SYNTHESIS AND DYEING PROPERTIES OF METALLISABLE AND NON METALLISABLE ACID DYES

By

YAKUBU, Mohammad Kabir, B.Sc, M.Sc.

(Textile Science and Technology) A.B.U.

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Department of Textile Science and Technology,

Faculty of Science, Ahmadu Bello University,

Zaria.

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DECLARATION

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any other University or Institution. The information derived from the published work of others have been duly acknowledged in the text by means of reference.

Date: 21/09/2000



YAKUBU, M.K.

CERTIFICATION

This thesis entitled "Synthesis and dyeing properties of metallisable and non-metallisable acid dyes" by Yakubu, M.K. meets the regulations governing the award of the degree of doctor of philosophy of Ahmadu Bello University and is approved for its contribution to scientific knowledge and literary presentation.

Dr. K.A. Bello
Chairman, Supervisory Committee

Date

Prof. P.O. Nkeonye
Member Supervisory Committee

Date

Dr. K.A. Bello
Head of Department

Date

Professor S.B. Ojo
Dean, Post Graduate School

12/03/01
Date

DEDICATION

It is for you that is weak in social status, weak in educational background, weak in knowledge, weak in financial position and perhaps too weak in spirit. I assure you that you can more than make it. But don't forget that Rome was not built in a day, nor was New York, nor also was the whole universe so that we can learn to steadily progress.

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The choicest and most pleasant thanks are due to Allah alone. He is the only one, whose existence only guaranteed the survival of the universe far beyond the recognition and comprehension of science. Development, evolution and growth of science will to the end of time explain only an infinitesimal if ever of this mystery that is the so diverse yet so unified, the so disorderly yet so synchronized, the aimless, yet so purposeful, the so secretive yet so manifest truth. The epic achievement of science is to acknowledge the weakness of human knowledge and credit all wisdom to Him who is the fountain of all goodness the giver and provider of life to all that exists, the nourisher and enricher of the weak. And eventually the only sole inheritor of all that He created. Certainly, I owe my life to His bounteous and countless mercies if not for Him I would still have been engrossed in layers upon layers of darkness.

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ABSTRACT

The research thrust of this thesis investigated the role of acetylation on the colour and dyeing properties of mono azo dyes where H-acid was used as coupling component. It also studied the potentiality of 2-nitroso-l-naphthol both as a pigment when used as a ligand with some selected heavy metals and as a dye to nylon and wool substrates with a possibility of being postmetallized with some metallic salts. In addition, characterization and dyeing properties of dyes where p-amino toluenesulphon-N-ethylanilide was used as diazo component was investigated.

In the first case, H-acid was acetylated. Two sets of dyes were synthesized from this and the unacetylated intermediate by coupling with different diazo components. The two groups were characterized and then applied to wool and nylon 6.6 fabrics and their color fastness assessed. Generally, the acetylated dyes gave hypsochromic effects on color. However, color fastness to wet treatments such as washing and perspiration was improved on both substrates as a result of acetylation. Whereas, a general improvement was made on acetylated dyes when applied to wool fabric, no noticeable improvement on light fastness with respect to nylon 6.6 was observed.

2-Nitroso-1-naphthol was synthesized and coupled to two diazo components under alkaline condition. The three compounds were in turn complexed to several heavy metals. Two types of pigments the 1:1 and 1:2 were identified. In the 1:1, one molecule of the organic compound was complexed to one atom of the metal whereas in the 1:2, two molecules of the organic compound were complexed to one atom of the metal. The results showed that both the parent nitroso and its azo derivatives are strong ligands. They formed complexes by mere shaking the solution of the nitroso with an aqueous solution of the heavy metals. However, unlike the complexes derived from the nitroso phenols, the two types of complexes cannot be differentiated by solubility. Similarly, the two types of complexes seemed to absorb at basically the same region. The complexes from different metals gave distinct color differences. Following the success of this, we extended the range of diazo components to increase the number of azo dyes. Their uv-visible and ir-spectroscopies were studied. The dyes obtained were applied to wool and nylon 6.6 fabrics. The kinetics and thermodynamics of dyeing were quantified. The postmetallisability of the dyed substrates with heavy metals was then investigated. The effect of pH on adsorption by wool and nylon 6.6 substrates confirmed that acid-dyeing mechanism could explain the dyeing system. Overdyeing phenomenon observed with the

dyeing of polyamide fibres with conventional acid dyes was however, not indicated by these dyes. A dyeing mechanism from this observation was proposed. As with many cases in the literature, thermodynamic and kinetic of dyeing didn't outline any general trend with respect to the influence of molecular size, volume and the degree of sulphonation etc. The dyed substrates proved metallisable with the aqueous solutions of heavy metals. The influence of pH on metallisation showed that the best region is between the pH of 7-9. It also indicated that a very short liquor ratio is more desirable with a very dilute solutions of the metals. The distinct shade changes confirmed that the nitroso and hydroxyl groups are still intact in their relative positions and therefore formed the complexes in situ. These findings added yet another post metallisable dye in addition to the already existing ones. Its characteristics are however, similar to the dyes with salicylic acid residue. The dyeings showed moderate to excellent wet fastness treatments, but poor light fastness ratings on both substrates, the effect of post metallisation showing little influence.

p-Aminololucnesulphon-N-ethylanilide was diazotised and coupled to five different coupling components. After uv-visible and ir-characterisations, the dyes were applied to wool and nylon 6.6 substrates. Thermodynamic and kinetic parameters were quantified together with wet

and light fastness indices. The results showed that tautomcrism greatly affected the extinction coefficients of the dyes. The wash and perspiration fastness ratings were also good. The light fastness properties of the dyes were moderate on nylon 6.6 but ranged from good to excellent on wool substrate.

TABLE OF CONTENTS

		Page
	Title	i
	Declaration	ii
	Certification	iii
	Dedication	iv
	Acknowledgement	v
	Abstract	viii
	Table of Contents	xii
	List of Tables	xix
	List of Figures	xxiii
	Chapter 1: Literature Survey	
1.1	Introduction	1
1.2	Historical development of the synthetic dye industry	3
1.3	Development of colour and constitution theory	12
1.4	Qualitative methods of color assessment	19
1.4.1	Predictive methods of color assessment	19
1.4.2	Resonance theory	21
1.4.3	Pertubational molecular orbital theory	24
1.4.4	The triad theory of Dahne	28
1.5	Quantitative molecular orbital methods	30
1.5.1	The free electron model (FEMO)	31
1.5.2	The Huckel molecular method (HMO)	32

1.7.3 Nitroso dyes

1.8 Diffusion and rate of dyeing

1.8.1 Diffusion infinite bath

1.8.2 Diffusion in finite bath

1.9 Thermodynamic of dyeing nylon and wool with acid dyes

1.9.1 Mechanism of dyeing nylon with acid dyes

1.9.2 Mechanism of dyeing wool with acid dyes

Chapter 2: Effects of Acetylation on Color and Fading of some azo dyes on wool and nylon fabrics

2.1 Introduction

2.2 Results and discussions

2.2.1 Synthesis of the intermediates and dyes

2.2.2 UV-visible spectroscopic properties of the dyes

2.2.3 Dyeing fastness properties

4.2 Results and discussions

4.2.1 Synthesis of the dyes

4.2.2 UV-visible spectroscopy of the dyes

4.2.3 Effect of pH on the dyeing of the dyes on nylon 6.6 and wool

4.2.4 Determination of coefficient of diffusion

4.2.5 Determination of the thermodynamic parameters of the dyes on wool and nylon 6.6

4.2.6 The effect of pH on the fixation of the nitroso dyes on nylon

Chapter 5: Synthesis and properties of monoazo acid dyes Derived from p-amino toluene-sulphone-N-Ethylanilide as diazo component

5.1 Introduction

5.2 Results and discussions

5.2.1 Synthesis, characterizations and spectroscopic properties of the dyes

5.2.2 Diffusion coefficient and activation energy on wool and nylon 220

5.2.3 Thermodynamic parameters of the dyes on wool and nylon 6.6 245

5.2.4 Wash and perspiration fastness properties of the dyes on wool and nylon 6.6 253

5.2.6 Light fastness ratings of the dyes on wool and nylon 6.6 259

Chapter 6: Experimental

6.1 General information 263

6.1.1 Melting point determination 263

6.1.2 Spectra 263

6.1.3 Calibration curves 263

6.1.4 Determination of the diffusion coefficient 265

6.1.5 Determination of affinity 267

6.1.6 Determination of the wash fastness 270

6.1.6.1 I.S.O. 3 (CO3) 271

6.1.6.2 I.S.O. 4 (CO4) 271

6.1.6.3 I.S.O. 5 (CO5) 271

6.1.7 Determination of the fastness to perspiration 271

6.1.7.1 Alkali solution 272

6.1.7.2 Acid solution 273

6.1.8 Determination of color fastness to light 273

6.1.9 Dyeing properties 274

6.1.9.1 Dyeing procedure 274

6.1.9.2 Measurement of exhaustion 275

6.2	Synthesis of the intermediates and dyes (1-12)	275
6.2.2	General method for diazotisation of the amines for dyes (1-12)	276
6.2.3	General method of coupling dyes (1-12)	277
6.3	Synthesis of the nitroso dyes (65-73)	277
6.3.1	Procedure for nitrosation of 1-naphthol	278
6.3.2	Diazotisation of the amine	278
6.3.2.1	Diazotisation of aniline and 4-aminobenzoic acid	278
6.3.2.2	Diazotisation of 2-cyano-4-nitroaniline and 4-nitroaniline	279
6.3.2.3	Diazotisation of J, H, sulphanilic acids and 4-aminophenol	279
6.3.3	General procedure for coupling	279
6.4	General procedure for premetallisation	279
6.4.1	The 1:1 complex	280
6.5	Synthesis of the dyes (74-78)	280
6.5.1	Diazotisation of p-amino toluene-N-ethylanilide	281
6.5.2	Coupling	281
	Chapter 7: Conclusion	310
	Bibliography	315

LIST OF TABLES

Table	Page
1. Substituent R_0, R_1, and R_2	81
2. Visible absorption properties of the dyes	82
3. Fastness properties of the dyes on nylon 6.6 fabrics	88
4. Fastness properties of the dyes on wool	89
3.1 Yield and some properties of the 1:1 complex from 2-nitroso-1-naphthol	97
3.2 Yield and some properties of the 1:2 complex from 2-nitroso-1-naphthol	98
3.3 Yield and other properties of diazotised aniline derivatives of 2-nitroso-1-naphthol, 1:1 premetallized complex	99
3.4 Yield and other properties of diazotised aniline derivatives of 2-nitroso-1-naphthol, 1:2 premetallized complex	100
3.5 Yield and other properties of diazotised 4-amino benzoic acid Derivative of 2-nitroso-1-naphthol, 1:1 premetallized complex	101
3.6 Yield and other properties of diazotised 4-amino benzoic acid Derivatives of 2-nitroso-1-naphthol 1:2 premetallized complex	102
4.1 Characterisation data for 2-nitroso-1-naphthol and its azo dyes Derivatives	111

4.2 The effect of pH on dyeing wool samples 131

4.3 The effect of pH on dyeing nylon 6.6 samples 132

4.3.1 pH of maximum exhaustion for nylon 6.6 and wool 137

4.4 Diffusion data of dye (65) on wool and nylon 6.6 at 303 and 323K 138

4.5 Diffusion data of dye (66) on wool and nylon 6.6 at 303 and 323K 139

4.6 Diffusion data of dye (67) on wool and nylon 6.6 at 303 and 323K 140

4.7 Diffusion data of dye (68) on wool and nylon 6.6 at 303 And 323K 141

4.8 Diffusion data of dye (69) on wool and nylon 6.6 at 303 And 323K 142

4.9 Diffusion data of dye (70) on wool and nylon 6.6 at 303 And 323K 143

4.10 Diffusion data of dye (71) on wool and nylon 6.6 at 303 And 323K 144

4.11 Diffusion data of dye (72) on wool and nylon 6.6 at 303 And 323K 145

4.12 Diffusion data of dye (73) on wool and nylon 6.6 at 303

	And 323K	146
4.13	Thermodynamic parameters of the dyes on wool substrates	173
4.14	Thermodynamic parameters of the dyes on nylon 6.6	175
4.15	The heat and entropy of dyeing for the dyes on wool and nylon 6.6	184
4.16	Effect of pH on the fixation value of dye (65) on nylon 6.6 Mordanting with different metallic salts	187
4.17	Effect of pH on the fixation value of dye (66) on nylon 6.6 Mordanting with different metallic salts	188
4.18	Effect of pH on the fixation value of dye (67) on nylon 6.6 Mordanting with different metallic salts	189
4.19	Wash fastness ratings of the nitroso dyes on wool using ISO 3	194
4.20	Wash fastness ratings of the nitroso dyes on nylon using ISO 3	195
4.21	Acid and alkaline perspiration ratings for the 2-nitroso-1-Naphthol and azo derivative dyes on wool	196
4.22	Acid and alkaline perspiration ratings for the 2-nitroso-1-Naphthol and azo derivative dyes on nylon 6.6	197
4.23	Light fastness ratings of the dyes on wool and nylon 6.6	205
5.1	Yield, melting point and spectroscopic properties of the dyes	210
5.2	Diffusion coefficient and activation energy of dye (74) on	

Wool at 333 and 353K 221

5.3 Diffusion coefficient and activation energy of dye (75) on Wool at 333 and 353K 222

5.4 Diffusion coefficient and activation energy of dye (76) On wool at 333 and 353K 223

5.5 Diffusion coefficient and activation energy of dye (77) On wool at 333 and 353K 224

5.6 Diffusion coefficient and activation energy of dye (78) on Wool at 333 and 353K 225

5.7 Diffusion coefficient and activation energy of dye (74) on Nylon 6.6 at 333 and 353K 226

5.8 Diffusion coefficient and activation energy of dye (75) on Nylon 6.6 at 333 and 353K 227

5.9 Diffusion coefficient and activation energy of dye (76) on Nylon 6.6 at 333 and 353K 228

5.10 Diffusion coefficient and activation energy of dye (77) on Nylon 6.6 at 333 and 353K 229

5.11 Diffusion coefficient and activation energy of dye (78) on Nylon 6.6 at 333 and 353K 230

5.12 Thermodynamic parameters of the dyes on wool 246

5.13 Thermodynamic parameters of the dyes on nylon 6.6 247

5.14 Wash fastness ratings of the dyes on wool 254

5.15 Wash fastness ratings of the dyes on nylon 6.6 255

5.16 Acid and alkali perspiration ratings for the dyes 256

5.17 Light fastness ratings of the dyes on wool and nylon 6.6 260

LIST OF FIGURES

Title	Page
Fig 3.1: uv-visible spectrum of dye (19)	106
Fig 3.2: uv-visible spectrum of dye (28)	107
Fig 3.3: uv-visible spectrum of dye (32)	108
Fig 3.4: uv-visible spectrum of dye (59)	109
Fig 4.0: i.r spectrograph of the solvent, DMF	121
Fig 4.1: i.r spectrograph for dye (65)	122
Fig 4.2: i.r spectrograph for dye (66)	123
Fig 4.3: i.r spectrograph for dye (67)	124
Fig 4.4: i.r spectrograph for dye (68)	125
Fig 4.5: i.r spectrograph for dye (69)	126
Fig 4.6: i.r spectrograph for dye (70)	127
Fig 4.7: i.r spectrograph for dye (71)	128
Fig 4.8: i.r spectrograph for dye (72)	129
Fig 4.9: i.r spectrograph for dye (73)	130
Fig 4.10: The effect of pH on dyeing of wool	135
Fig 4.11: The effect of pH on dyeing of nylon 6.6	136
Fig 4.12: Rate curve for dye (65) on wool	147
Fig 4.13: Rate curve for dye (66) on wool	148

Fig 4.14: Rate curve for dye (67) on wool 149

Fig 4.15: Rate curve for dye (68) on wool 150

Fig 4.16: Rate curve for dye (69) on wool 151

Fig 4.17: Rate curve for dye (70) on wool 152

Fig 4.18: Rate curve for dye (71) on wool 153

Fig 4.20: Rate curve for dye (72) on wool 154

Fig 4.21: Rate curve for dye (73) on wool 155

Fig 4.22: Rate curve for dye (65) on nylon 6.6 156

Fig 4.23: Rate curve for dye (66) on nylon 6.6 157

Fig 4.24: Rate curve for dye (67) on nylon 6.6 158

Fig 4.25: Rate curve for dye (68) on nylon 6.6 159

Fig 4.26: Rate curve for dye (69) on nylon 6.6 160

Fig 4.27: Rate curve for dye (70) on nylon 6.6 161

Fig 4.28: Rate curve for dye (71) on nylon 6.6 162

Fig 4.29: Rate curve for dye (72) on nylon 6.6 163

Fig 4.30: Rate curve for dye (73) on nylon 6.6 164

Fig 4.31: Effect of pH on the post metallization of dye (65)
On nylon 6.6 190

Fig 4.32: Effect of pH on the post metallization of dye (66) on
Nylon 6.6 191

Fig 4.33: Effect of pH on the post metallization of dye (67) on Nylon 6.6 192

Fig 5.1: HPLC spectrograph of p-amino toluene sulphon-N-Ethylanilide 212

Fig 5.2: i.r spectrum of dye (74) 213

Fig 5.3: i.r spectrum of dye (75) 214

Fig 5.4: i.r spectrum of dye (76) 215

Fig 5.5: i.r spectrum of dye (77) 216

Fig 5.6: i.r spectrum of dye (78) 217

Fig 5.8: Rate curves for dye (74) on wool 231

Fig 5.9: Rate curves for dye (75) on wool 232

Fig 5.10: Rate curves for dye (76) on wool 233

Fig 5.11: Rate curves for dye (77) on wool 234

Fig 5.12: Rate curves for dye (78) on wool 235

Fig 5.13: Rate curves for dye (74) on nylon 6.6 236

Fig 5.14: Rate curves for dye (75) on nylon 6.6 237

Fig 5.15: Rate curves for dye (76) on nylon 6.6 238

Fig 5.16: Rate curves for dye (77) on nylon 6.6 239

Fig 5.17: Rate curves for dye (78) on nylon 6.6 240

Fig 6.10: Calibration curve for the NaOH solution of dyes (65-67) 283

Fig 6.11: Calibration curve for the NaOH solution of dyes (68-70) 283

Fig 6.12: Calibration curve for the NaOH solution of dyes (71) 285

Fig 6.13: Calibration curve for the NaOH solution of dyes (72) 286

Fig 6.14: Calibration curve for the NaOH solution of dyes (73) 287

Fig 6.20: Calibration curve for wool/NaOH solution of dyes(65 & 69) 288

Fig. 6.21: Calibration curve for wool/NaOH solution of dyes(66 & 72) 289

Fig. 6.22: Calibration curve for wool/NaOH solution of dyes(67 & 70) 290

Fig. 6.23: Calibration curve for wool/NaOH solution of dye (68) 291

Fig. 6.24: Calibration curve for wool/NaOH solution of dye (71) 292

Fig. 6.25: Calibration curve for wool/NaOH solution of dye(73) 293

Fig. 6.30: Calibration curve for solution of dyes(65 & 66)in
2 cm^3, 0.2M NaCl 294

Fig 6.31: Calibration curve for solution of dyes(68 – 70)in 2 cm^3,
0.2M NaCl 295

Fig 6.32: Calibration curve for solution of dyes(67)in 2 cm^3,
0.2M NaCl 296

Fig 6.33: Calibration curve for solution of dyes(71)in 2 cm^3,
0.2M NaCl 297

Fig 6.34: Calibration curve for solution of dyes(72)in 2 cm^3,
0.2M NaCl 298

Fig 6.35: Calibration curve for solution of dyes 73 in 2 cm^3, 0.2M NaCl 299

Fig. 6.40: Calibration curve for dye (74) in 20% pyridine solution 300

Fig. 6.41: Calibration curve for dye (75) in 20% pyridine solution 301

Fig. 6.42: Calibration curve for dye (76) in 20% pyridine solution 302

Fig. 6.43: Calibration curve for dye (77) in 20% pyridine solution 303

Fig. 6.44: Calibration curve for dye (78) in 20% pyridine solution 304

Fig. 6.50: Calibration curve for dye (74) in NaOH/wool solution 305

Fig. 6.51: Calibration curve for dye (75) in NaOH/wool solution 306

Fig. 6.52: Calibration curve for dye (76) in NaOH/wool solution 307

Fig. 6.53: Calibration curve for dye (77) in NaOH/wool solution 308

Fig. 6.54: Calibration curve for dye (78) in NaOH/wool solution 309

CHAPTER 1

Literature Survey

1.1 Introduction

Dyes are described as chemical substances that are colored and can be imparted onto a given substrate. They are characterized in accordance with their ability to absorb in the visible part of the electromagnetic radiation. Visible light represents a very small part of the electromagnetic spectrum and corresponds roughly with radiation within the wavelength range 400-780 nm.

The absorption of light by colored substances is due to electronic transitions between different orbitals within the molecule and the wavelengths absorbed are determined by energy differences between the orbitals. Every dye or pigment therefore exhibits a pattern of absorption arising from its chemical structure and this may be represented by an absorption spectrum consisting of a graph in which the degree of absorption is plotted as ordinate against wavelength as abscissa.

The visible spectrum contains regions recognized by the human visual system in terms of color and the approximate wavelength ranges corresponding to the colors are as shown in Table 1.1.

When light of a given color is absorbed the complementary color is transmitted or reflected. For example, a dye absorbing light within the blue range is seen in daylight as yellow.

The absorption spectrum of a dye may be complex, and the purity of the color observed depends on the shape of the curve. Bright colors are the result of narrow absorption bands with sharp peaks and dullness is associated with broader bands lacking

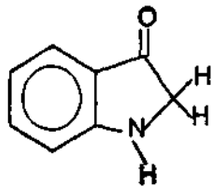
Table 1.1 Relationship of Colors observed to Wavelengths absorbed.[2]

Light absorbed		Complementary
Wavelength (nm)	Color	Color seen
400-435	Violet	Green-Yellow
435-480	Blue	Yellow
480-490	Green-Blue	Orange
490-500	Blue-Green	Red
500-560	Green	Purple
560-580	Yellow-Green	Violet
580-595	Yellow	Blue
595-605	Orange	Green-Blue
606-750	Red	Blue-Green

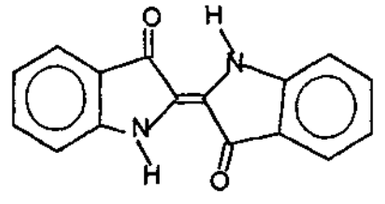
such peaks. Non-spectral colors such as brown are associated with absorption spread fairly evenly over a wide wavelength range. Black is the result of absorption throughout the visible spectrum.

1.2 Historical Development of the Synthetic Dye Industry

Before the mid-nineteenth century, virtually all dyes originated from animal and mineral sources. In fact, ancient Egyptian hieroglyphs contain a thorough description of the extraction of natural dyes and their application in dyeing.[3] Further development extending many thousand years led to rather complicated dyeing processes and high-quality dyeings. Among these, indigo, Turkey red ancient purple deserve special mention. Indigo is a natural blue colorant of vegetable origin. The major source of this dye was the plant indigofera tinctoria. The leaves of the plant is rich in indoxyl (1) , which is a glycoside derivative. Fermentation of the leaves liberates free indoxyl and this is rapidly oxidized by air to the desired, water insoluble indigo (2). In Europe the woad plant was used to provide the dye.



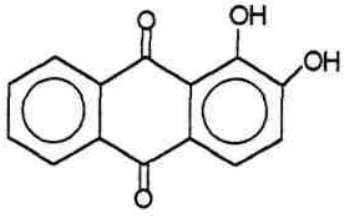
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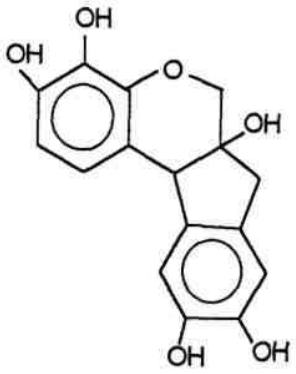
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The superior wash- and light fastness properties of indigo meant that none of the early synthetic blue dyes posed a threat to it. Madder was also

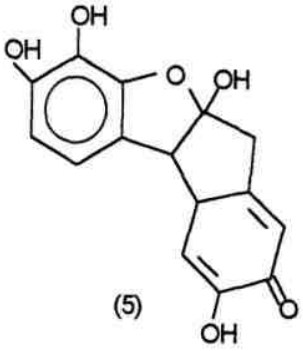
vegetable based. It is obtained from the root of the Rubia tinctorum plant. The principal component being alizarine (3). The popular Turkey Red is from the same source. Cellulosic fabrics were dyed with this material by a mordant dyeing process. Perhaps the only natural dye that is still in production on a large scale is logwood. It is derived from the wood of the tree Haematoxylon campechianum which is cultivated in Central America. When freshly cut the wood contains haematoxylin (4). This is oxidized to haematin (5) during ageing or deliberate oxidation of the extract. Logwood is still used for dyeing wool, silk, nylon, viscose and acetate fibres to a cheap black shade with good fastness properties.[4]



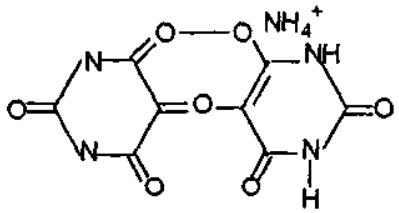
(3)



(4)



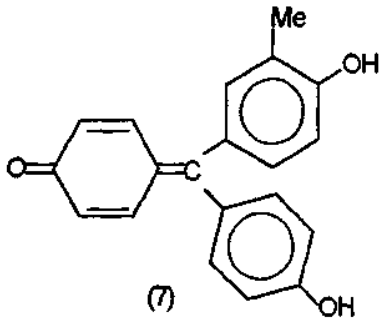
In 1771, picric acid was obtained by Woulfe by heating indigo with nitric acid. Although it was found that picric acid dyed silk greenish yellow, it was not until 1845 that an economic route to picric acid from phenol could be found and the dye commercialized. It was however not a successful dye because of its poor light fastness. In 1818, Prout discovered Murexide (6). It was made by the reaction of uric acid with concentrated nitric acid followed by ammonia. Like picric acid, its poor fastness properties limited its usefulness.



(6)

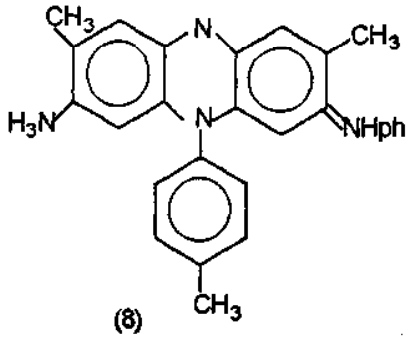
Another historical antecedant to the development of synthetic dye industry was the discovery of Aniline by the distillation of indigo by Unverdorben in 1826. In 1825, Faraday discovered benzene and by 1845, Zinin and Hoffmann had found how to nitrate this chemical and how to reduce the product to aniline.

In 1834, Runge synthesized Rosolic acid (7) by the oxidation of crude carbolic acid. However, it was not until 1861 when it was obtained by heating phenol with oxalic acid and sulphuric acid.

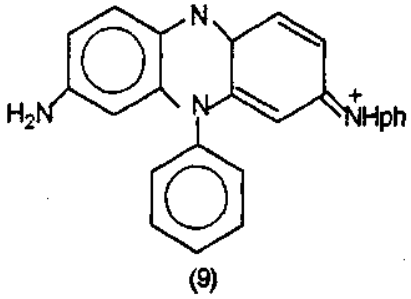


(7)

The foundation of the synthetic dye industry was laid in 1856 when Perkin synthesized Aniline purple otherwise called Mauvein while attempting to produce quinine by oxidizing aniline, a dirty brownish product was obtained. By extracting with alcohol he obtained mauvein. He showed that the dye was in fact a mixture of two dyes; (8) and (9).



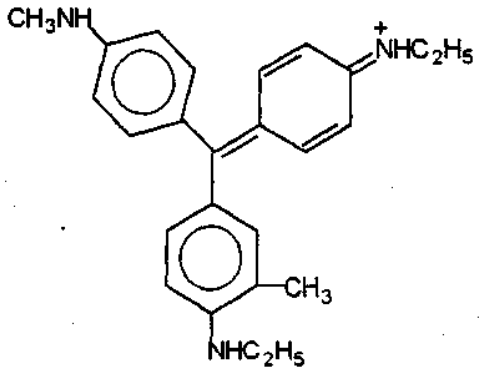
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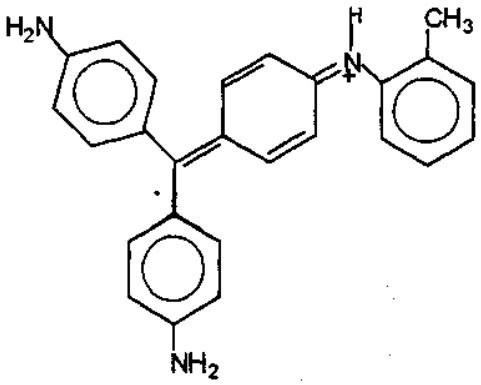
(9)

Another success story was Magenta. This was discovered in 1856 in Natanson and commercially by Verguin in 1959. Verguin obtained this dye by oxidizing crude aniline with stannic chloride. One of the principal contents of the dye was homorosaniline (10) together with rosaline. Magenta proved a greater commercial success than Aniline purple. Other

notable discoveries in the 1950's and 60's were Hofmann's violet (11) 1863, and Girard's violet Imperial (12) 1860. But, the first systematic approach to dye synthesis came independently from Nicholson and Gilbee in 1862 when they deliberately sulphonated N-phenyl derivatives of magenta to confer water solubility. These proved to be the pioneering research in acid dye field for wool with good water solubility and protein fibre affinity.

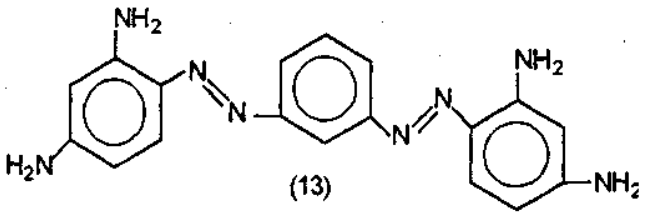


(11)



(12)

In 1863 a major break through was made with the synthesis of an azo dye Bismarch Brown by Martin (13). The structure of the dye was only discovered when Griess demonstrated the azo coupling reaction.



(13)

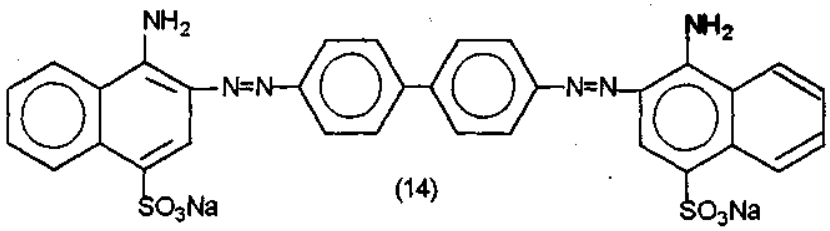
After the decisive work by Kekule on the quadrivalence of carbon in 1858 and on the constitution of benzene in 1865 a way was opened for the planned preparation of purely synthetic dyes as well as for the artificial production of natural dyes. The first success to be mentioned is the elucidation of the constitution and the synthesis immediately afterwards of alizarin by Graebe and Liebermann in 1868. They synthesized alizarin by bromination of anthraquinone followed by alkali fusion. The high cost of bromine prevented commercialization of this method until Perkin and Caro discovered an alternative route in 1869 by the sulphonation of anthraquinone in the 2-position followed by alkali fusion.

In 1866 Martins and Griess showed that Aniline Yellow was actually 4-amino azo benzene formed by coupling diazotised aniline to aniline itself, followed by acid-catalyzed rearrangement of the diazo amino compound. The coupling reaction between diazonium ions and phenols was discovered by Kekule in 1870. In 1875 Caro made the basic azo dye chrysoidine. 1876 saw the synthesis of the first azo dyes for wool Orange I and Orange II by Roussin.

In 1873 Croissant produced what came to be known as sulphur dyes by heating saw dust with sodium polysulphide to give deeply colored products. By 1880 a completely new dyeing method was discovered by the

introduction of azoic dyeing. It involved saturating the fabric with an alkaline solution of a phenol or naphthol and then treating the fabric with a solution of a diazotised aromatic amine.

In the early 1880's, cotton was still the most important textile fibre, the dyeing of which was only limited to Indigo and mordant dyeing with alizarin, the shade of which were very narrow coupled with troublesome and at times unreproducible. Thus a major step forward was made in 1883 when Griess developed disazo sulphonated dyes which had natural affinity for cellulose without the need of a mordant. These dyes were later named direct dyes. Thus in 1884 Bottinger synthesized Congo Red (14).

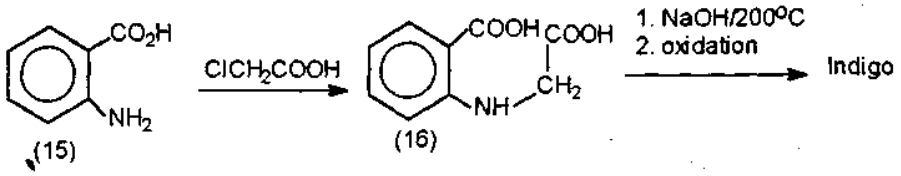


(14)

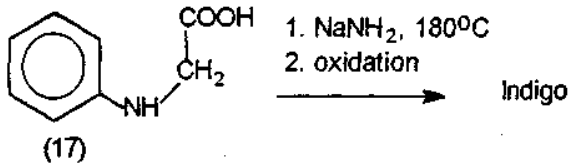
By 1885 also, Meldula and Nietzki prepared dyes from the coupling reaction between diazonium ions and salicyclic acid which could by mordanting with chromium produce good fastness properties on wool. This was the beginning of metal-complex azo dye chemistry.

In the 1890's, Indigo was perhaps the only natural dye that had any commercial importance, a lot of research was intensified to synthesize it.

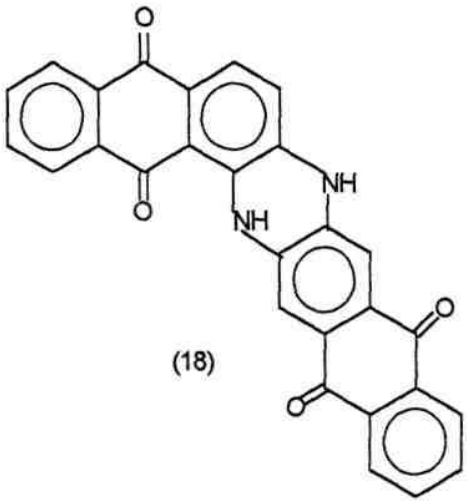
After economically non viable attempts by Baeyer in 1878 by the o-nitrophenylacetic acid or the o-nitrocinnamic acid route neither was the BASF's anthranilic acid (15) though o-carboxy-phenylglycine (16) was any success.



In 1902 a more economic route was established by Roessler by using phenylglycine (17) and cyclizing it to Indoxyl at moderate temperatures by using sodamide.



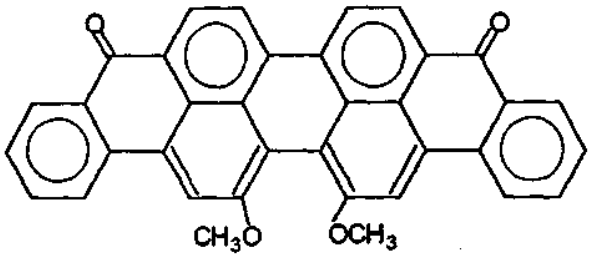
Concurrently in 1901, Bohn in an attempt to synthesize Indigo structure containing anthraquinone residues by reacting 2-amino anthraquinone with chloroacetic acid and subjecting to alkaline fusion obtained a blue dye which was subsequently shown by Scholl to be an Indanthrone (18) believed to contain a quinonoid structure.



(18)

The recognition of quinones as potential vat dye systems encouraged intensive investigation of other related structures and many new vat colours were introduced in the 1900-1910 period.

From the 1901 to the 1930's notable achievements included the J-acid direct dyes, naphthol AS and its analogues in the azoic dyeing field, blue acid dyes from bromamine acid and arylamines. Others included the Neolan dyes which were the pre complexed mordant azo dyes for wool and silk. In 1920 the ICI marketed Caledon Jade Green (19) thus filling the gap in the vat dye range. It became possible to market stabilized diazonium salts and sulphuric esters of pre-reduced vat dyes increasing the versatility and convenience of the azoic and vat dyeing processes. The introduction of cellulose acetate fibres opened a totally new approach in the dyeing technology. The Ionamine dye ranges in the 1920's solved the problem.



(19)

These dye ranges were believed to be water soluble but hydrolyse to a water insoluble dye inside the fibre. Subsequently disperse dye chemistry was born. In 1934, the most important new chromophore of the century, copper phthalocyanine was marketed by ICI.

Essentially, the 1940's saw the marketing of Nylons, polyesters and the acrylic fibres which meant a more intensive research in the disperse dye area, culminating in the discovery of the more innovative cationic dyes for acrylic fibres.

When the cotton reactive dyes were introduced in 1956, it proved to be the most significant advance in dye application chemistry of the century.[5]

1.3 Development of Color and Constitution Theory

Apparently synthetic chemists were advancing faster than the theoretical chemists. It was not until the Kekules cyclohexatriene formulation of the benzene ring in 1865[6] that structural chemistry started to

be appreciated. This was however later modified to a dynamic structure involving a continuous oscillation between the two triene forms. Electron was only discovered in 1897 and the concept of the electron-pair-bond formulated only in 1916[7].

The first observation on the relation between chemical constitution and color was made by Graebe and Liebermann.[8] They postulated that color arise from the presence of unsaturation in a molecule. This idea was based on the experimental observation that all known dyes could be reduced and the color disappeared on reduction. In 1879, Professor Nietzki[9] extended this idea and formulated a rule that the color of a dye was deepened by the addition of groups to the molecule thus increasing the molecular weight. This rule was however left open to criticism due to ready availability of practical exceptions, however, the rudiments of the ideas of extended conjugation can be recognized in it.

Hewitt and Mitchel[10] stated the rule correctly in terms of the dependence of color on the conjugation length in a molecule. Schutze[11] in 1892 examined Nietzkis rule in depth pointing out many exceptions and in so doing coined the terms bathochrome and hypsochrome.

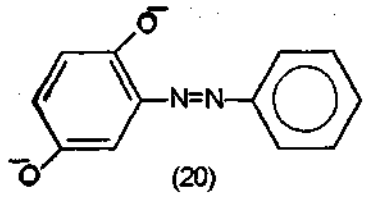
The first real attempt to establish a general theory relating depth of color to molecular constitution was by Witt in 1876.[12] He considered that a

dye molecule could be dissected into discrete units, the total combination of which gave rise to color. He noted that all dyes known at that time contained a benzene or naphthalene moiety and that attached to this moiety were simple unsaturated groups such as $-NO_2$, -NO, -N=N-, -C=O, which he termed chromophores. Combination of an aromatic nucleus and chromophores give rise to feeble color or non at all. Such a union was called a chromogen. Intense colour could be developed from a chromogen by attaching weakly basic groups i.e $-NH_2$, $-NR_2$, -OH etc. called auxochromes. In modern times a chromophore is more clearly defined as a –M (mesomerically electron withdrawing) and auxochrome as a +M (mesomerically electron donating) substituents. This approach was adopted by Kauffmann[13] in the 1907 systematically extended and developed. He established that the relative effectiveness of the common auxochromes for producing color is:

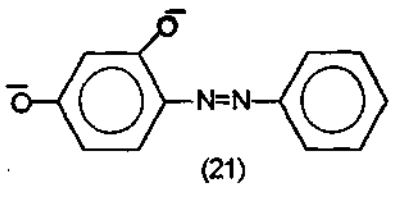
$$C_2H_5- < OCH_3 < NHAc < -NH_2 < Nme_2 < NHph.$$

Recognizing that chromophores were opposite in Acid-Base characteristics to auxochromes, Kauffmann redesignated them antiauxochrome. Kauffmann also examined the influence of multi auxochromic substitution on color and the importance of the relative position of auxochrome and antiauxochromes in a dye molecule.

Kauffmann showed that the deepest color was obtained when two auxochromes were ortho, meta relative to a single anti auxochrome. The organic chemist however thinks that ortho and para arrangement is potentially the most bathochromic. This is well exemplified by the two azo dye anions (20) and (21).



(20)
Blue



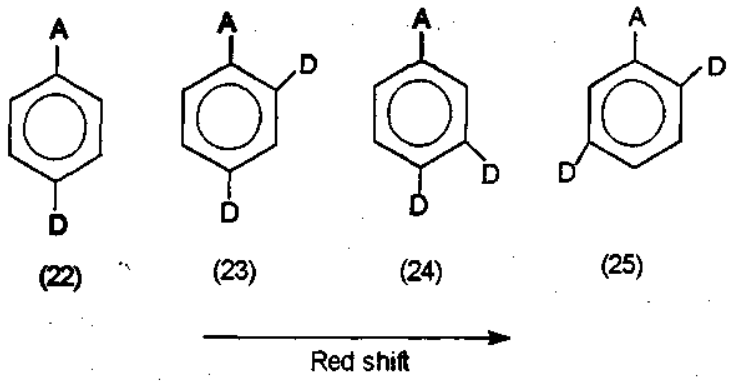
(21)
Orange

Although a greater number of low energy resonance structures can be drawn for (21) than (20), it is the latter compound that aborbs at longer wavelength. This highlighted one of the weakness of the resonance interpretation of color in which seemingly resonance forbidden structures are often ignored, yet these can make very important contribution to the excited state of the molecule and hence its color. Adequate consideration of such structures predict (20) to have lower transition energy.

Witts theory was developed further by Pfeffer, Delthy and Wizinger[14] to explain the intense color of the di- and triaryl- methane cationic and anionic dyes which contain no obvious chromophores. The concept of Ionogenes was introduced (e.g $\overset{+}{C}$-, -$\bar{C}$-, -$\bar{N}$-)

which were poweful antiauxochromic groups. Witts theory as it was, though applicable to quinone and azo dyes could not be applied to the cationic dye known at that time.

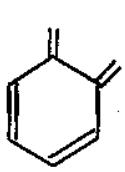
Wizinger[15] also pointed out that it is impossible to understand the so called distribution principle of auxochromes on the basis of the resonance theory to be discussed later. This refers to the fact that the introduction of a further donor into a benzene derivative that already carries one electron acceptor and a donor causes the following shifts relative to the 1,4-donor-acceptor compound:



It is seen here too[16] that the cause of this shift to longer wavelengths lies in the fact that the energy in the excited state does not correspond to that which could be expected from the customary concepts of the resonance theory.

In 1888 the quinonoid theory was proposed by Amstrong.[17] This approach enjoyed wide acceptance in its day because of its immediate

relevance to the cationic dyes which were most numerous at that time. The theory was based on the idea that the exocyclic double bonds peculiar to ortho and para quinonoid structures (26) and (27) were in some way strained and this was associated with color.

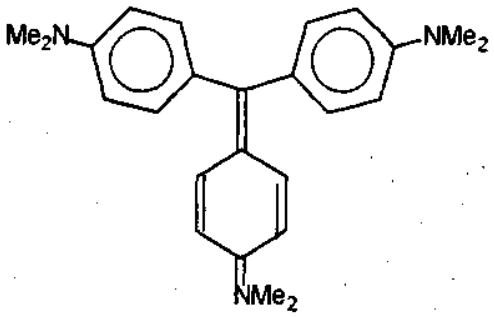


(26)

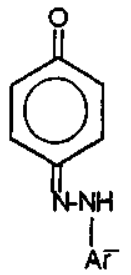


(27)

Thus any molecule that had such quinonoid units in its structure would exhibit color. Cationic dyes e.g (28) also owe their intense color to the quinonoid structures. The azo dyes are adopted to this theory by, assuming that they actually existed as hydrazone tautomers e.g (29).

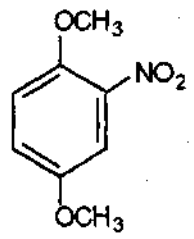


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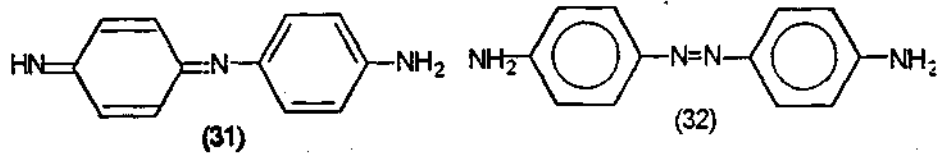


(29)

Many exceptions to the quinonoid theory were advanced. Some quinonoid compounds were synthesized with no colors e.g 1,4-benzoquinone diamine and also many intensely colored compounds with no possibility of quinonoid substituents were synthesized e.g 1,4-dimethoxy-2-nitrobenzene (30).

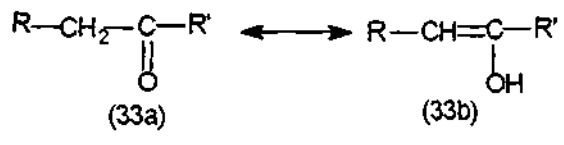

(30)

Watson[18] in 1913 suggested that if a dye could show a quinonoid structure in all its possible tautomeric forms, then it would be deeply colored however small its molecular size. An example of this is Indamine (31) which is blue contrasted with 4,4'-diamino azo benzene (32) which is yellow and yet the latter has the greater degree of conjugation.


(31) (32)

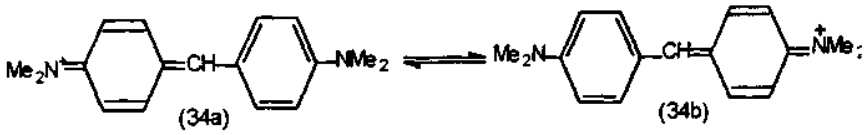
It was then possible to rationalize various pronounced differences between dyes of similar molecular size, as Watson demonstrated for hydroxy anthraquinones, triarylmethane, indophenol dyes and many others.

In 1904, Baly and Desch[19] promoted by the discovery of the phenomenon of keto enol tautomerism, presumed that near uv light absorption was associated with the rapid bond alternation occuring between tautomeric forms of a molecule e.g (33a) and (33b)


(33a) (33b)

However, many colored compounds are incapable of exhibiting tautomerism. Analogous oscillation theories were proposed by Von Baeyer[20] for triarylmethane dyes and by Willstatter[21].

Watson[18] extended these ideas to include other dye systems and suggested that the oscillating process in a dye molecule corresponded to the reversal of double bond and single bonds along the whole conjugated chain i.e.



(34a) (34b)

The longer the chain the slower the period of the oscillation and then one could account qualitatively for the effect of conjugation length on absorption. The idea that light absorption involved the electrons in a molecule was introduced later but was accepted reluctantly by organic chemists. Drude[22] showed theoretically that whereas atomic vibration correspond to frequencies in the IR range, uv frequencies required the oscillation of particles of much smaller mass i.e electron and visible region involved interactions of the radiation with electrons.

1.4 Qualitative Methods of Color Prediction

1.4.1 Predictive Methods of Color Assessment

Colored organic molecules have been classified into the following chromogenic types by Griffiths[23];

(i) n-π^*

(ii) donor-acceptor

(iii) polyene

(iv) cyanine

Most organic dyes however belong to the donor-acceptor class. Such chromogens are characterized by having one or more substituents with lone pair of electrons (donor groups) and one or more electron attracting substituents (acceptor groups) attached to the same conjugated π-electron systems (conjugating bridge). Absorption of visible light results in the migration of π-electrons density from the donor groups to the acceptor groups. The transition energy of such process will depend critically on the relative strengths of the donor and acceptor residues and also the nature of the bridging group. Most empirical quantitative work is based on the numerical definition of the donor strength (ionization potential) and acceptor strength (electron affinity Hammett σ constants), and the correlation of these quantities with absorption maxima. The order of electron donor strengths for some common donors based on ionization potential is:-

$$Oac < OH < NHAc \cong Ome < SH < NH_2 < Sme < O^- < NH^-$$

The color of donor-acceptor chromogens generally deepens as the donor strength is increased. An example of a linear correlation between absorption wavelength and ionization potential of donor is given by the 2-donor substituted anthraquinone [24], corresponding compounds substituted in the 1-position are complicated by steric interaction and hydrogen bonding effects.

Prediction of spectral properties based on electron acceptor strength using the Hammetts substituents σ-constant are met with complexities because the σ-constant derived on the basis of ground state properties of aromatic compounds containing the relevant acceptor group, may have little relevance in the excited state of the chromogen.

1.4.2 Resonance Theory

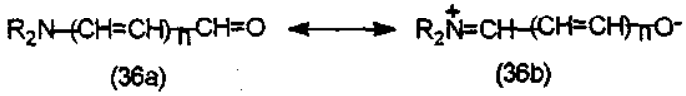
This theory states that if an unsaturated organic molecule can be represented reasonably as a hybrid of two extreme canonical forms, then, the closer the two forms are in energy, the smaller will be the gap between the ground and first excited state i.e the more bathochromic will be the light absorption band. (35a) and (35b) are two canonical forms of a cyanine dye; they are equal in energy, thus resonance theory suggests that these should absorb at particularly long wavelength. Such chromogens are generally the

most bathochromic of all organic n → π* chromogens for a given molecular size:



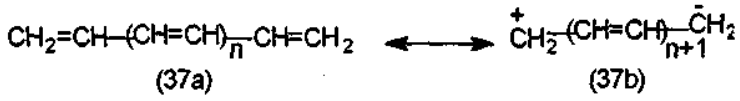
(35a) (35b)

The merocyanines (36) have none equivalent extreme forms (36a) and (36b), they are predicted to absorb at shorter wavelengths than the cyanines of equivalent chain length. The merocyanines and related chromogens have a ground state structure corresponding more closely to the neutral form and thus show some degree of double-single bond alteration along their conjugated systems.



(36a) (36b)

The hydrocarbon polyenes on the other hand represent an extreme situation where one canonical form (37a) is much lower than the charge separated form (37b) in energy. These are thus relatively hypsochromic chromogen.



(37a) (37b)

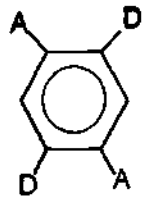
All general qualitative treatments of color and constitution recognise the fundamental significance of the transition of a chromogen from the ideal

so called polymethine state (35) to the polyene state as in (37) although some place greater stress on this than others.

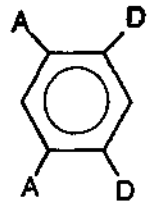
When several low energy resonance forms for a molecule are possible, it is generally assumed that the greater the number of these, the more bathochromic will be the molecule. However, the main weakness of resonance theory lies in the assumption that only a few low energy canonical forms contribute to the hybrid molecular structure. It has been found out that various high energy forms may make an important contribution to the excited state of a molecule, neglect of this can lead to the prediction of high energy absorption bands where infact low energy transition exist.

Some of the exceptions to the above rule predicted by resonance theory is given in (22) to (25) above. It is observed that the relative order of λ_{max} values for these systems will be (22) < (23) < 24) < (25). The reverse order is predicted by the resonance theory. The ionized dihydroxyazo benzene derivatives (20) and (21), provide other examples of such systems.

Other exception can be seen in the case of benzene derivatives bearing one donor and one acceptor group, as in (38) and (39), the *meta* isomer in most cases absorbs at longer wavelength than the *para* isomer, the resonance theory predicts otherwise.

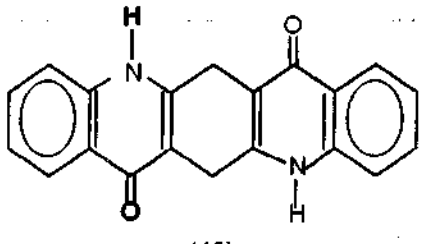


(38)

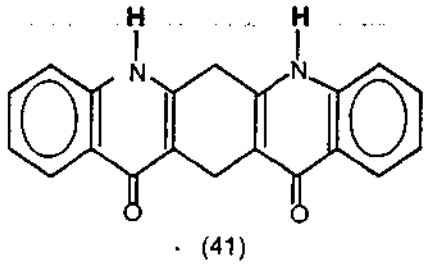


(39)

Similarly, quinacridone (40) is red violet, whereas its isomer (41) is only yellow in color.



(40)



(41)

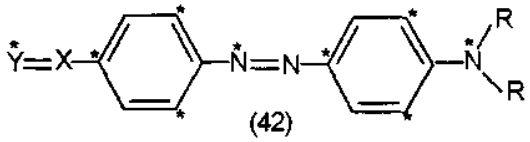
Resonance theory is of considerable value in helping one to understand the color and constitution behaviour of cyanine type chromogens because of its conceptual simplicity. However, this approach cannot be extended with any confidence to other more complex types of chromogens.

1.4.3 Perturbational Molecular Orbital Theory (PMO)

This method considers the electronic structure of a complex molecule to arise by the modification or perturbation of a simpler model compound[25]. Such a perturbation might result from the attachment of substituents to the model structure or the replacement of a carbon atom in the molecular frame

work by a heteroatom. By focussing attention on the highest unoccupied molecular orbital (HUMO) and the lowest unoccupied molecular orbital (LUMO), Dewar[26] was able to draw up a set of rules for predicting the effect of structural changes on the color of alternant molecules.

An alternant molecule is defined as one that contains a system of overlapping atomic p-orbitals such that the contributing atoms are linked to form open chains or even numbered rings. If the contributing atoms are indexed by starring every alternate atom, it is found that in such systems no two adjacent atoms will carry the same index. Starring is initiated at any of the terminal positions of the π-electron system and it is found that all odd alternants have at least one more starred atom than there are unstarred atoms. The following scheme can be used to explain the starring in the Dewar's analysis.



(42)

Y=X- represent typical electron acceptor group such as $-NO_2$, -CN, -CHO etc.

Generally, slight modification as summarised below have been made to the general rule:

(i) Alteration of the electronegativity of an atom in an even numbered alternant system has only a small effect on the wavelength of the first absorption band.

For odd numbered alternants the following rules apply:

(ii) Replacing a carbon atom at a starred position by a more electronegative heteroatom will cause a hypsochromic shift of the first absorption band whereas similar replacement at an unstarred position will cause a bathochromic shift.

(iii) Attaching electron donating substituents (+M, + I) to a starred position will cause a bathochromic shift of the first absorption band, attaching them to an unstarred position will cause hypsochromic shift. The reverse is true of electron withdrawing substituents (-M, -I).

(iv) Attachment of a neutral conjugating specie (± M) i.e phenyl, vinyl to any position in the chromogen will result in a bathochromic shift.

So many examples can be given to confirm the rules, but still some limitations to the rules have been found out. One of the problems concerns what is meant by an electron donating or withdrawing groups. For some substituents both characteristics are observed depending on their particular

relationship to the reaction centre in a given molecule. The methoxy group ($-OCH_3$) for example shows typical donor properties when in the *para* position of a phenyl ring and in this case the (+M) effect of the group is dominant. In contrast, the same substituent in the *meta* position of a phenyl ring is weak electron acceptor and in such case the (-I) effect is dominant. Many substituents have similar opposed inductive and mesomeric effects (e.g –OH, $-NH_2$, -F, -Cl).

Dewar's rules are based on the orbital pairing properties peculiar to alternant hydrocarbons and as long as heteroatomic dye structures bear a close similarity to such compounds, the rules should work well.

However, there is evidence that in more complex systems containing several heteroatoms and exhibiting some polyene character, the anology between such systems and iso-π-electronic odd alternant hydrocarbon breaks down and the rules are inapplicable e.g the aminoazo benzenes illustrated by (42). Rule (iii) would suggest that attachment of electron donor group e.g Ome, NHAc, Me to the 2-position (formally unstarred) should produce a hypsochromic shift, whereas it is well known that such structural modifications give useful bathochromic shifts. Conversely, hypsochromic displacements were produced when electron acceptor groups were attached to the same position.

Failure of Dewar's rules also occurs in other systems e.g the anthraquinones and in certain cases, the rules cannot be applied at all, if a chromogen is non alternant system e.g the Indigoid). In such cases, the starring procedure breaks down.

1.4.4 The Triad Theory of Dahne

Dahne[27] developed some ideas concerning the basic theories of color and constitution in organic chemistry. This theory developed in 1965 is an overall restatement of the well known molecular orbital and electronic properties of alternant hydrocarbon and the extension of these principles to include heteroatomic dye structures and complex donor-acceptor chromogens containing several donor and acceptor groups. He postulated that there are three ideal states for unsaturated compounds:

(i) The aromatic state structure. This is believed to have a stabilized electronic structure with equal π-bond orders and equal π-electron densities at all atoms.

(ii) The polyene state. In this system, there is no special resonance stabilisation of the conjugated system and thus there is a high degree of single-double bond alternation.

(iii) Polymethine state: Structures falling under this, correspond to the odd-alternant hydrocarbon anions and cations and also include the even alternant polyene radical anions and cations, such system possess a high resonance energy, equal π bond orders and a strongly alternating π-electron density.

Electronic excitation gives a maximum change in π-electron density at all atoms. Dahne's general formula is represented by structure (43).

$$X\!\left(\!-Y\!-\right)_{n-2}\!X^{-} \qquad (N\pm1)\pi$$

Based on this, the following rules are made for predicting color and constitution.

(i) If a polymethine system is perturbed by replacing carbon atom by a heteroatom or attaching a substituent, if the characteristic charge density alternation of the polymethine is preserved, then the first absorption band will be unaffected or displaced slightly to shorter wavelength.

(ii) If modifications such as described alters the characteristic polymethine charge alternation, then, the resultant chromogen will absorb at significantly longer wavelength than the parent system.

(iii) If an alternating or non-alternating polymethine can adopt a more favourable aromatic structure, the chromogen will absorb generally at shorter wavelength than the corresponding unbranched polymethine chromogen.

(iv) The gradual transition from an ideal polymethine structure to an aromatic or polyene structure results in an increasing hypsochromic shift.[28]

Some criticism of the Dahnes approach to color and constitution theories is that it attempts to interpret the behaviour of all donor-acceptor chromogens within the polymethine concept, as a result, in a few cases lead to the wrong prediction.

1.5 Quantitative Molecular Orbital Methods

The most successful procedures for computing the transition energies and intensities of complex organic molecules are based on the linear combination of atomic orbitals (LCAO) theory. This assumes that the molecular orbitals of a particular structure can be represented as a linear combination of the individual atomic orbitals present in the system. By calculating the energy of each molecular orbital it is then possible to calculate the transition energies for the promotion of an electron from a low

energy orbital to the various high energy unoccupied orbitals. From the LCAO form of the orbitals involved in a transition, it is possible to estimate the absorption intensities.

It is assumed that the σ and π orbitals of an unsaturated molecule can be treated independently and attention is directed to the higher energy set of π-orbital only. Electron repulsion effects are ignored hopefully to be compensated for by suitable choice of empirical parameters. We have various methods under this category, some of the important ones are:

1.5.1 The Free Electron Model (FEMO)

The FEMO method is the simplest molecular orbital calculation procedure and works surprisingly well with polymethine systems because of their high degree of bond uniformity along the molecular axis. The approach restricts attention to the conjugated π-electron systems which are regarded as mainly responsible for the color of dyes.

It is assumed that the electrons are free to move within the conjugated system, based on this, Kuhn[29] showed that the wavelength of the maximum absorption over the first absorption band (λ) is calculated by means of the Schroedinger expression.[30]

$$\lambda_1 = \frac{8mcl^2}{h(n+1)} \quad \ldots\ldots\ldots\ldots \quad (1)$$

and the transition energy is given by:-

$$\Delta E_{n \rightarrow n+1} = \frac{h^2}{8ml^2}(2n+1) \quad \ldots\ldots\ldots (2)$$

where, m = mass of electron, c = velocity of light, h = Plank's constant, n = number of π-electron, l = length of the conjugated chain.

One important source of error identified with this approach is due to its assumption that all bond lengths along the molecular axis are identical which assumes a constant potential energy along the chain, this situation does not hold for polyenes which are known to exhibit strong bond alternations.

Though many refinements of the method have been suggested, these are more of academic than practical value because of ready availability of other far superior methods.

1.5.2 **The Huckel Molecular Method (HMO)**

The Huckel method is based on the assumption that a molecular orbital wave function (w) can be expressed as a linear combination of the component atomic orbital wave functions (ψ).

Thus, for a system of n overlapping p orbital, with each atomic orbital having the wave function ψ_i, w can be written as a linear sum:

$$w = c_1\psi_1 + c_2\psi_2 + + + \quad c_n\psi_n \qquad \ldots\ldots\ldots \quad (3)$$

c's are the mixing coefficients, E, of the molecular orbital is defined by the equation:-

$$H_w = E_w \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Where H = Hamilton operator,

$$E = \int_{-\infty}^{+\infty} \frac{E_nC_n\psi_n + E_nC_n\psi_n dr}{(E_nC_n\psi_n)^2 dt} \qquad \ldots\ldots\ldots (5)$$

Thus the energy of a molecular orbital is expressed in terms of the atomic orbital wave functions.

The HMO model provides the π-orbital energies of a molecule, these energies can be expressed in the general form:

$$E_n = \alpha + X_n\beta \qquad \ldots\ldots\ldots (6)$$

The transition energy for the promotion of one electron from one orbital to the other is given by the energy difference between the two relevant π-orbital energies.

Although the HMO method is more generally applicable than the latter, it suffers from the same major disadvantage, namely that it neglects electronic interaction effects.

The method can however, be refined in various ways and in particular, it can be made self-consistent by carrying out several consecutive calculations on the same molecule, adjusting the parameters at each state to allow for the charge densities and bond orders predicted by the previous calculation. Eventually, convergence is achieved i.e, predicted charge densities and bond orders show no change between two consecutive calculations. Such a procedure has been used to calculate the spectra of a wide range of heteroatomic conjugated molecules including retinal and porphyrins.[31]

1.5.3 The Pariser-Parr-Pople (PPP) Method)

Both the HMO and FEMO methods suffer serious disadvantages especially in the calculation of electronic transition energies and thus can only be used in the prediction of spectra for some few cases. The PPP method takes into account electronic interaction and because it is self-consistent, it is well suited to handle heteroatomic structures.

Since it is also based on the LCAO approach, it assumed that each molecular orbital can be expressed as a linear sum of the individual atomic orbitals. A set of equations are obtained which are similar in general form to the HMO equations, differing only in the energy term α, (Coulomb integral), β, (resonance integral) which include repulsion energies due to the presence of electronic interactions.

Thus, it can be seen that the transition energy for the promotion of a single electron from orbital I to orbital j without reversal of spin (singlet-singlet transition) is given by[32]

$$\Delta E_i \rightarrow j = (E_j - E_i) - \Upsilon_{ij} + 2\delta_{ij} \quad \ldots\ldots (7)$$

E_i and E_j are the eigen values for orbital I and j respectively.

The energy quantity δ_{ij} is the total repulsion energy between the molecular orbital i and j assuming there is one electron each.

Additional advantages of the method over the previous two are that:

(i) The ability to distinguish molecular geometry like the cis-trans isomers

(ii) The ability to distinguish between singlet and triplet states.

The main disadvantage of this method is that it relies on the assumption that the σ and π electrons behave independently of each other and thus, the σ-electron are ignored.

1.5.4 All-Valence-Electron Method

All valence electron MO calculations are based more or less on the same formula as the PPP procedure, but with the major differences that all orbitals involved in bonding i.e. both σ and π electrons are specifically considered. Obviously, the choice of parameters is a greater problem than in π-electrons methods, and in addition, the demands made on computer time are much greater.

Important calculations of spectra is the CNDO/s method designed by Jaffe and Del Bene,[32] this was applied for the polyenes[33] and polyacetylenes,[34] acetylinic, cyanines[35] porphyrins[36] and the aminoazo benzene[36].

1.5.4 Molecules In Molecule Method

Molecules in molecules (MIM) calculations have both quantitative and qualitative applications in color and constitution studies. When MIM and PPP are combined, the procedure is known as configuration analysis.[36]

The MIM procedure was developed by Languet-Higgin and Murrel[37] and is consequently also known as the LHM method.

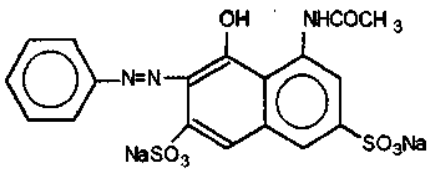
In this method a complex unsaturated molecule is dissected into smaller sub units, the molecular orbital properties of which are known and

the state wave function for the complete molecule are calculated on the basis of these smaller units. For example, a donor-acceptor chromogen is considered to consist of three units, the donor, a single atom with lone pair of electrons; the acceptor, consisting of two atoms linked together by a double bond; and the conjugating bridge, a more complex system of conjugated double bonds. If the units are brought together and still retain their separate identities, then various electronic excitation processes are possible. These may be classed as local excitation, where an electron is promoted from a bonding orbital to an anti-bonding orbital within the same unit, and gives rise to locally excited (LE) configuration. Alternately they can be classed as charge transfer transition, where an electron from the bonding orbital of one unit is promoted to the anti-bonding orbital of a different unit and gives rise to charge transfer (CT) configuration.

To obtain a closer approximation to the true situation, the ground state or no bond (NB) configuration, the LE and CT configuration are considered to interact and the configuration interaction procedure gives rise to state wave function and energies, the former expressed as a linear sum of the NB, CT and LE configurations, which is later retained and simplified in the work of Baba Suzuk and Tekemma[36] where they based their calculations on the PPP-CI method on the concept of delocalized molecular orbitals.

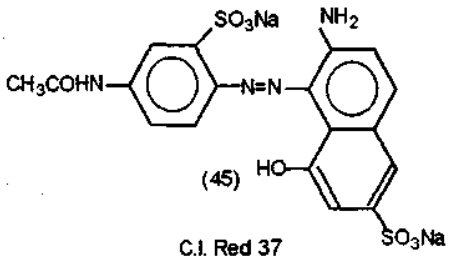
1.6 **Acid Dyes**

From application point of view acid dyes are classed as either levelling or milling types. The levelling sometimes called equalising dyes have fairly simple chemical structures, migrate readily on wool and are easily applied from strongly acid baths. However, their wet fastness properties are low. These dyes are much influenced by the presence of salts such as sodium sulphate. Some examples of the leveling dyes are:[38]



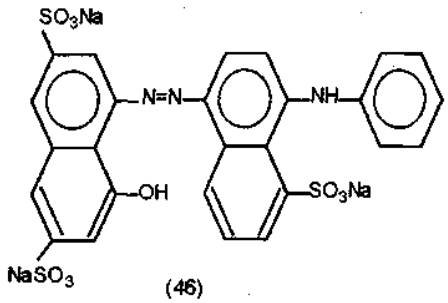
(44)

C.I. Red 1



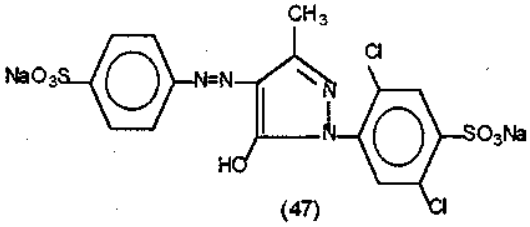
(45)

C.I. Red 37



(46)

C.I. Blue 92

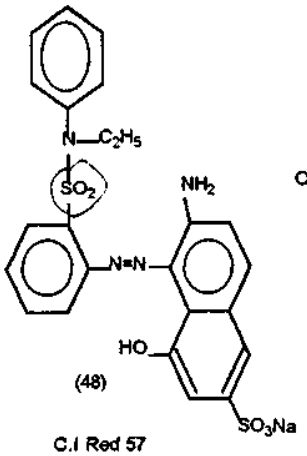


(47)

C.I. Acid Yellow 23

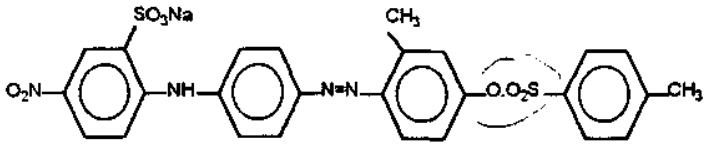
The milling dyes are structurally more complex, have high affinity, form colloidal state in aqueous conditions, medium rate of dyeing and slow migration. These dyes are much faster to wet treatments, perspiration and

milling than levelling dyes. A weak acid, usually formic or acetic acid is used in the dyebath together in some cases, with an auxiliary to control the rate of dyeing.[39] Some of these dyes are shown in structures (48) – (51).



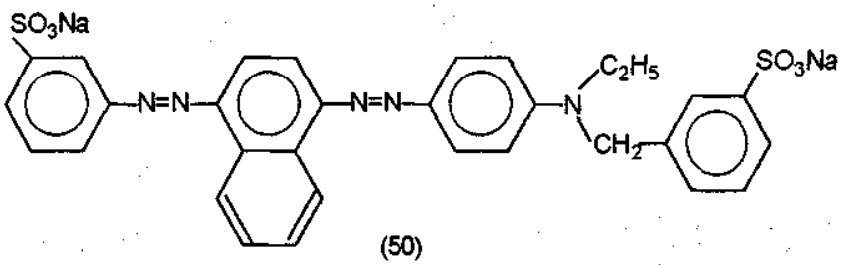
(48)

C.I Red 57



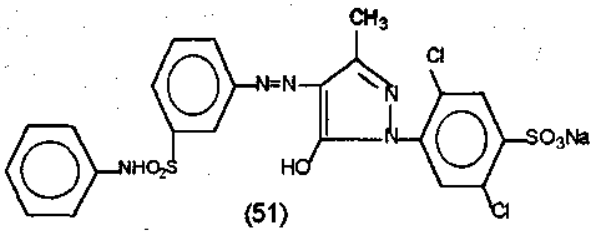
(49)

C.I. Acid Orange 67



(50)

C.I. Acid Red 119



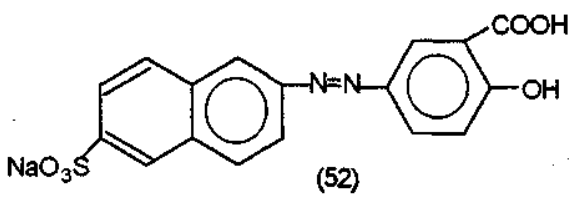
(51)

C.I. Acid Yellow 29

1.6.1 **Mordant Dyes**

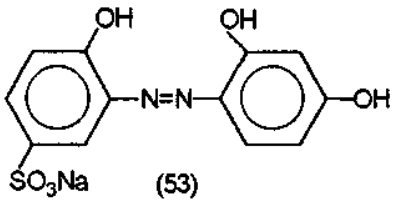
The term mordant dyes which was properly applied to most of the old natural dyes now also covers acid dyes metallised in various ways during the application process and the synthetic polyhydroxyanthraquinone of Alizarine discovered earlier. Mordant dyes as a class still represent some 30% of all dyes for wool on a world-wide basis and can be used at all stages in wool processing.

Nietzki[40] in 1889 is credited with the discovery of an azo dye containing a salicyclic acid residue that could be rendered faster to washing by treatment with a chromium compound. It was not until the beginning of the 20th century that any real progress was made, particularly in the case of dyes containing o,o'-dihydroxy, o-hydroxy-o'-carboxylic acid group, o-amino-o'-hydroxy azo groups and the arylazo pyrazolone dyes. Below are typical examples of mordant dyes:



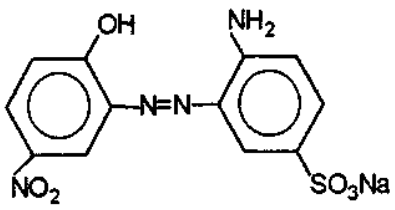
(52)

C.I. Mordant Yellow 3



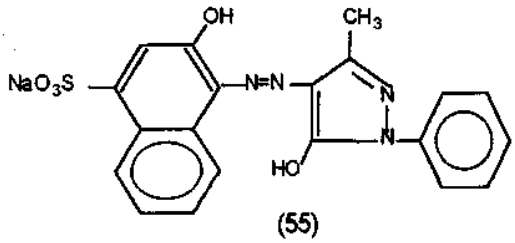
(53)

C.I. Mordant Red 5



(54)

C.I. Mordant Brown 33



(55)

C.I. Mordant Red 7

Three application techniques are used. The on-chrome, after-chrome and the meta chrome methods.

In the on-chrome method, the material is treated initially with a dichromate solution and then with a reducing agent such as formic acid. The material is then treated with the dye solution.

In the after chrome method, the material is dyed in an acid bath until exhausted due regard being taken for the possible need to include auxiliaries to control the rate of dyeing to give levelness. After a slight reduction in temperature, dichromate is added and the temperature raised to the boil until a full shade is developed.

In the meta chrome method, only selected dyes are used. In this method, the dye is applied simultaneously with a chromating agent consisting of a mixture of a chromate with ammonium sulphate. The chromating agent is usually prepared from a dichromate with ammonium sulphate and ammonia. Whereas, dichromates usually cause chromium

derivatives of dyes to be precipitated in the bath, this does not occur with the chromates formed by the action of ammonia. In the boiling dyebath, acid is liberated slowly so that dichromate is formed at a steady rate and the chromium complex is fixed on the fibre. The role of ammonium salts has been studied by Goodall and his collaborators.[41-43]

In all these processes a deepening and dulling of shade occur especially when monoazo dyes are used.

The processes whereby chromium complexes are formed on the fibre were studied by Speakman and his co-workers.[44] They considered the possibility that 1:1 complexes are obtained in which union with the fibre might depend on (I) co-ordinate valencies of chromium (ii) residual cationic valency of chromium and (iii) ionic attraction between sulphonic acid groups in the dye and basic groups in wool fibre. These experiments showed that in at least some dyes a 1:2 complex is formed and they pointed out that in such cases, the co-ordinate valencies of chromium are satisfied within the dye molecule and are therefore not available for combination with the fibre. The larger molecules of 1:2-chromium complexes would result in stronger attachment by van der Waal forces and perhaps also in physical entrapment of dye molecule within the fibre.[45]

1.6.2 **Pre-Metallised Dyes**

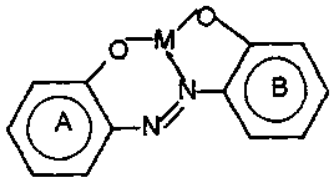
Due to the disadvantages associated with the mordanting methods described above, some of which include; matching difficulty, dullness, selectability for the meta chrome dyes etc, dye chemists synthesized dyes already metallised. There are two types of these dyes:

(i) 1:1 Complexes

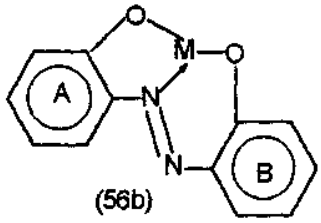
As long ago as the 1912, Bohr succeeded in isolating chromium complexes of dyes containing salicylic acid residues. Seven years later BASF obtain chromium complexes from sulphonated o,o'-dihydroxyazo dyes. Production of the dyes entails heating an o,o'-dihydroxy or an o-hydroxy-o'-carboxylic acid azo derivative in an acid medium with chromium III compounds often under pressure. The 1:1 complex is indicative that one molecule of dye is linked to one atom of the metal. Since the dye molecule occupies only three of the six coordination sites of the chromium atom, the remaining sites are occupied by water molecules or hydroxyl ions. It is possible that the ligands are water molecules in acid or neutral media but their place is taken by hydroxyl ion in alkaline condition.[46-49]

A study of molecular models shows that in complex compounds of trans o.o'-dihydroxyazo structures, the metal atoms (M) can be linked to

only one of the nitrogen atoms, but in unsymmetrical compounds, two isomers are possible which may be represented thus:



(56a)

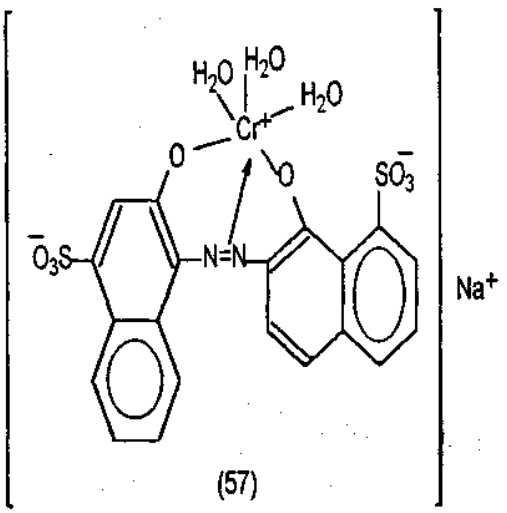


(56b)

However, metal complexes of o-carboxy-o'-hydroazo dyes probably exist in one form only, the nitrogen atom nearer the carboxy substituted ring being linked to the metal atom so that six-membered rings are formed.

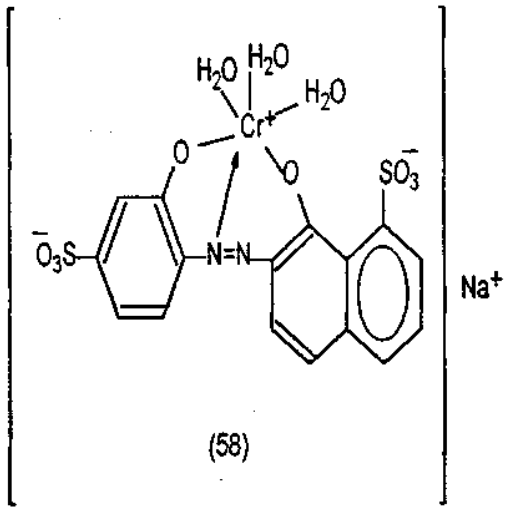
With one or more sulphonic acid groups, these dyes are soluble in water but need to be applied from a 5-8% H_2SO_4 with 10% sodium sulphate to achieve level results.[50]

The dyeing of these dyes gives rather brighter shades than the mordant dyes and there is better provision of the lighter hues. Light fastness is comparable with that of the mordant dyes but there is however, a slight inferiority in washing fastness. As the operation is completed in a single stage, shades can be matched without difficulty. Typical of this class of dyes are shown in structures (57) – (60).



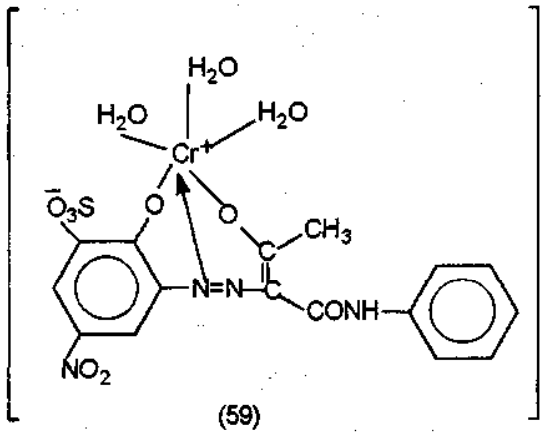
(57)

C.I. Acid Blue 158



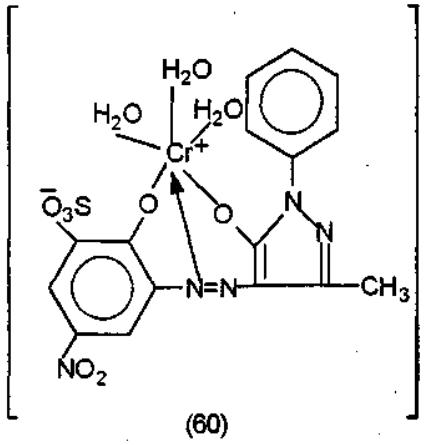
(58)

C.I. Acid Blue 159



(59)

C.I. Yellow 99



(60)

C.I. Acid Orange 74

(ii) 1:2 Complex

The main disadvantage of the 1:1 complex was the requirement for a strongly acidic bath which often resulted in appreciable degradation of wool fibre. This led to a demand for fast dyes suitable for milder application conditions. After an extensive study it was discovered that a 1:1 complex

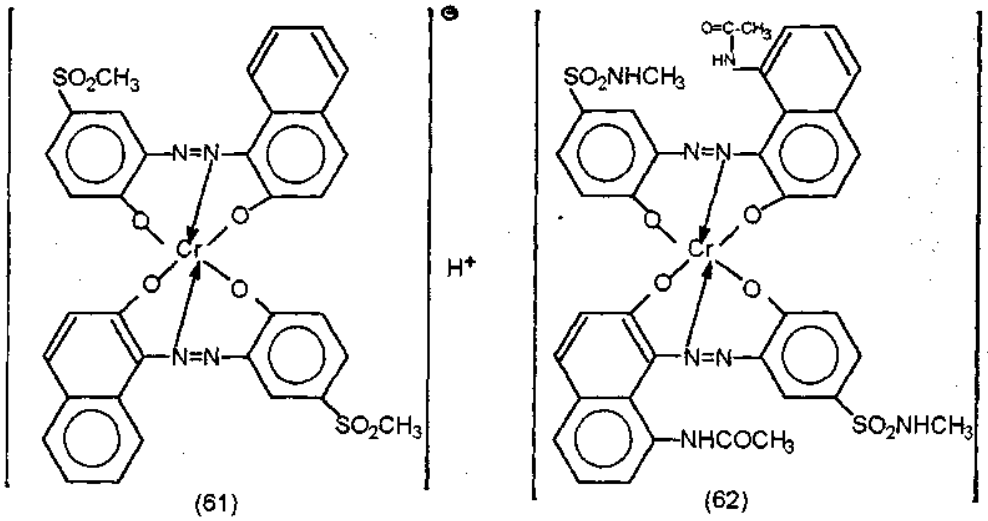
will react in alkaline or weakly acid medium with a second molecule of the same dye to give a complex containing two molecules of dye and one atom of chromium. Drew and Fairbaim[51] provided structures of some of these complexes.

Early products were found to have insufficient solubility to be commercially acceptable other than in a dispersed form. Some of the solubilizing groups used include methyl sulphonyl, sulphonamide, acetylamino. However, sulphonic and carboxylic groups were found to be exceptionally sensitive to natural variations in the fibre, given rather unlevel dyeings.[52-55]

The 1:2 complexes which contain the same dye chromogen are described as symmetrical, but if the 1:1 complex reacts with a molecule of a different dye an unsymmetrical or mixed complex results. The range of available shades can be extended by using such mixed structures. It is also possible to use two dyes of which only one contains a sulphonic acid group and in this way relatively cheap products having good solubility have been obtained which give level dyeings on wool from neutral baths with negligible damage to the fibre.[56]

Other octahedrally coordinating metals may be used in place of chromium but of these only cobalt yields dyes of technical importance. The

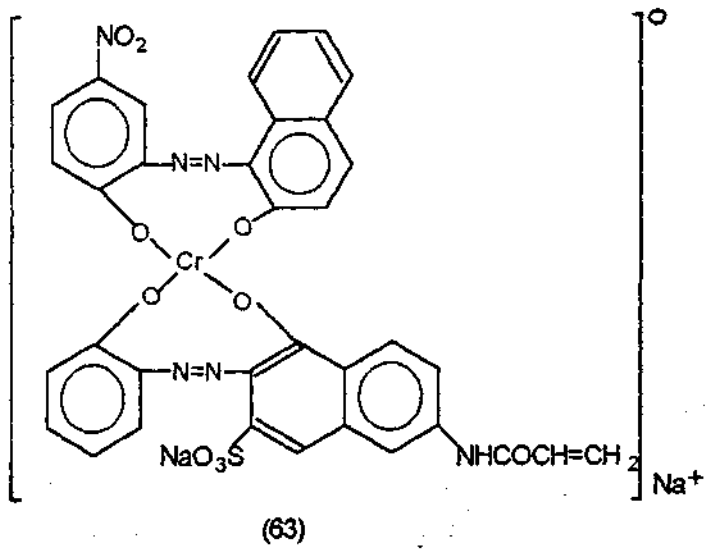
bathochromic effect of cobalt is less than that of chromium in corresponding structures, the cobalt complexes often have somewhat higher light fastness. The general enhancement of light fastness resulting from metallisation of an azo dye may be attributed to stabilisation of the azo group towards electrophilic attack by lone pair withdrawal and the effectiveness of cobalt is due to its high affinity for nitrogen donor ligands. Illucidation of the structural natures of the metal complex dye have been documented.[57-60] Examples of the 1:2 complex are shown with structures (61) and (62).



(61)
C.I. Acid Violet 78

(62)
C.I. Acid black 60

It has been found possible to combine a metal complex dyes with reactive groups to give dyes with extremely good wet and light fastness[61] e.g (63).

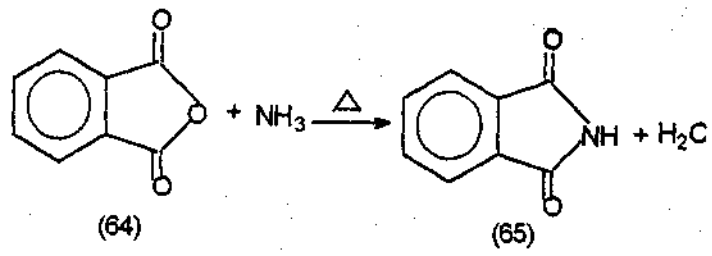


(63)

1.7 Other Metallized Chromogens

1.7.1 Phthalocyanines

This was described as the only chromogen of major commercial importance discovered in the nineteenth centry. It was discovered by accident during the routine manufacture of phthalimide from phthalic anhydride and ammonia, a blue contaminant was found.

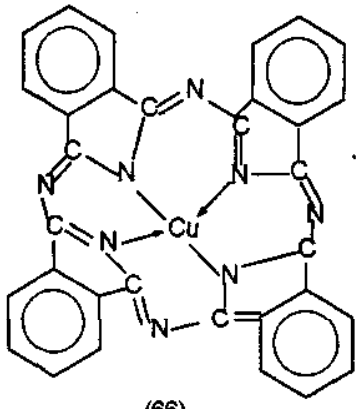


(64) (65)

Dandridge et al[62,63] synthesized the pigment by passing ammonia into molten phthalic anhydride containing iron filings. After removal of alkali-soluble components the product was purified either by vatting or by

fractional precipitation from solution in concentrated sulphuric acid, it gave a blue shade on cotton when applied from a vat. A similar preparation in which iron was replaced by cuprious chloride gave a blue pigment which could not be vatted and another non-vattable product was obtained by using a nickel salt.[64-65]

Linstead represented the copper derivative as (66) and assigned the name phthalocyanine. His structure was soon confirmed by Robertson.[66-69]

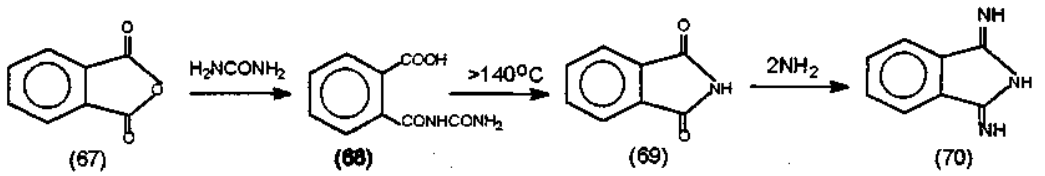


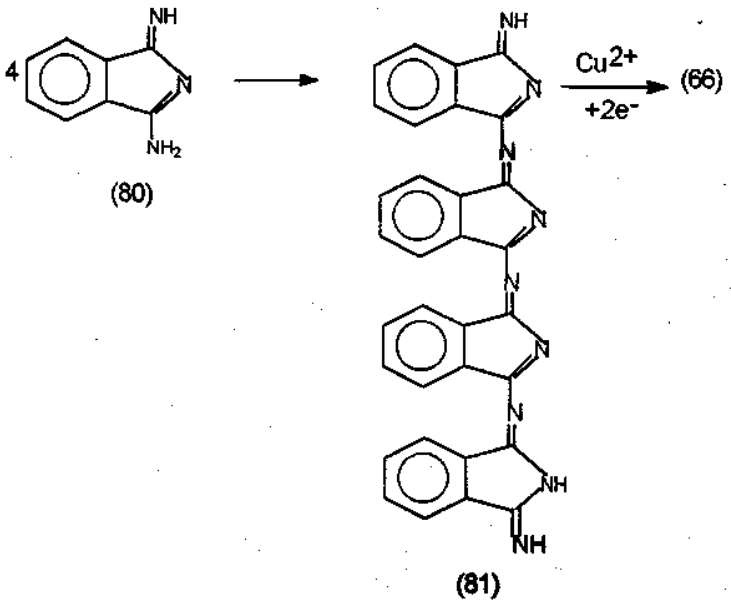
(66)

Linstead found that many metallic phthalocyanine derivatives can be prepared conveniently by heating o-cyanobenzamide with the metal concerned, or its oxide, sulphide or carbonate at a temperature of about 250°C.[70-71] Later phthalonitrile was used, this reacts with copper or its salts at 190-210°C.[72]

The production of the pigment from phthalonitrile required the presence of air or a little cupric chloride.[73]

Wyler found that copper phthalocyanine can be produced by fusing phthalamide or diammonium phthalate with ammonium salt of sulphamic acid in the presence of copper salts.[74] He later used phthalic anhydride, urea and cupric chloride.[75] To improve the yield he used boric acid.[76] Riley later used the catalyst of ammonium molybdate, ammonium phosphate or any element in the Group V or VII.[77] Peterson and co-workers gave the course of the production of copper phthalocyanine from phthalic anhydride and urea as shown below.[78]



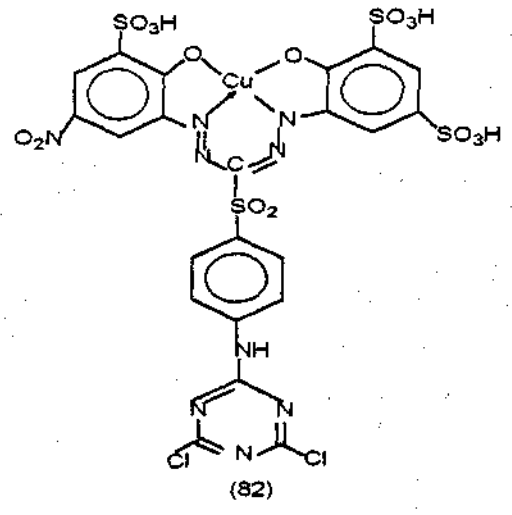


Metal-free phthalocyanine is a bright greenish blue pigment formed by heating phthalonitrile in a heated glass vessel at 350-360°C either alone[79] or with an acid amide, phenol, naphthol or triethanolamine.[80-82] It is also obtained by eliminating metal from phthalocyanine complexes with labile metals such as magnesium or calcium by reaction with a strong acid[83] or even more easily by treatment of disodium phthalocyanine with cold methanol.[84]

Sulphonation of the copper phthalocyanine for application to cellulose, wool and nylon is reported elsewhere.[62] Similarly, temporarily solubilised derivatives of copper phthalocyanine has been produced to be applied to cellulose.[85-87]

1.7.2 **Formazan Dyes**

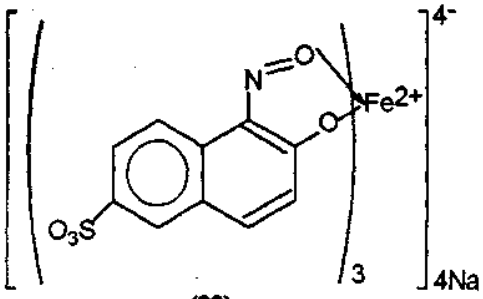
Only the copper complexes of the formazan dyes are considered in this case e.g (82). It is a reactive dyes for cotton.[88-91]



(82)

1.7.3 Nitroso Dyes

The only important metal complex dyes in this series are the sulphonated ferrous sulphate complexes of the 1-nitroso-β-naphthol and the α-naphthol isomer. Pigment Green B is derived from the -β-naphthol. Its other name is C.I. Acid Green 1. It gives yellowish green shades rather lacking in brightness.[92-94] It is used in emulsion paints and also for coloring paper.



(83)

Bello and Griffiths in their attempts to synthesise near infra-red absorbing dyes from the nitroso dyes confirmed that substitution in the naphthol does not alter the absorption wavelength significantly, similarly the extinction coefficient does not change.[94]

1.8 Diffusion and Rate of Dyeing

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motion. This eventually leads to an equalisation of chemical potential and concentration

Throughout the system. Where there is more than one phase, the chemical potential of the diffusant is constant throughout the system once true dynamic equilibrium has been achieved, even though the concentrations in each phase may differ considerably.

The diffusion of dye molecules into a textile fibre is believed to take place in three stages.

(i) Migration of dye through the bulk solution of dyebath to the surface of the fibre.

(ii) The adsorption of the dye molecules onto the surface of the fibre.

(iii) Diffusion of the dye molecule from the surface to the interior of the fibre.

The third stage is the most important in dyeing process since it is the rate determining step. It is the part that is given more prominence in rate of dyeing.

Fick's Laws of Diffusion

Fick was the first person to appreciate the fundamental similarities between mass transfer to heat transfer by conduction concepts.[96] The theory was earlier developed by Fourier[97] to cover quantitative diffusion in an isotropic medium. Fick stated that the rate of transfer of a diffusant through

a section of unit area is proportional to the concentration gradient measured normal to the section.

$$F = -D \frac{dc}{dx} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

F is the rate of transfer per unit area of section. C is the concentration of diffusing substance, x is the space co-ordinate measured normal to the section and D is the diffusion coefficient. dc /dx is the concentration gradient.

Equation (1) otherwise called Fick's first law describes the rate of transfer in a steady state of flow across the section when the concentration gradient is constant. It applies only to an isotropic medium in which the diffusion properties at any point are the same relative to all directions. In an

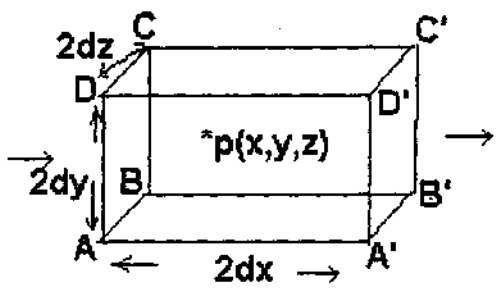


Figure 1

anistropic medium, the diffusion properties depend on the direction in which they are measured.

at p. Similarly, the rate of loss of diffusant through the plane A'B

given by:

$$\text{rate of loss} = 4dydz\left(Fx + \frac{dFx}{dx}.dx\right) \quad \ldots\ldots\ldots (3)$$

equations (3) – (2) gives the rate of increase,

$$\text{rate of increase} = -8dxdydz \frac{dFx}{dx} \quad \ldots\ldots\ldots\ldots (4)$$

Similarly for the other two faces;

$$-8dxdydz \frac{dFy}{dy} \quad \ldots\ldots\ldots\ldots (5)$$

$$- 8dxdydz \frac{dFz}{dz} \quad \ldots\ldots\ldots\ldots (6)$$

However, since the rate at which the diffusant accumulates in the element is also given by:

$$8dxdydz\left(\frac{dc}{dt}\right) \quad \ldots\ldots\ldots (7)$$

It follows that for the three faces,

$$- 8dxdydz\left(\frac{dFx}{dx} + \frac{dFy}{dy} + \frac{dFz}{dz}\right) = - 8dxdydz \quad \ldots\ldots (8)$$

It follows that

$$\frac{dc}{dt} = \frac{dFx}{dx} + \frac{dFy}{dy} + \frac{dFz}{dz} \quad \ldots\ldots\ldots\ldots (9)$$

If the diffusion coefficient D is constant and independent of x, y and z direction and Fx, Fy and Fz given in equation (1), then equation (9) becomes:

$$\frac{dc}{dt} = D\left(\frac{d^2c}{dx^2} + \frac{d^2c}{dy^2} + \frac{d^2c}{dz^2}\right) \quad \ldots\ldots\ldots (10)$$

Limiting (10) to only x-direction it becomes,

$$\frac{c}{dt} = D\frac{d^2c}{dx^2} \qquad \ldots\ldots\ldots\ldots\ldots (11)$$

equation (11) is the expression of Fick's second low of diffusion.

All of the above equations are based on the assumption that the diffusion coefficient is constant. In many real systems however, the value of D depends on the concentration of the diffusant in the fibre. Also when the medium is not homogenous D may be a function of the co-ordinates x, y and z. In such case, equation (10) becomes:

$$\frac{dc}{dt} = \frac{d}{dx}\left(D\frac{dc}{dx}\right) + \frac{d}{dy}\left(D\frac{dc}{dy}\right) + \frac{d}{dz}\left(D\frac{dc}{dz}\right) \qquad \ldots\ldots\ldots (12)$$

Considering the x-direction only equation (12) becomes

$$\frac{dc}{dt} = \frac{d}{dx}\left(D\frac{dc}{dx}\right) \qquad \ldots\ldots\ldots (13)$$

In Carthesian coordinates equation (12) becomes;

$$\frac{dc}{dt} = \frac{D}{r}\left(\frac{d}{dr}r\left(\frac{dc}{dr}\right) + \frac{d^2c}{rd\theta^2} + \frac{rd^2c}{dr^2}\right) \qquad \ldots\ldots (14)$$

r is the radius θ is the direction angle whereas z is the length coordinate.

To solve the differential equations generated, in (14) and (12), it is assumed that the independent variables are separable. In this case the concentration is a function of two functions each of which is a function of only one independent variable.

$$C = X(x)T(t) \quad \ldots\ldots\ldots \quad (15)$$

X(x) and T(t) are functions only of x and t respectively.

$$\left(\frac{dc}{dt}\right)_x = X\frac{dT}{dt} \quad \ldots\ldots\ldots (16)$$

$$\left(\frac{dc}{dy}\right)t = T\frac{dX}{dx} \quad \ldots\ldots\ldots (17)$$

Substituting (16) and (17) into eqution (10)

$$X\frac{dT}{dt} = DT\frac{d2X}{dx^2} \quad \ldots\ldots\ldots (18)$$

$$\frac{1}{T}\frac{dT}{dt} = \frac{D}{X}\frac{dx^2}{d2X} = \qquad -\lambda^2 D \quad \ldots\ldots (19)$$

λ^2 is a constant

Integrating both sides of the equation;

$$T = e^{-\lambda^2 Dt} \quad \ldots\ldots (20)$$

$$X = A\mathrm{Sin}\lambda x + B\cos \lambda x \quad \ldots\ldots (21)$$

Since the diffusion equation is a linear equation, the general solution is the combination of the particular solution. The general solution of equation (10) is therefore;

$$C = \sum_{M=1}^{\infty}(A_m \mathrm{Sin}\lambda_m x_m + B_m \mathrm{Cos}\lambda_m x_m) - e^{-\lambda 2mDt} \quad \ldots\ldots (22)$$

$A_m B_m \lambda_m$ are constants depending on the boundry conditions. When D is dependent only on the concentration, Matano[98] analysed and described by Crank.[99,100]

$$D(c) = -\frac{1dx}{2cdc} \int xdC \quad \ldots\ldots\ldots (23)$$

When the results of experimental measurement correlating either the distribution of dye concentration or the total dye uptake with time of dyeing, the next problem is to evaluate the diffusion coefficient from the data.

An exact analytical solution of the diffusion equation is required in all cases, the diffusion coefficient is assumed to be independent of c, t and x.

The solution is found by evaluating either of two data.

(i) The dye concentration (c) as a function of space co-ordinates

(ii) The dye uptake (M) as a function of time.

As a first approximation, the substrate is assumed to be cylindrical with cylindrical co-ordinates. The dye penetrates from the periphery towards the centre of the cylinder in radial direction. There are two particular solutions obtainable from two particular situations.

- The dye bath is considered as being infinite in which case it is assumed that the dye concentration in the bath stays constant at its initial value during the entire dyeing time, irrespective of the amount of dye absorbed by the substrate.

- The dye bath is considered finite. This is the situation whereby the concentration of the dye is changing. It is however assumed that the dye extracted from the bath equals the amount taken-up by the substrate.

The two situations under which the data can be analysed are:

(i) Steady state condition: here is a situation whereby initially the substrate contains no diffusant, with time the diffusant accumulates until it can take no more after which it is assumed that the amount of dye leaving equals the amount of dye adsorbed.

(ii) Non-steady state condition, here the amount of dye taken up by the substrates keeps changing with time.

1.8.1 **Diffusion in Infinite Bath**

(i) Steady State Condition

Consider diffusion through a plane sheet of thickness L whose surface x = 0 and x = c maintained at constant concentrations c_1 and c_2 respectively. Initially the sheet contains no diffusant, but accumulates and after a time a steady state is reached. At this condition, provided the diffusion coefficient is constant, in equation (11)

$$\frac{d^2c}{dx^2} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (24)$$

On integrating twice with respect to x and introducing the boundary concentration condition at x = 0 and x = L then;

$$\frac{C - C_1}{c_2 - c_1} = \frac{x}{L} \quad \ldots\ldots\ldots\ldots \quad (25)$$

The concentration changes linearly through the sheet and the rate of transfer across one plane in the sheet is the same as the rate of transfer across any other plane, the rate of transfer F is:

$$F = -D\frac{dc}{dx} = D\left(\frac{c_1 - c_2}{L}\right) \quad \ldots\ldots \quad (26)$$

The use of this condition is explained in detail in the literatures.[101-104]

(ii) Non-steady state

During the initial period before m_t against t plot becomes linear, diffusant accumulates in the film under a non-linear concentration gradient. If the contribution to mass transfer through the ends of a filament or through the edges of a film is considered negligible, the dye penetrates the empty filament or film along a non-linear concentration gradient from both sides of the film or from the surface of the filament. When the dye molecules reach the centre of the material the overall concentration gradient begins to decrease owing to accumulation from both sides until finally no measurable gradient exists. The total amount of diffusant taken up in time t is determined by integrating Fick's second equation (11) over the period t = 0 to t = t, for small times. One solution,[105] for diffusion into a film is given by:

$$\frac{m_t}{m_\infty} = 4\left(\frac{Dt}{L^2}\right)^{1/2}\left(\frac{1}{\pi} + 2\sum_{n=0}(-1)^n\right) e^{\frac{nL}{2(Dt)^{1/2}}} \quad \text{..... (27)}$$

m_t = diffusant accumulated after t, m_∞ is the amount accumulated at equilibrium.

Within the limits of experimental error, this graph is linear up to a value of $m_t/m_\infty = ½$ or to larger values when the diffusion coefficient is a function of concentration which increases with increasing concentration.

Vickerstaff[106] approximated bath in the early stages of diffusion which relies on the fact that until the diffustant penetrates to the centre of the substrate, the sheet is considered to be infinitely thick into which diffusion is occuring from one face, he simplified that:

$$\frac{m_t}{m_\infty} = 2\sqrt{\frac{D_t}{\pi}} \qquad \ldots\ldots\ldots (28)$$

A plot of mt/m_∞ against $\sqrt{t}$ should be linear. For moderate and large time Crank[107] simplified the Fick's second law thus:

$$\frac{m_t}{m_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\left(\frac{D(2n+1)_\pi^2 t}{L^2}\right)} \qquad \ldots\ldots\ldots (29)$$

At $t_{1/2}$, or time of half dyeing, where $m_t/m_\infty = ½$, equation (29) is simplified thus;

$$\frac{t\,½}{L^2} = \frac{1}{\pi^2 D}\left[\ln\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^4\right] \qquad \ldots\ldots\ldots (30)$$

Which reduces to;

$$D = 0.04919\, L_2/t_{½} \qquad \ldots\ldots\ldots (31)$$

linear of the graph has been investigated by Frensdorff.[108]

Earlier expressions have been given by Mcbain[109] and Hills has been reduced by Vickerstaff[111] to be of the general form;

$$\frac{Mt}{m_\infty} = 1 - Ae^{-B\beta} - C_e^{E\beta} \quad \ldots\ldots\ldots (33)$$

where $\beta = D_t/r^2$ or D_t/l^2, ABCE are known constants.

Equation (21) was used by Peters[112] to plot a data for a Similarly numerical solutions of the equation for diffusion into a pl immersed in a solution of constant concentration have been Newmann[113] and Crank.[114] Vickerstaff[115] presented the data in form.

1.8.2 **Diffusion in Finite Baths**

If there is only a limited amount of solution, the solute; concentration in the bath will decrease as solute diffuses into the substrate. The sole condition for diffusion evaluations in this case is that the total amount of the diffusant in the system remains constant. The practical implication makes it easy to determine the rate of sorption of the solute by the substrate by measuring the changes in concentration in the solution with time rather than the rate of increase in solute concentration in the substrate. The only source of error is contained by ensuring that loss of diffusant by adsorption on the vessel surfaces or loss by volatisation either of the solute or solvent does not occur.

A method for determining the diffusion coefficient from finite baths under the restriction of the above condition has been given in the form of mathematical solution to Fick's second equatuion by Caman and Haul.[116] If D is constant it has been solved by Wilson[117] for plane sheet and Crak[118] for cylindrical fibre respectively that:

$$\frac{m_t}{m_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1 + \alpha + \alpha^2 q_n^2} e^{-\frac{4Dq_n^2 t}{L^2}} \quad \text{..... (34)}$$

$$\frac{m_t}{m_\infty} = 1 - \Sigma \frac{4\alpha(1+\alpha)}{4 + 4\alpha + 4\alpha^2 q_n^2} e^{-\frac{q_n^2 Dt}{r^2}} \quad \ldots\ldots (35)$$

where α is related to the fractional equilibrium exhaustion E by

$$\alpha = \frac{1 - E}{E} \quad \ldots\ldots (36)$$

q's are the non zero roots of equation (37) $\alpha q_n J_o(q_n) + 2J_1(q_n) = 0$ ... (37)

where $J_o(q_n)$ and $J_1(q_n)$ are the Bessel function of the first kind.[119]

When the rate curves for different percentage exhaustions are plotted using these equations it is found that as exhaustion decreases from 90% to 30%, t ½ increases from about 2 to 60 minutes i.e the rate of dyeing increases with increasing exhaustion.[120]

According to Boulton,[121,122] it is best to compare dyeing rates under conditions of the same percentage exhaustion. The overall dyeing rate is dependent on a wide variety of factors under technical dyeing conditions e.g affinity, liquor ratio, electrolyte concentration, agitation rate, pH, temperature and substrate geometry). In general, rapidly diffusing dyes

show good levelling and penetration and are easily applied, contrary behaviour is shown by slowly diffusing dyes.[121-122]

All of the above systems apply to ideal situations. They all assume that the diffusion coefficient is constant and independent of the concentration of dye in the substrate. In actual dyeing processes there are a number of factors which contribute to a variable diffusion coefficient in addition to those of concentration dependence and affinity of the dye for the substrate. A number of other parameters which may be variable and interrelated also influence the diffusion processes and rates of dyeing, these are assessed as:[123]

(i) Variation in the nature and concentration of ionisable groups both in the dye and in the polymer substrate.

(ii) Interraction between all species present in both phases.

(iii) Changes in physical structure of the substrate and release and formation of stresses together with changes in amorphous or available regions.

(iv) Changes in structure and molecular orientation of the solvent in both main phases and in boundary layers.

A number of approaches have been documented to solve this difficult matter with respect to different dye-substrate systems.[124-144]

1.9 Thermodynamics of Dyeing of Nylon and Wool With Acid Dyes

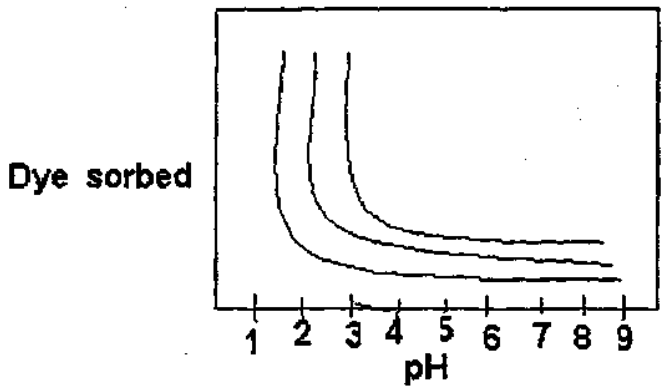
1.9.1 Mechanism of Dyeing Nylon with Acid Dyes

Nylon contains carboxyl and amine end groups which can ionize to produce $-COO^-$ and $-NH_3^+$ ions. In general there is usually a greater number of carboxyl end groups than amine end groups so that some of the carboxyl end groups remain in the unionized form. The fibre also contains weakly basic regularly spaced amide groups along the polymer chain. Though the zwitterion form shown below is a matter of great speculation. Zollinger[145], from a comparative study of the properties of normal nylon 6.6 and of specially prepared polyamide fibres with double number of carboxyl groups concluded that the zwitterion form for nylon is favoured.

$$\overset{+}{N}H_3—Ny—COO^-$$

Marshall[146] on the absorption of simple acids by nylon indicated that the process is equivalent to the back titration of carboxyl groups in the polymer and nylon was regarded as existing in the zwitterion form. Similar observation was made by Daruwalla.[147]

The equilibrium sorption of acid dyes by nylon fibres as a function of pH generally follows curves of the type shown in Figure 2[148] which can be regarded as the titration curves of nylon with anionic dyes.



The titration of nylon with hydrochloric acid[149,150] gives similar sigmoid curve except that the more or less horizontal portion of the curve corresponding to the saturation of amine end groups occurs in a narrow region around pH 3 and is not spread out over a wide range of pH. In most cases, the curve can be divided into three portions. In the first, at high pH values, the carboxyl group will be almost completely ionized and amine end group would begin to lose their protons.

Adsorption of anionic dyes would therefore be small. With decrease in pH the amine end groups will get protonated and dissociation of the carboxyl groups will be gradually supressed. The dye anions sorption therefore gradually increases to a maximum value equivalent to the stoichiometric amine end group content. At lower pH values there is a sharp

increase in dye uptake that is generally attributed to dye adsorption on protonated imido groups. This phenomenon is usually referred to as overdyeing.

It is generally assumed that there is a stoichiometric relationship between the amino end group content and the amount of dye adsorbed.[148,151,152] The dyeing mechanism that emerge from the results of all these studies in the amine dyeing region is that hydrogen ions are adsorbed by carboxyl groups when nylon fibres are immersed in a dyebath containing an acid and an acid dye, while the dye ion attaches itself to positively charged amino groups.

$$\overset{+}{N}H_3\text{—Ny—}COO^- + H^+ \longrightarrow \overset{+}{N}H_3\text{—Ny—}COOH + A^- \longrightarrow \overline{A}\overset{+}{N}H_3\text{-Ny-}COOH$$

Myagkon and Pakshver[153,154] have proposed that a simple ion-exchange equilibrium of the type shown below exists for the polyamide-acid dye system.

$$H\overset{-+}{O}NH_3\text{-Ny-}COOH_{(s)} + \overline{A}_{(aq)} \rightleftharpoons A\text{-}\overset{+}{N}H_3\text{-Ny-}COOH_{(s)} + \overline{OH}_{(aq}$$

Ferrini and Zolliger[155] have observed that adsorption of anionic monoazo dyestuffs on polyamides follows a Langmuir isotherm with a stoichiometric relationship between the dye adsorbed and amino group

concentration, the mechanism of adsorption being a simple ion-exchange process.

However, several other workers have observed that the equilibrium sorption as a function of pH in the amine dyeing region deviates from the stoichiometric relationship between amine end group content and concentration of adsorbed dye.[150,156,152,157] In some cases there is agreement between these quantities only at particular pH values.[157-158] This non-stoichiometric relationship is attributed to the degree of sulphonation and the affinity of the acid dye.

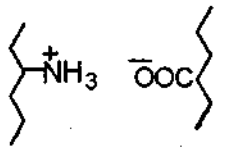
From the aforementioned some researchers are of the opinion that overdyeing need not occur always at low pH, but can occur to a greater or lower extent even at higher pH once the saturation of amino groups has been achieved.[159-161]

Though Remington[152] explained overdyeing at low pH as being due to adsorption on new amine end groups formed by acid hydrolysis of amido group, but O' Brian and Peters[162] showed that the uptake of dye in this region of low pH is considerably in excess of the number of new amine end groups. Bhat and Daruwalla[163] though confirming hydrolysis at low pH, observed that the amount of dye adsorption is considerably in excess of the

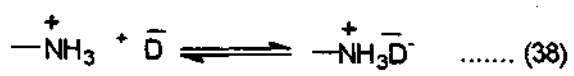
concentration of the new amine end groups formed at all stages of the dyeing process.

1.9.2 Mechanism of Dyeing Wool with Acids Dyes

A wool fibre consists of the protein keratin which is built up by the condensation of about 18 α-amino acids to give long polypeptide chains. Some of the side chains terminate in amino groups and others in carboxyl groups, these basic and acidic side chains being present in approximately chemically equivalent quantities as shown below:



When the amphoteric protein fibre is immersed in an aqueous acid solution, the weak carboxyl groups are back-titrated to –COOH, resulting in the absorption of H^+ ions. The capacity of a protein fibre for acids is equivalent to the free amino group content. In the dyeing of wool with acid dyes, the acid dye anions (D^-) is believed to be attached to the positively charged amino groups.[164]



..... (38)

1.9.3 Affinity Determination of Acid Dyes on Wool and Nylon

$$\frac{[H^+][-COO^-]}{[-COOH]} \cdot \frac{[\quad][\quad]}{[\overset{+}{N}H_3D]} = K_{HD} \quad \ldots\ldots (42)$$

$$K_{HD} = K_H \times K_D \qquad \ldots\ldots (43)$$

If the total number of –COOH and $–COO^-$ groups is c at a hydrogen ion concentration a fraction θ_H will be in the undissociat $(1-\theta_H)$ will be dissociated. Similarly if the total number of $–NH_3$ N^+H_3 group is B at any given anion concentration the fraction of sites occupied by anions can be written as θ_D and the remainder is 1-

$$\frac{[H^+][1-\theta_H]}{\theta_H} \cdot \frac{[D^-][1-\theta_D]}{\theta_D} = K^1H_D \qquad \ldots\ldots (44)$$

If the pH is adjusted such that H_D is 50% ionised, so that $\theta_D = \theta$

that,

$$-\Delta\mu^{\circ}_{HD} = 2.303RT(\log[D^{-}] - pH) - 2.303RT\log \frac{\theta_H}{(1-\theta_H)} \cdot \frac{\theta_D}{(1-\theta_D}$$

Equation (41) to (49) assumes that the acid dye is monobasi

the dye anion carries z negative charges equation (49) becomes,

$$-\Delta\mu_{H2D} = RTIn[H^{+}]^2[D^{2-1}] + (2+1)RTIn \frac{\theta}{1-\theta} - RTIn \frac{z-\theta}{1-\theta}$$

Gilbert and Rideal assumes that C = B which means that $\theta_H = \theta$

Equation (49) becomes,

$$-\Delta\mu^{\circ} = 2.303RT(\log[D^{-}] - pH) - 2.303RT\log\left[\frac{\theta}{1-\theta}\right]^2 \quad \ldots\ldots$$

This approach is used to estimate the affinity of acid dyes on wool.[165-166]

(ii) **Displacement Method**

Gilbert[164] also devised a method of comparing the affinity of dye anions with that of chloride or sulphate ions by finding how much dye is displaced by given concentration of sodium chloride or sodium sulphate. He assumed the amount of sodium ions taken up by the fibre to be negligible in comparison with that of the hydrogen ions and assumed further that the number of basic and acidic sites in wool is the same, hence,

$$\theta_H = y\theta_y + 2\theta_D \qquad \ldots\ldots\ldots (52)$$

θ_y is the fraction of sites occupied by anions of the added salt each having y negative charges and occupying y sites.

The affinity of the dye anion is;

$$-\Delta\mu^{\circ}_D = RT\ln \frac{\theta_D}{1-2\theta_D - y\theta_y} - RT\ln[D]_i + 2\psi F \qquad \ldots\ldots (53)$$

whilst that of the salt anion is;

$$-\Delta\mu^{\circ}_y = RT\ln \frac{\theta_y}{1-2\theta_D - y\theta_y} - RT\ln[Y]_i + y\psi F \qquad \ldots\ldots\ldots (54)$$

By eliminating ψF,

$$-y\Delta\mu^{\circ}_{D} + 2\Delta\mu^{\circ}_{y} = RTIn\left(\frac{\theta_D}{1-2\theta_D - y\theta_y}\right)^{y}\left(\frac{1-2\theta_D - y\theta_y}{\theta_y}\right)^{z} - RTIn\frac{[D]_i}{[Y]_i} \quad \ldots (55)$$

assuming that $1-2\theta_D - y\theta_y = 1 - \theta_H$, therefore,

$$-(y\Delta\mu^{\circ}_{D} - 2\Delta\mu^{\circ}_{y}) = RTIn\left(\frac{\theta_D}{1-\theta_H}\right)^{y}\left(\frac{1-\theta_y}{\theta_y}\right)^{z} - RTIn\frac{[D]_i}{[Y]_I} \quad \ldots (56)$$

Lemin and Vickerstaff[165] pointed out that if a monovalent salt is chosen for a monosulphonic acid dyes, a divalent salt for disulphonic dyes etc i.e y = z, equation (56) becomes,

$$-(\Delta\mu^{\circ}_{D} - \Delta\mu^{\circ}_{y}) = RTIn\frac{\theta_D}{\theta_y}\frac{[Y]_i}{[D]_i} \quad \ldots\ldots (57)$$

if dyeing is carried out at low pH, $\theta_H = 1$, and equation (57) becomes,

$$-(\Delta\mu^{\circ}_{D} - \Delta\mu^{\circ}_{y}) = RTIn\frac{\theta_D}{1-\theta_D}\frac{[Y]_i}{[D]_I} \quad \ldots\ldots (58)$$

Mcgrew and Schneider[167] applied the same analysis for nylon. Allenton et al.[168] used a different approach to estimate affinities of acid dyes in nylon.

They derived by using statistical thermodynamic argument that

$$-(\Delta\mu^{\circ}_{D} - \Delta\mu^{\circ}_{y}) = RT\ln \frac{\theta_D}{1-\theta_D} \frac{[D]_i}{[Y]_i} - RT\ln z/y \quad \ldots\ldots (59)$$

The acid dyes have the formular Na_2D, whereas the desorbing salts has a charge of y.

Earlier, Remington et al.[152] generalized the Gilbert-Rideal equations and used it for nylon as follows:

$$-\Delta\mu^{\circ}_{HD} = RT\ln \frac{[H]_o}{C-[H]_o} \cdot \frac{[D]_o}{B-[D]_o} - RT\ln[H]_i[D]_I \quad \ldots\ldots (60)$$

Where C = total carboxyl content, -COOH + $-COO^-$

B = amine group in the nylon

$[H]_o$ = concentration of carboxyl group in –COOH

$[D]_o$ = concentration of the dye in solution.

They assume that because equal amount of dye anion and hydrogen ion are absorbed.

$$C - [H]_o = B - [D]_o \quad \ldots\ldots (61)$$

$$-\Delta\mu^{\circ}_{HD} = RT\ln k \quad \ldots\ldots (62)$$

$$\text{where } k = \frac{[D]_o(C - B + [D]_o)}{(B - [D]_o)^2[H]_i[D]_I} \quad \ldots\ldots (63)$$

if C – B = x, and rearranging equation (63)

$$r = \left(\frac{[D]_o([D]_o + x)}{[H]_i[D]_f}\right)^{1/2} = B\sqrt{K} - [D]_o\sqrt{K} \quad \ldots\ldots (64)$$

By plotting r against $[D]_o$, a straight line graph is obtained from where the slope gives $\sqrt{K}$ and the intercept given $B\sqrt{K}$ from which the affinity and maximum dye uptake is calculated.

A more direct method of finding the affinity of acid dyes on wool and polyamides is the one of the formula.[169]

$$\Delta\mu = -RTIn \frac{[D]_f}{v[D]_s} \quad \ldots\ldots (65)$$

where v is the volume of internal phase of fibre.

CHAPTER 2

2.0 Effects of Acetylation on Color and Fading of Some Azo Dyes on Wool and Nylon 6.6 Fabrics

2.1 Introduction

Light and weather fastness are important factors in the determination of the useful life span of textiles. Light may produce two different changes in dyed fibrous materials. On the one hand the color can fade, on the other hand photochemical degradation of the fibrous material can take place. Many works have been done in the understanding of photochemical mechanisms.[170-174] Similarly the photo-chemistry of dyes both in solution and on textile and other substrates has been actively studied.[175-181]

It is well known that certain yellow and orange vat dyes sensitise the photo degradation of cellulosic fibres such as cotton, while acid metal-complex dyes serve to protect nylon fibres.[182-183] Baumann[184] concluded from experimental results obtained from amino acids that certain reactive dyes linked to the side chain slow down the photo degradation of wool while they promote reaction when attached to the principal polypeptide chain.

It has also been reported that acetylation of free amino groups of some dyes lead to an improvement in the light fastness to such an extent as much

as 3-4 units on wool fabric[185] and it has been proved that both $-NH_2$ and –OH groups are the source of furgitiveness of the dyes containing them.[178-179] It was therefore considered of interest to study the effects of acetylating only the free amino group contained in acid dyes derived from H-acid to study the effects on fading behaviours of the resulting dyes on wool and nylon 6.6. The –OH group is left intact.

2.2 RESULTS AND DISCUSSIONS

2.2.1 Synthesis of the Intermediates and Dyes

Commercial grade of the sodium salt of H-acid was used. Acetylation of the H-acid was carried out with acetic anhydride as the acetylation agent. After the reaction was completed, soda ash was added to hydrolyse off any acetyl group that may have substituted the hydrogen atom in the hydroxyl group of the H-acid.

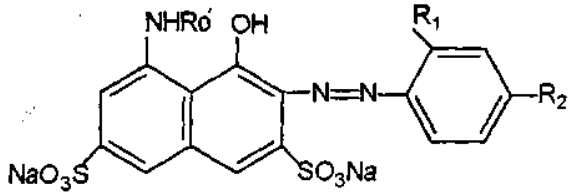


Figure 1

Table 1: Substituents R_o, R_1 and R_2

Dye No	Substitutents			Molecular weight
	R_o	R_1	R_2	
1	-H	-H	-COOH	511
2	$-COCH_3$	-H	-COOH	553
3	-H	-CN	$-NO_2$	537
4	$-COCH_3$	-CN	$-NO_2$	579
5	-H	-Cl	$-NO_2$	546
6	$-COCH_3$	-Cl	$-NO_2$	589
7	-H	-Cl	$-SO_2CH_3$	580
8	$-COCH_3$	-Cl	$-SO_2CH_3$	622
9	-H	$-NO_2$	-Cl	547
10	$-COCH_3$	$-NO_2$	-Cl	589

The acetylated H-acid and the unacetylated one, in each case was coupled to diazo salts of p-aminobenzoic acid, 2-chloro-4-nitro aniline, 2-nitro-4-chloroaniline, 2-cyano-4-nitro aniline and 2-chloro-4-methylsulphoneaniline. Dyes of the general formula 1 are produced. The impure dyes were recrystalized from ethanol-water mixture and their purity controlled by TLC.

2.2.2 **UV-Visible Spectrometric Properties of the Dyes**

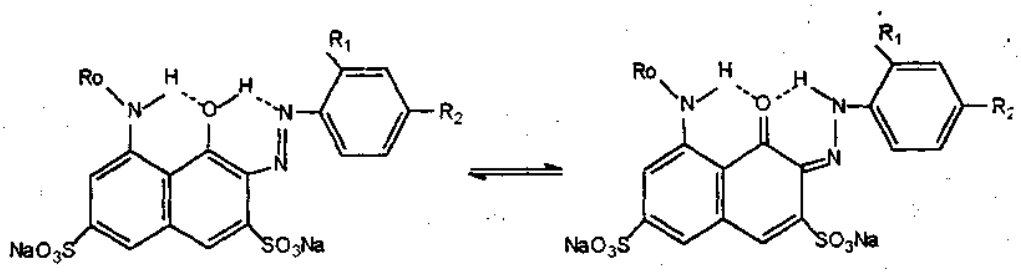
Visible spectra of the dyes were obtained with a Specord uv-vis-spectrophotometer using water solutions at concentrations of 1 x 10^{-4} – 10^{-5} mol/l. The extinction coefficient was also determined in aqueous solution. The result is shown in Table 2.

Table 2: Visible absorption Properties of the Dyes

Dye No	λ_{max} (nm)	$\varepsilon \times 10^4$ l $mol^{-1}cm^{-1}$	$\Delta\lambda^*$	$\Delta\varepsilon^* \times 10^4$ $lmol^{-1}cm^{-1}$
1	539	2.39	29	0.54
2	510	1.85		
3	569	1.55	70	0.29
4	499	1.26		
5	557	1.72	42	- 0.13
6	515	1.85		
7	537	2.06	06	0.00
8	531	2.06		
9	541	1.37	46	0.20
10	495	1.17		

*$\Delta\lambda$ = [λ_{max} unacetylated - λ_{max} acetylated]; $\Delta\varepsilon$ = (ε unacetylated - ε acetylated)

The dyes exhibit azo-hydrazone tautomerism because of the presence of the azo linkage close to the hydroxyl molecule, this is explained in Scheme 1, below:



Scheme 2.1: Azo-hydrazone tautomer

It can be seen that the electron withdrawal tendency of an amido group will increase the intramolecular hydrogen bonding between the hydrogen atom attached to the nitrogen atom bearing the amido group and the central oxygen atom. Consequently, the intra molecular association will increase at the expense of the inter molecular interactions. With this in mind it can be argued that the dominant form is the hydrazone form. That is the acetylated dye will have more ratio in favor of the hydrazone form.

The visible absorption property of the dyes was measured in water and the molar absorption coefficient calculated in the same solvent. The results obtained are summarised in Table 2. The dyes are classified as donor-acceptor chromogen in which the phenyl ring is serving as electron acceptor half and the naphthalene ring is acting as the electron donating half of the chromogen. Dye (1) contains a carboxylic group as electron withdrawing substituent in the acceptor half as a result absorbs at 539 nm in water with a molar extinction coefficient of 2.39 x 10^4 l/molcm, however when the electron donating amino group in it is substituted with an acetyl group as in

dye (2) the resulting dye (2) absorbs at 510 nm which is at a shorter wavelength of 29 nm and also a lower molar absorption coefficient of 5.4 x 10^3 $lmol^{-1}cm^{-1}$. These indicated hypsochromic and hypochromic effects respectively.

In dye (3) the carboxylic group in the parent dye (1) has been substituted with a nitro group and an additional electron withdrawing cyano group which is ortho to the azo group, in this case the dye absorbs at relatively longer wavelength which is 569 nm. This is expected since the electron withdrawing strength of the acceptor has increased lowering the ionization potential, and easing the electron transfer between the ground and excited states. Quantitatively a bathochromic shift of 30 nm in relation to dye (1) was recorded. However, a hypochromic effect of 8.4 x 10^3 $lmol^{-1}cm^{-1}$ was suffered. This could be attributed to the crowdness of the two groups in the same moiety. The acetylation of the amino group in dye (3) to give dye (4), suffers a hypsochromic shift of 70 nm and a hypochromic defect of 2.9 x 10^3 $lmol^{-1}$ cm^{-1}. This is consistent with the result obtained when dye (1) is acetylated to give dye (2). The acetyl group is in effect a weaker electron donating group substituted in the electron donor half of the chromogen.

The results obtained with dyes (5) and (6) also follow the same trend with respect of absorbance wavelength but in contrast a hyperchromic shift of 1.3 x 10^3 $lmol^{-1}cm^{-1}$ was achieved. Dye (5) absorbs at 557 nm whereas dye (6) in which the amino group has been acetylated absorbs at 515 nm, showing a hypsochromic shift of 42 nm. In dye (9) and (10), the relative positions of chlorine and nitro groups are interchanged from the positions they occupied in dyes (5) and (6). Comparing the two pair reveals that nitro group in the para position to the azo group gives dyes which are more bathochromic than the corresponding dyes with chloro group in this position. However, explanation for this is given from the possible steric overcrowding which the nitro group in ortho position to the azo group could produce as is the case with dyes (9) and (10) which absorb at shorter wavelength as compared to their counterparts, of course the volume factor of a nitro group is higher than that of a chloro group.[187-191] When compared, dye (5) has a bathochromic shift of 16 nm over dye (9), whereas dye (6) recorded about 20 nm over dye (10). This over crowding explanation is further accentuated when the extinction coefficients are compared. Dye (5) with nitro group at para position to the azo group recorded an extinction coefficient of 1.72 x 10^4 $lmol^{-1}$ cm^{-1} whereas dye (9) where the nitro group at ortho position recorded only 1.37 x 10^4 $lmol^{-1}$ cm^{-1} which is a hypochromic defect of 3.5 x

10^3 $lmol^{-1}$ cm^{-1} over dye (5). Similar hypochromic effect of about 6.8 x 10^3 $lmol^{-1}$ cm^{-1} was suffered. However, the same acetylation effect observed previously still reflects. Dye (9) absorbs at 541 nm while dye (10) absorbs at 495 nm, a hypsochromic effect of 46 nm with a hypochromic effect of 2 x $10^3 lmol^{-1}cm^{-1}$.

When dye (7) and (8) are compared the hypsochromic effect of 6 nm is the smallest. Interestingly, acetylation did not produce any extinction coefficient difference. When this pair is compared to dye (5) and (6), it is observed that $-NO_2$ group proved to be a better electron withdrawing specie than the $-SO_2CH_3$ group with respect to dye (5) compared to dye (7) with a hypsochromic effect of 20 nm. However, when dye (6) and dye (9) are compared a bathochromic effect of 16 nm is recorded, this is rather difficult to explain. However, with respect to extinction coefficients, dyes (7) and (8) produced hyperchromic effect of 3.4 x 10^3 $lmol^{-1}cm^{-1}$ and 2.1 x 10^3 $lmol^{-1}cm^{-1}$ over dyes (5) and (6) respectively.

The results summarised in Table 2 generally show that acetylation of amino group in the azo dyes under study leads to hypsochromic effects when the corresponding pairs of dyes are compared. However, the result on extinction coefficient is not so straight, while three of the pairs produced hypochromic effect, one recorded a hyperchromic effect whereas the

remaining one produced no difference. The observed bathochromic shifts when the electron withdrawing strength is the phenyl moiety was increased confirmed the donor-acceptor disposition claimed for this type of chromogen.

As a result, the hypsochromic effect observed for corresponding pairs is explained as being due to the fact that the strength of the electron donating half of the chromogen has been reduced when an acetyl group replaces a hydrogen atom in the amino group. When the relative strength of the electron withdrawing groups incorporated in the acceptor half of the chromogen is compared, the nitro group para to the azo group influenced a powerful electron withdrawing strength, when a cyano group is ortho to the azo group the most bathochromic dyes in the series is obtained.

It is also observed that dye (1) for which R_1 is a proton is the most hyperchromic dye. Explanation for this may be due to the spatially unrestricted resonance of the lone pair of electron on the 'azo' nitrogen.

2.2.3 Dyeing Fastness Properties

The results of the ISO 3 wash fastness test summarised in Tables 3 and 4 show that all the dyes give dyeing of excellent wet fastness on nylon 6.6 materials, however, the wet fastness ratings obtained with the dyeings of the

dyes on wool are not as good. This is however the general trend for acid dyes on nylon and wool as they have better affinities on nylon. This is attributed to their greater affinity for hydrogen ion. The higher exhaustion recorded by wool as against that of nylon is testimony of the free amine

Table 3: Fastness Properties of the Dyes on Nylon 6.6 fabrics

Dye No	Exhaustion (E) (%)	Wash fastness		Perspiration fastness				Light fastness
		Change in shade	Degree of staining	Alkali		Acid		
				Change in shade	Degree of staining	Change in shade	Degree of staining	
1	52	3	5	4	4	4-5	4-5	2
2	71	4	5	3-4	3	4-5	4	2-3
3	88	2	5	2-3	5	4-5	3	3-4
4	39	4-5	5	4	4-5	3	4	2
5	71	2-3	5	2	4-5	2	4-4	4
6	61	3	5	3-4	5	5	5	2
7	76	3	4	3	4	3	4-5	3
8	68	4	4-5	4	4	2	3-4	2-3
9	67	2-3	5	2-3	3	2-3	4-5	2
10	67	4-5	5	2-3	5	2-3	5	1

contents of wool of about 800 – 900 mmolkg^{-1} as against the 30 – 50 mmolkg^{-1} in nylon.[192-193] It is also seen that for the same pairs, always the acetylated dyes is about 1 higher than the unacetylated dyes. Explanation of this can be deduced from two reasons; in the first reason, acetylation reduces the solubility of the dyes in alkaline solutions, this was investigated by Nichols in detail.[194] The other explanation was due to Giles,[197] and Fern.[196]

Table 4: Fastness Properties of the Dyes on Wool

		Wash fastness		
Dye No	Ehaustion (E) (%)	Change in shade	Degree of staining	Light fastness
1	93	4	5	6
2	97	4-5	5	7
3	98	3	4-5	3
4	96	3-4	5	4
5	99	4	4-5	4
6	99	4-5	4-5	5-6
7	97	4-5	4-5	4
8	94	5	5	6
9	99	3-4	5	6
10	99	3-4	5	7

They all found out that wash fastness of dyes with molecules of the same degree of sulphonation increase with molecular or anionic weight or volume.

The results of the perspiration test also show that both the alkaline and acid perspiration fastness are good on nylon 6.6 materials and it couldn't be determined whether the acetylation has any effect on this fastness property.

The results of light fastness test summarised in Table 4 for wool fabrics clearly show the effects of acetylation on light fastness. When all the dyes are compared, it is seen that acetylated dyes have good resistant to light than the unacetylated dyes. All the dyes that contain free amino group gave reduced light fastness rating. This is much in agreement with earlier works.[195,198-201] Watson observed that fading of azo dyes is due to oxidation of that part of the molecule containing –OH or $–NH_2$ groups. It has long been established that fading of acid dyes on wool is a reductive process.[197] It can be advanced that free amino group in azo dyes increases the surface activity of the molecule and consequently reduces its photostability. The decrease in the photostability of the dye molecule allows the dye molecule to react with surrounding materials such as free oxygen in the air when some form of light is absorbed. In this respect the dye molecule decomposes and looses color.[202]

When the light fastness properties of these dyes are compared with respect to wool and nylon, it is observed that they have better fastness on wool. If it is assumed that mechanism of fading is the same for nylon as in wool, the presence of histidine residue is believed to provide hydrogen, thus retarding reductive fading.[203] Even if fading is oxidative, the presence of many different amino acids in wool as against nylon could provide particular amino acid residue retarding photo oxidation. Another reason for increased light fastness of the dyes on wool rather than nylon can be seen from the percentage exhaustion of dyes on both fabrics. The dyes are generally more exhausted on wool than nylon 6.6 and therefore, the amount of dyes contained by wool fabric in each case, are more, they are more likely to be in a greater aggregated form as a result, light destruction will take place over a very long period before it is noticed on wool because they are present in larger amount than on nylon 6.6.[204]

From the results of light fastness in Table 3, there is no improvement on nylon 6.6 when the dyes are acetylated. This may suggest different mechanism of fading in nylon than in wool. It is well known that resistance of a dye or pigment to chemical or photochemical attack is related to the chemical structure and physical characteristics of the fibre itself.[205]

CHAPTER 3

3.0 Synthesis and Properties of Metal Complex Pigments Derived From 2-Nitroso-1-Naphthol

The study of the nitrosation of phenols and its derivatives and their heavy metal complexes started as long as the year 1902.[232-245] Their naphthols counterparts started even earlier.[92-94] However, it seemed that, the most important complexes studied were the sulphonated derivatives. The main extension carried out in the area was in 1987 by Bello[246] in his attempt to prepare near infra-red absorbing dyes. He found out that the iron II complexes of the dyes did not record any significant change in the wavelength of maximum absorption inspite of substitution within the naphthyl ring system. It was also observed that to a certain extent the extinction coefficient didn't change much.

However, it is not evident of any earlier work done in attempting to use other metallic salts, apart from iron II.

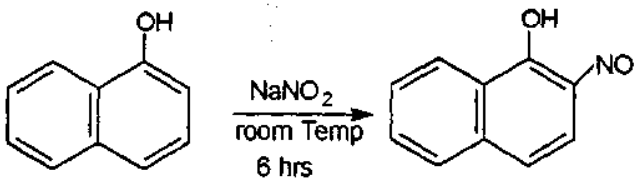
The present work attempted not only to study the preparation or characteristics of the 2-nitroso-1-naphthol and its purified iron II complexes but also other metallic complexes. We also identified two complexes as 1:1 and 1:2. We extended the work by diazotising and coupling aniline and 4-amino benzoic acid to 2-nitroso-1-naphthol under alkaline conditions,

formed the two types of complexes using several metallic salts and characterized them. It is obvious from the yield of the complexes that both the complexes from the free nitroso and the 'azo' derivatives are more reactive than the nitrosophenol described elsewhere.[232-245] There was no need for pyridine catalysis to get quantitative yields.

3.2 Results and Discussions

3.2.1 Synthesis of Pigments and Intermediates

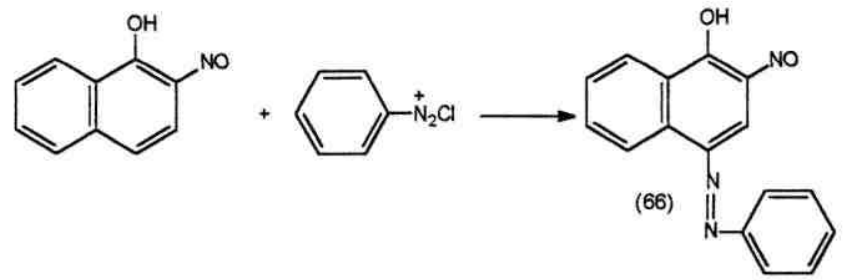
The main intermediate, 2-nitroso-1-naphthol was synthesised from 1-naphthol by direct nitrosation with sodium nitrite at room temperature.

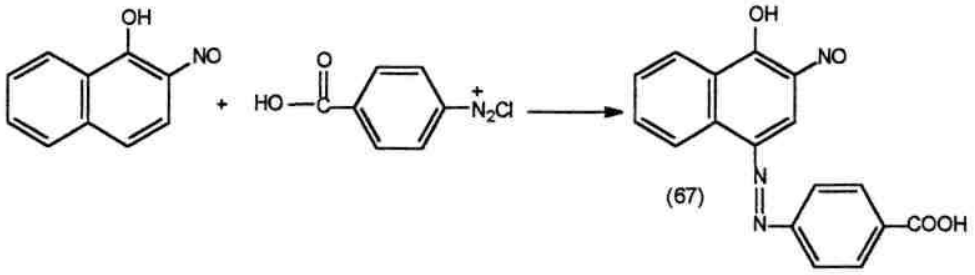


(65)

The yield, melting point and other characterisation data are reported in Chapter 4, Table 4.1

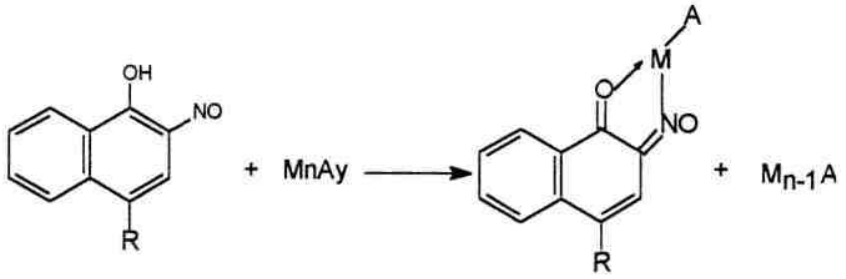
The two azo dyes derivative of 2-nitroso-1-naphthol were synthesized by diazotising aniline and 4-amino benzoic acid and coupling to (65) under alkaline medium as shown below:

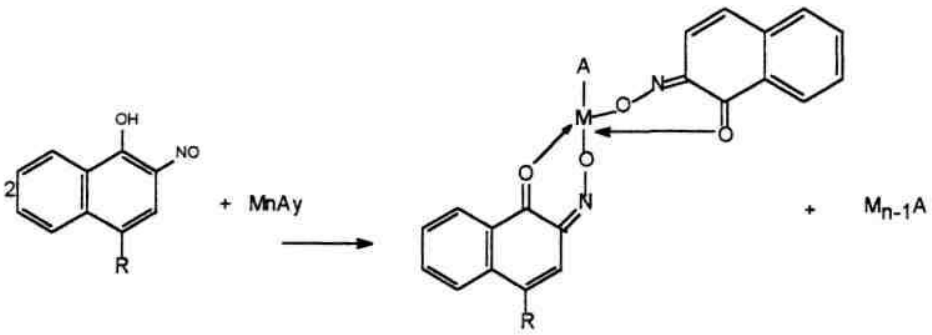




The yield, melting points and characterisation data are reported in Table 4.1

(65), (66) and (67) were treated with nine different metallic salts to produce two sets of complexes in each case as shown below:





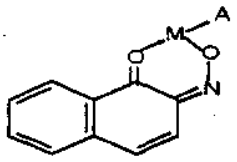
M is the metallic radical whereas A is the acidic radical.

UV-visible, melting point and the yield in grams of the pigments (11) –(64) are reported in Tables 3.1 – 3.6

In contrast to the nitrophenols reported,[224-225] none of the either complexes of the 2-nitroso-1-naphthol could dissolve in water. Neither also are the metallic salts derivatives of the aniline and 4-amino benzoic acid azo pigments. However, all the pigments studied are soluble without exception in DMF and ethanol and majority in toluene. But only a few are actually sparingly soluble in the least polar hexane. Some of the complexes that gave any solubility distinguishing differences with respect to the solvents used are: The 1:1 complex of the parent nitroso $Co(NO_3)_2$ complex is soluble in toluene but its 1:2 complex is not. Similarly, the $Pb(CH_3COO)_2$ 1:1 complex is not soluble in toluene but the 1:2 complex is. The 1:1 complex of $ZnSO_4$ of the same pigment is sparingly soluble in hexane but 1:2 complex is not. Similar observation is made with respect to the $Co(NO_3)_2$ complex in hexane.

All of the diazotised aniline 1:1 and 1:2 complexes are soluble in DMF, ethanol and toluene. However, the $Co(NO_3)_2$, $ZnSO_4$ and $FeCl_3$ 1:1 complexes are only sparingly soluble in hexane, whereas their 1:2 complexes are not.

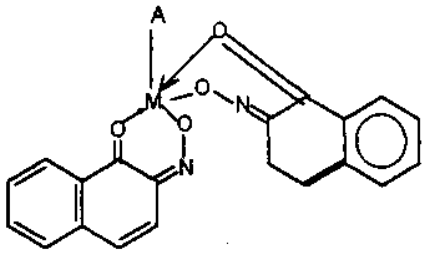
Table 3.1: Yield and Some Properties of 1:1 Complex From 2-Nitroso-1-Naphthol



No	(M)	Yield (crude) (g)	M.pt (°C)	Solubility in:					λ_{max} (nm) in:		
				H_2O	DMF	EtOH	Toluene	Hexane	EtOH	DMF	Formic acid
11	$FeSO_4$	3.34	184	-	+	+	+	-	380 350	360 299	355
12	$CuCl_2$	5.34	164	-	+	+	+	-	390 310	369 295	350
13	MCl_2	3.62	139	-	+	+	+	-	372	342 292	355 291
14	$Co(NO_3)_2$	7.96	179	-	+	+	+	+ Sp	360	292 370	368
15	$ZnSO_4$	3.70	137	-	+	+	+	+ Sp	380	392 290	343 292
16	$Pb(CH_3COO)_2$	12.41	151	-	+	+	+	-	370	357 296	355 306
17	$MnCl_2$	3.60	182	-	+	+	+	-	367	356 305	360 355
18	$Cr_2(SO_4)_3$	5.82	138	-	+	+	+	-	380	350 291	358 304
19	$FeCl_3$	3.98	180	-	+	+	+	+ Sp	370	357 308	350 290

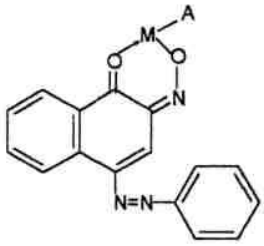
M = Complexing Salt; Sp = Sparingly soluble

Table 3.2: Yield and Some Properties of the 1:2 Complex from 2-nitroso-1-naphthol



No	(M)	Yield (g)	M.pt (°C)	Solubility in:					λ_{max} (nm) in:		
				H_2O	DMF	EtOH	Toluene	Hexane	EtOH	DMF	Formic acid
20	$FeSO_4$	10.14	188	-	+	+	+	-	375	357 301	360
21	$CuCl_2$	9.70	186	-	+	+	+	-	380	357 296	355 293
22	MCl_2	9.70	167	-	+	+	+	-	375	357 301	395 293
23	$Co(NO_3)_2$	9.96	169	-	+	+	+	-	375	377 316	350 295
24	$ZnSO_4$	10.14	182	-	+	+	+	-	388	367 301	350 290
25	$Pb(CH_3COO)_2$	17.00	159	-	+	+	+	-	370	362 301	355 308
26	$MnCl_2$	9.30	174	-	+	+	+	-	380	357 301	355 305
27	$Cr_2(SO_4)_3$	11.10	181	-	+	+	+	-	380	357 301	348 290
28	$FeCl_3$	8.90	172	-	+	+	+	-	380	357 301	355 305

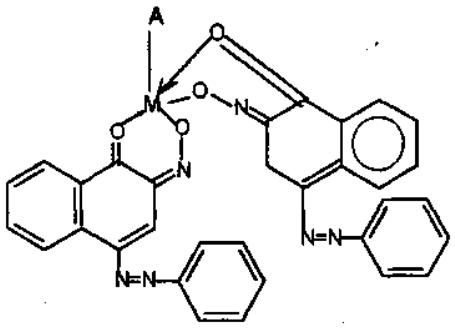
Table 3.3: Yield and Other Properties of Diazotised Aniline derivatives of 2-Nitroso-1-Naphthol 1:1 Premetallized Complex



No	(M)	Yield (g)	M.pt (°C)	Solubility in:					λ_{max} (nm) in:		
				H_2O	DMF	EtOH	Toluene	Hexane	EtOH	DMF	Formic acid
29	$FeSO_4$	1.33	182	-	+	+	+	-	380	381 306	355 300
30	$CuCl_2$	1.06	89	-	+	+	+	-	382	347 291	475 355
31	MCl_2	2.47	164	-	+	+	+	-	360	352 301	360
32	$Co(NO_3)_2$	0.73	157	-	+	+	+	+ Sp	370	357 396	485 355 305 285
33	$ZnSO_4$	1.07	167	-	+	+	+	+ Sp	380	357 300	355 300 290
34	$Pb(CH_3COO)_2$	1.88		-	+	+	+	-	-	-	-
35	$MnCl_2$	1.32	157	-	+	+	+	-	350	352 342	295
36	$Cr_2(SO_4)_3$	1.77	175	-	+	+	+	-	375	357 301	360 259
37	$FeCl_3$	1.33	181	-	+	+	+	+ Sp	384	387 306	355 305

M = Complexing salts; Sp = sparingly soluble

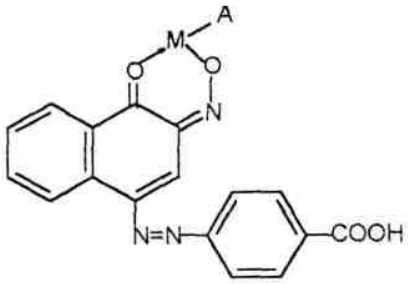
Table 3.4: Yield and other Properties of diazotised aniline derivative of 2-nitroso-1-naphthol 1:2 premetallized complex



No	(M)	Yield (g)	M.pt (°C)	Solubility in:					λ_{max} (nm) in:		
				H_2O	DMF	EtOH	Toluene	Hexane	EtOH	DMF	Formic acid
38	$FeSO_4$	1.88	118	-	+	+	+	-	380	352 295	478 260
39	$CuCl_2$	1.88	114	-	+	+	+	-	370	347 391	264
40	MCl_2	2.10	129	-	+	+	+	-	370	347 296	459 365
41	$Co(NO_3)_2$	1.82	124	-	+	+	+	-	375	357 292	470 355 287 265
42	$ZnSO_4$	1.83	129	-	+	+	+	-	350	352 281	470 355 304
43	$Pb(CH_3COO)_2$	2.42	143	-	+	+	+	-	No	No	-
44	$MnCl_2$	2.07	98	-	+	+	+	-	380	357 281	470 345 300
45	$Cr_2(SO_4)_3$	2.43	167	-	+	+	+	-	380	357 396	358 295
46	$FeCl_3$	1.90	175	-	+	+	+	-	380	357 306	368

M = Complexing salts

Table 3.5: Yield and other properties of diazotised 4-amino benzoic acid derivative of 2-nitroso-1-naphthol 1:1premetallized complex

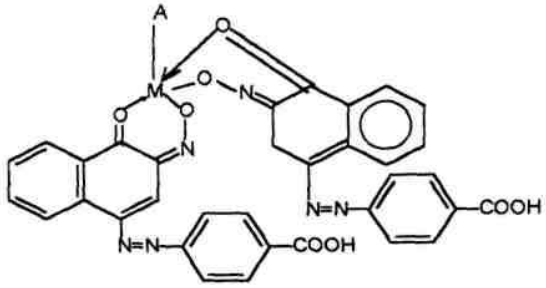


No	(M)	Yield (g)	M.pt (°C)	Solubility in:					λ_{max} (nm) in:		
				H_2O	DMF	EtOH	Toluene	Hexane	EtOH	DMF	Formic acid
47	$FeSO_4$	1.28	190	-	+	+	-	-	322	366 306	365 273
48	$CuCl_2$	1.27	188	-	+	+	+	-	297	352 273	365 275
49	MCl_2	1.24	136	-	+	+	+	-	297	352 293	359 285
50	$Co(NO_3)_2$	1.08	169	-	+	+	-	-	281	357 306	370 369
51	$ZnSO_4$	0.97	137	-	+	+	+	-	-	357 286	350 267
52	$Pb(CH_3COO)_2$	1.65		-	+	+	+	-	355 265	-	-
53	$MnCl_2$	1.06	168	-	+	+	+	-	350 290	347 286	358 288
54	$Cr_2(SO_4)_3$	1.83	139	-	+	+	-	-	298	377 300	376 273
55	$FeCl_3$	1.56	169	-	+	+	+	+	309	-	-

M = Complexing salts

Table 3.6: Yield and other Properties of Diazotised 4-amino benzoic acid

Derivatives of 2-Nitroso-1-Naphthol 1:2 premetallized complexes



No	(M)	Yield (g)	M.pt (°C)	Solubility in:					λ_{max} (nm) in:		
				H_2O	DMF	EtOH	Toluene	Hexane	EtOH	DMF	Formic acid
56	$FeSO_4$	1.83	155	-	+	+	-	-	310	352 298	360 290
57	$CuCl_2$	1.81	168	-	+	+	-	-	292	357 347	375 274
58	MCl_2	1.75	159	-	+	+	-	-	310	252 296	355 268
59	$Co(NO_3)_2$	1.88	167	-	+	+	+	-	307	364 347	359 289
60	$ZnSO_4$	1.89	177	-	+	+	-	-	303	362 357	355 290
61	$Pb(CH_3COO)_2$	2.08	180	-	+	+	+	-	310	357 257	358 289
62	$MnCl_2$	1.90	169	-	+	+	-	-	315	352 296	355 290
63	$Cr_2(SO_4)_3$	2.33	157	-	+	+	+	-	297	349 269	358 288
64	$FeCl_3$	2.27	169	-	+	+	-	+	306	359 300	375 298

M = Complexing salts

All of the diazotised 4-amino benzoic acid 1:1 and 1:2 complexes are soluble in DMF and ethanol. However, the $CuCl_2$ 1:1 complex is soluble in toluene whereas the 1:2 complex is not. Similar observation is made with respect to the $NiCl_2$, $MnCl_2$ and $FeCl_3$ complexes. Conversely is the case of the $Co(NO_3)_2$ complex in which the 1:2 complex is soluble in toluene whereas the 1:1 complex is not. Also the $Cr_2(SO_4)_3$ gave similar converse results. The 1:2 complex is soluble in toluene whereas the 1:1 complex is not. Of all the 4-amino benzoic acid pigments only the $FeCl_3$ complexes are soluble in hexane.

A comparative analysis of the absorbance maxima between the two types of complexes in each pigment system in each of the three solvents run as follows. The pigments recorded at least two distinct absorbance bands in DMF and formic acid.

With respect to the 1:1 complex of the parent 2-nitroso-1-naphthol pigment, there is a hypsochromic shift of about 5 nm in ethanol, 3 nm in DMF and a bathochromic shift of 5 nm in formic acid compared to the 1:2 complex all of $FeSO_4$. The more bathochromic peak chosen where there are two peaks.

When the $CuCl_2$ complexes are compared, in ethanol, there is a hypsochromic shift of 10 nm, 12 nm in DMF and a bathochromic shift of 5 nm in formic acid.

The same observation is seen in all cases with the exception of the $ZnSO_4$ complexes where a bathochromic shift of 8 nm was recorded comparing 1:2 complex against the 1:1 complex. Similarly a bathochromic shift of 25 nm was recorded in DMF with a hypsochromic shift of 7 nm in formic acid. Another notable exception is the $Pb(CH_3COO)_2$ complexes where there is no differences between the absorbance bands of the two types of complexes.

With respect to the diazotised aniline derivatives of 2-nitroso-1-naphthol complexes, it is observed that compared to the 1:1 complexes, there was no difference in absorbance maxima in ethanol for the $FeSO_4$ complexes. Hypsochromic shift of 9 nm was recorded in DMF and a bathochromic shift of 123 nm in formic acid. The $CuCl_2$ complexes suffered a hypsochromic shift of 12 nm in ethanol, no difference in DMF and a hypsochromic shift of about 211 nm in formic acid.

With the $NiCl_2$ complexes, bathochromic shift of 10 nm was recorded in ethanol etc. The same trend is observed with virtually all the remaining complexes. The main observation that is prevalent even for the diazotised 4-

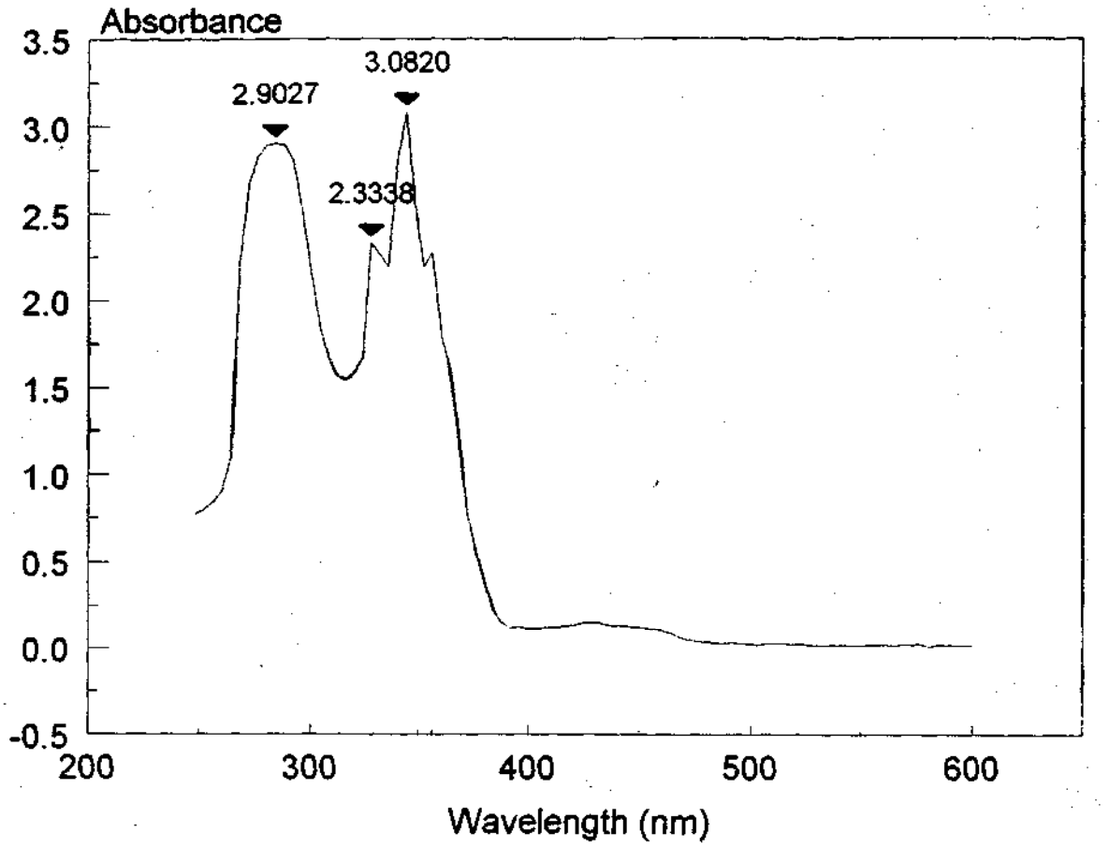
amino benzoic acid derivative is that the absorbance maxima differences is not so conclusive. For all purposes and usage the pigment seem to have the same hue with the only main difference that the 1:1 complexes produce brighter colors compared to the 1:2 complexes. The typical shape and nature of the pigment uv-visible curves in ethanol using a different spectrophotomer is shown in Figure 3.1 and 3.2. Figure 3.1 is the 1:1 $FeCl_3$ complex of the parent 2-nitroso-1-naphthol, whereas Figure 3.2 is the 1:2 complex. It can be observed that there can be observed a subdued absorbance around 400 to 460 nm in both complexes, there are absorbances at 344, 328 and 284 nm but the 1:1 complex gave sharper peaks with the exception of the peak at 284 nm where the 1:2 complex recorded shaper peak. There is also a sharp absorption with respect to the 1:1 complex at 356 nm.

Figure 3.3 is also another typical curve, it is due to diazotised aniline derivative 1:2 $Co(NO_3)_2$ complex. There are sharp absorbances at 356, 350 and 285 nm. The 1:1 complex of the same pigment absorbs also around 285 nm, 360 and 348 nm, the curve is shown in Figure 3.4. The point to note is the sharpness of the peak in the case of the 1:1 complex compared to the 1:2 complex. It is also observed here that there is a subdued absorbance

UNICAM UV-VISIBLE SPECTROMETRY ~ VISION SOFTWARE V3.32

Operator Name	S. T. Diete-Spiff		
Department	Inst. Unit	Date of Report	1/13/99
Organisation	NARICT	Time of Report	11:25:25
Information	Sample4		

Fig. 3.1: uv-visible spectrum of dye 19



Results Table - scan005,Sample001,Cycle01

nm	A	**Peak Pick Results Table Method**
284.00	2.9027	Find 8 Peaks Above -3.0 A
328.00	2.3338	Start Lambda 250.0 nm
344.00	3.0820	Stop Lambda 600.0 nm
		Sort By Wavelength

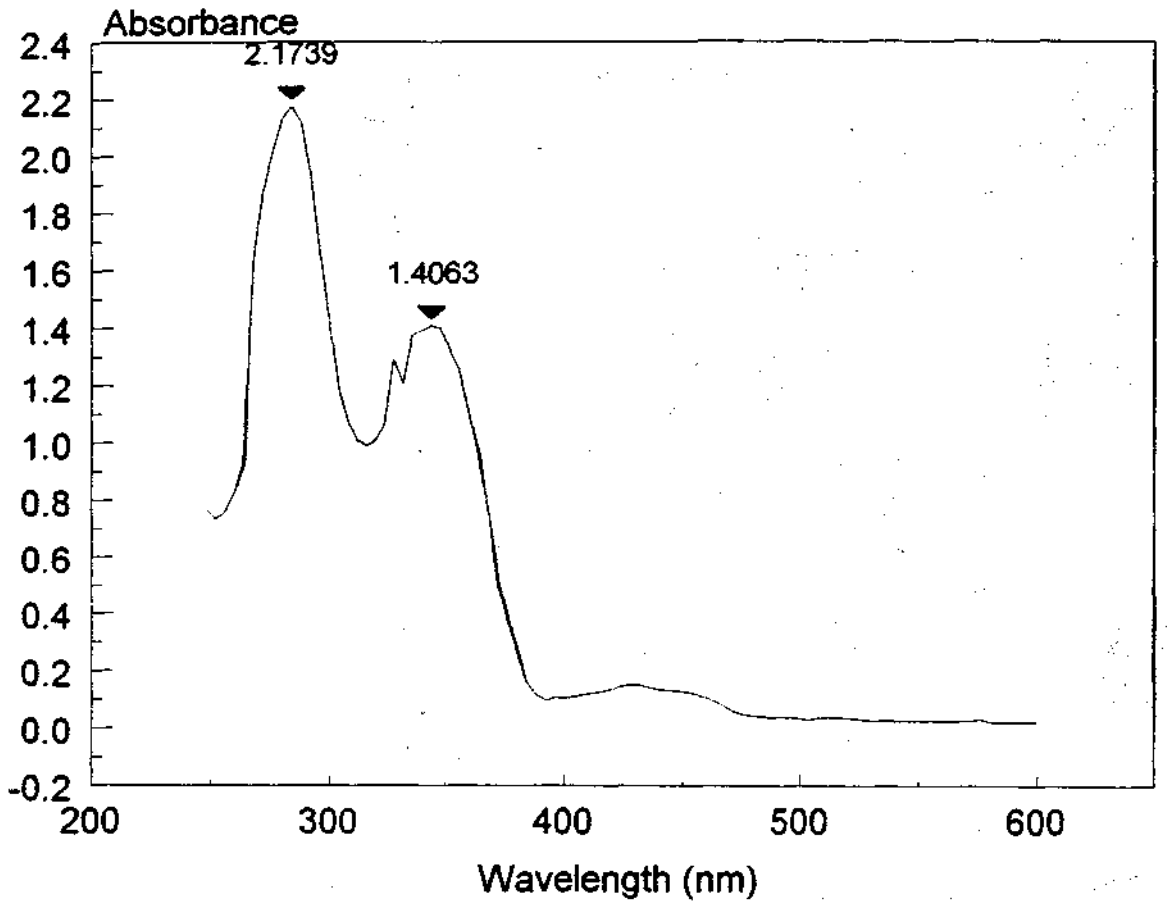
Description	Sample4		
Date Collected	1/13/99	Time Collected	11:23:43
Operator Name	S. T. Diete-Spiff	Instrument ID	051003

Page 1, Scan Graph

UNICAM UV-VISIBLE SPECTROMETRY ~ VISION SOFTWARE V3.32

Operator Name	S. T. Diete-Spiff		
Department	Inst. Unit	Date of Report	1/13/99
Organisation	NARICT	Time of Report	11:20:08
Information	Sample14		

Fig, 3.2: uv-visible spectrum of dye 28



Results Table - scan004,Sample001,Cycle01

nm	A
284.00	2.1739
344.00	1.4063

Peak Pick Results Table Method

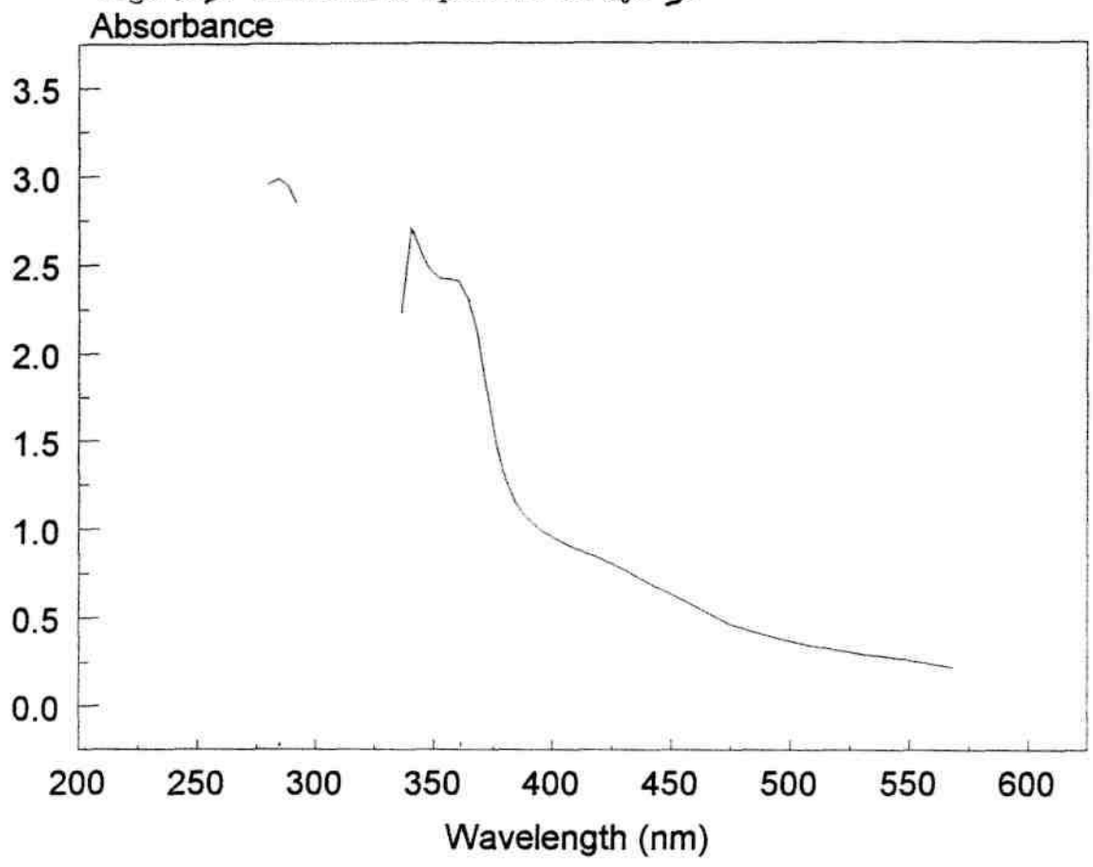
Find 8 Peaks Above -3.0 A
Start Lambda 250.0 nm
Stop Lambda 600.0 nm
Sort By Wavelength

Description	Sample14		
Date Collected	1/13/99	Time Collected	11:18:23
Operator Name	S. T. Diete-Spiff	Instrument ID	051003

UNICAM UV-VISIBLE SPECTROMETRY ~ VISION SOFTWARE V3.32

Operator Name	S. T. Diete-Spiff		
Department	Inst. Unit	Date of Report	1/13/99
Organisation	NARICT	Time of Report	11:06:57
Information	Sample23		

Fig. 3.3: uv-visible spectrum of dye 32



Results Table - scan008,Sample001,Cycle01

nm	A

Peak Pick Results Table Method
Find 8 Peaks Above -3.0 A
Start Lambda 250.0 nm
Stop Lambda 600.0 nm
Sort By Wavelength

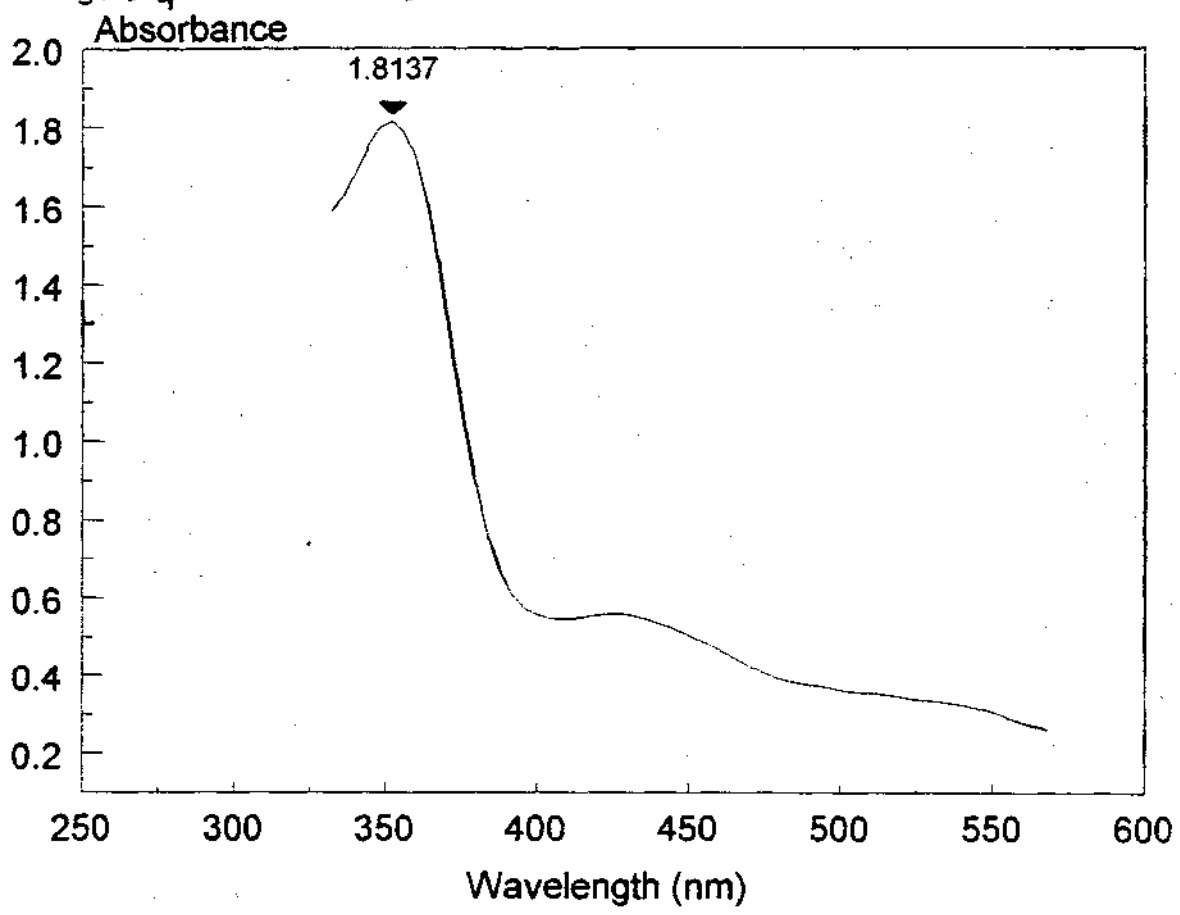
Description	Sample23		
Date Collected	1/13/99	Time Collected	11:04:07
Operator Name	S. T. Diete-Spiff	Instrument ID	051003

Page 1, Scan Graph

UNICAM UV-VISIBLE SPECTROMETRY ~ VISION SOFTWARE V3.32

Operator Name	S. T. Diete-Spiff		
Department	Inst. Unit	Date of Report	1/13/99
Organisation	NARICT	Time of Report	10:58:01
Information	Sample 55		

Fig. 3.4: uv-visible spectrum of dye 59



Results Table - scan006,Sample001,Cycle01

nm	A
352.00	1.8137

Peak Pick Results Table Method
Find 8 Peaks Above -3.0 A
Start Lambda 300.0 nm
Stop Lambda 600.0 nm
Sort By Wavelength

Description	Sample 55		
Date Collected	1/13/99	Time Collected	10:55:54
Operator Name	S. T. Diete-Spiff	Instrument ID	051003

Page 1, Scan Graph

CHAPTER 4

4.0 Synthesis, UV-visible Specoscopy and Dyeing Properties of 2-Nitroso-1-Naphthol, Its Azo Acid Dyes Derivatives and Their Post Metallisation on Wool and Nylon 6.6.

4.1 Introduction

As already mentioned in Chapter 3, success of premetallizability of the nitroso derivative dyes encouraged us to study post-metallizability of the nitroso dyes on wool and nylon 6.6. Another justification for the study is provided from Bello's[206] review on the development of non-carcinogenic dyes. Freeman[207-208] also studied mordant dyes with respect to environmental friendliness. He concluded that iron II and iron III as mordanting salts provided better alternatives to chromium ions as complexing agents even though at times the light fastness was not as good and the hue on the substrates did not quite match.

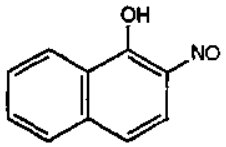
This chapter investigates the uv-visible, ir spectrophotometric properties of the azo dyes derived from 2-nitroso-1-naphthol. This was followed by the study of the dyeing properties of these dyes on wool and nylon 6.6 substrates.

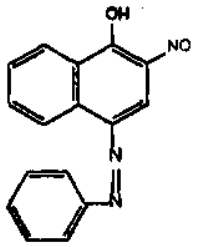
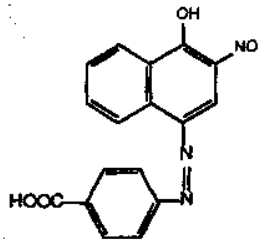
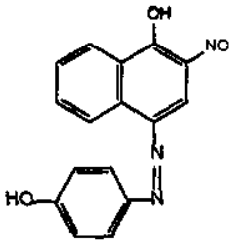
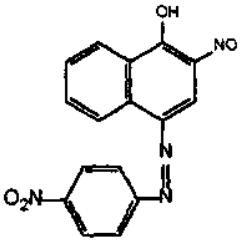
4.2 RESULTS AND DISCUSSIONS

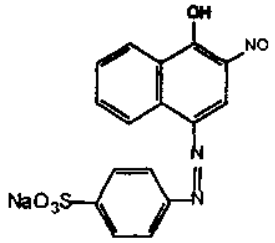
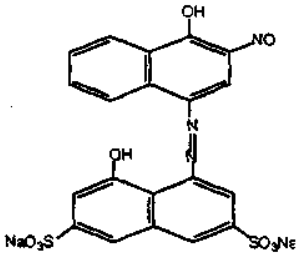
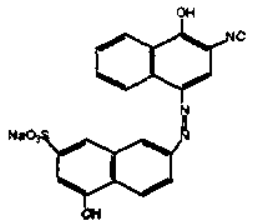
4.2.1 Synthesis of the dyes

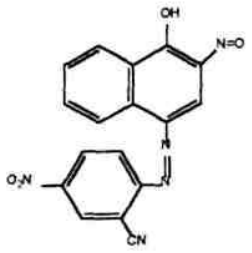
In addition to the 2-nitroso-1-naphthol and its aniline and 4-amino-benzoic acid azo dyes derivatives synthesized in Chapter 3, 4-aminophenol, 4-nitroaniline, sulphanilic acid, J-acid, H-acid, 2-cyano-4-nitroaniline were also diazotised and coupled to 2-nitroso-1-naphthol. The dyes were purified by dissolving in ethanol and then precipitated with water. The pure dyes were analysed by ir, uv-visible spectroscopies and melting point determinations. The results are summarised in Table 4.1 and Figures 4.0 – 4.9.

Table 4.1: Characterisation Data for 2-Nitroso-1-Naphthol and its Azo Dyes Derivatives.

Dye No	Structure of the Dyes	Yield (%)	M. Pt.	λ_{max} in H_2O	$\varepsilon \times 10^4$	Characteristics ir peaks[261,262]
65		98	140**	472	6.4311	1329, 1303 – NO 3448 - -OH 771 – C-H, OH 974 – N-OH 922 – C-H 1413 - -C=N

66		66	172*	485	3.5614	1328, 1303 – N=O 3472 - -OH 770 C-H, -OH 973 -N-OH 920 –C-H 1413 - -C=N
67		50	172*	475	1.605	1328, 1303 -N=O 3470 –OH 772 C-H, -OH 974 -N-OH 920 -C-H 850 -N=O- 1413 -C=N
68		56	142*	452	1.4504	1328, 1303 -N=O 3465 –OH 766 -CH, -OH 920 -C-H 822 ..... N=O 1413 -C=N 973 -N-OH
69		75	140*	512	0.5796	1328, 1304 -N=O 3452 –OH 769 C-H, -OH 973 -N-OH 921 -C-H 850 ..... –N=O- 1413 -C=N

70		40	130*	450	1.2295	1328, 1303 -N=O 3477 –OH 770 -C-H, -OH 973 -N-OH 920 -C-H 864 ..... -N=O- 1413 -C=N
71		31	130*	478	1.129	1328, 1303 -N=O 3466 –OH 1148 -SO_3Na 771 C-H, -OH 973 -N-OH 920 C-H 851 .....N=O- 1413 -C=N
72		62	150*	551	0.8844	1328, 1303 -N=O 3467 –OH 770 C-H, -OH 973 -N-OH 920 -C-H 864 .....-N=O- 1413 -C=N

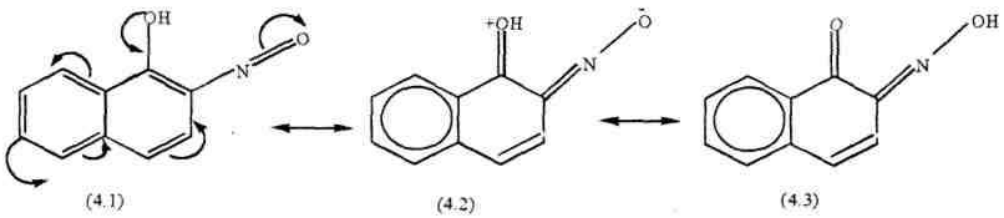
73		79	130*	480	0.8328	1324, 1303 3464 770 974 920 850 1413	N=O –OH C-H, -OH -N-OH -C-H –N=O- -C=N

* **Decomposed**

4.2.2 UV-Visible Spectroscopy of the Dyes

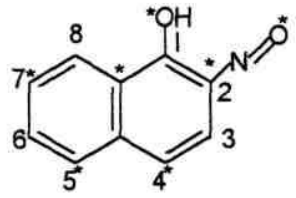
UV-visible spectra of the dyes were obtained with a Pye-Unicam uv-visible spectrophotomer SP 800 using 5% NaOH solution of the dyes at concentration of 1 x 10^{-5} – 10^{-6} mole/dm^3. The extinction coefficients were determined in 5% NaOH solution.

The parent dye, 2-nitroso-1-naphthol (65) absorbs at 472 nm. The origin of the colour in the molecule can be ascribed to a donor-acceptor chromogen character as shown in structure 4.1. However, the molecule also exhibits tautomerism with the form 4.3. This is an ortho quinonoid structure which according to Armstrong theory is a chromophore.[17]



(4.1) (4.2) (4.3)

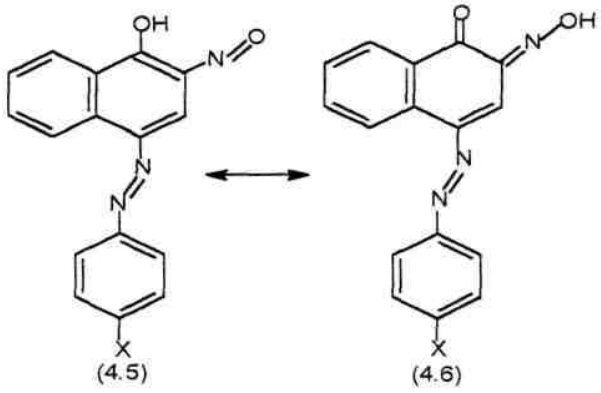
If molecule (4.1) can be regarded as playing a more prominent contribution to the color of the dye, then, applying Dewar's starring technique to it, structure (4.4) is obtained.



(4.4)

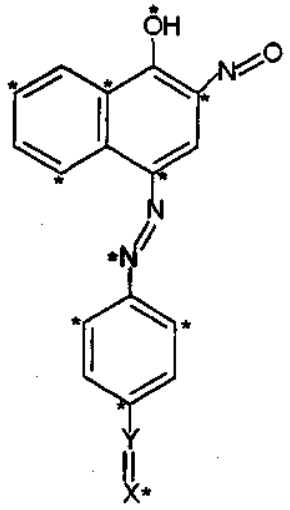
According to Dewar's[25-26] rules attaching electron donating species to positions 4,5 and 7 could lead to bathochromic shifts whereas electron withdrawing groups in the same positions will lead to hypsochromic shifts. Similarly, one of the rules said that attaching a neutral conjugating specie (±M) i.e phenyl to any position will result in a bathochromic shift.

When the parent dye (65) was coupled to different diazo component, the coupling position is '4'. Dyes (66) – (73) were produced. Since the molecule can exist as in molecule (4.3). Therefore, the azo dyes can also exist as tautomers (4.5) and (4.6).



(4.5) (4.6)

The wavelength of maximum absorbances given in Table 4.1 can only be explained when this fact of tautomerism is taken into account. For ease of analysis, the synthesized dyes can be grouped under four groups. In the first group, the terminal group –X in structure (4.5) is replaced by (-Y = X) to produce structure (4.7). This is because the dyes have electron withdrawing groups attached, in this form (-OH) group is the electron donating specie whereas the remaining part of the chromogen forms the electron withdrawing moeity. When Dewar's starring technique is applied to it, the nitroso group (-N=O), which is electron withdrawing is seen to be in a starred position. This is believed to lead to hypsochromic shift.

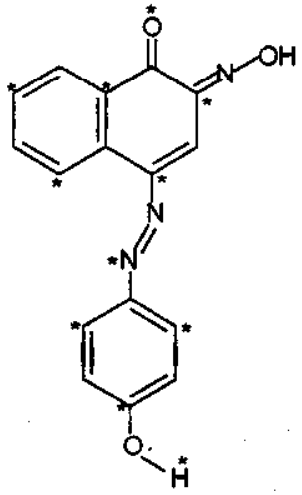


(4.7)

This is the case with dyes (67), (69), (70) and (73). Out of these dyes, it is observed that dye (69) is the most bathochromic with about 512 nm followed by dye (73). Dye (69) evidently is more bathochromic over dye

(73), because a cyano group is attached to a starred position; being electron withdrawing, it suffered a hypsochromic shift. Dye (73) is followed by dye (67) with 475 nm and lastly dye (70) with 450 nm. It can be seen from this that a carboxylic acid group is more electron withdrawing than a sulphonic acid group. It is infact the case.

The second group is typified by the presence of an electron donating specie as the (-X) group in (4.5), dye (68). Explanation of its color quality from Dewar's procedure can be derived from two approaches. The first approach is to assume that it exists in the tautomeric form (4.6), starring procedure gives the structure (4.8).



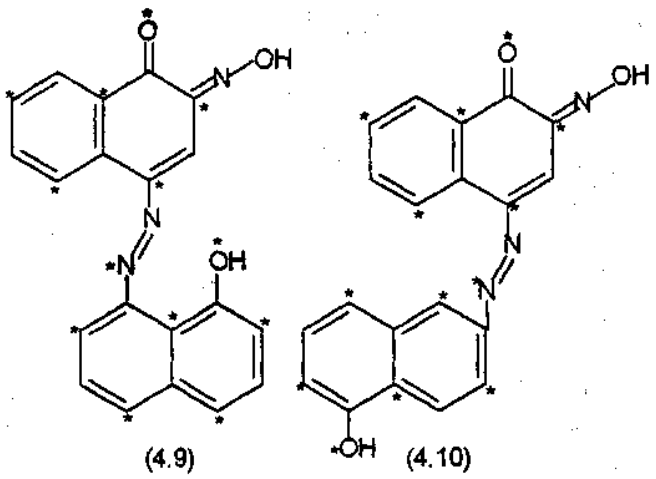
(4.8)

From the structure (4.8), it can be seen that the dye suffered weak absorption wavelength by having an electron withdrawing specie (-C=N) in a starred position making the dye to be even weaker compared to dye (65)

with structure (4.1) or (4.3). The second approach is to consider that an –OH group can be electron withdrawing by virtue of its (-I). By which structure (4.7) and the corresponding analogy applies. In this case too, the presence of an electron withdrawing group could lead to a hypsochromic effect. In addition, the fact that an –OH group has an electron donating tendency by mesomeric effect, this will further reduce the absorption wavelength. Perhaps this explains the relative hypsochromic effect of dye (68) compared to dye (65).

The third group is typified by the attachment of a diazotised aniline to dye (65). This is the case with dye (66). In this case the dye can be compared to the parent dye (65). Structure (4.4) can be used to explain its color quality. According to Dewar's starring procedure, a neutral phenyl group attached to a starred position will lead to a bathochromic shift. Infact, dye (66) recorded 485 nm, which is a bathochromic shift of about 13 nm over dye (65).

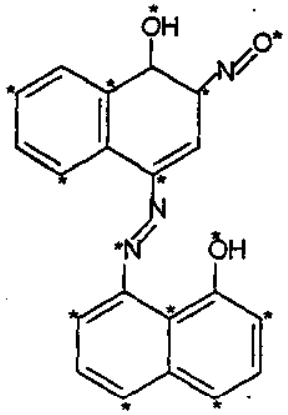
The fourth group is typified by the attachment of a naphthalene ring to the parent dye. Since H- and J-acids were used as the diazo component. Structures (4.9) and (4.10) resulted.



(4.9) (4.10)

It can be reasoned that with respect to Dewar's rules, dye (71) in contrast to the result obtained, should record higher wavelength of absorption relative to dye (72). This is because, there are two electron withdrawing groups in an unstarred positions in dye (71) as against one in dye (72). Possible explanation for this is given below. However, the higher wavelength of absorption for dye (71) over even dye (69) is explainable by having an electron withdrawing group (SO_3Na) in an unstarred position which impoved its absorbance wavelength in addition to the increased length of conjugation. To explain the rather lower recorded wavelength of maximum absorption for dye (71), the dye molecule is assumed to exist as shown in structure (4.11) below. In this form, the hydroxyl group is believed to be the electron donating group, whereas, the rest of the chromogen is the electron withdrawing part. However, even if structure

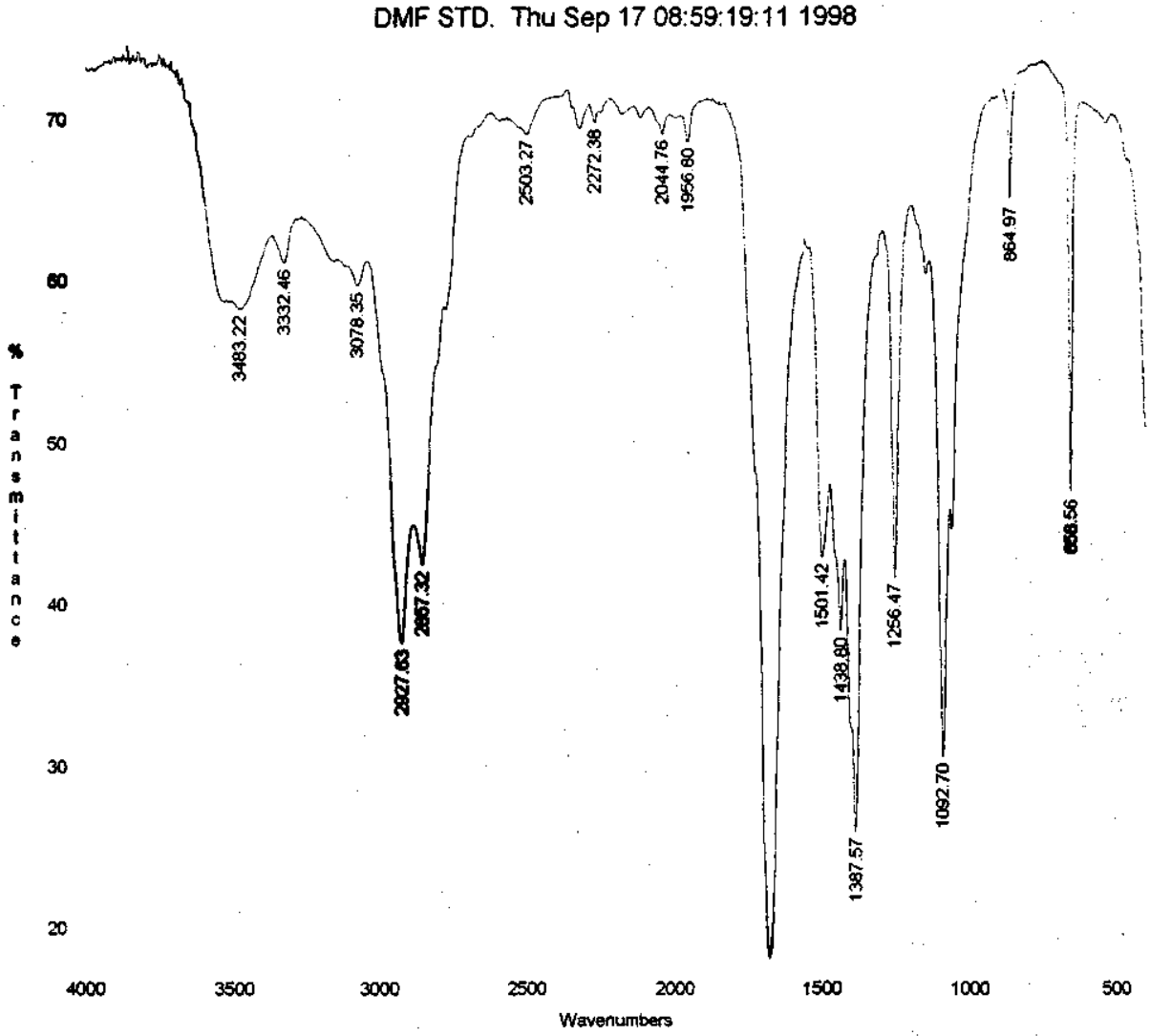
(4.9) is the actual prominent form of the dye in the relative positioning of the –OH group in relation to the azo group compared to dye (72) can influence the dominant effect of the –OH group. In dye (72), the dominant effect may be mesomeric electron donating, whereas, in dye (71) it is inductomeric electron withdrawing, hence the observed differences.



(4.11)

In the form (4.11) too, there are two electron withdrawing groups attached to unstarred positions which is expected to lead to bathochromic effect. This tendency has been dampened by the attachment of an electron donating substituent in an unstarred position believed to lead to hypsochromic shift.

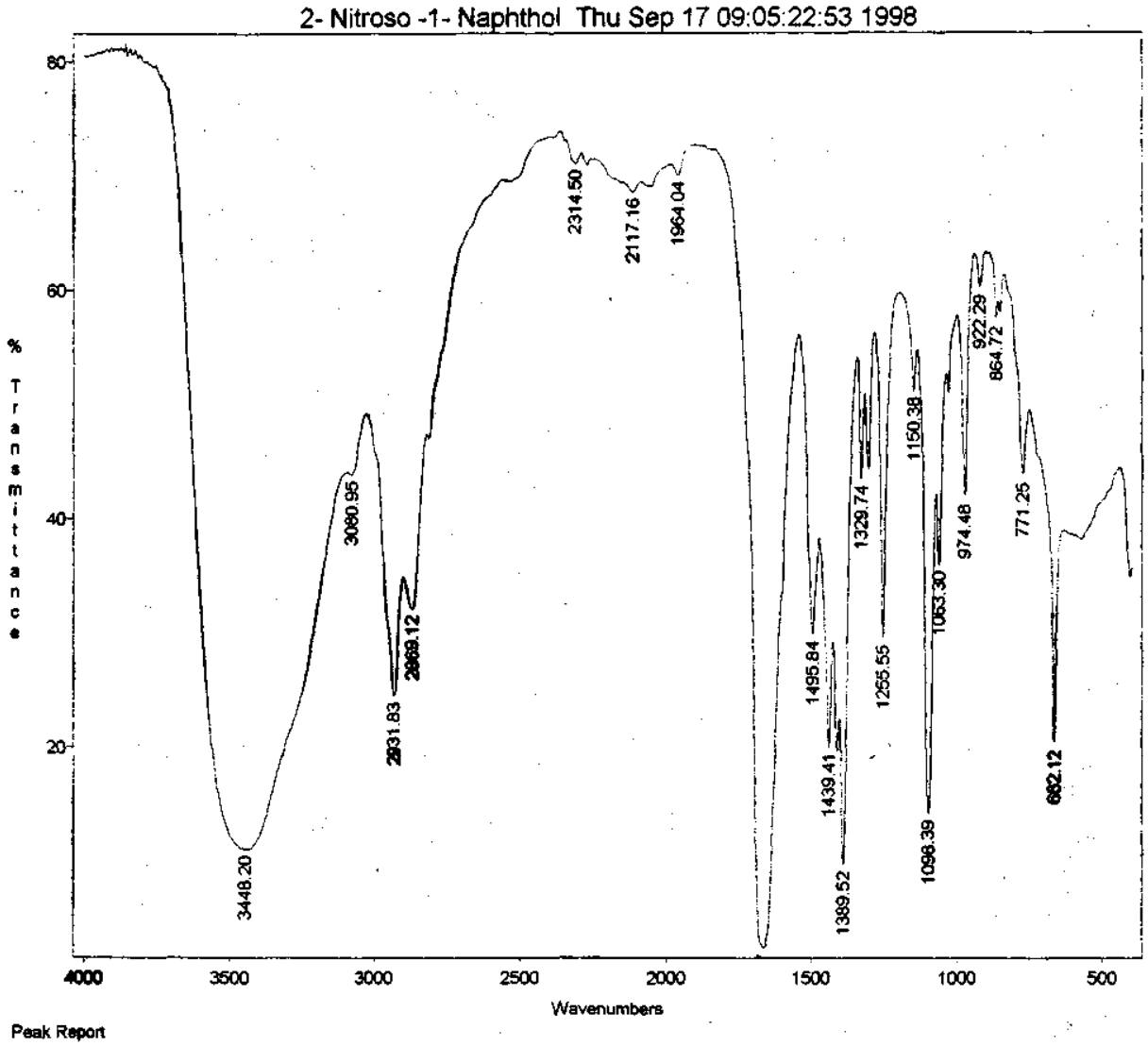
Fig. 4. 0: ir-spectrograph of the solvent, DMF



Peak Report
File: c:\first\data\galaxy\tmp416.ras
Title: DMF STD. Thu Sep 17 08:59:19:11 1998
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
3483.22	58.21	3332.46	61.05	3078.35	59.66
2927.63	37.59	2857.32	42.40	2503.27	69.03
2272.38	69.72	1956.80	68.52	1673.51	18.10
1501.42	42.86	1438.80	38.28	1387.57	25.95
1256.47	41.62	1092.70	30.53	864.97	64.95
658.56	46.99	2044.76	68.98		

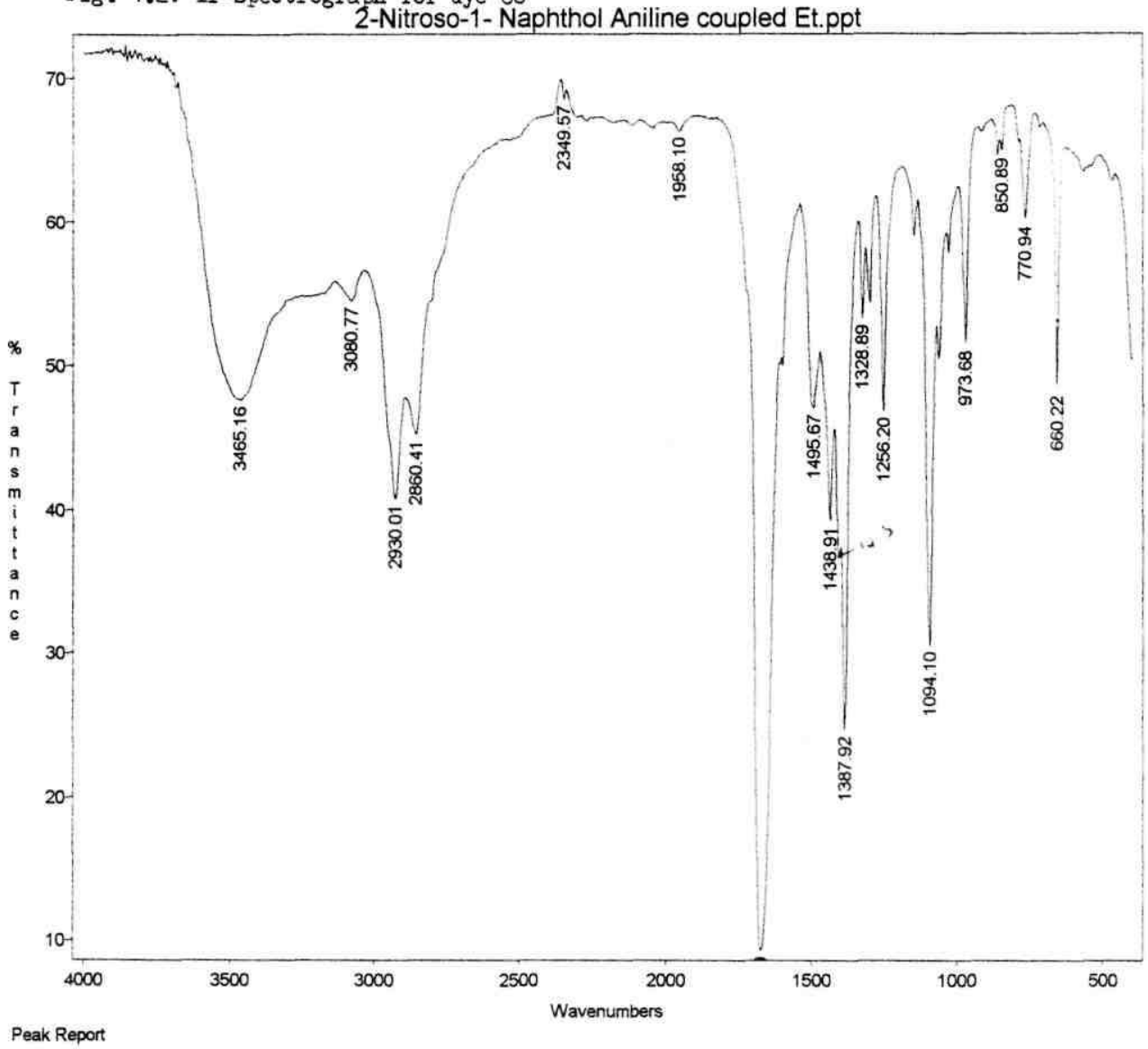
Fig. 4.1: ir-spectrograph for dye 65



Peak Report
File: c:\first\data\galaxy\tmp417.ras
Title: 2- Nitroso -1- Naphthol Thu Sep 17 09:05:22:53 1998
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
3448.20	10.99	3080.95	43.79	2931.83	24.47
2869.12	32.08	1664.77	2.40	1495.84	29.87
1439.41	19.95	1389.52	9.66	1329.74	43.45
1255.55	29.48	1150.38	51.18	1098.39	14.12
1063.30	35.95	974.48	41.96	771.25	43.89
662.12	20.40	864.72	57.56	922.29	60.35
1964.04	70.03	2314.50	71.06	2117.16	68.61

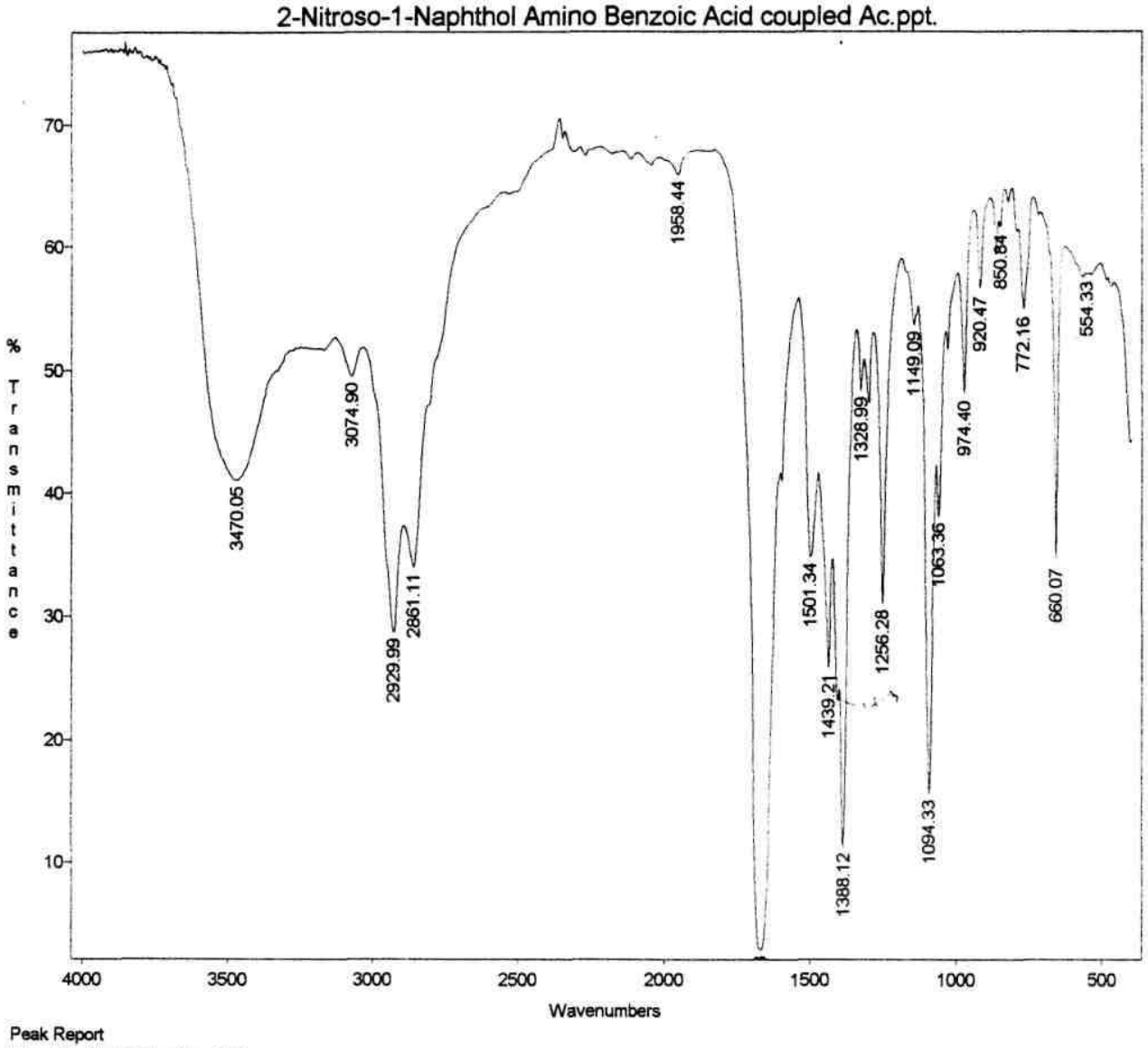
Fig. 4.2: ir-spectrograph for dye 66



Peak Report
File: c:\first\data\galaxy\tmp418.ras
Title: tmp418 Thu Sep 17 09:14:59:50 1998
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
3465.16	47.62	3080.77	54.48	2930.01	40.81
2860.41	45.21	1958.10	66.33	2349.57	68.53
1672.09	9.27	1495.67	47.08	1438.91	39.25
1387.92	24.62	1328.89	53.23	1256.20	46.84
1094.10	30.50	973.68	51.64	850.89	65.02
770.94	60.29	660.22	48.50		

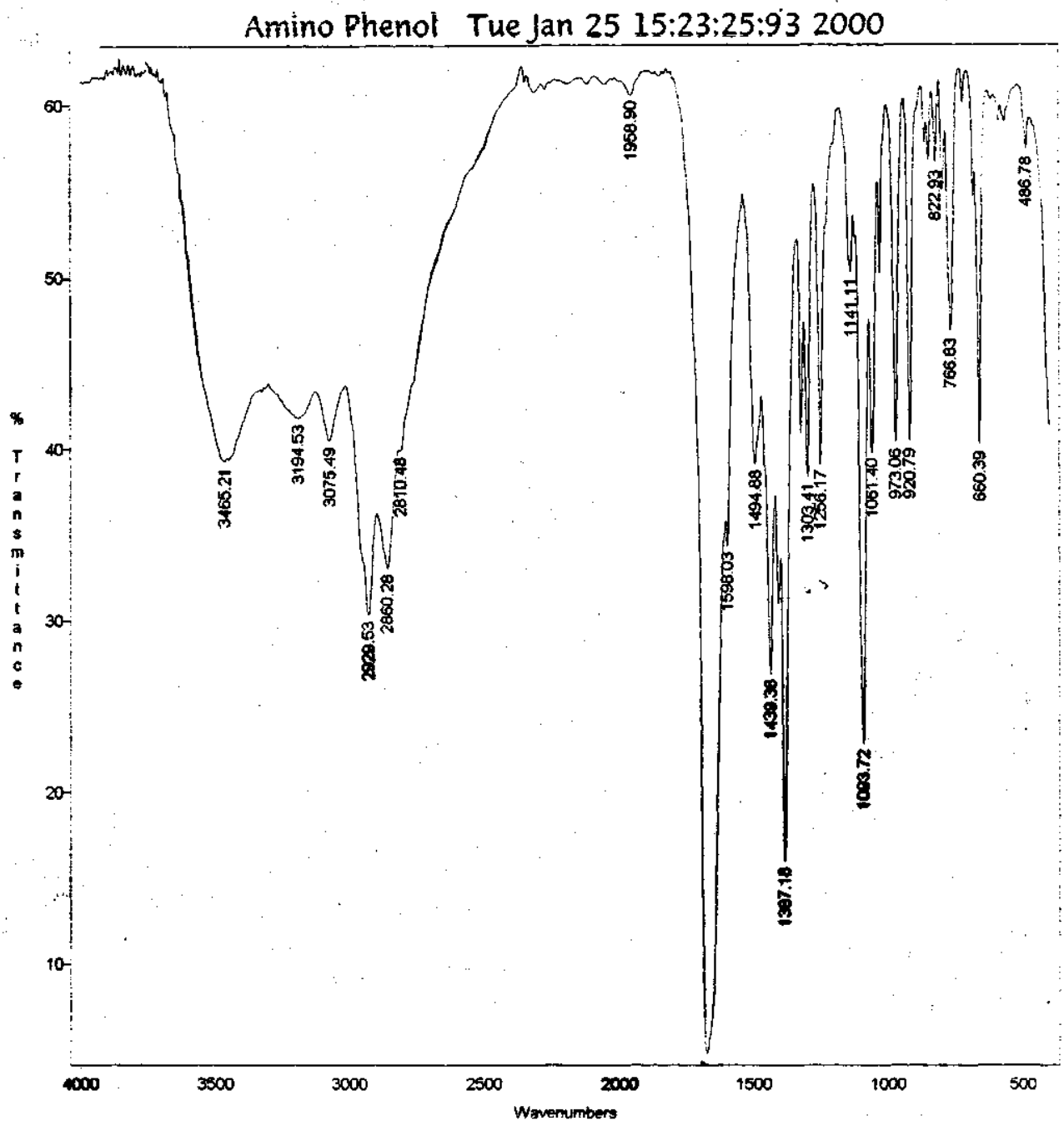
Fig. 4.3: ir-spectograph for the dye 67



Peak Report
File: c:\first\data\galaxy\tmp419.ras
Title: 2-Nitroso-1-Naphthol Amino Benzoic Acid coupled Ac.ppt.
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
3470.05	41.07	3074.90	49.50	2929.99	28.66
2861.11	33.93	1958.44	65.88	1670.93	2.91
1501.34	34.81	1439.21	25.80	1388.12	11.27
1328.99	48.34	1256.28	31.00	1149.09	53.62
1094.33	15.62	1063.36	38.10	974.40	48.20
920.47	56.60	850.84	61.64	772.16	54.94
660.07	34.52	554.33	57.78		

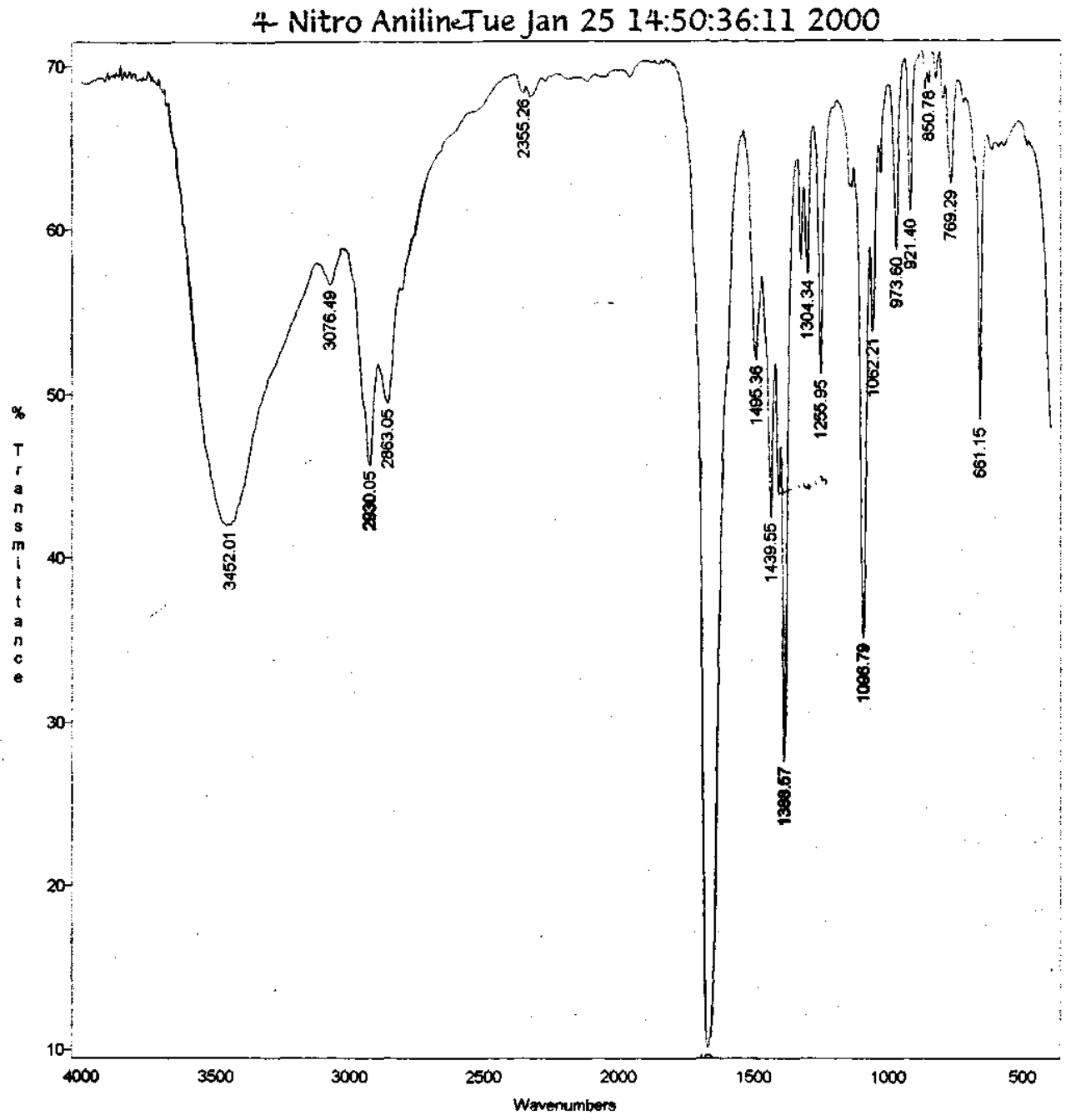
Fig. 4.4: ir-spectrograph for dye 68



Peak Report
File: c:\first\data\galaxy\cfir1931.ras
Title: Amino Phenol Tue Jan 25 15:23:25:93 2000
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
2810.48	39.85	2860.28	33.04	2929.53	30.29
3075.49	40.44	3194.53	41.77	3465.21	39.28
1958.90	60.53	1674.07	4.71	1598.03	34.32
1494.88	39.08	1439.38	26.85	1387.18	15.98

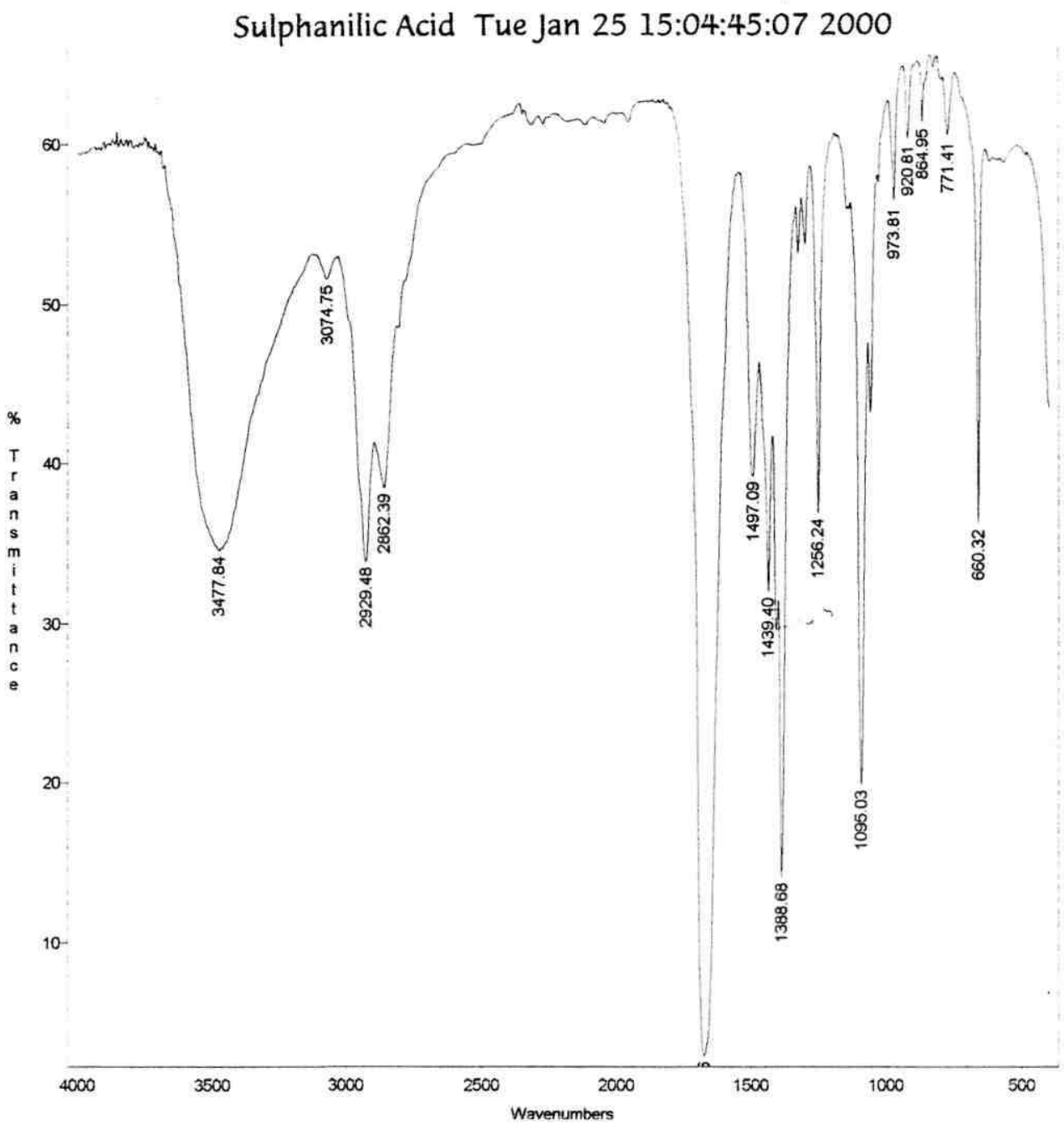
Fig. 4;5: ir-spectrograph for dye 69



Peak Report
File: c:\first\data\galaxy\cfir1928.ras
Title: 4- Nitro Anilin Tue Jan 25 14:50:36:11 2000
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
661.15	48.40	769.29	62.79	850.78	68.88
921.40	61.02	973.60	58.69	1096.79	35.10
1062.21	53.73	1255.95	51.17	1304.34	57.19
1388.57	27.61	1439.55	42.43	1495.36	52.02

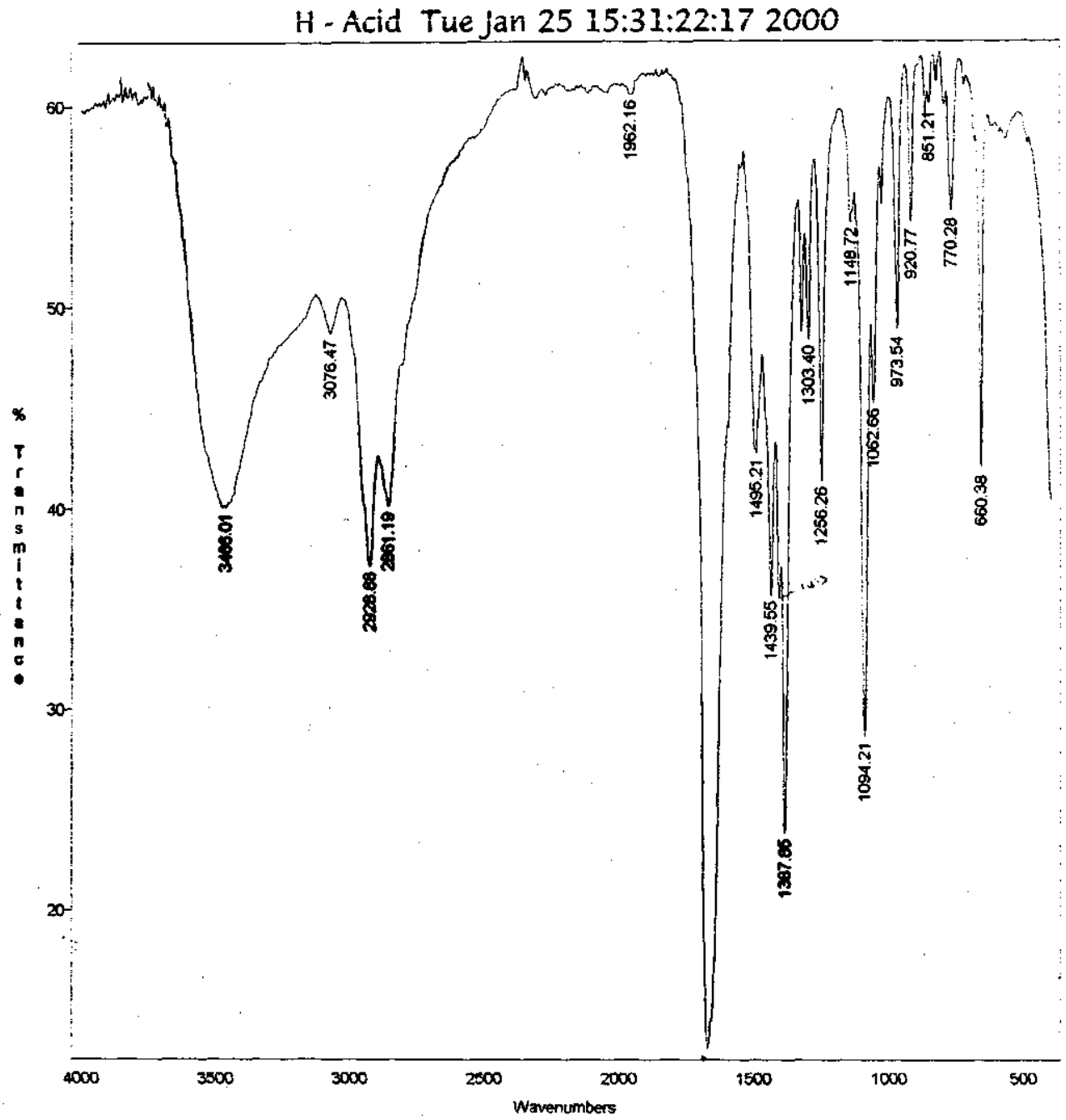
Fig. 4.67: ir-spectrograph for dye 70



Peak Report
File: c:\first\data\galaxy\cfir1929.ras
Title: Sulphanilic Acid Tue Jan 25 15:04:45:07 2000
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
660.32	36.28	771.41	60.52	920.81	60.33
864.95	61.36	973.81	56.39	1095.03	19.84
1256.24	36.87	1388.68	14.10	1439.40	31.93
1497.09	39.18	1673.76	2.85	2862.39	38.43

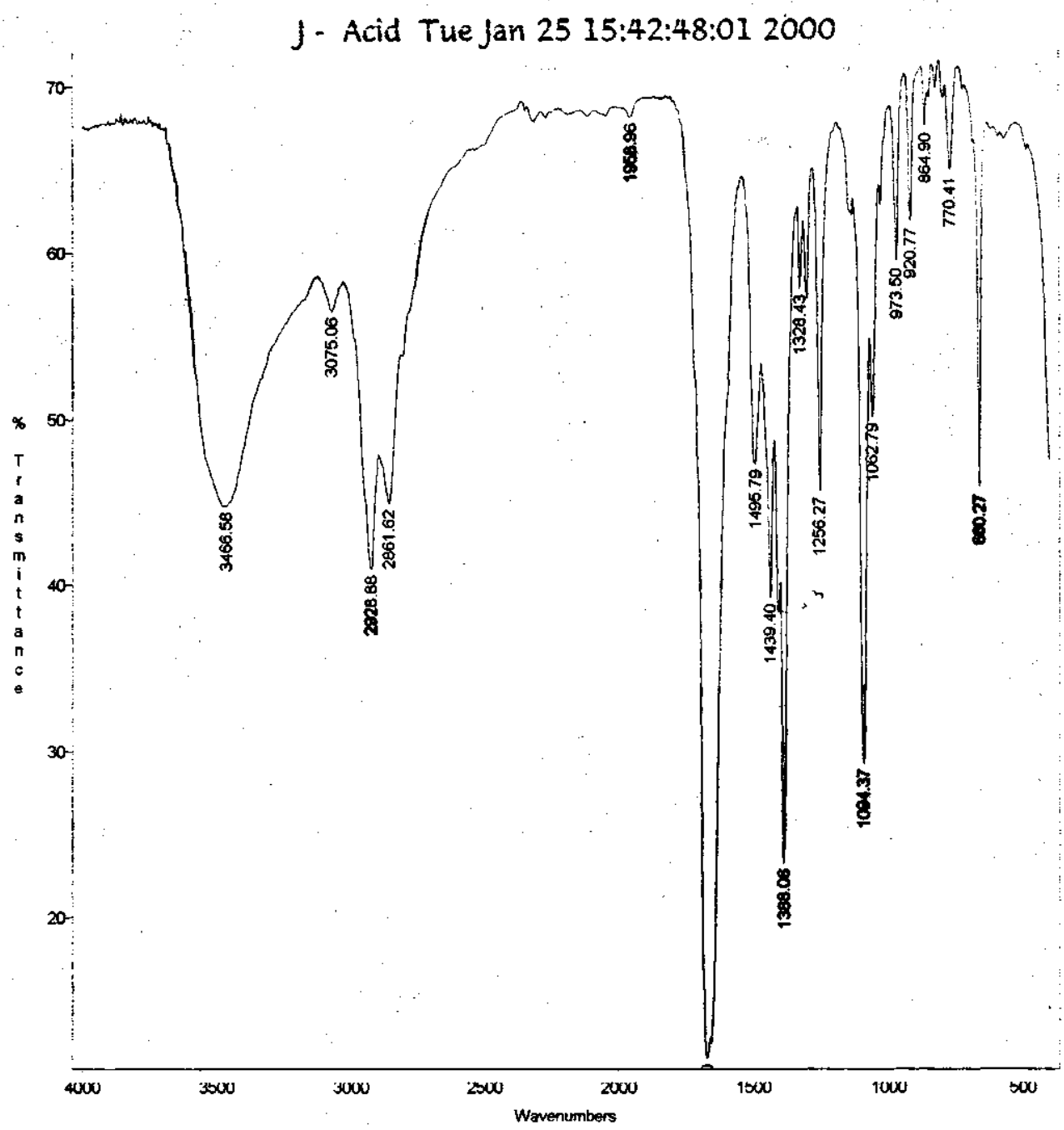
Fig.4.7 : ir-spectrograph for dye 71



Peak Report
File: c:\first\data\galaxy\cfir1932.ras
Title: H - Acid Tue Jan 25 15:31:22:17 2000
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
3466.01	40.10	3076.47	48.71	2928.68	37.14
2861.19	40.11	1962.16	60.55	1674.17	13.11
1495.21	42.76	1439.55	35.65	1387.85	23.85
1303.40	48.36	1256.26	41.37	1094.21	28.64

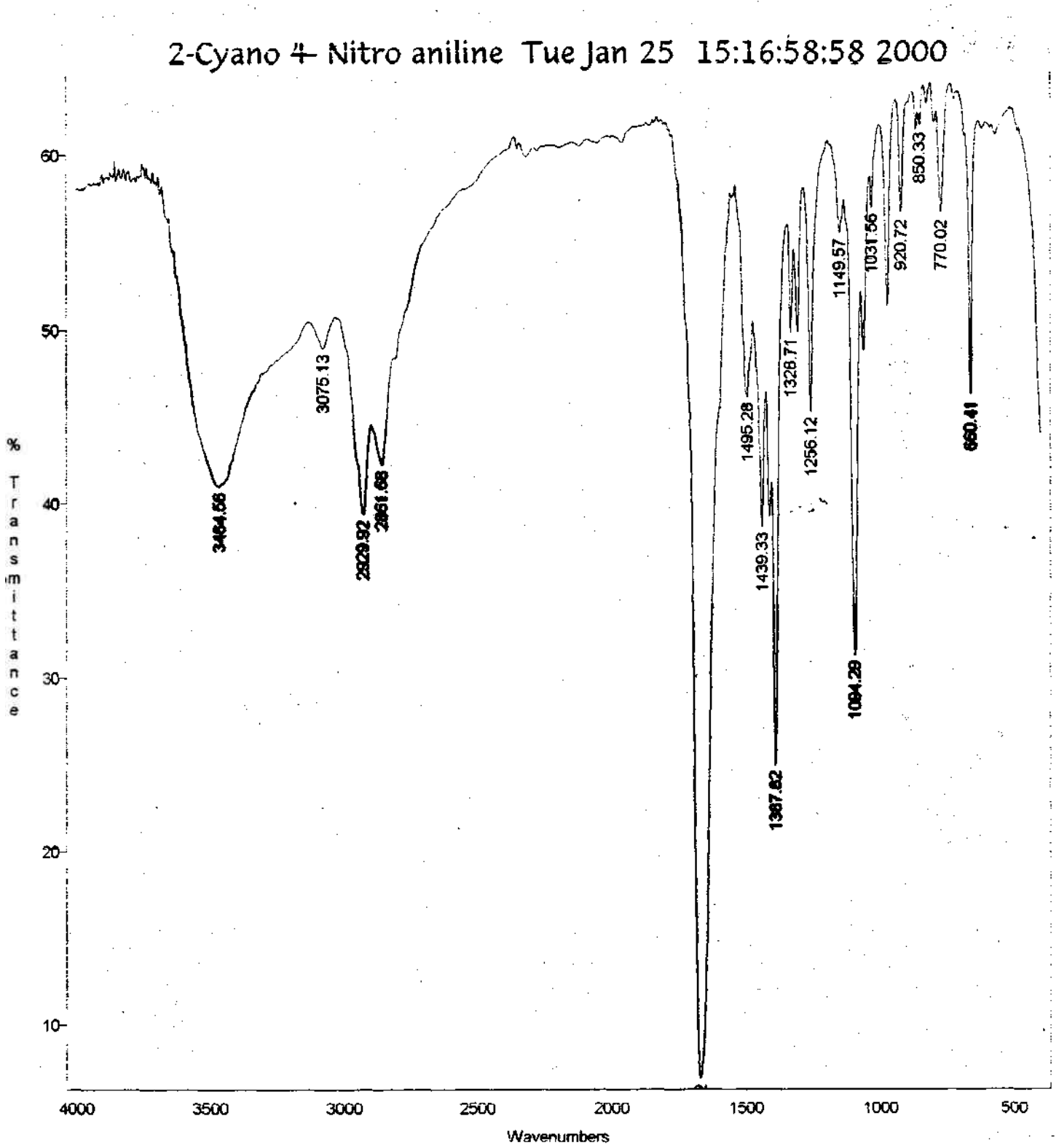
Fig. 4.8: ir-spectrograph for dye 72



Peak Report
File: c:\first\data\galaxy\cfir1933.ras
Title: J - Acid Tue Jan 25 15:42:48:01 2000
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
3466.58	44.77	3075.06	56.49	2928.88	40.94
2861.62	44.88	1958.96	68.10	1674.00	11.54
1495.79	47.27	1439.40	39.19	1388.06	23.22
1328.43	57.78	1256.27	45.60	1094.37	29.27

Fig. 4.9: ir-spectrograph for dye 73



Peak Report
File: c:\first\data\galaxy\cfir1930.ras
Title: 2-Cyano 4- Nitro aniline Tue Jan 25 15:16:58:58 2000
Filter: Three Point Center of Gravity

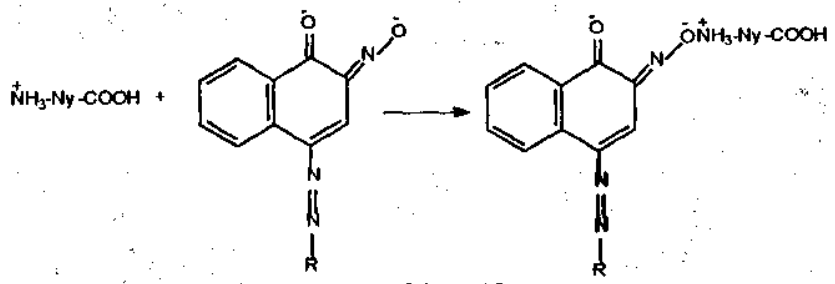
cm-1	%T	cm-1	%T	cm-1	%T
3464.56	40.98	3075.13	48.92	2929.92	39.37
2861.68	42.19	1673.22	6.87	1495.28	46.09
1439.33	38.63	1387.82	24.86	1328.71	49.80
1256.12	45.24	1149.57	55.46	1094.29	31.27

4.2.3 Effect of pH on the Dyeing of the Dyes on Nylon 6.6 and Wool

The dyes were applied to wool and nylon fabrics using 1% shade omf at a liquor to goods ratio of 50:1. 0.1% HCl solution was used to adjust the pH. Dyeing was carried out at the boil for 30 minutes. No wetting agent was used. The results obtained are shown in Tables 4.2 and 4.3 and illustrated graphically in Figures 4.10 and 4.11.

Table 4.2: The Effect of pH on Dyeing of Wool Samples

Dye 65		Dye 66		Dye 67		Dye 73		Dye 69		Dye 68		Dye 70		Dye 72		Dye 71	
pH	E %	pH	E %	pH	E %	pH	E %	pH	E %	pH	E %	pH	E %	pH	E %	pH	E %
7.3	24	6.9	75	7.3	46	7.3	33	8.2	37	7.2	42	6.8	47	7.8	63	7.2	40
6.2	25	5.7	81	5.8	47	5.9	35	6.5	37	6.4	42	6.0	55	6.8	65	6.1	50
5.2	26	5.1	95	5.0	49	4.9	42	4.9	38	5.0	43	5.0	45	5.5	73	4.9	68
4.4	27	3.9	87	4.1	52	4.2	44	4.5	39	3.9	48	3.7	45	4.2	78	4.3	62
3.3	29	3.2	86	3.1	52	3.5	46	3.5	40	3.2	45	3.2	44	3.3	78	3.6	57
2.9	29	2.9	83	2.9	51	3.1	48	3.1	37	2.9	44	2.9	40	3.0	74	3.0	54



Scheme 4.3

However, when the pH is rather too low below 4, it is observed that most of the dye will be precipitated and is assumed to exist in the un-ionized form of Scheme 4.2 which is also assumed to be in the quinonoid tautomer shown in Scheme 4.1, which does not have any tendency of ionizing and as such can not form salt linkages.

The observation made with respect to nylon also extended to wool. Table 4.31 summaries the pH for both wool and nylon when the exhaustion is maximum.

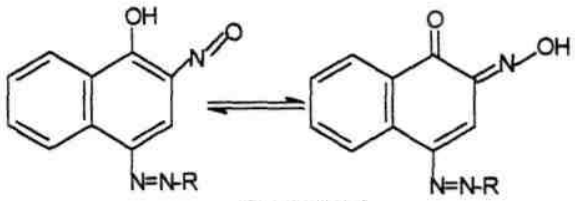
It can be observed from Table 45th that the dyes containing sulphonic acid groups (70), (71) and (72) generally showed that the pH for maximum exhaustion was higher for wool than for nylon. This indicated the role of sulphonic acid groups is providing alternate sites for salt linkages. At these relatively high pH for wool the more abundant sites are still sufficiently

Table 4.3: The Effect of pH on Dyeing of Nylon 6.6 Samples

Dye 65		Dye 66		Dye 67		Dye 69		Dye 73		Dye 70		Dye 68		Dye 72		Dye 71	
pH	E %	pH	E %	pH	E %	pH	E %	pH	E %	pH	E %	pH	E %	pH	E %	pH	E %
6.8	31	6.8	40	7.4	30	7.6	20	6.8	34	7.9	29	7.2	59	7.0	21	7.1	35
5.0	34	6.2	52	6.6	34	6.1	30	6.3	39	6.4	41	6.2	73	6.0	21	6.4	43
4.6	55	5.6	86	5.4	34	5.0	37	5.4	72	5.6	58	4.8	83	5.5	30	5.3	54
3.7	55	3.7	76	4.2	44	4.4	40	4.3	80	4.2	62	3.8	88	3.9	68	4.0	61
3.1	47	3.2	60	3.6	36	3.6	42	3.8	77	3.7	70	3.0	95	3.2	72	3.2	60
2.7	47	2.9	62	2.8	18	3.0	40	3.3	77	3.0	70	2.7	76	2.8	72	2.6	51

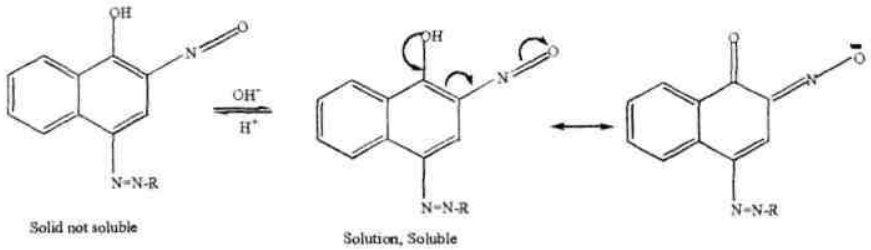
As explained elsewhere in the literature, the attraction of acid dyes by nylon is regarded as a back-titration of carboxylic groups in the polymer with the nylon assumed to be existing in the zwitterion form.[14t)] It was also stated that apart from ionized -COO" and -NH_3^T ions, there are also weakly basic regularly spaced amide groups along the polymer chain. Majority of work carried out to study the effect of pH on the adsorption of conventional acid dyes produced a curve already explained.[148] The shape is that of very weak absorption at high pH's gradually increasing as the pH increases flattening at pH's around 3-5, and rising almost without limit about the pH of 3. Surprisingly, the application of the acid nitroso dyes under study gave." rather different curves. While there is obvious evidence of increases as the pH decreases from about pH 6-4.5, the exhaustion falls after pH 4. Inspite

of the controversies with respect to overdyeing mechanism at low pHs[150,152,157,156,162,163] a different mechanism is hereby proposed for the obvious non conformity with the rules with respect to these dyes. The nitroso dye structure can be seen to exist in the tautomeric forms as shown in Scheme 4.1.



Scheme 4.1

At moderately low pH, the polymer existed with the $-COO^-$ back titrated leaving a protonated amino group. Similarly, the nitroso dye exists in a partially ionized form in equilibrium with a dispersion of unionized dye.



Scheme 4.2

It is assumed that the soluble ionized second form, forms a salt link with the protonated polymer in the usual manner.

Fig 4.10: The effect of pH on dyeing wool

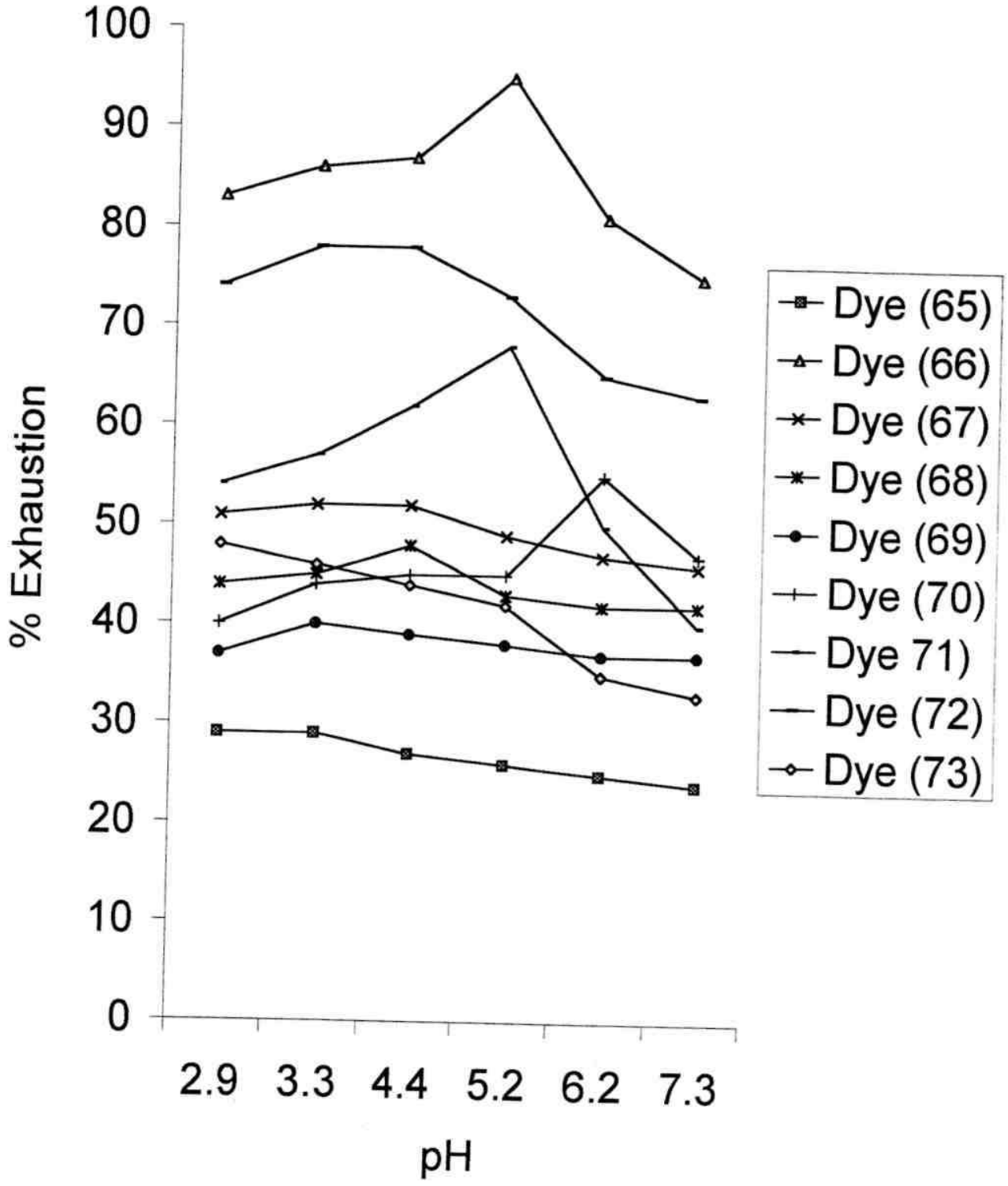


Fig 4.11: The effect of pH on dyeing Nylon 6.6

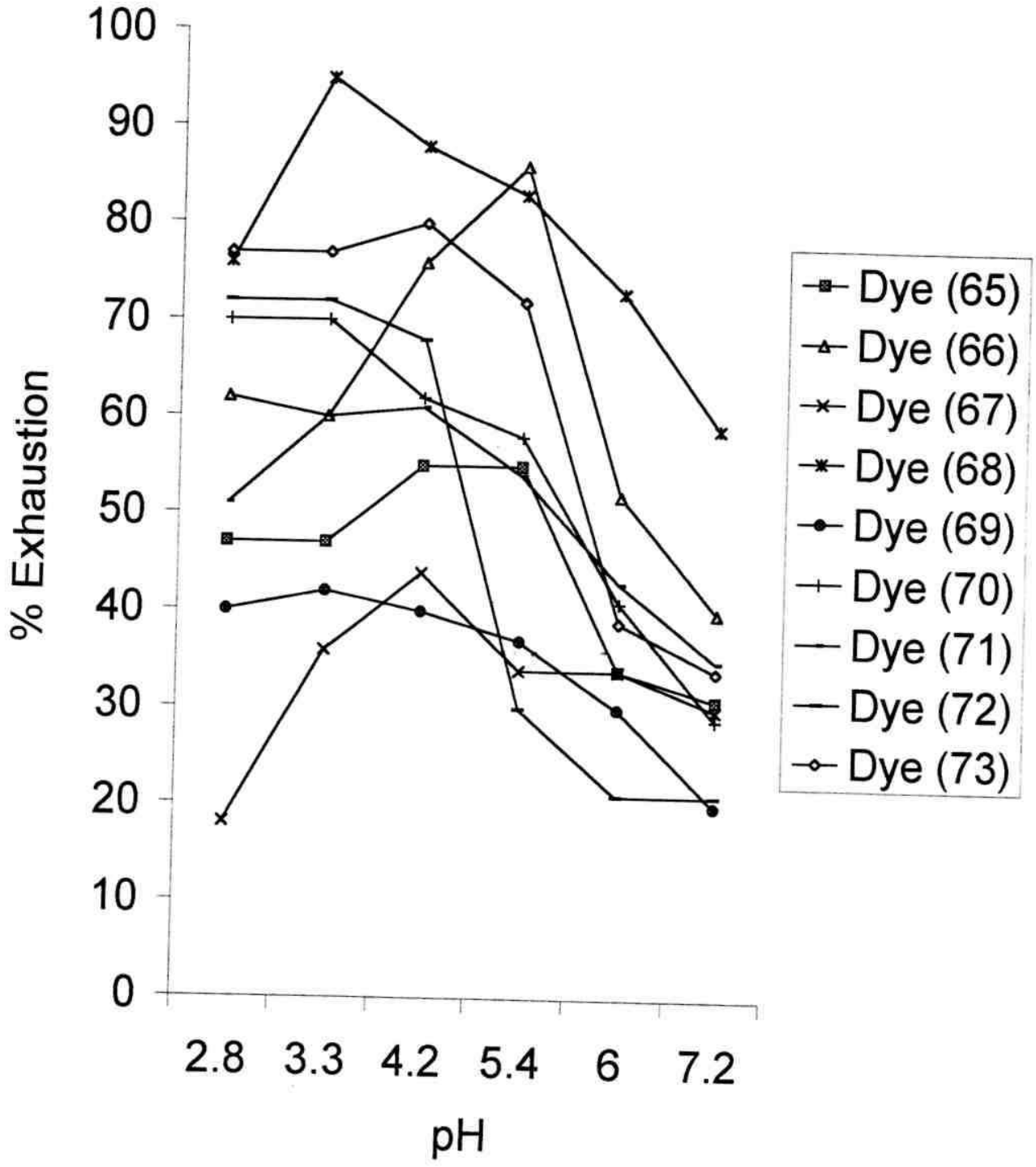


Table 43 pH of Maximum Exhaustion for Nylon and Wool

Dye No	Nylon 6.6	Wool
65	4.6	3.3
66	5.6	5.1
67	4.2	4.1
68	3.0	3.9
69	4.4	3.5
70	3.7	6.0
71	4.0	4.9
72	3.2	4.2

activated to get linked up compared to nylon 6.6. It is also generally observed that with the exception of dye (66) all the dyes recorded maximum exhaustion below or at the pH 4. Another important observation of note is that nylon 6.6 is more sensitive to pH change than wool.

4.2.3 Determination of Coefficient of Diffusion

Non-steady state condition, t½ method of the determination of diffusion coefficient was used.[106] It depends on the assumption that until the diffusant penetrates to the centre of the substrate, the sheet is considered to

be infinitely thick. The concentration of the dye in solution is designed in such a way that the amount of dye adsorbed is infinitestimally small to alter it. The results are as shown in Tables 4.4 – 4.12 and Figures 4.12 – 4.30.

Table 4.4: **Diffusion Data of Dye (65) on Wool and Nylon 6.6 at 303 and 323°K.**

Time		303K				323K			
t (s)	t ½	Wool		Nylon 6.6		Wool		Nylon 6.6	
		Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞
600	24.5	0.065	0.23	0.089	0.41	0.068	0.29	0.096	0.44
900	30.0	0.065	0.23	0.0998	0.46	0.072	0.31	0.114	0.525
1200	34.6	0.066	0.23	0.114	0.53	0.078	0.34	0.115	0.53
1500	38.7	0.067	0.235	0.113	0.52	0.079	0.34	0.136	0.625
1800	42.4	0.070	0.25	0.121	0.56	0.083	0.36	0.145	0.67
2100	45.8	0.070	0.25	0.126	0.58	0.087	0.375	0.158	0.73
2400	49.0	0.071	0.25	0.126	0.58	0.104	0.45	0.158	0.73
2700	52.0	0.073	0.257	0.138	0.635	0.094	0.405	0.169	0.78
3000	54.8	0.074	0.26	0.141	0.65	0.09	0.39	0.179	0.82
3600	60.0	0.076	0.267	0.152	0.70	0.097	0.42	0.191	0.88
∞		0.284		0.217		0.232		0.217	
Slope:		1.231×10^{-3}		8.276×10^{-3}		3.92×10^{-3}		1.389×10^{-2}	
D/r^2 (sec^{-1}):		2.9754×10^{-7}		1.3448×10^{-5}		3.0172×10^{-6}		3.7882×10^{-5}	
Activation energy: 94280 J/mol								42134 J/mol	

Table 4.5: **Diffusion Data of Dye (66) on Wool and Nylon 6.6 at 303 and 323°K.**

Time		303K				323K			
t (s)	t ½	Wool		Nylon 6.6		Wool		Nylon 6.6	
		Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞
600	24.5	0.059	0.39	0.054	0.245	0.085	0.57	0.07	0.402
900	30.0	0.062	0.41	0.063	0.285	0.089	0.59	0.077	0.445
1200	34.6	0.065	0.43	0.076	0.345	0.092	0.61	0.080	0.460
1500	38.7	0.065	0.435	0.074	0.335	0.098	0.65	0.087	0.500
1800	42.4	0.069	0.46	0.078	0.355	0.0998	0.67	0.111	0.638
2100	45.8	0.070	0.465	0.087	0.395	0.102	0.68	0.097	0.560
2400	49.0	0.070	0.47	0.078	0.355	0.107	0.715	0.100	0.575
2700	52.0	0.072	0.48	0.095	0.430	0.107	0.715	0.104	0.600
3000	54.8	0.074	0.495	0.099	0.450	0.112	0.748	0.100	0.575
3600	60.0	0.077	0.51	0.108	0.49	0.117	0.778	0.117	0.675
∞		0.150		0.22		0.15		0.174	
Slope:		3.33×10^{-3}		6.8×10^{-3}		6.00×10^{-3}		7.5×10^{-3}	
D/r^2 (sec^{-1}):		2.181×10^{-6}		9.079×10^{-6}		7.069×10^{-6}		1.1045×10^{-5}	
Activation energy:		47855 J/mol						7978 J/mol	

Table 4.6: **Diffusion Data of Dye (67) on Wool and Nylon 6.6 at 303 and 323°K.**

Time		303K				323K			
t (s)	t ½	Wool		Nylon 6.6		Wool		Nylon 6.6	
		Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞
600	24.5	0.046	0.41	0.023	0.18	0.076	0.66	0.038	0.32
900	30.0	0.048	0.43	0.028	0.21	0.073	0.635	0.040	0.34
1200	34.6	0.051	0.45	0.032	0.24	0.080	0.69	0.045	0.38
1500	38.7	0.052	0.465	0.033	0.25	0.082	0.71	0.050	0.42
1800	42.4	0.054	0.48	0.035	0.27	0.084	0.73	0.053	0.45
2100	45.8	0.056	0.50	0.038	0.29	0.089	0.775	0.059	0.50
2400	49.0	0.058	0.52	0.039	0.30	0.092	0.800	0.061	0.515
2700	52.0	0.058	0.520	0.040	0.305	0.097	0.844	0.064	0.545
3000	54.8	0.060	0.535	0.043	0.33	0.0998	0.870	0.068	0.58
3600	60.0	0.062	0.555	0.045	0.345	0.105	0.915	0.074	0.63
∞		0.112		0.131		0.115		0.118	
Slope:		4.167×10^{-3}		4.4×10^{-3}		9.211×10^{-3}		9.5×10^{-3}	
D/r^2 (sec^{-1}):		3.4094×10^{-6}		3.8013×10^{-6}		1.6659×10^{-5}		1.772×10^{-5}	
Activation energy:		64565 J/mol						62652 J/mol	

Table 4.7: **Diffusion Data of Dye (68) on Wool and Nylon 6.6 at 303 and 323°K.**

Time		303K				323K			
t (s)	t ½	Wool		Nylon 6.6		Wool		Nylon 6.6	
		Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞
600	24.5	0.067	0.70	0.09	0.33	0.039	0.37	0.108	0.49
900	30.0	0.067	0.71	0.096	0.355	0.040	0.38	0.113	0.535
1200	34.6	0.0679	0.72	0.09	0.33	0.041	0.39	0.20	0.63
1500	38.7	0.0689	0.725	0.105	0.39	0.043	0.405	0.192	0.60
1800	42.4	0.069	0.73	0.10	0.37	0.045	0.42	0.204	0.64
2100	45.8	0.070	0.74	0.115	0.425	0.046	0.43	0.210	0.655
2400	49.0	0.071	0.74	0.118	0.44	0.047	0.44	0.228	0.71
2700	52.0	0.071	0.75	0.122	0.45	0.047	0.445	0.227	0.71
3000	54.8	0.074	0.775	0.127	0.47	0.049	0.46	0.234	0.73
3600	60.0	0.075	0.785	0.131	0.485	0.050	0.475	0.248	0.775
∞		0.095		0.27		0.106		0.32	
Slope:		1.569×10^{-3}		4.343×10^{-3}		3.023×10^{-3}		8.00×10^{-3}	
D/r^2 (sec^{-1}):		4.834×10^{-7}		3.7035×10^{-6}		1.7943×10^{-6}		1.2566×10^{-5}	
Activation energy:		53376 J/mol						49722 J/mol	

Table 4.8: **Diffusion Data of Dye (69) on Wool and Nylon 6.6 at 303 and 323°K.**

Time		303K				323K			
t (s)	t ½	Wool		Nylon 6.6		Wool		Nylon 6.6	
		Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞
600	24.5	0.080	0.33	0.035	0.18	0.053	0.52	0.053	0.23
900	30.0	0.080	0.33	0.040	0.20	0.059	0.58	0.060	0.265
1200	34.6	0.081	0.34	0.041	0.21	0.065	0.64	0.071	0.31
1500	38.7	0.083	0.35	0.048	0.24	0.071	0.70	0.078	0.34
1800	42.4	0.083	0.35	0.060	0.30	0.070	0.69	0.099	0.43
2100	45.8	0.090	0.375	0.052	0.26	0.078	0.775	0.093	0.41
2400	49.0	0.092	0.380	0.055	0.28	0.081	0.80	0.100	0.44
2700	52.0	0.092	0.385	0.057	0.29	0.083	0.825	0.108	0.475
3000	54.8	0.096	0.40	0.060	0.305	0.087	0.86	0.114	0.500
3600	60.0	0.099	0.415	0.064	0.325	0.089	0.88	0.124	0.545
∞		0.2396		0.198		0.101		0.228	
Slope:		2.9268×10^{-3}		4.286×10^{-3}		1.241×10^{-2}		7.00×10^{-3}	
D/r^2 (sec^{-1}):		1.68196×10^{-6}		3.607×10^{-6}		3.0239×10^{-5}		9.621×10^{-6}	
Activation energy:		117586 J/mol						39928 J/mol	

Table 4.9: **Diffusion Data of Dye (70) on Wool and Nylon 6.6 at 303 and 323°K.**

Time		303K				323K			
t (s)	t ½	Wool		Nylon 6.6		Wool		Nylon 6.6	
		Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞
600	24.5	0.035	0.32	0.060	0.23	0.048	0.49	0.101	0.46
900	30.0	0.040	0.36	0.068	0.26	0.052	0.53	0.116	0.525
1200	34.6	0.044	0.40	0.087	0.33	0.060	0.61	0.135	0.61
1500	38.7	0.046	0.415	0.085	0.325	0.061	0.62	0.139	0.635
1800	42.4	0.050	0.45	0.089	0.34	0.066	0.67	0.160	0.73
2100	45.8	0.052	0.47	0.096	0.37	0.070	0.71	0.161	0.732
2400	49.0	0.053	0.48	0.105	0.40	0.070	0.71	0.171	0.77
2700	52.0	0.058	0.525	0.107	0.41	0.077	0.785	0.180	0.82
3000	54.8	0.058	0.53	0.120	0.46	0.079	0.81	0.170	0.77
3600	60.0	0.062	0.565	0.124	0.475	0.084	0.86	0.194	0.79
∞		0.11		0.76		0.098		0.22	
Slope:		7.142×10^{-3}		6.842×10^{-3}		1.135×10^{-2}		1.27×10^{-2}	
D/r^2 (sec^{-1}):		1.002×10^{-5}		9.1917×10^{-6}		2.529×10^{-5}		3.1669×10^{-5}	
Activation energy:		37680 J/mol						50350 J/mol	

Table 4.10: **Diffusion Data of Dye (71) on Wool and Nylon 6.6 at 303 and 323°K.**

Time		303K				323K			
t (s)	t ½	Wool		Nylon 6.6		Wool		Nylon 6.6	
		Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞
600	24.5	0.064	0.56	0.068	0.25	0.037	0.32	0.134	0.36
900	30.0	0.066	0.58	0.074	0.275	0.042	0.36	0.156	0.425
1200	34.6	0.077	0.68	0.081	0.30	0.047	0.41	0.183	0.50
1500	38.7	0.072	0.635	0.089	0.33	0.049	0.425	0.202	0.55
1800	42.4	0.092	0.81	0.091	0.34	0.050	0.43	0.238	0.65
2100	45.8	0.076	0.67	0.095	0.35	0.056	0.48	0.237	0.645
2400	49.0	0.078	0.63	0.11	0.41	0.060	0.52	0.241	0.655
2700	52.0	0.079	0.69	0.104	0.385	0.061	0.52	0.272	0.74
3000	54.8	0.080	0.70	0.109	0.405	0.062	0.53	0.286	0.78
3600	60.0	0.084	0.74	0.115	0.425	0.070	0.60	0.313	0.85
∞		0.114		0.27		0.116		0.368	
Slope:		5.00×10^{-3}		5.128×10^{-3}		7.63×10^{-3}		1.382×10^{-2}	
D/r^2 (sec^{-1}):		4.909×10^{-6}		5.1633×10^{-6}		1.143×10^{-5}		3.7501×10^{-5}	
Activation energy:		34397 J/mol						80697 J/mol	

Table 4.11: **Diffusion Data of Dye (72) on Wool and Nylon 6.6 at 303 and 323°K.**

Time		303K				323K			
t (s)	t ½	Wool		Nylon 6.6		Wool		Nylon 6.6	
		Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞
600	24.5	0.079	0.36	0.043	0.22	0.12	0.27	0.074	0.40
900	30.0	0.096	0.435	0.053	0.265	0.14	0.30	0.083	0.45
1200	34.6	0.100	0.45	0.051	0.26	0.15	0.33	0.109	0.59
1500	38.7	0.101	0.46	0.064	0.32	0.17	0.38	0.104	0.56
1800	42.4	0.104	0.47	0.073	0.365	0.18	0.40	0.11	0.59
2100	45.8	0.105	0.475	0.075	0.375	0.20	0.44	0.116	0.525
2400	49.0	0.107	0.47	0.080	0.40	0.21	0.46	0.123	0.66
2700	52.0	0.110	0.50	0.083	0.415	0.22	0.495	0.126	0.68
3000	54.8	0.110	0.50	0.089	0.445	0.23	0.50	0.135	0.73
3600	60.0	0.114	0.52	0.095	0.475	0.25	0.55	0.143	0.775
∞		0.22		0.20		0.45		0.185	
Slope:		2.73×10^{-3}		7.347×10^{-3}		8.50×10^{-3}		1.063×10^{-2}	
D/r^2 (sec^{-1}):		1.4634×10^{-6}		1.0599×10^{-5}		1.4186×10^{-5}		2.219×10^{-5}	
Activation energy:		92447 J/mol						30072 J/mol	

Table 4.12: **Diffusion Data of Dye (73) on Wool and Nylon 6.6 at 303 and 323°K.**

Time		303K				323K			
t (s)	t ½	Wool		Nylon 6.6		Wool		Nylon 6.6	
		Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞	Ct	Ct/C∞
600	24.5	0.065	0.33	0.059	0.21	0.064	0.32	0.103	0.41
900	30.0	0.070	0.35	0.074	0.26	0.073	0.365	0.113	0.45
1200	34.6	0.075	0.38	0.087	0.31	0.079	0.40	0.135	0.54
1500	38.7	0.078	0.39	0.092	0.325	0.085	0.425	0.135	0.54
1800	42.4	0.082	0.41	0.103	0.36	0.085	0.43	0.138	0.55
2100	45.8	0.085	0.425	0.114	0.40	0.095	0.475	0.154	0.615
2400	49.0	0.087	0.44	0.118	0.42	0.099	0.50	0.163	0.65
2700	52.0	0.090	0.45	0.125	0.44	0.105	0.525	0.171	0.685
3000	54.8	0.094	0.47	0.135	0.475	0.11	0.548	0.174	0.70
3600	60.0	0.098	0.49	0.43	0.505	0.129	0.585	0.186	0.75
∞		0.200		0.284		0.20		0.250	
Slope:		4.6429×10^{-3}		8.22×10^{-3}		7.5862×10^{-3}		1.00×10^{-2}	
D/r^2 (sec^{-1}):		4.2326×10^{-6}		1.3267×10^{-5}		1.13×10^{-5}		1.9635×10^{-5}	
Activation energy:		39966 J/mol						15955 J/mol	

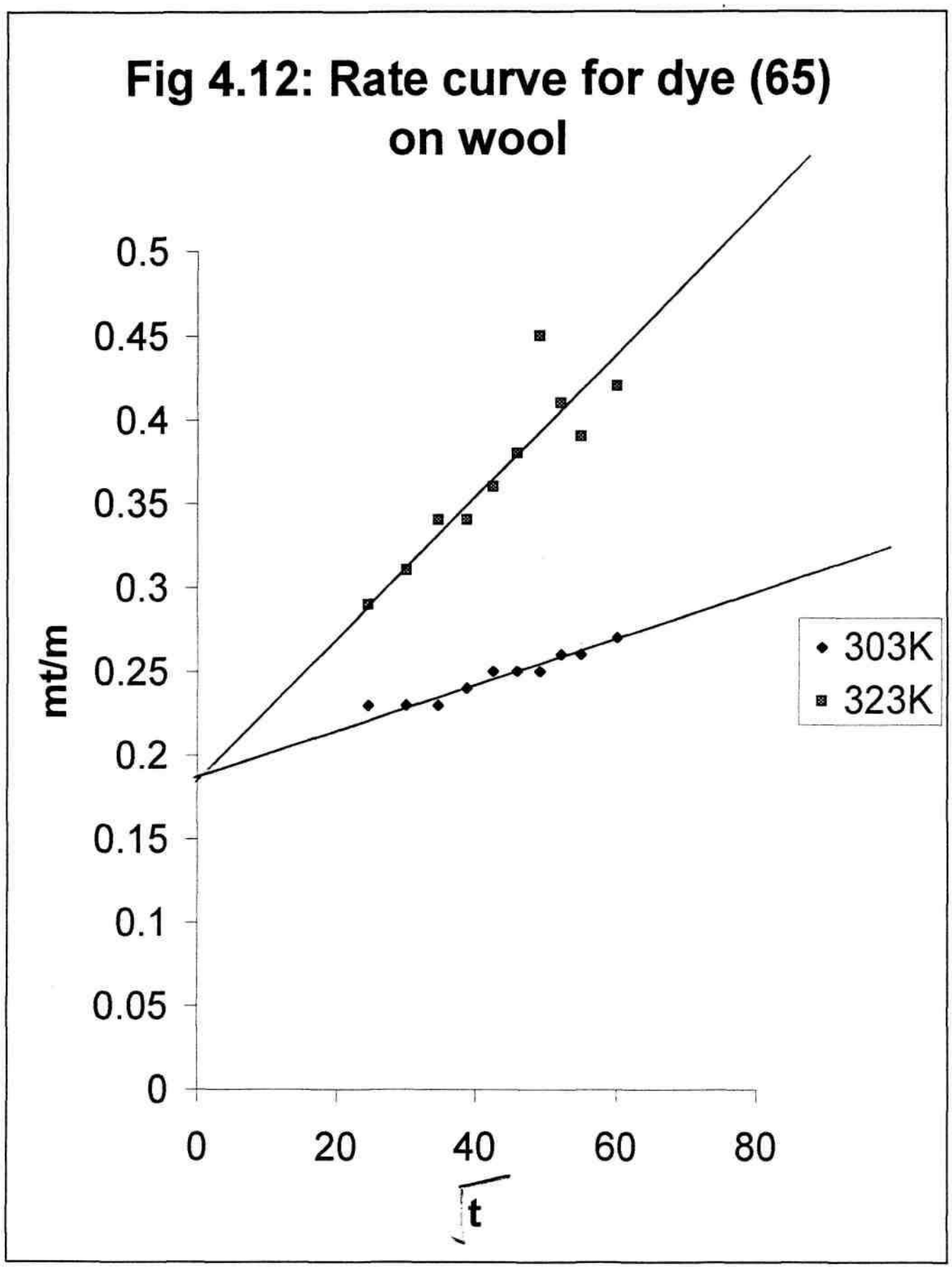

Fig 4.12: Rate curve for dye (65) on wool
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
mt/m
0
20
40
60
80
√t
303K
323K

Fig 4.13: Rate curve for dye (66) on wool

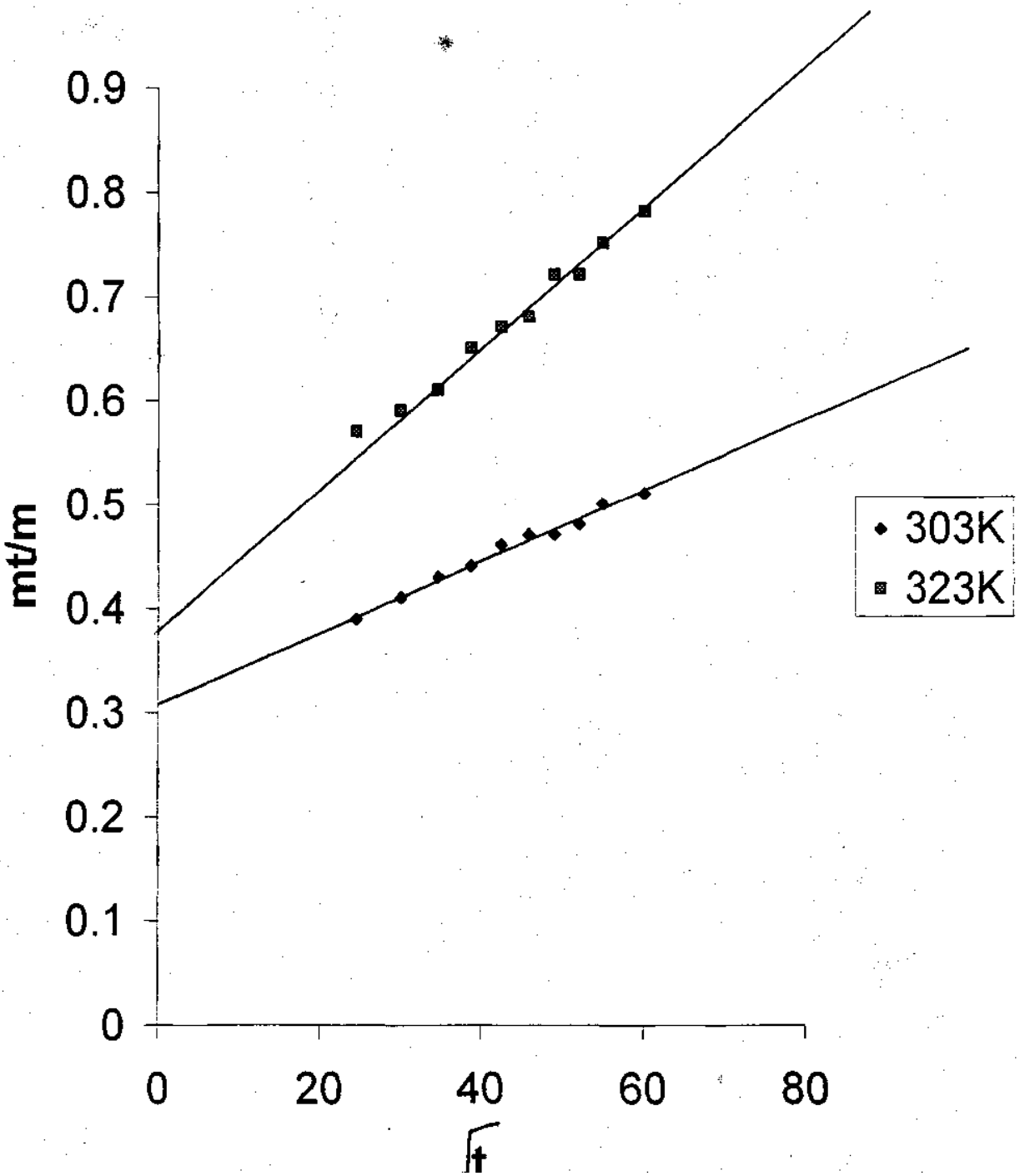


Fig. 4.14: Rate curves for dye (67) on wool

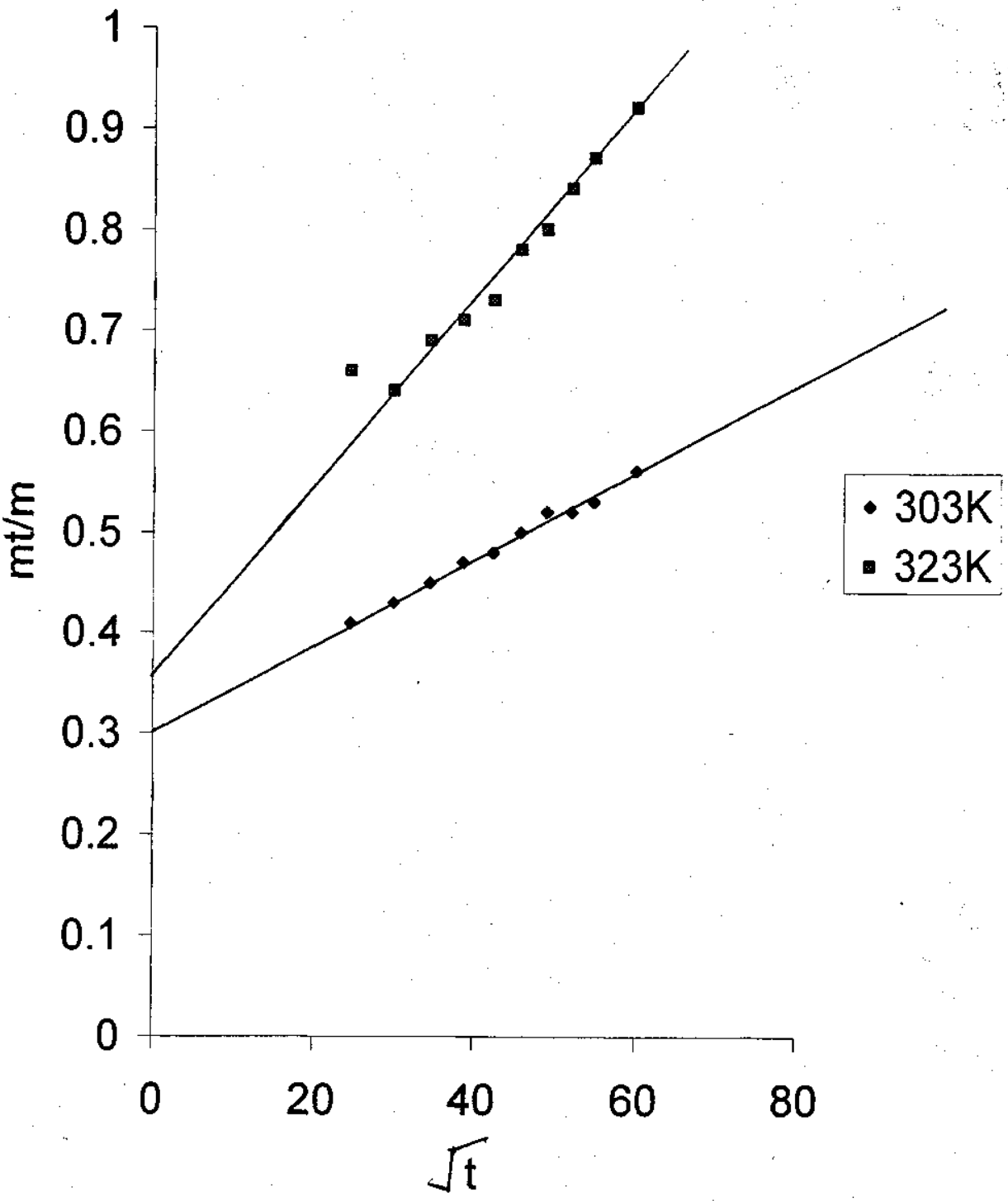


Fig 4.15: Rate curves for dye (68) on wool

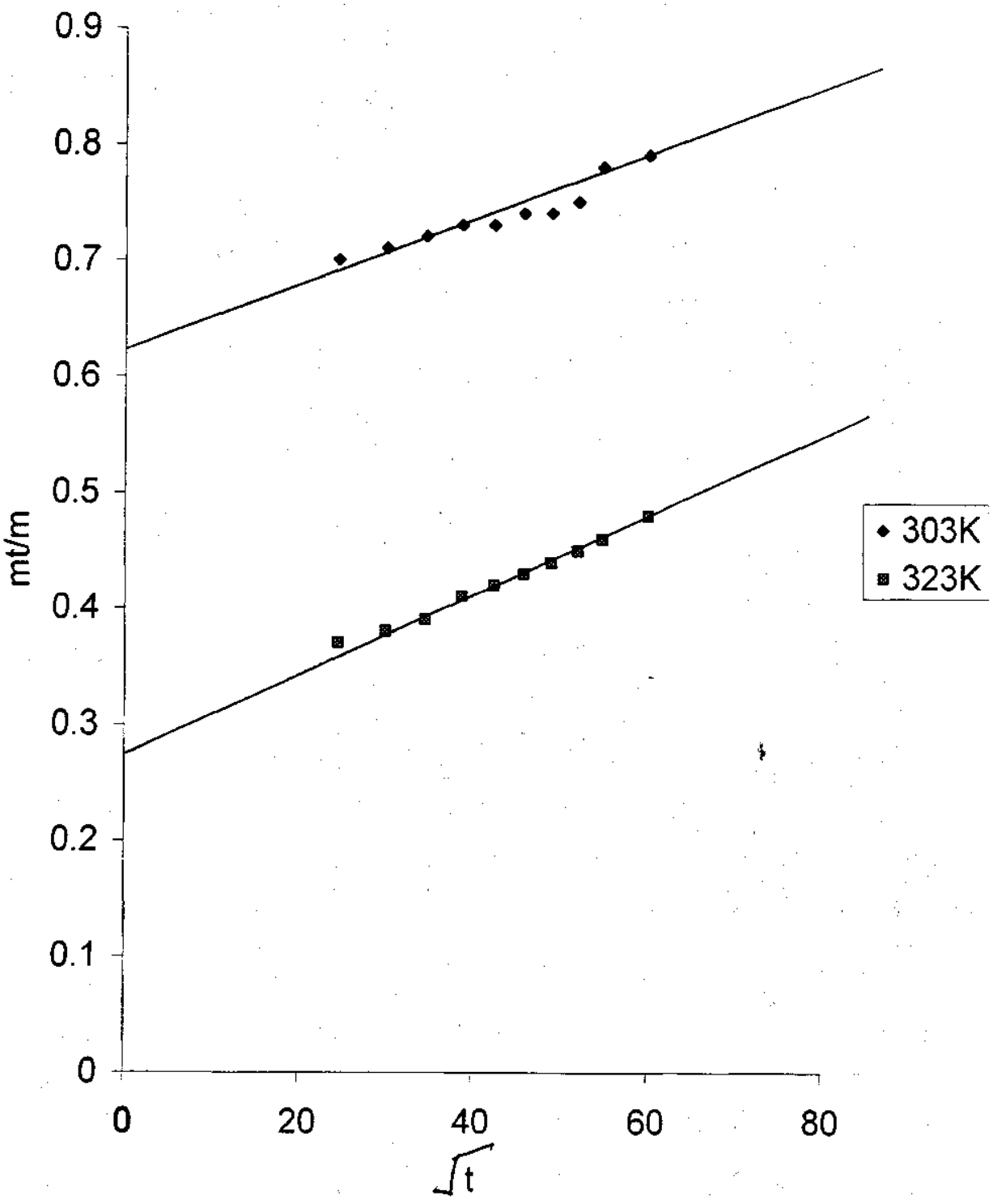


Fig 4.16: Rate curves for dye (69) on wool

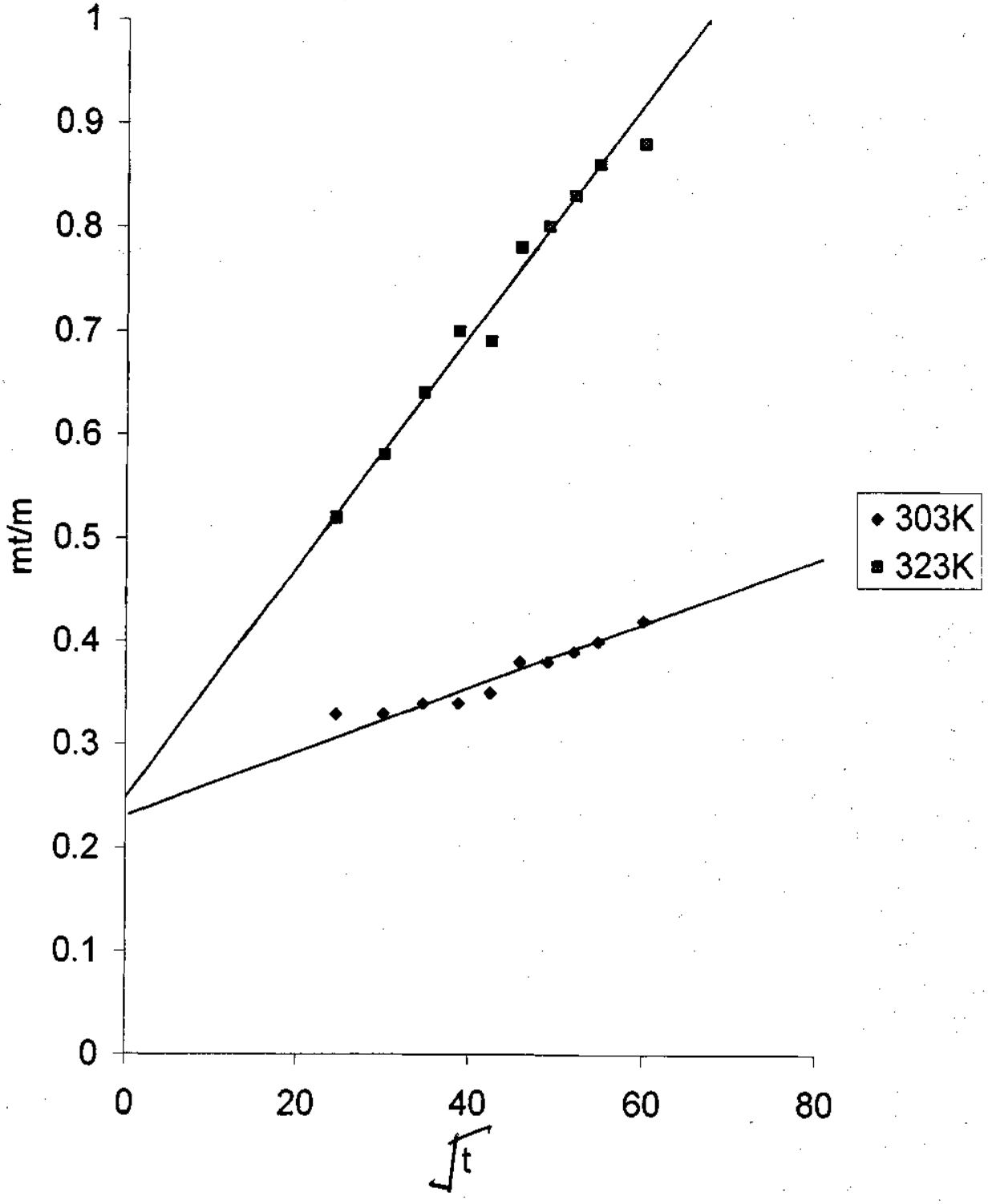


Fig 4.17: Rate curves for dye (70) on wool

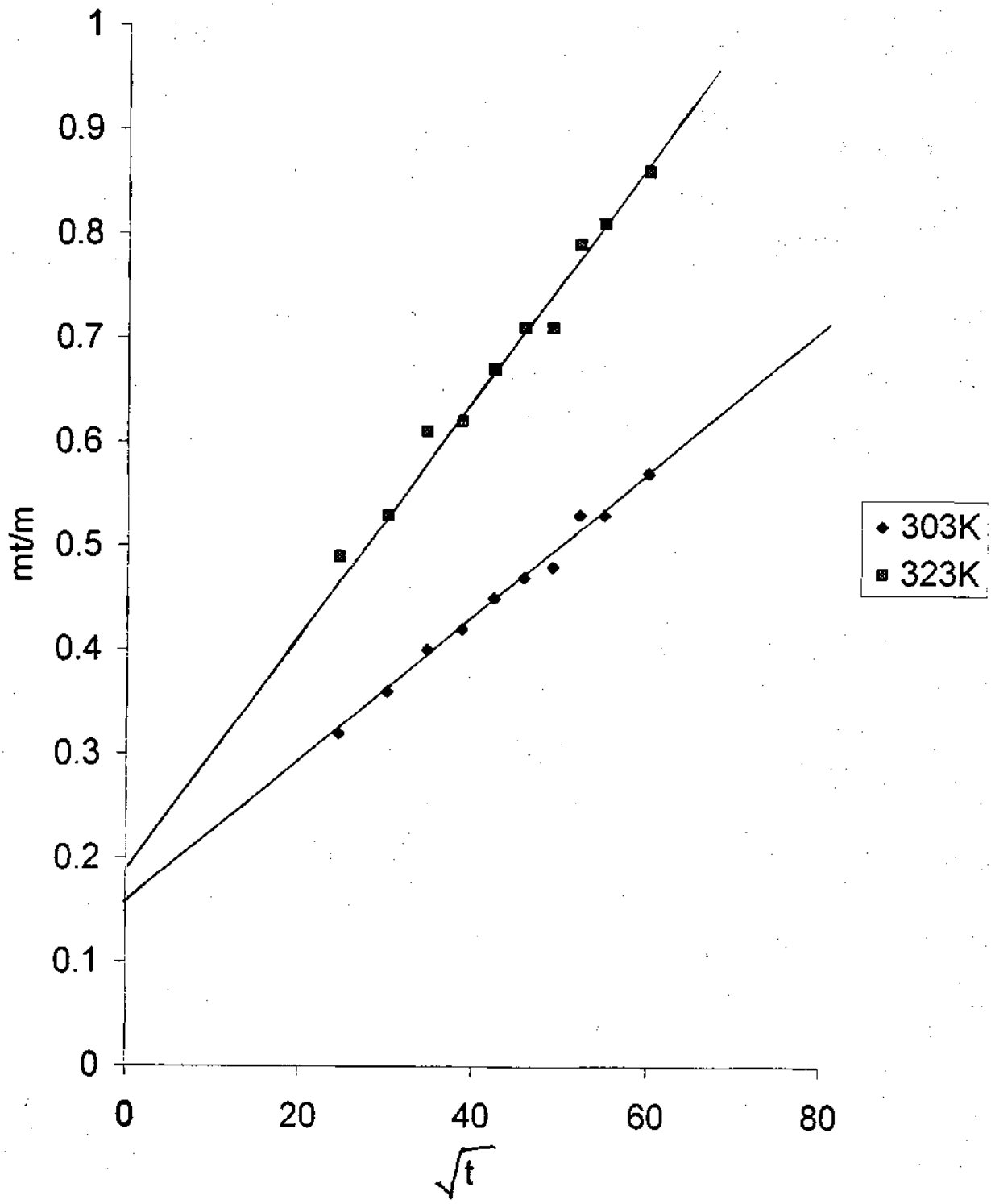


Fig 4.18: Rate curves for dye (71) on wool

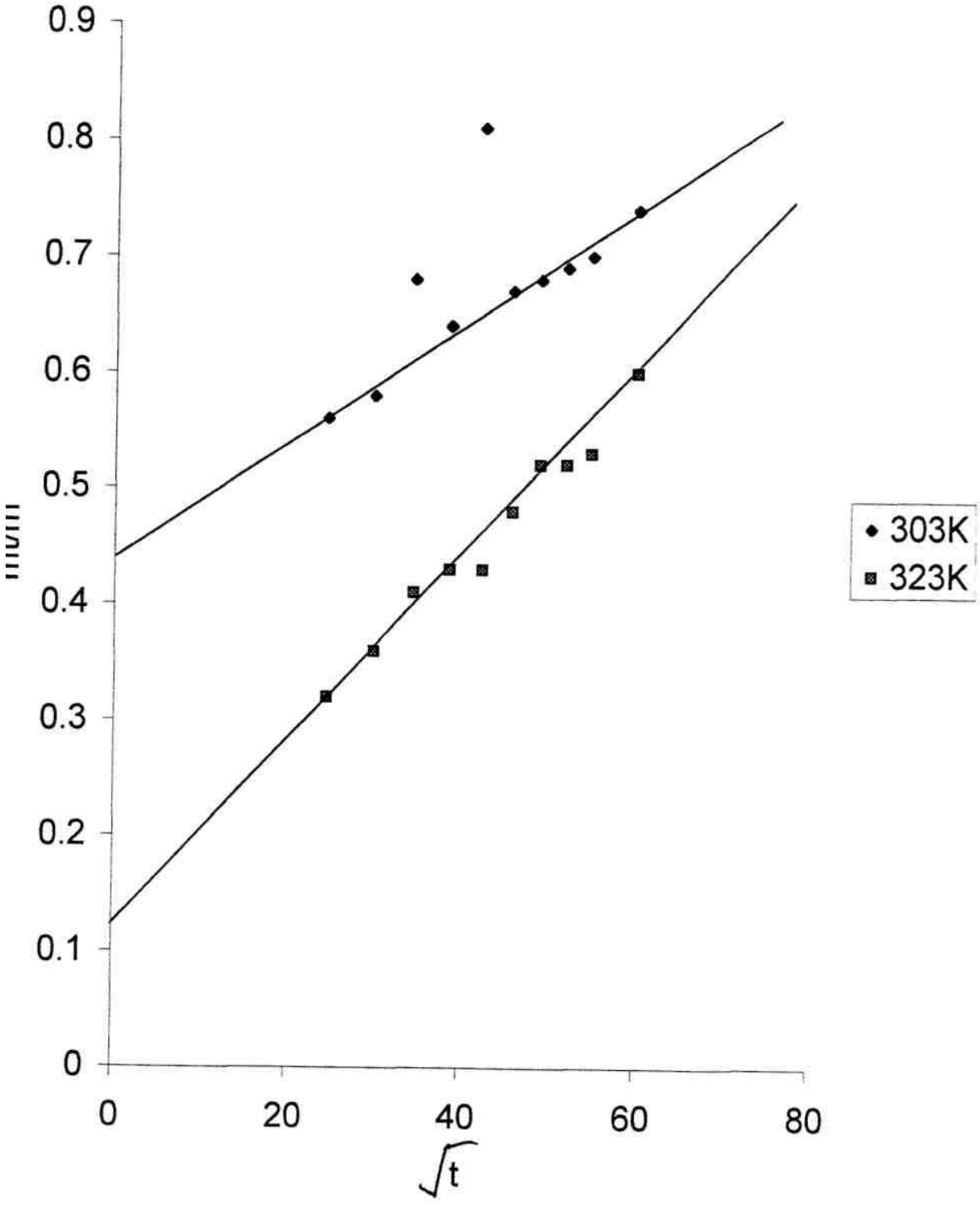


Fig 4.20: Rate curves for dye (72) on wool

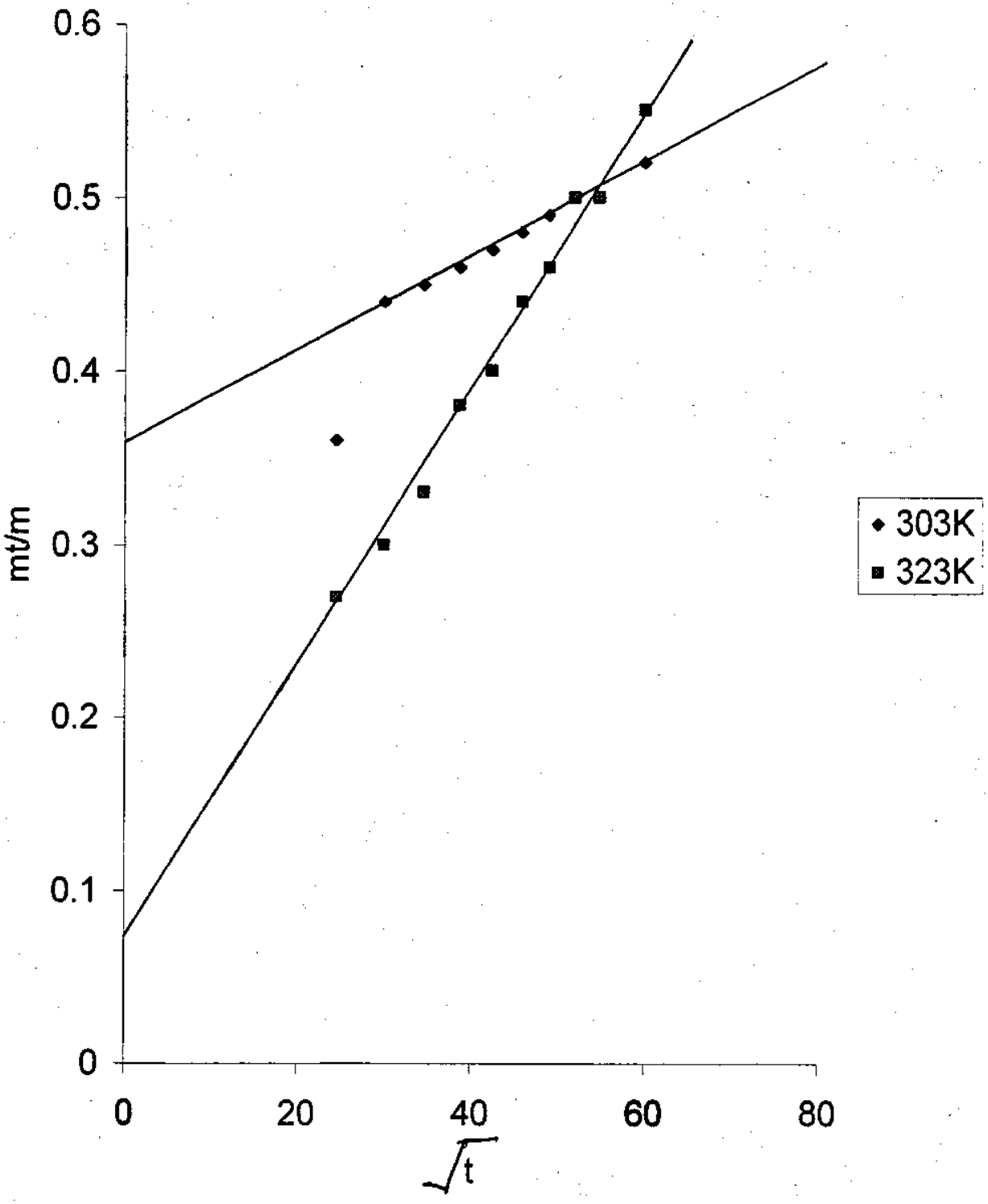


Fig 4.21: Rate curves for dye (73) on wool

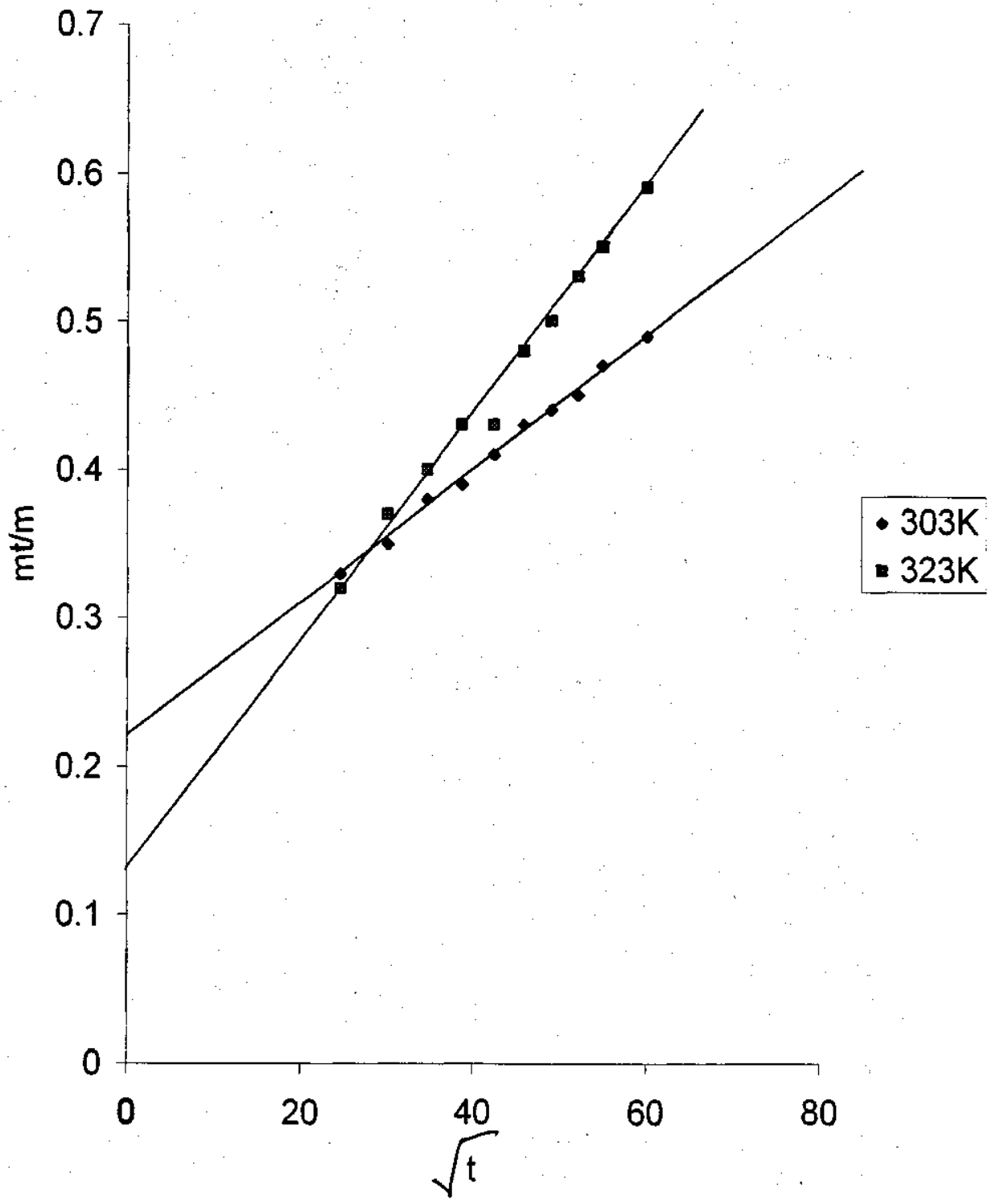


Fig 4.22: Rate curves for dye (65) on nylon 6.6

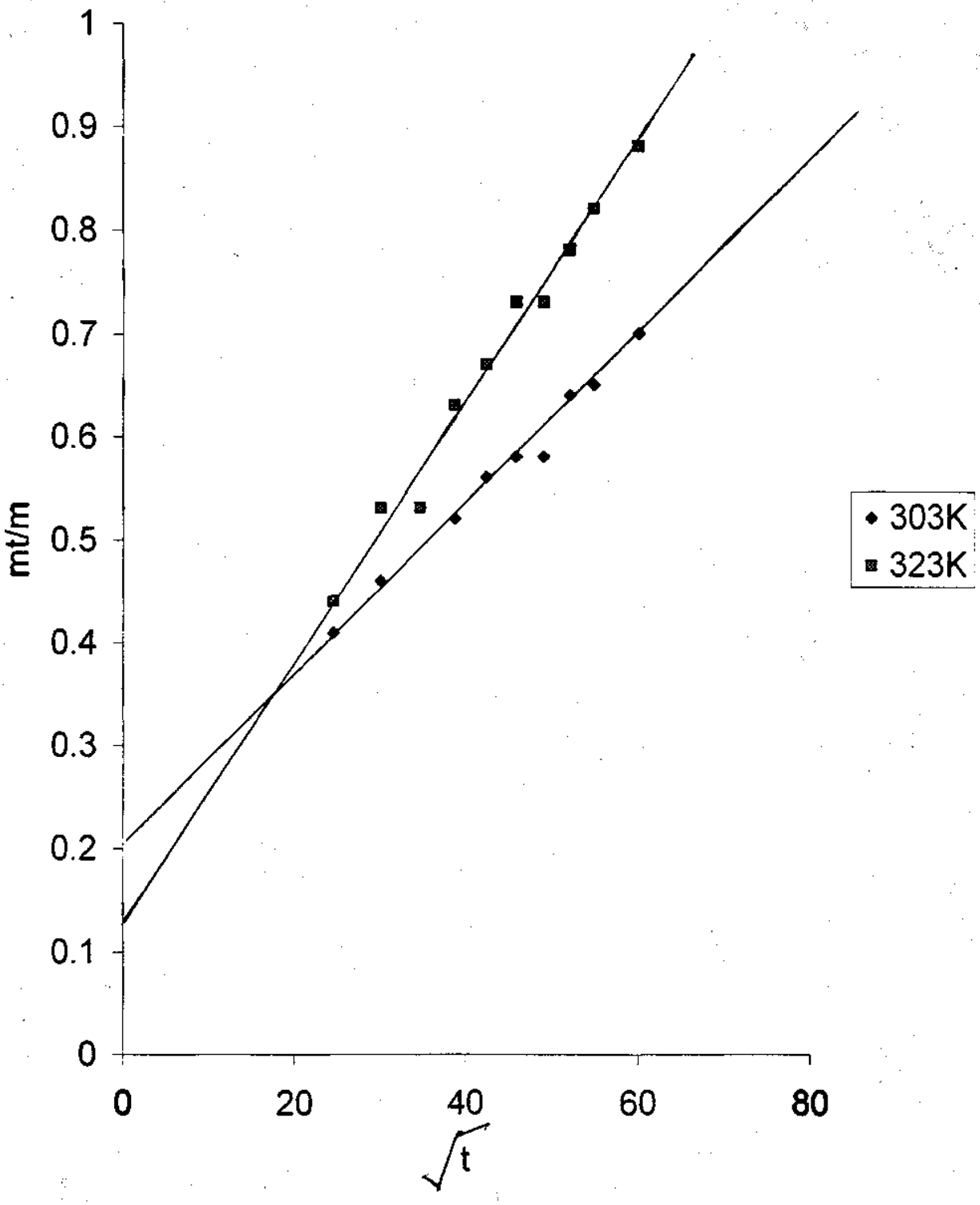


Fig 4.23: Rate curves for dye (66) on Nylon 6.6

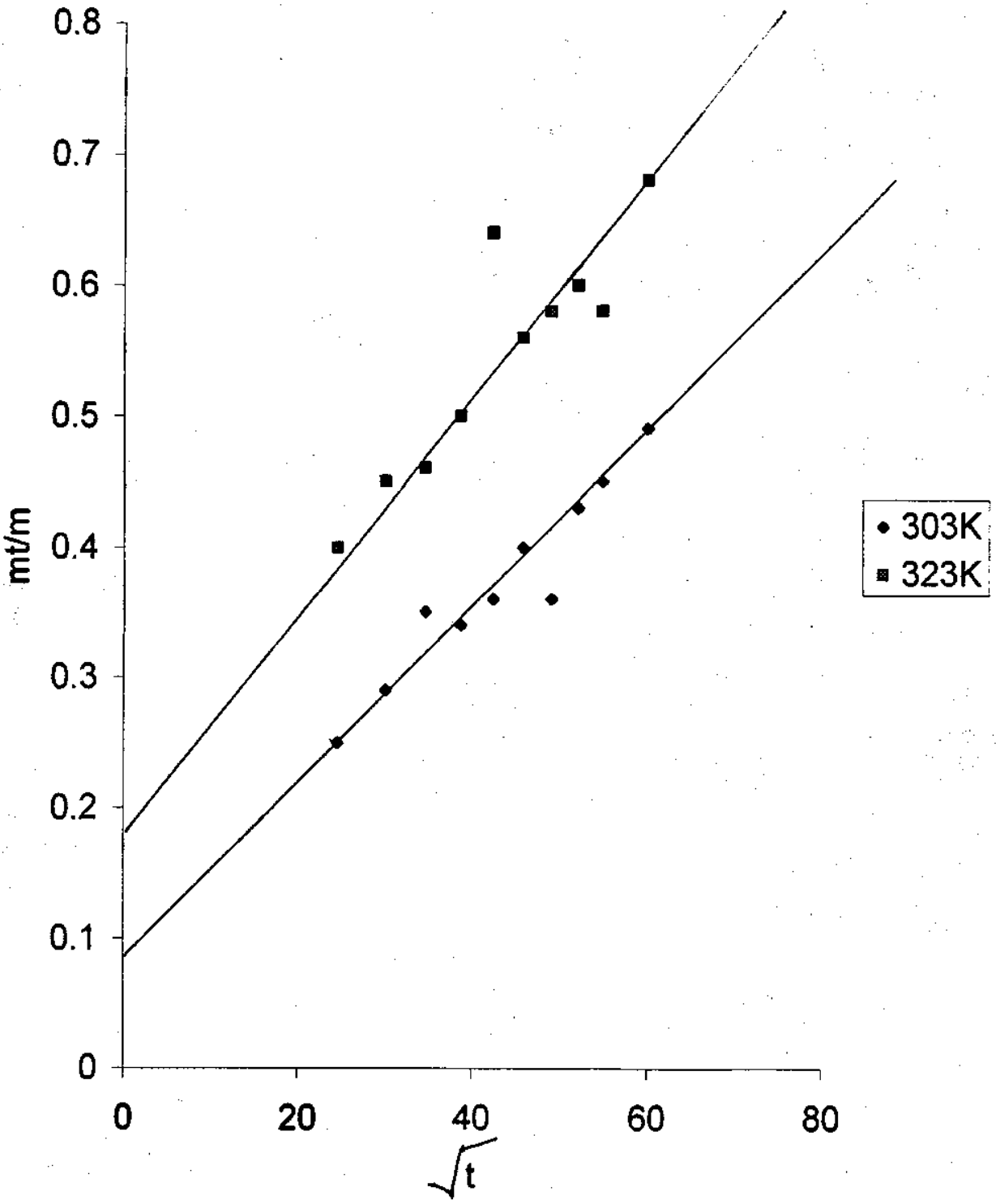


Fig 4.24: Rate curves for dye (67) on nylon 6.6

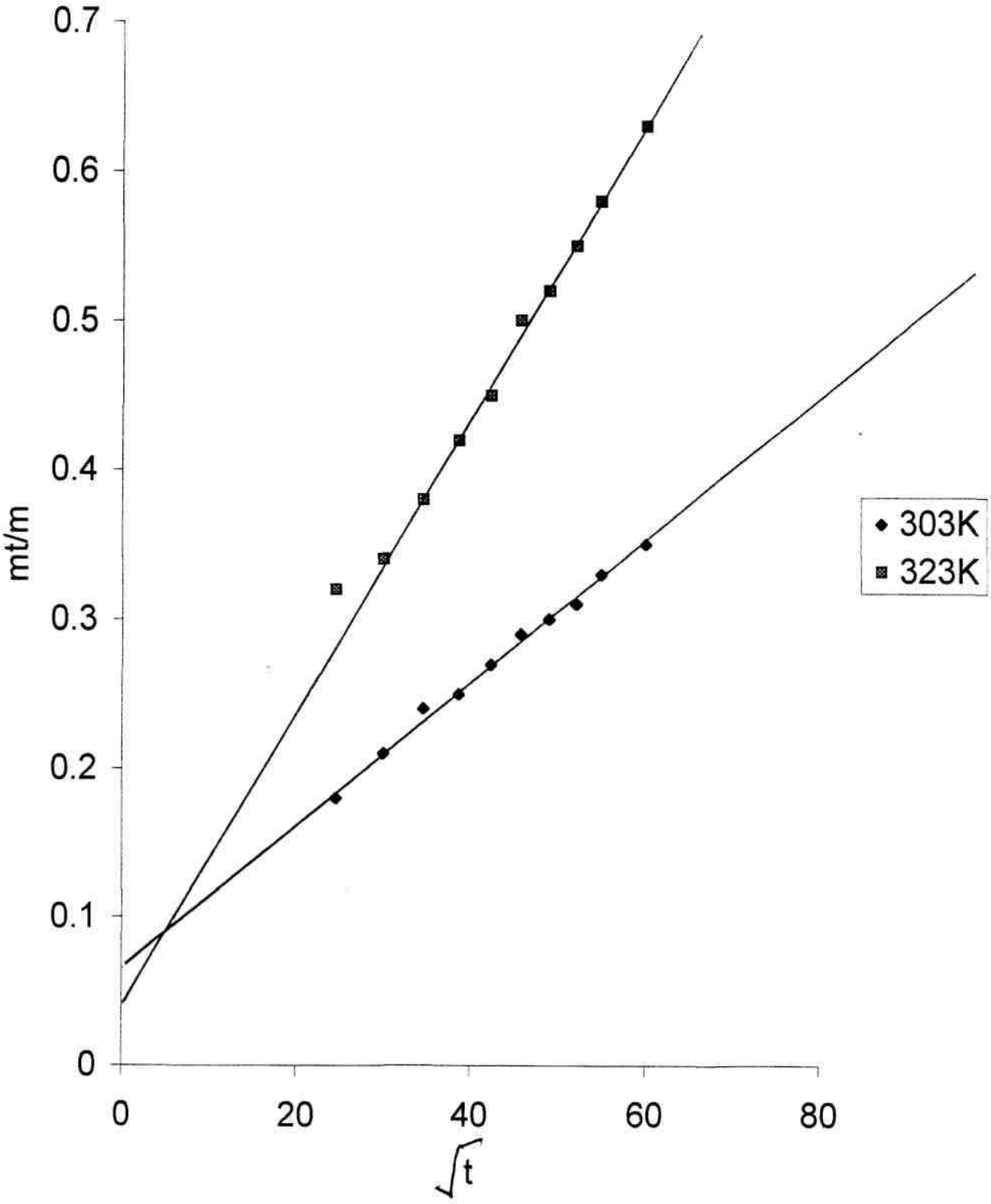


Fig 4.25: Rate curves for dye (68) on nylon 6.6

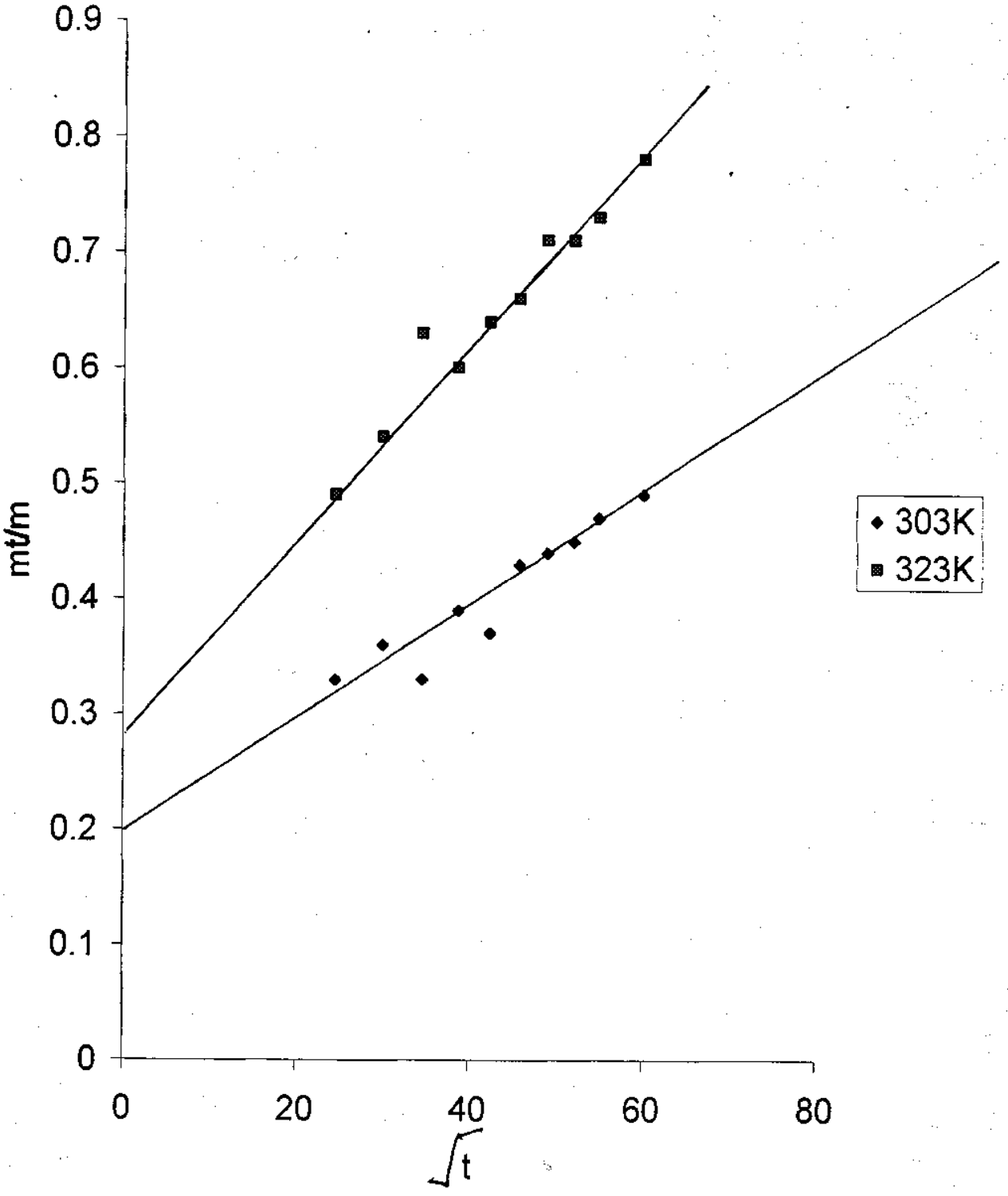


Fig 4.26: Rate curves for dye (69) on nylon 6.6

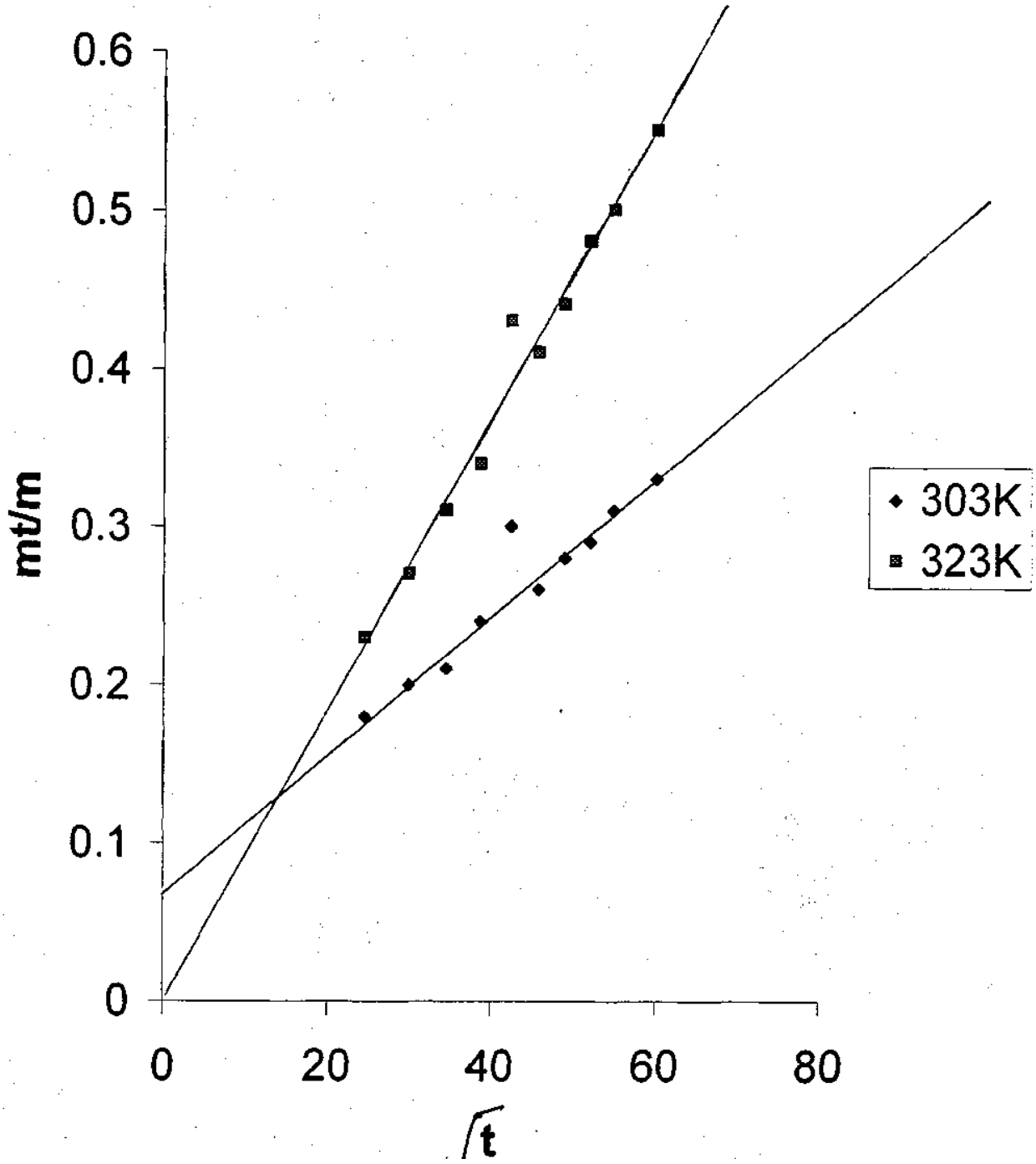


Fig 4.27: Rate curves for dye (70) on nylon 6.6

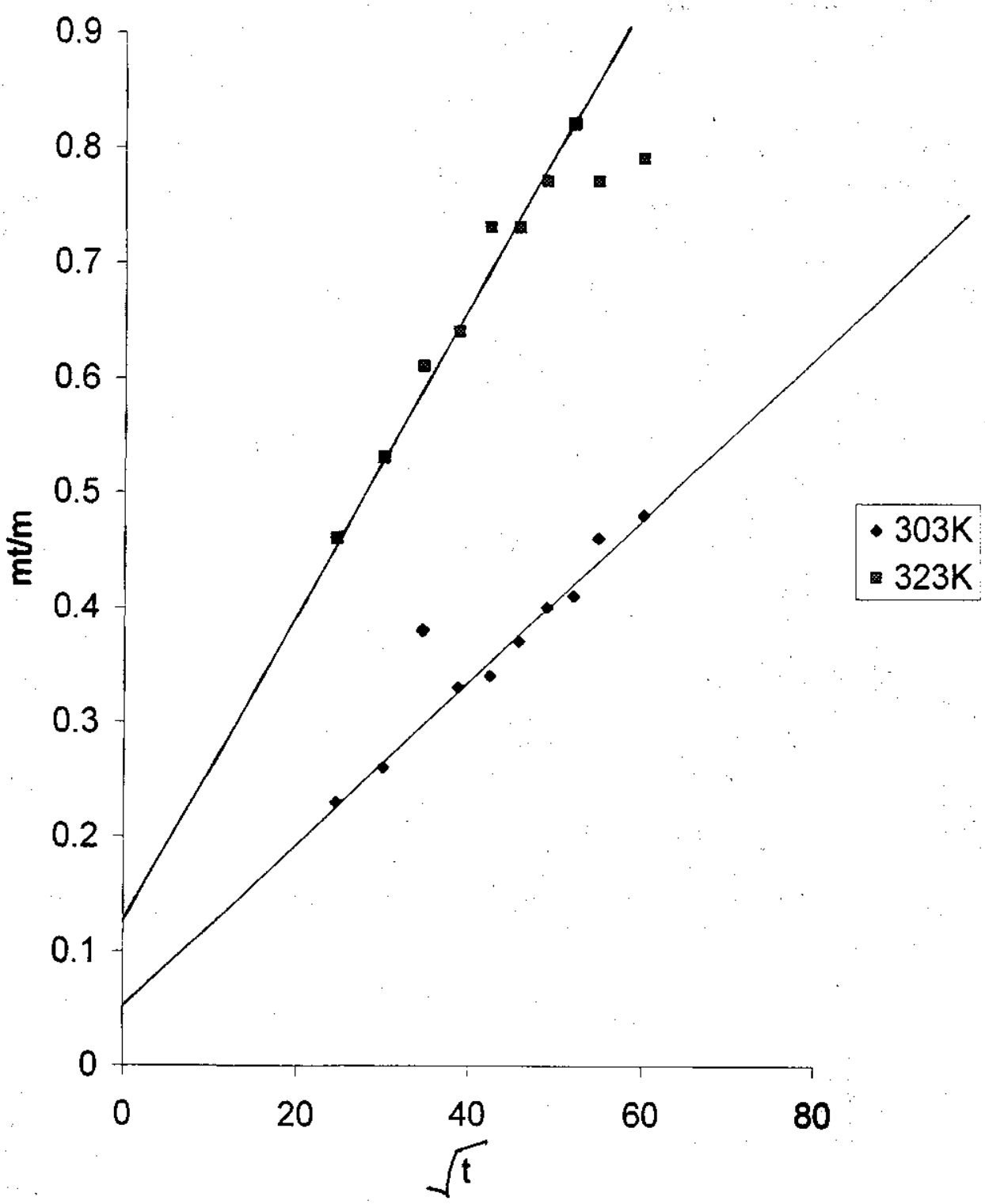


Fig 4.28: Rate curves for dye (71) on nylon 6.6

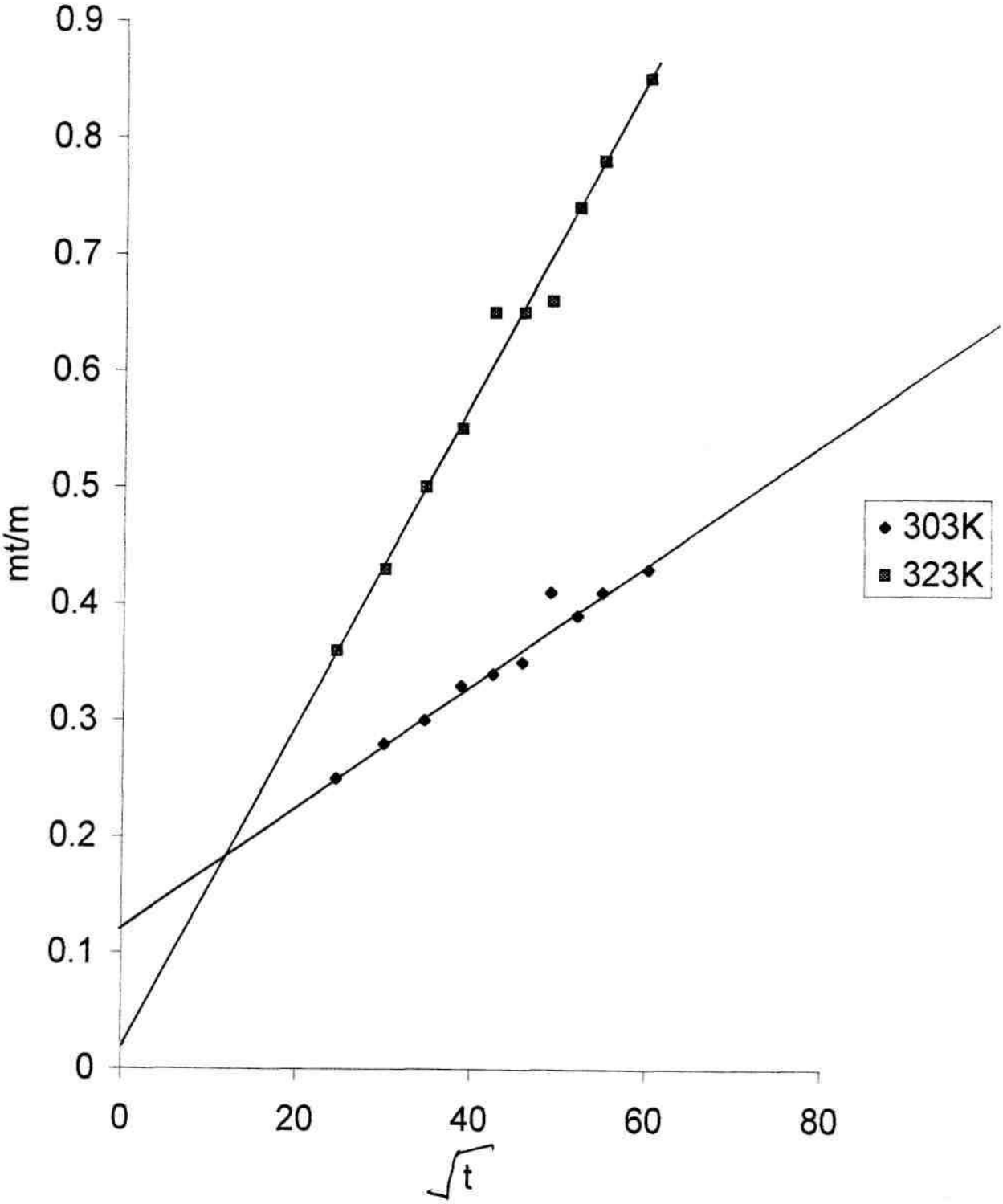


Fig 4.29: Rate curves for dye (72) on nylon 6.6

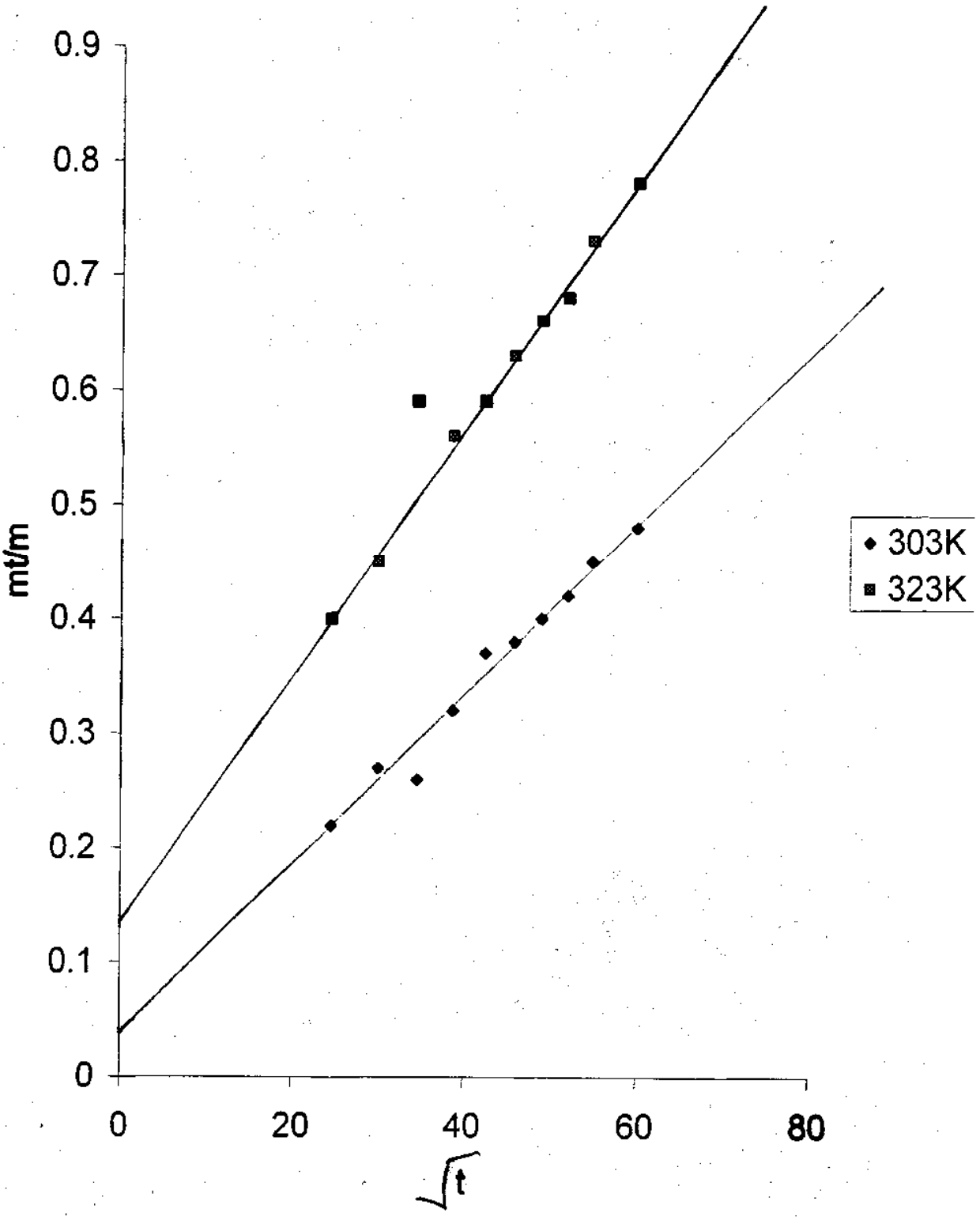
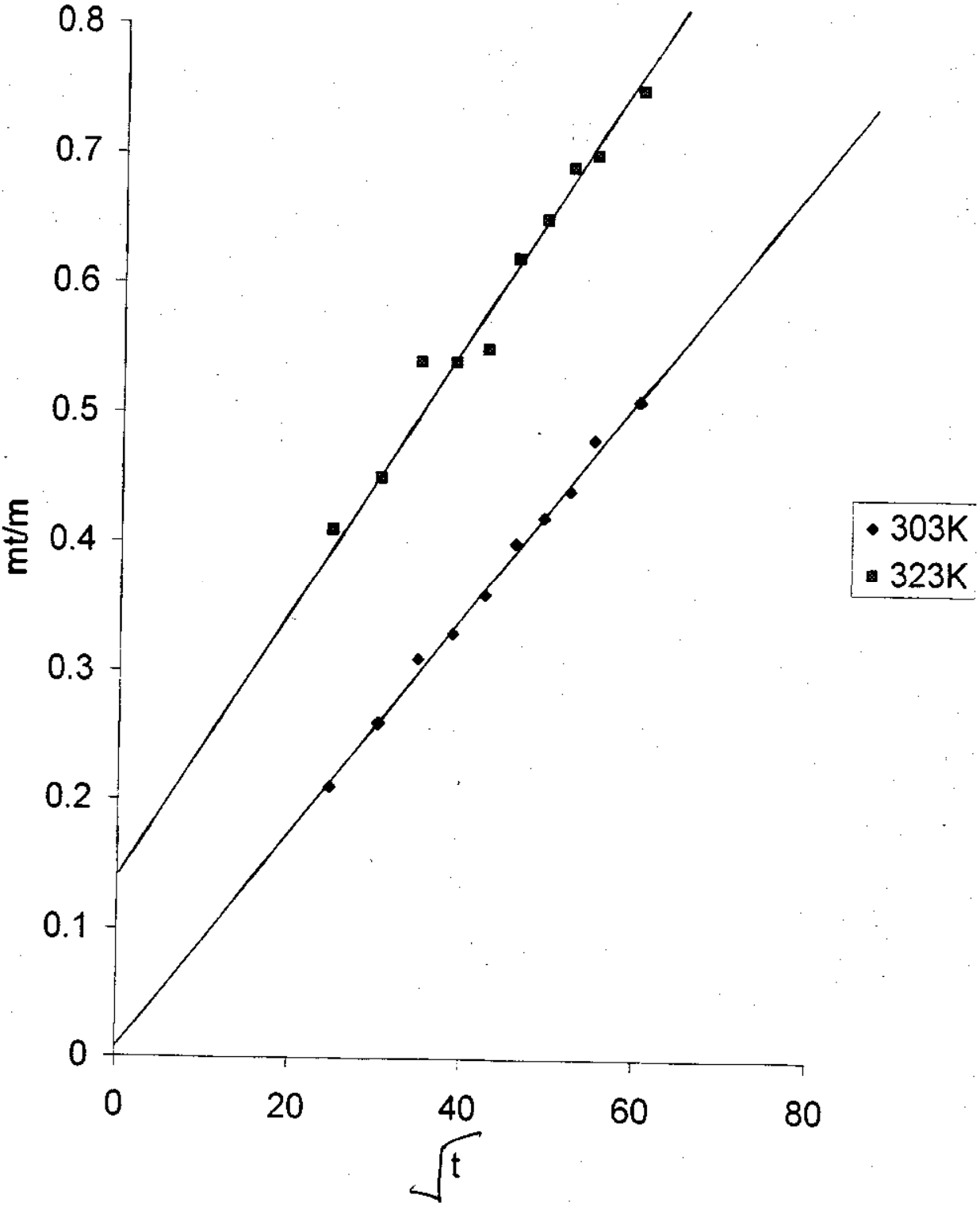


Fig 4.30: Rate curves for dye (73) on nylon 6.6



Tables 4.4 to 4.12 were used to plot Figures 4.12-4.30. Their slopes were determined after which the apparent diffusion coefficients per square of the radius of the fibres were determined according to the method used by Peters et. al.[168] The activation energies were calculated using Arrhenius equation.

Diffusion coefficient is believed to depend on several factors, some of these are: the affinity of the dye for the fibre, the size and structure of the dye molecule, the hydrophobic character, dye aggregation in the solution and fibre phases, the influence of electrical factors due to charges on the fibre surface and on the dye if both fibre and dye contain ionizable groups, the crystallinity or otherwise of the fibre, the pH, presence or absence of electrolytes, etc.

To make the comparison meaningfully, the pH was made constant at pH 4.

It could be seen quite easily that for the type of wool and nylon 6.6 samples under consideration that the diffusion coefficient of nylon 6.6 was in most cases higher than that of wool. Since the rate of aggregation of the dye in solution, pH, temperature etc are the same for both substrates, then, logically, the cause of these difference is associated with the natures of the different fibres. For dye (65), the speed factor by which the dye is faster in nylon than in wool is 45 at 303K and 13 at 323k; for dye (66), it is 4 at 303k

and 2 at 323k; it is 1.1 at 303k and 1.06 at 323k for dye (67); for dye (69) it is 2 at 303k and 0.32 at 323k; 0.917 at 303k and 1.25 at 323k for dye (70); 7.66 at 303k and 7 at 323k for dye (68); 3.13 at 303k and 1.74 at 323k for dye (73); 1.05 at 303k and 3.28 at 323k for dye (71), and 7.24 at 303k and 1.564 at 323k for dye (72). It is also observed that for majority of the dyes the speed factor decreases with increase in temperature. Two reasons can be advanced to explain these differences. The first being the fact that wool fibres contain a membrane on the outer surface, called the epicuticle that offers a great resistance to dye diffusion.[209-210] The second reason being that the sites for adsorption are more in wool than in nylon. This would mean that the nylon substrate will become saturated much faster than wool. The higher the temperature, the faster to approach saturation level for both fibres and the easier to break the resistance posed by the epicuticle.

It is seen as well that with increase in molecular weight of the dyes the speed difference also reduced. The effect seemed to be caused by the increase in the rate for wool and a reduction in the rate for nylon. It is seen that for wool at 303k the coefficient of diffusion trend is dye (65) < dye (66) < dye (67) < dye (70). Between dye (69) and dye (73), they have almost the same structure, dye (73) has (higher molecular weight) and is seen to have higher diffusion coefficient, it is also true with dye (71) and dye (72) where

dye (71) recorded higher diffusion coefficient. The same observation can be made at 323k as well.

In the case of nylon 6.6, the trend does not seem quite simple to follow. While dye (65) has higher diffusion coefficient compared to dye (66), dye (66) having lower molecular weight produced higher diffusion coefficient than dye (67). While comparing dye (69) to dye (73), the higher molecular weight , dye (73) recorded higher diffusion coefficient all at 303k.

Bird et al[211] found that dye diffusion coefficient in cellulose acetate decreased with increasing molecular weight. But in addition to the molecular weight, the shape factor as shown by Vickerstaff is equally important. This was confirmed in the dyeing of nylon 6.6 with aminoazobenzene derivatives which gave a decreasing diffusion coefficient with increasing molecular size whereas anthraquinone derivatives showed no such correlation. Glenz et al[212] observed a general linear relationship between a parameter related to the molecular volume of the dye and the reciprocal of its diffusion coefficient. It was also observed that those dyes with -OH, $-NH_2$ groups which have greater affinity by virtue of H bond formations, have their coefficient of diffusion better explained by this factor rather than the size factor.

In general, it is observed that for wool the diffusion coefficient decreased with increasing molecular weight, however, for nylon to agreater extent the reverse is the case.

Activation energy of diffusion is an estimate of the total number of dye molecules having an activation energy (E) in excess of the average energy needed by the diffusing molecules to overcome the restraints to diffusion and move inside the fibres. It can also be defined as the energy required by a diffusing molecule to jump from one adsorption site to an adjacent vacant site. The higher the activation energy the higher the obstacles to diffusions. Technically, it is also a measure of the effect of temperature on diffusion coefficients. The higher the activation energy the higher the diffusion coefficient increase for a given temperature gradient. Activation energy depends on a number of factors both related to the polymeric fibre such as crystallinity, surface characteristics etc to the nature of the diffusing molecule such as molecular weight, molecular volume, presence of attraction sites etc.

For the dyes in consideration, it could be observed that for wool, dye (65) has an activation energy of 94.3 KJ/mole (22.5 KC/mol) dye (66) gave 47.9 KJ/mol (11.4 KC/mol). It is not immediately clear why the higher molecular weight dye (66) should give a dye of half the activation energy

than that of the parent dye. But when dye (67) is considered with an activation energy of 64.6 KJ/mol (15.4 KC/mol), this has a higher activation energy than dye (66), it has a higher molecular weight, additionally, it has double salt link sites, $-COO^-$ and O^-. This would mean that more energy is needed to push the adsorbing molecules between absorbing sites, or to jump between sites. The same explanation is expected for dye (70), but it provided the least activation energy for wool. Similarly based on the advantage of weight alone, dye (73) should register higher activation energy than dye (69), but dye (69) gave the highest activation energy for wool of all the dyes.

Between dyes (71) and (72), contrary to expectation, on weight ground alone, dye (72) gave the higher activation energy. All these are pointing to the fact that other intrinsic properties of the dye molecules such as slimness, molecular volume rather than weight, etc do play tremendous role in analysing activation energy results.[89]

The observations made with respect to wool are also extended to nylon. Dye (65) recorded 42.13 KJ/mole whereas dye (66) recorded 8 KJ/mole. But dye (67) recorded 62.7KJ/mol. Dye (70) recorded 50.4KJ/mole. In nylon too, dye (69) has higher activation energy (40KJ/mol) than dye (73) (16KJ/mol). Contrary to what was observed for

species. The negative chemical potential gradient is directly propor
the temperature and inversely proportional to the concentration
molecules.

The resistance to the diffusional flow is provided by the
resistance. By equating the two opposing forces, the diffusion coeff
obtained to be inversely proportional to the radius which is itself
proportional to the molecular weight of the diffusing molecules. B
this consideration, it can be advanced that a molecule that has more
groups such as H-acid compared to J-acid everything being equal
expected to have a higher mobility in a given substrate. This may
explain why the dye based on H-acid recorded lower activation ener
J-acid in wool. The opposite is the case with nylon partly because

the fibre is inversely proportional to the basicity of the dye. This is
butressing the point that molecules containing ionizable groups such
and sulphonic acids should record slower diffusion coefficient as
higher activation energies. This theory was obeyed only to few cases
dyes under consideration in both fibres.

4.2.4 Determination of the Thermodynamic Parameters of the D

Wool And Nylon 6.6

The final stage of a dye adsorption process is usually reached
state of equilibrium is attained in the system. This equilibrium proce
be described in terms of dye adsorption isotherms under a given
conditions. In the case of acid dye-nylon fibres or acid dye-woo

systems, the equilibrium isotherms are generally expressed as functional relationships between the extent of dye adsorption and the pH of the system at a given dye bath concentration or the extent of dye adsorption as a function of equilibrium dyebath concentration at a fixed pH. Many different approaches have been developed to explain the complex equilibria obtained.[165-168] The sole aim of the theories is to enable the determinations of the different thermodynamic parameters such as the free energies (affinity), enthalpies and entropies of dyeing. Such data give valuable information on the magnitude of the driving force behind the dyeing process, the interplay of forces between all the components in the system resulting from molecular interactions in both the fibre and dyebath and the extent of orientation of the observed dye molecules. Studies on entropy changes are also useful in relation to the extent of hydrophobic bonding that plays an important part in some dye adsorption processes.

The direct method of measuring affinity was used in the case of nylon.[169] Whereas, in the case of wool the displacement method was adopted because of the difficulty in attaining true equilibrium.[165] The results are shown in Tables 4.13 and 4.14.

Table 4.13: Thermodynamic Parameters of the dyes on wool substrate. It is assumed that the saturation value of the substrate is 0.9m/kg[218] , the concentration of the sodium chloride desorbing solution is 0.2M, affording a $[Cl^-]$ of 2.338×10^{-2} g/kg.

Dye No	65		66		67		68		69	
$[D]_f$/ $[Cl]_f$	3.373×10^{-2}		8.68×10^{-1}		9.639×10^{-2}		2.759×10^{-2}		3.229×10^{-2}	
	339K	363K	339K	363K	339K	363K	339K	363K	339K	363K
	4.031	7.21	1.469	4.062	2.485	5.094	2.08	4.03	2.39	
	5.020	6.18	1.396	4.990	2.510	6.910	2.10	3.91	2.48	6.001
	4.130	5.83	1.520	4.41	3.490	6.12	1.89	4.167	3.01	5.980
	3.390	5.64	1.630	4.13	3.290	5.890	2.17	4.04	2.94	6.02
	4.230	5.17	1.55	4.058	3.125	6.326	1.95	4.07	2.00	5.82
Average	4.17×10^{-5}	6.006×10^{-5}	$1..513 \times 10^{-5}$	4.33×10^{-5}	2.98×10^{-5}	6.068×10^{-5}	2.038×10^{-5}	4.043×10^{-5}	2.559×10^{-5}	$5.996.13 \times 10^{-5}$
$-\Delta\mu^\circ$ J/mol	14340	14254	26355	25047	18247	17393	15793	14842	15594	14129
$-\Delta H^\circ$ J/mol	15509		44831		30310		29226		36287	
$-\Delta S^\circ$ J/mol	3.45		54.5		35.6		40		61.04	

Table 4.13 continued:

70		71		72		73	
4.458×10^{-2}		3.032×10^{-2}		6.24×10^{-2}		2.412×10^{-2}	
339K	363K	339K	363K	339K	363K	339K	363K
3.13	6.81	3.65	9.30	1.30	2.34	6.14	1.53
3.24	6.77	3.59	8.98	1.22	2.41	7.05	1.42
3.04	7.06	4.21	9.14	1.23	3.29	6.13	1.38
3.19	5.92	3.57	9.42	1.08	3.12	5.09	1.12
3.35	6.82	4.88	9.35	1.20	3.14	5.89	1.35
3.19×10^{-5}	6.676×10^{-5}	3.98×10^{-6}	9.238×10^{-6}	1.205×10^{-5}	2.86×10^{-5}	6.112×10^{-6}	1.36×10^{-5}
15882	14777	20663	19584	19575	18352	18809	17726
31490		35904		36850		34106	
46		45		51		45	

Table 4.14: Thermodynamic Parameters of the Dyes on Nylon 6.6

[D]f/0.05g fabric; V = 0.02

Dye No	65		66		67		68	
	329K	363K	329K	363K	329K	363K	329K	363K
	7.2195	3.707	5.60	2.80	3.091		5.534	3.1469
	7.82	4.10	6.20	3.10	3.50	1.273	6.020	3.02
	6.89	3.50	4.80	2.78	2.99	2.030	4.99	2.89
	7.3	3.70	5.30	3.05	3.42	1.49	6.13	3.12
	8.4	3.80	5.80	1.96	3.07	1.18	5.85	2.910
Average	7.53 x 10^{-5}	3.76 x 10^{-5}	5.54 x 10^{-5}	2.74 x 10^{-5}	3.21 x 10^{-5}	1.431.17 x 10^{-5}	5.705 x 10^{-5}	3.02 x 10^{-5}
[D]f/Kg	1.506	0.752	1.108	0.548	0.642	0.287	1.141	0.604
[D]s/L	0.0425	0.0462	0.0445	0.0473	0.0468	0.0496	0.0443	0.470
-Δμ°J/mol	20,467	20233	19501	19207	17870	17109	19594	19.520
-ΔH°J/mol	22731		22346		25230		20310	
-ΔS°J/mol	6.88		8.65		22.4		2.18	

Table 4.14: Continued

69		70		71		72		73	
329K	363K	329K	363K	329K	363K	329K	363K	329K	363K
2.0	8.00	4.536	2.258	4.39	2.1302	5.601	3.501	6.484	3.203
1.98	7.80	4.800	1.980	4.23	1.9100	6.200	3.25	7.13	3.010
2.01	8.01	5.300	2.010	4.34	2.000	5.800	3.30	6.80	2.980
1.99	7.90	4.900	2.12	4.53	2.080	5.59	2.80	6.70	3.120
1.89	9.00	5.000	1.89	3.99	1.980	5.580	2.70	7.10	2.870
1.97 x 10^{-5}	8.14 x 10^{-6}	4.91 x 10^{-5}	2.05 x 10^{-5}	4.25 x 10^{-5}	2.02 x 10^{-5}	5.76 x 10^{-5}	3.11 x 10^{-5}	6.84 x 10-5	3.04 x 10-5
0.394	0.1628	0.982	0.41	0.850	0.404	1.152	0.622	1.368	0.608
0.048	0.04919	0.0451	0.0480	0.0458	0.0480	0.0442	0.0469	0.0432	0.0470
16465	15424	19134	18286	18697	18242	19626	19615	20159	19540
26538		27340		23100		19732		26149	
30.6		24.9		13.4		0.32		18.2	

As expected the heat of dyeing in all the dyes and in both substrates gave negative values, indicating, as is long established that dyeing is an exothermic process. In both substrates as reported in respect to the work carried out by McGrew et al[156] there is no simple correlation between affinity and dye structure as regard to molecular weight, the number of sulphonic acid groups or the molecular structure. A tenable explanation given by McGrew is that, affinity determined from aqueous solution represents the difference between the standard free energy of the dye on the fibre and in water.

With respect to the sulphonated dyes such as dyes (70), (71) and (72) on nylon, it can be seen that dye (71) is the least in affinity at both temperatures followed by dye (70), with dye (72) being the highest in affinity values. Explanation advanced is that adsorption is believed to be caused by the intrinsic affinity of the dye anion. As adsorption commences there is a decrease in the free energy and also since the dye anion is negatively charged there is an increase in the surface free energy due to an increase in the surface potential. Therefore a polysulphonated dye like the H-acid has a larger negative charge than monosulphonated dyes such as J and sulphanilic acids derivatives, the increase in surface potential due to adsorption will be more even at low levels of adsorption. In contrast, the

molecular structures and also the same basicity. The only likely exp
of this is that the salt link strength in a sulphonic acid group is grea
in a carboxylic acid group with the substrate. This can be ascertain
the dissociating constants of the two groups in which that of t
sulphonic acid bond dye is higher, suggesting that a greater exhaust
be obtained with respect to the sulphonic acid dye anion more t
carboxylic acid dye anion.

When non dissociatable dyes other than nitroso group d
compared i.e dyes (66), (69) and (73) on nylon, dye (73) (20,159 J
329K, 19540 at 363K) is followed by dye (66) (19501 J/mol at 329K
J/mol at 363K) and lastly dye (69) (16465 J/mole at 329K, 15,424 J
363K) is the trend. No available parameters at our disposal seem to

to explain this observation. The superiority of dye (73) seemed to be the contribution of hydrophobic bond formation with the alkyl groups in the nylon substrate. It has larger surface area and the dye can lie flat because a cyano group is sterically advantaged. In contrast the dye (69) with its spatial disposition may not be as alligned as to lead to greater hydrophobically bonded as the unsubstituted aniline. This is however mere speculation. Contribution of hydrophobic bonding between the hydrophobic groups in both the fibre and the dye have been investigated in details by Peters et al.[218]

The affinity of the parent dye (65) is seen to be very competitive with respect to the other dyes under investigations. As already mentioned earlier in the chapter, affinity is believed to be caused by electrostatic salt linkage between the ionized hydroxyl group attached to the nitrogen promoted by the electron withdrawing strength of the nitroso group and the protonated amine groups in both nylon and wool substrates. The dye is seen to be the least in all aspect of weight or volume parameters by virtue of which it can be anticipated to be adsorbed in great quantity at least comparatively before equilibrium as a balance between the negative surface potential and the decrease in the free energy due to adsorption could set in.

With respect to the wool substrate, only slight correlation exist as compared to nylon. The tris of dyes (66), (69) and (73) showed that dye (69)

is still the least, dye (66) has the highest affinity whereas dye (73) came in between. Of course, the tenable explanation of this is that wool is a hydrophilic fibre with a regain of about 30%. It may be that the contribution due to hydrophobic attractions is less important as that between the more adsorption required with respect to dye (66) over the more polar dye (73) to strike a balance between the increase in the negative surface potential and the decrease in the free energy due to adsorption. When dye (67) and dye (70) are compared, dye (67) recorded higher affinities at both temperatures (18,247KJ/mol at 339K; 17393KJ/mol at 363K) as against 15,882KJ/mol at 339K and 14,777KJ/mol at 363K) for dye (70). This is also in contrast to the observation made with respect to nylon. However, sulphanilic acid is the more polar group and more ionized group, its adsorption may be discouraged by the negative surface potential on the wool surface which consideration will bring about an edge with respect to the 4-aminobenzoic acid derived dye (67). Even though these points seem to be clashing, many similar explanation have been advanced pertaining to similar cases. For example, in their attempt to propose a unified interaction theory for all dye-fibre system, Derbyshire and Peters[218] supported primarily by calorimetric investigation postulated that the fundamental contribution to the standard affinity of dyeing arises from non polar van der Waals forces. They

suggested that electrostatic interactions between charged groups of fibres and dye ions, the dipole interactions and hydrogen bonding are all of secondary importance and that hydrophobic parts of the dye molecule have adequate affinity for the hydrophobic parts of the fibre. On this explanation, the case of dye (67) having higher affinity than dye (70) rests. Another explanation proposed by Vickerstaff[166] suggested that the polar group in wool internal surface is hydrated which reduces the substantivity of the fibre for negatively charged dye anions. This will then mean that the driving force will be the hydrophobic interaction forces or the slowly diffusing controlled elimination of the hydrated water by polar dye anions enabling the dye molecule to come sufficiently close to the fibre so that the dispersion forces can be effectively operative and bind the dye to the surface. Strong indication of the strength of these hydrophobic interaction was further butressed when Peters et al [218] found out that the heat of dyeing for CI Acid orange 7 with wool at infinite dilution was equal to the heat of dimerization of the acid dye. This suggested that the same type of force exists in the adsorption of this dye by wool and also in dye aggregation. Zahn[220] explained that in a swollen fibrous protein such as wool, salt linkages or ionic pair bonds as well as hydrogen bonds are weak as a result of the hydration of the polar groups in the fibre. He further stated that hydrophobic

interactions have a stabilizing effect. Ferrini[221] and Zollinger[222] also obtained results that showed that the decrease in dye adsorption in a group of dyes that have the same basic structure differing only in the nature of side chains, is consistent with hydrophobic bonding. Similar interpretations were made by Sivaraja et al.[254]

When the sulphonated dyes were observed with respect to wool, dye (71) gave the highest affinity followed by dye (72) and finally dye (70). This result is much similar with what was obtained in the case of nylon, if not for the swapping of positions between dye (71) and (72). The main reason for the swapping may be due to the assumptions made in the experiment that is the salt-linkage involves only the hydroxylate anion in the dye. The same hydrophobic interaction explanation is maintained in this case as well.

Contrary to the findings in nylon substrate, the parent dye (65) produced the least affinity values at all temperatures. Probably because the dislodgements of the hydration water on the polar groups could not be accomplished as completely which would mean that the hydrophobic force that would strengthen the interactions will be weak.

Some of these interpretations are not clear-cut evidence because of the influence of aggregation equilibria superimposed on the adsoption equilibria for these dyes.[220-221]

As a general observations, the dyes under investigation recorded higher affinity values at the temperatures used in the determination for nylon than wool. This is in conformity with the established facts. The main reason for this is attributable to the hydration water that shields easy accessibility to the interaction sites on the wool substrate which is about 30% water. Coupled to this will be the allignment of the chains in nylon fibres making them more amenable for hydrophobic and other non polar van der Waal forces of attractions. A confirmation of the above inference can be seen by comparing the heats of dyeing and entropy shown in Table 4.15

With the exception of the parent dye (65), the heat of dyeing in the case of wool are generally higher than that of nylon. This infers that the coulombic forces are higher stressing that hydrophobic forces are greater in the case of nylon. This is further strengthened by the more increase in the entropy term for nylon than wool. As a rule, dye adsorption process is regarded as one in which the dye undergoes a transition from a state of random distribution of dye ions in solution to a state of restricted movement and a more ordered arrangement of adsorbed dye on the fibre surface. To

Table 4.15: The Heat and Entropy of Dyeing for the Dyes on wool and Nylon 6.6

Dye No	$-\Delta H^{\circ}$ (J/mol)		$-\Delta S^{\circ}$ (J/mol)	
	Wool	Nylon 6.6	Wool	Nylon 6.6
(65)	15509	22731	3	7
(66)	44837	22346	55	9
(67)	30310	25230	36	22
(68)	29226	20310	40	2
(69)	36287	26538	61	31
(70)	31490	27340	46	25
(71)	35904	23100	45	13
(72)	36850	19732	51	00
(73)	34106	26149	45	18

support their claims for hydrophobic forces interplay in the dyeing of wool, Sivaraja et al[219] used the principle of minimum structural changes by substituting methyl, butyl and phenyl side chains into an acid dye. The thermodynamic parameters indicated an increase in affinity, decrease in heat of dyeing and an increase in the entropy as side chain increases in size and molecular weights. They concluded that hydrophobic interaction resulted in the more influence of increased entropy meaning either more positive entropy value or less negative value and less heat of dyeing since it is space-related force. Similar observations are hereby also extended when the thermodynamic parameters are compared with nylon relative to wool of the given dyes under investigation.

The less entropy observed for the dyes in wool is attributed from the changes in the structure of water in the system. Water molecules in liquid water are highly aggregated and therefore the introduction of a hydrophobic dye ion results in the disaggregation of water molecules.[254]

4.2.5 The Effect of pH on the Fixation of the Nitroso Dyes on Nylon 6.6

Test runs confirmed our anticipation that it would be possible to post metallize nitroso dyeings by acid fixation mechanism on wool and nylon 6.6. The dyes proved unable to dye cellulosic fibres and polyester even by

mordanting techniques. Attempt is hereby made to study the effect of pH on the fixation of the parent 2-nitro-1-naphthol and the coupled azo dyes that resulted after diazotising aniline and 4-amino benzoic acid as examples. Test runs showed that only $FeSO_4$, $Co(NO_3)_2$, $CuCl_2$ and $NiCl_2$ gave distinctive hue differences as a result of mordanting. Therefore, these metals were used to investigate this effect. Further test runs showed that to manifest distinctive hue difference the dyes needed to be applied at shallow shades, therefore, 0.5% shade was selected for applying the dyes using 0.2% acetic acid at a liquor to goods ratio of 50:1 at the boil for 30 minutes. Preliminary investigations showed that there was no increase in the degree of fixation by using salt concentration from 0.5% to 5%, infact, the effect proved to be a decrease. As a result a 0.5% treatment of the salt concentration was used. Further more higher liquor ratio proved detrimental to the fixation value. A liquor to goods ratio of 5:1 was used, treatment time being 15 minutes at the boil. 1% HCl and 1% NaOH were used to control the pH. The drastic conditions used in this study made wool unsuitable.

Table 4.16: Effect of pH on the Fixation value of Dye (65) on Nylon 6.6 Mordanting with different Metallic Salts.

$FeSO_4$		$Co(NO_3)_2$		$CuCl_2$		$NiCl_2$	
pH	% F	PH	% F	pH	% F	pH	% F
1.5	23	1.4	30	1.4	25	1.5	25
1.7	23	1.6	41	1.6	33	3.5	29
2.0	25	1.9	44	1.8	34	5.2	40
3.5	33	5.4	52	3.6	40	7.3	75
7.0	60	7.0	82	7.2	65	8.4	79
9.0	65	9.2	86	9.0	70	9.0	81
9.4	70	9.7	82	10.1	74	10.0	85

Table 4.17: Effect of pH on the Fixation value of Dye (66) on Nylon 6.6 Mordanting with different Metallic Salts.

$FeSO_4$		$Co(NO_3)_2$		$CuCl_2$		$NiCl_2$	
pH	% F	PH	% F	pH	% F	pH	% F
1.7	22	1.6	23	1.6	8	1.1	13
2.0	32	1.9	27	1.8	13	1.5	15
3.5	42	3.5	32	3.7	42	5.2	56
5.3	55	5.4	45	5.4	52	6.3	73
7.0	68	7.0	75	7.2	69	7.0	80
9.0	70	9.2	86	9.0	72	8.4	87
9.4	72	9.7	83	10.1	84	9.0	81

Table 4.18: Effect of pH on the Fixation value of Dye (67) on Nylon 6.6 Mordanting with different Metallic Salts.

$FeSO_4$		$Co(NO_3)_2$		$CuCl_2$		$NiCl_2$	
pH	% F	PH	% F	pH	% F	pH	% F
1.5	10	1.4	27	1.6	14	1.7	10
1.7	12	1.6	29	1.8	14	2.3	14
2.0	23	3.7	37	3.6	24	3.7	23
3.5	27	5.4	54	5.3	53	5.7	45
7.0	64	7.0	69	7.3	68	7.2	65
9.0	71	9.2	76	9.0	73	8.4	67
9.4	77	9.7	78	10.1	77	9.0	79

Fig 4.31: Effect of pH on the post-metallization of dye (65) on Nylon 6.6

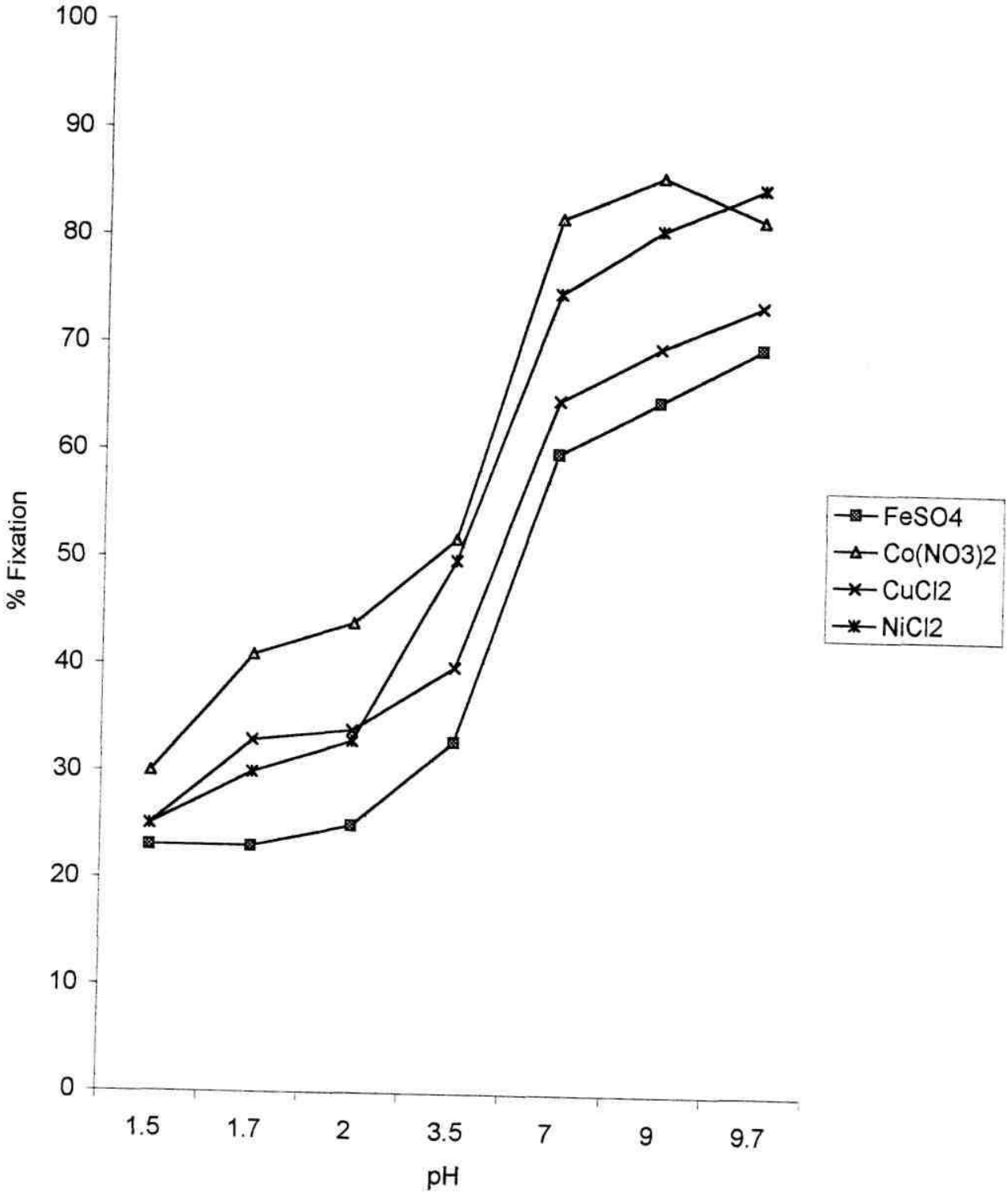


Fig 4.32: Effect of pH on the post-metallization of dye (66) on Nylon 6.6

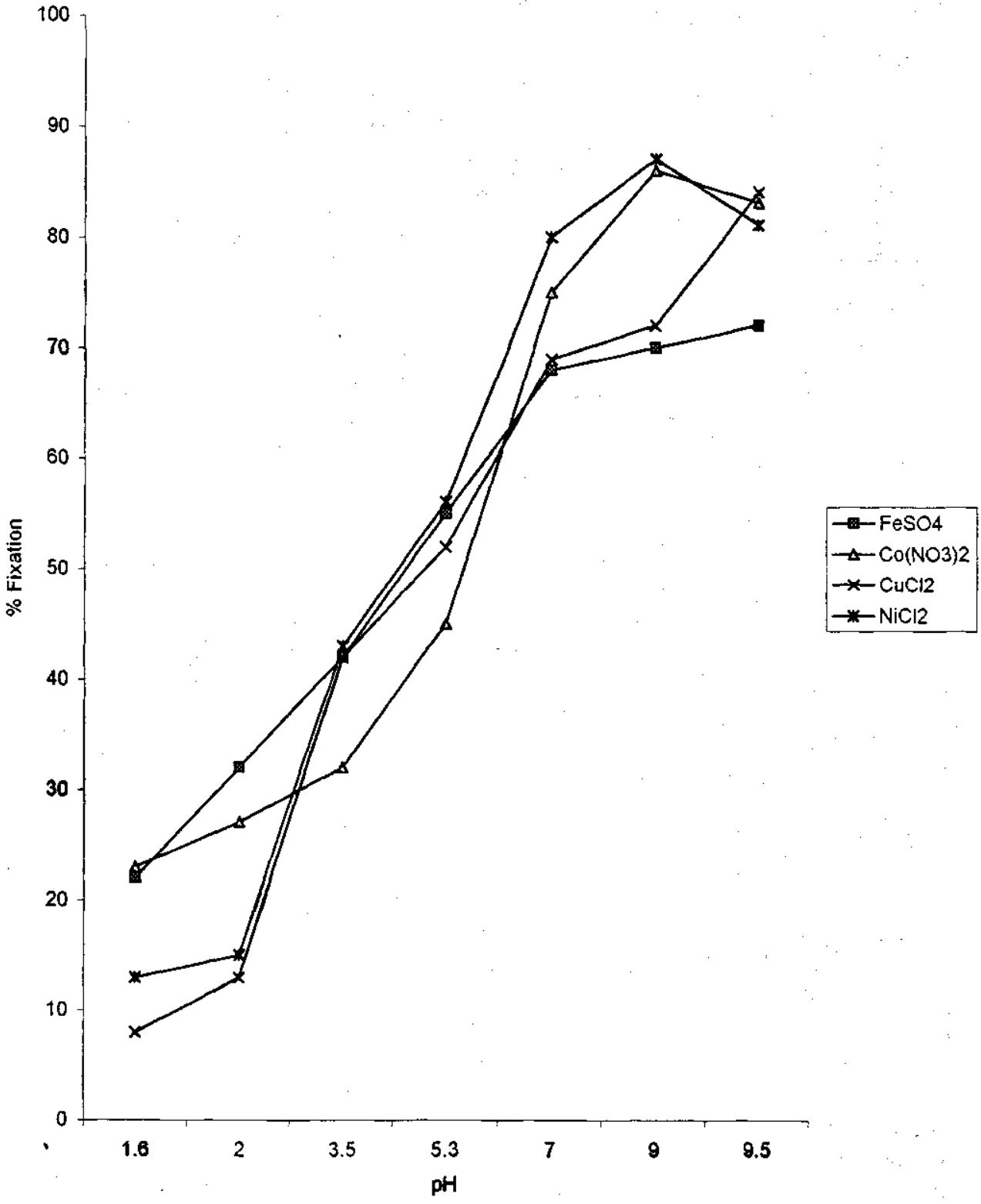
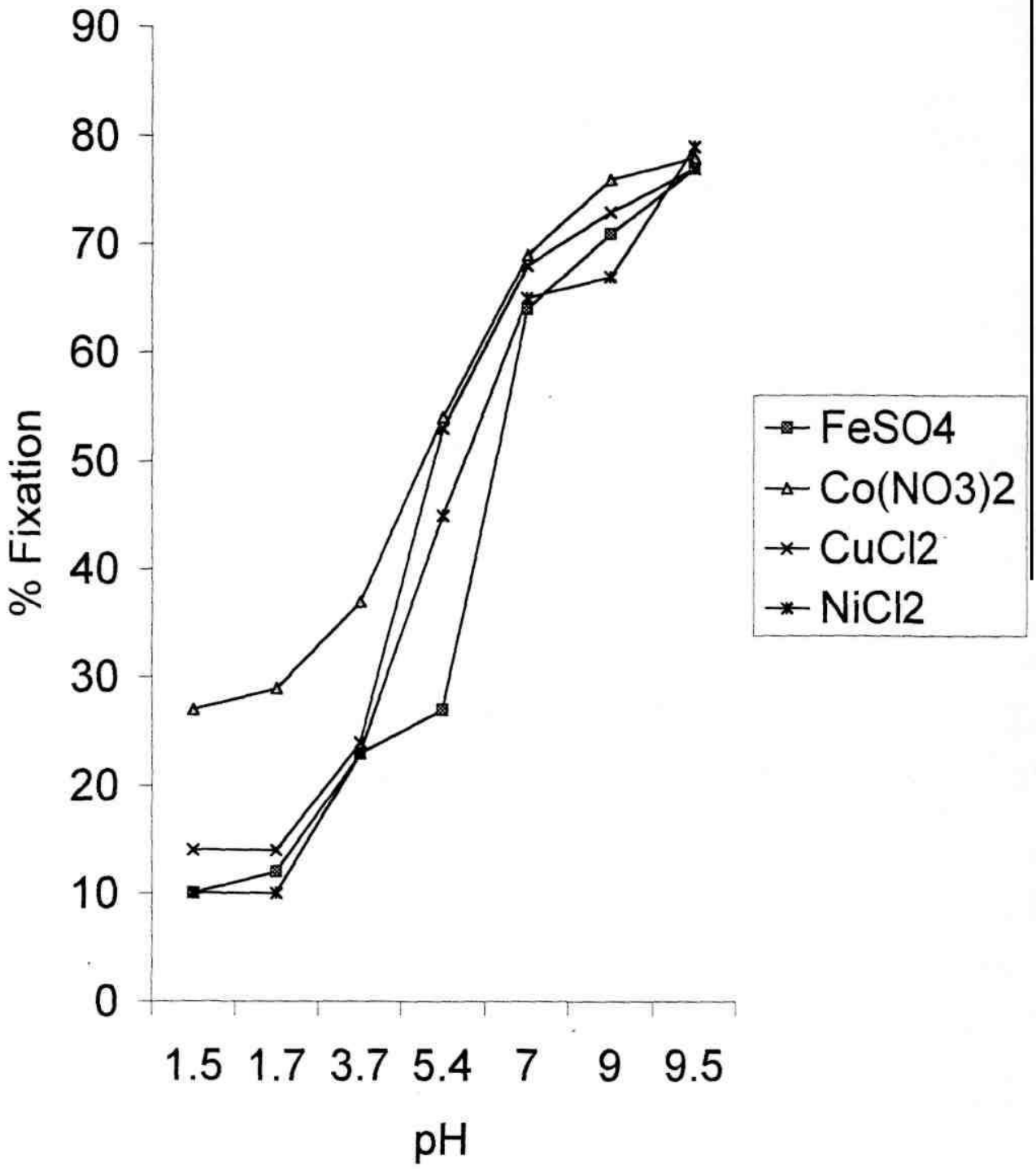


Fig 4.33: Effect of pH on the post-metallization of dye (67) on nylon 6.6



Generally, as shown in Figures 4.31-4.32 a marked increase in fixation was noted as the pH increased. The marginal increase over the neutral pH made higher pH unrealistic. The unfixed dye is thought to be mostly the 1:1 complex. This perhaps explains why higher metal concentration and long liquor to goods ratio in the test run gave poor fixation values. Comparatively all the three dyes showed almost the same extent of difference as the pH is changed.

Proof for the formation of 1:2 complex has been provided very recently by Freeman et al.[207]

4.2.6 Wash and Perspiration Fastness Properties of the 2-nitroso-1-Naphthol and Its Azo Dyes Derivatives and Their Post-Metallized Products on Wool and Nylon 6.6

Wool and nylon 6.6 samples are dyed to 0.5% shade with the assistance of 0.1% Lissapol C, 0.2% acetic acid, 50:1 liquor ratio at the boil for 1 hour. The low shade was chosen to avoid deeper shades whose post-metallization hue is not apparent.

Table 4.19: Wash Fastness Ratings of the Nitroso Dyes on Wool using ISO No. 3

Dye No	Complexing Salts															
	None		$FeSO_4$		$Co(NO_3)_2$		$CuCl_2$		$ZnSO_4$		$NiCl_2$		$MnCl_2$		$Cr_2(SO_4)_3$	
	C	ST	C	St	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST
65	3-4	5	2-3	5	4	5	4	5	3-4	5	2-3	5	4-5	5	3	5
66	4	5	4	5	4	5	3-4	5	3-4	5	3-4	5	4-5	5	5	5
67	4	5	3-4	5	3-4	5	4-5	5	2-3	5	5	5	2-3	5	3	5
68	3	5	3-4	5	4-5	5	4	4	5	5	4-5	5	3	5	4	5
69	3-4	5	4	5	4	5	4	5	3-4	5	5	5	4	5	3-4	5
70	3-4	5	3-4	5	3-4	5	4	5	4	5	3-4	5	3	5	3-4	5
71	4	5	3-4	5	4-5	2-3	4-5	5	2	5	4	5	2-3	5	3	5
72	1-2	5	2-3	5	2-3	3	4	5	1-2	5	2	5	2-3	5	2-3	5
73	3-4	5	5	5	3	5	4	5	2-3	5	5	5	2-3	5	3	5

C = Change in Shade; ST = Staining of Adjacent White

Table 4.20: Wash Fastness Ratings of the Nitroso Dyes on Nylon 6.6 using ISO No. 3

Dye No	Complexing Salts															
	None		$FeSO_4$		$Co(NO_3)_2$		$CuCl_2$		$NiCl_2$		$ZnSO_4$		$MnCl_2$		$Cr_2(SO_4)_3$	
	C	ST	C	St	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST
65	3	5	5	5	4-5	5	4	5	3	5	2	5	2	5	3	5
66	2	5	5	5	4	5	4	5	2	5	3	5	2	5	3	5
67	4	5	5	5	4	5	4	5	4	5	4	5	3	5	3	5
68	3	4-5	5	5	4	5	4	5	3	5	3	5	4	5	2-3	5
69	3	5	3	5	3	5	3	5	3	5	4	5	3	5	3	5
70	3	5	5	5	5	5	5	5	4	5	2	5	4	5	3	5
71	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
72	4-5	3	5	5	5	5	5	5	5	5	5	5	5	5	5	5
73	2	5	-	-	-	-	-	-	-	-	-	-	-	-	-	-

C = Change in Shade; ST = Staining of Adjacent White

Table 4.21: Acid and Alkali Perspiration Ratings for the 2-Nitroso-1-Naphthol and azo Derivatives Dyes on Wool

Complexing salts	65				66				67				68				69			
	Acid		Alkali		Acid		Alkali		Acid		Alkali		Acid		Alkali		Acid		Alkali	
	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST
None	3	4	4-5	3	4	5	4	5	4-5	5	4	5	4	5	2	5	5	5	3	5
$FeSO_4$	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
$Co(NO_3)_2$	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
$CuCl_2$	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
$NiCl_2$	5	5	4	5	5	5	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5
$ZnSO_4$	5	5	4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
$MnCl_2$	5	5	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
$Cr_2(SO_3)_4$	5	5	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5

KEY: C = Change in shade; ST = Staining of Adjacent White

Complexing Salts	70				71				72				73			
	Acid		Alkali		Acid		Alkali		Acid		Alkali		Acid		Alkali	
	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST
None	4	5	4	5	4-5	5	4	5	4	3	4	3	5	5	5	5
$FeSO_4$	5	5	5	5	5	5	5	5	5	3	5	3	5	5	5	5
$Co(NO_3)_2$	5	5	5	5	5	5	5	5	5	3	5	3	5	5	5	5
$CuCl_2$	5	5	5	5	5	5	5	5	5	3	5	4	5	5	4	5
$NiCl_2$	5	5	4	5	5	5	4	5	5	3	5	3	5	5	5	5
$ZnSO_4$	5	5	5	5	5	5	4-5	5	5	3	5	3-4	5	5	5	5
$MnCl_2$	5	5	5	5	5	5	5	5	5	3	5	3-4	5	5	5	5
$Cr_2(SO_3)_4$	5	5	5	5	5	5	5	5	5	3	5	4	5	5	5	5

C = Change in Shade; ST = Staining of adjacent White

Table 4.22: Acid and Alkali Perspiration Ratings for the 2-Nitroso-1-Naphthol and azo Derivatives Dyes on Nylon 6.6

Complexing salts	65				66				67				68				69			
	Acid		Alkali		Acid		Alkali		Acid		Alkali		Acid		Alkali		Acid		Alkali	
	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST
None	4	5	4	5	5	5	5	5	5	5	5	5	4-5	5	5	5	5	5	5	5
$FeSO_4$	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
$Co(NO_3)_2$	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
$CuCl_2$	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
$NiCl_2$	5	5	4	5	5	5	4-5	5	5	5	5	5	5	5	4	5	5	5	5	5
$ZnSO_4$	5	5	4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
$MnCl_2$	5	5	4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
$Cr_2(SO_3)_4$	4	5	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5

KEY: C = Change in shade; ST = Staining of Adjacent White

Complexing Salts	70				71				72				73			
	Acid		Alkali		Acid		Alkali		Acid		Alkali		Acid		Alkali	
	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST	C	ST
None	5	5	5	5	5	5	5	5	5	5	4	5	5	5	5	5
$FeSO_4$	5	5	5	5	5	5	5	5	5	5	5	5	-	-	-	-
$Co(NO_3)_2$	5	5	5	5	5	5	5	5	5	5	5	5	-	-	-	-
$CuCl_2$	5	5	5	5	5	5	5	5	5	5	5	5	-	-	-	-
$NiCl_2$	5	5	5	4	5	5	5	5	5	5	5	5	-	-	-	-
$ZnSO_4$	5	5	5	5	5	5	5	5	5	5	5	5	-	-	-	-
$MnCl_2$	5	5	5	5	5	5	5	5	5	5	5	5	-	-	-	-
$Cr_2(SO_3)_4$	5	5	5	5	5	5	5	5	5	5	5	5	-	-	-	-

C = Change in Shade; ST = Staining of Adjacent White

The wash fastness rating of the nitroso derivative dyes on wool showed that the dye derived from J-acid (dye 72) gave the least rating as far as the change in shade is concerned. This is closely followed by H-acid derivative dyes (dye 71), sulphanilic (dye 70) and 4-amino benzoic (dye 67) derived dyes. This observation to a larger extent is the trend irrespective of the complexing salt. The only exception is when $CuCl_2$ is the complexing salt, it gave a consistent rating of very good (4). When affinity of the three dyes are compared, dye (71) gave the highest, followed by dye (72) and finally dye (70) at the temperature considered. In contrast, dye (70) gave the highest diffusion coefficient followed by dye (71) and finally dye (72). Apparently there doesn't seem to be a direct correlation between affinity, dyeing properties as given by diffusion coefficient and wash fastness. This was also observed by Lemin et al[226] when they evaluated the affinity of six different dyes, they noted that there was no obvious correlation between affinity, dyeing properties and wash fastness with the chemical constitution of the dyes. Everything being equal, Speakman et al[227-228] have observed that the levelling properties is related to the capacity of dyes to form colloidal solution and consequently the ability of the dyes to form aggregates in the fibre. He found that the less the tendency to aggregate the greater the

levelling power; the tendency of a dye to become colloidal in the acid dyebath increases with the molecular weight and decreases with degree of sulphonation. Improved fastness to washing so far as this is concerned with the mechanical imprisonment of the dye within the fibre pores might conceivably result from an increase in the particle size of the dye by aggregation. From the foregoing, dye (71) is expected to have a poor fastness rating than dye (72). But surprisingly the correlation between affinity and wash fastness properties was observed. Dye (71) derived dye recorded the higher affinity than dye (72). When dye (72) and dye (70) are compared, of course, dye (72) has the higher molecular weight but has more ionic groups which makes it less prone to form colloidal solution than sulphanilic acid as such, which of the two gives the higher wash fastness rating is a balance between the molecular weight factor and solubilizing groups numbers as they affect the degree of aggregatability of the dyes. The fact that dye (70) gave the higher wash fastness rating is a direct consequence to the less number of solubilizing groups it possesses. However, this can not be explained from the affinity values computed in section 4.6 as J-acid derivative dye (72) gave the higher affinity value. 4-Amino benzoic acid derived dye (67) gave a rating higher than sulphanilic acid derived dye (70), this is also a consequence of the ability to form

aggregates which factor is stronger in 4-amino benzoic acid derived dye (67) than dye (70). However, the direct correlation between affinity and wash fastness is observed between the two dyes. Dye (67) has the higher affinity values at both temperatures considered than dye (70). Similar explanation will be difficult to advance when other dyes under study are considered. For example, when 4-amino phenol derived dye (68) is compared to dye (70), dye (70) gave the higher rating. This is an inverse relationship to the degree of ionizability in acid bath. The two dyes have almost the same affinities. The same analogy is equally applicable to the dyes of 4-amino phenol and 4-amino benzoic acid derived dyes (67) and (68). Dye (68) is expected to produce a dyeing of higher fastness rating as a consequence of ionizability in acid bath of the latter. But the reverse is the case, but this time the higher rating of the affinity of the 4-amino benzoic acid dye (67) can be sighted to explain the observation.

The wash fastness rating of the parent dye, dye (65) gave an average good rating, higher than the J-acid derived dye (72). This is despite its least affinity values at the temperature considered and least molecular weight. Explanation for this does not seem to be apparent from the coefficient of diffusion relatively of the dyes. However, dye (66) having high rating than

the parent dye (65) can be explained both from the advantage of molecular weight and affinity for which dye (66) is better in both factors.

When aniline is compared to 4-nitro aniline derivative dyes (66) and (69) respectively, dye (66) recorded the higher fastness rating inspite of the molecular weight advantage of the latter; but in accordance with affinity consideration aniline derivative dye (66) as is the case recorded higher fastness rating.

A comparison of the sulphonated dyes indicated that both J and H-acid derivative dyes (72) and (71) respectively recorded higher wash fastness rating than sulphanilic acid dye (70). The trend is not according to the affinities of the dyes. It had been investigated that replacement of a benzene by naphthalene residue should result in increase in wash fastness rating in a group of acid dyes on nylon substrates.[229] This should explain the superior fastness rating of both J and H-acid dyes (71) and (72) over the sulphanilic acid derived dye (70). 4-Amino benzoic acid derived dye (67) recorded higher fastness rating compared to the sulphanilic acid derived dye (70). This is in contrast to the trend in affinities of the two dyes where dye (70) gave the higher value. Here too, the degree of ionizability of sulphanilic acid is expected to be higher with the result that 4-amino benzoic acid derived dye (67) is expected to produce more colloidal solution in acid bath

as was actually observed. From earlier correlation,[227-228] it is expected to have higher aggregatability in the polymer and will as a consequence give higher fastness rating as observed. When 4-amino benzoic acid derived dye (67) is compared with 4-amino phenol dye (68), both ionizability/aggregatability and affinity factors pointed to the opposite. However, the lower activation energy of the 4-amino phenol derivative dye (68) (49,722 J/mol) could be advanced to explain the ease with each it slides in and out of the polymer as compared to the activation energy of 62652 J/mol of 4-amino benzoic acid derived dye (67).

Another dye system that defied explanation from molecular weight factor and ionizability considerations are 4-nitroaniline and 2-cyano-4-nitroaniline derived dyes (69) and (73). In both counts, dye (73) is expected to have a higher wash fastness rating but it gave almost the least rating on nylon substrate. A look at the activation energies however indicated that it has the least, 15955 J/mol as against 37928 J/mol for 4-nitroaniline derived dye (69) on nylon. In contrast to the observation with regards to wool between aniline and 4-nitroaniline derived dye, 4-nitroaniline dye (69) gave the higher rating. However, in this case, the explanation is not far fetched. Molecular weight consideration seemed to be the reason. Coupled to this is the very low activation energy of diffusion of aniline derived dye (66) (7978

J/mol) compared to the value for 4-nitro aniline derived dye (69) quoted above. The parent dye (65) also gave a higher rating compared to the aniline derived dye (66). But then, it has the advantage of both affinity (-20407 J/mol, at 329K) and activation energy 94280 J/mol compared to the affinity of 4-nitroaniline derived dye (69) (-19501 J/mol at 329k) and its activation energy given above.

With respect to nylon fibre and all the dyes, a general increase in wash fastness rating was observed as a result of post-metallization. The main reason is attributed to two distinct factors. The first is that a complex is formed between the dye and the metal which increases the molecular size of the dye. Secondly, a chemical combination is thought to be formed between the fibre, dye and the metal. The effect of post metallization is however not very apparent in the case of wool. No work has been done to ascertain the nature or likelihood of chemical association between the metals complexed to these types of dyes. However, the work carried out by Geog[224] with respect to phenols, indicated that the acid anions are retained by the metal even after forming a 1:2 metal complex dyes. This is indicative that a union between the fibre and the dye complex is not very likely compared to known metal complex systems. This being the case, then, the intrinsic affinities of the dyes on the substrates will only be improved by virtue of complexing. It

was observed that generally the free dyes had higher affinities on nylon than on wool. Aggregating the dyes on the substrate only consolidated the affinity of the dyes on the substrate. It can be seen that 2-cyano-4-nitro aniline dye (73) did not form any complex with respect to the nylon substrate. This may highlight yet another fundamental difference between the states of the complex, when the two substrates are compared. The same observation is made with respect to aniline and 4-nitroaniline derived dyes (66) and (69), even though they formed the complex with distinct hue differences, their wash fastness on nylon are only averagely good and are not as good as in wool. In between the complexing salts used, $FeSO_4$, $Co(NO_3)_2$ and $CuCl_2$ produced increasing better performance with respect to nylon substrate, whereas in the case of wool the trend changed. $CuCl_2$, $Co(NO_3)_2$, $FeSO_4$ seemed to be the trend.

The perspiration test results indicated that for wool substrate, there is a general improved fastness rating as a result of post metallization. It is only J-acid derived dye (72) that gave comparatively poor results with respect to staining for both acid and alkali tests. In a subdued manner alkali tests with respect to the free dyes proved poor in rating as expected with respect to wool.

The perspiration alkali and acid tests results on nylon gave an all-round excellent ratings.

4.1.4 Light Fastness Properties of the 2-Nitroso-1-Naphthol and its Azo Dyes Derivatives and Their Postmetallization Products on Wool And Nylon 6.6

The wool and nylon 6.6 substrates were dyed with the dyes and post metallized using the same condition as in section 3.8 The results obtained are shown in Table 4.23.

Table 4.23: Light fastness Rating of the Dyes on Wool and Nylon 6.6

Dye No	Complexing Salts															
	None		$FeSO_4$		$Co(NO_3)_2$		$CuCl_2$		$ZnSO_4$		$NiCl_2$		$MnCl_2$		$Cr_2(SO_4)_3$	
	W	NY	W	NY	W	NY	W	NY	W	NY	W	NY	W	NY	W	NY
65	1-2	1	2-3	2-3	3-4	3-4	2-3	1-2	1-2	1-2	3-4	1	1-2	1	1-2	1
66	1-2	1	4-5	1-2	3-4	1-2	2-3	1-2	1-2	1-2	3-4	1-2	2	1-2	2	1-2
67	1-2	1	2-3	3	2-3	2-3	3-4	2-3	2-3	1-2	2-3	1-2	1-2	1-2	1-2	1
68	1-2	1	3-4	1-2	2-3	1-2	2-3	1-2	2-3	2-3	2-3	1	1-2	1	1-2	1-2
69	1	1	5-6	2-3	4-5	1	2-3	1-2	1-2	1-2	2	1-2	1-2	1-2	1-2	1
70	1-2	1	3-4	1-2	2-3	1-2	2-3	1	2-3	1-2	2-3	1-2	1-2	1	1-2	1-2
71	1-2	1	4-5	1-2	3-4	1	2-3	1-2	1-2	1	2-3	1	1	1	1	1
72	2-3	1-2	4-5	1	4-5	3-4	3-4	3-4	2-3	1-2	4-5	1-2	2-3	1-2	2-3	1-2
73	1-2	1	5-6	1-2	4-5	1-2	2-3	1	1-2	1	2-3	1	1-2	1	1-2	1-2

KEY; W = wool; NY = Nylon 6.6

Clearly light fastness ratings of the dyes on the two substrates are generally not encouraging. The free dyes gave poor ratings on both substrates. As noted also in Chapter 2, wool substrate gave a unit higher rating than nylon 6.6. The same explanation about the presence of histidine and other amino acid believed to retard reductive and oxidative fading is also tenable here.[203] Generally it is observed that postmetallization only marginally improved the rating of the dyes with respect to nylon 6.6. But in the case of wool in certain cases a marked improvement has been obtained. For example the rating of the free dye (69) derived from 4-nitro aniline in wool was only 1, but the $FeSO_4$ post-metallized dye recorded 5-6, $Co(NO_3)_2$, 4-5, $CuCl_2$, 2-3 etc. Similarly, 2-cyano-4-nitroaniline dye (73) had a rating of 1-2 for the free dye but got improved to 5-6 by $FeSO_4$ post metallization, 4-5, by $Co(NO_3)_2$, 2-3 by $CuCl_2$, 2-3 $NiCl_2$ etc. Similar results were recorded by dyes (66), (71), (72) and (70).

Improvement in the fading rate was only moderate in the parent dye (65) and 4-aminobenzoic acid derived dye (67) even or wool. Similar observation is made with respect to 4-amino phenol derived dye (68). The dyes that recorded the highest improvement as a result of the post metallization are 2-cyano-4-nitroaniline dye (73), 4-nitroaniline dye (69) and

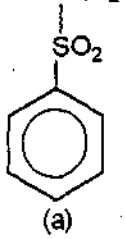
CHAPTER 5

5.0 Synthesis and Properties of Monoazo Acid Dyes Derived from p-Amino-toluenesulphon-N-ethylanilide as Diazo Component

5.1 Introduction

Acid dyes are the main group of dyes used for dyeing wool, silk and polyamide fibres, they have laso found use in leather dyeing.[259,247] The requirements of acid dyes vary depending on their end-use, but they are now mostly expected to show a high degree of exhaustion from the dyebath at a low or very low concentration of electrolytes and at a relatively high pH (5-6).

This study concerns the synthesis of some monoazo acid dyes in which p-aminotoluenesulphon-N-ethylanilide (a) was used as a diazo component. This amine was obtained from Wenzhou Rosi Dyestuff Company Ltd, China in 99% purity as shown by the HPLC spectrograph (Figure 5.1). It was used without further purification. The amine was diazotised and coupled to gamma acid also obtained from Wenzhou Rosi Dyestuff Company Ltd, J and H-acids donated from University of Leeds, Color Chemistry Department, chromatropic acid, a BDH laboratory reagents grade and 4-sulphophenyl-3-methyl-5-pyrazolone, also obtained from China. All the coupling components were coupled without further purification.



(a)

5.2 Results and Discussion

5.2.1 Synthesis, Characterisation and Spectroscopic Properties

Dyes

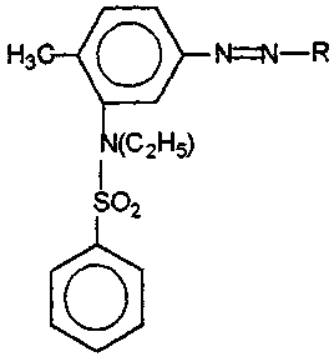
p-Amino toluene-sulphon-N-ethylanilide (a) was diazotise
direct method in the medium of acetic acid. The diazo salt was c
five different coupling components which are: H-acid, chromotropi
acid, gamma acid and 4-sulphonphenyl-3-methyl-5-pyrazolone to
of dyes (74) – (78) having the general formula (b).

Genesis series FTIR i.r-spectrophotometer. The results are shown
5.1 and Figures 5.2-5.7.

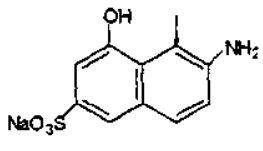
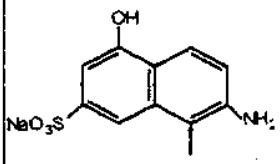
The yield of the dyes as shown in Table 5.1 is good. It is too
acid dyes most of which due to their high solubility are wasted awa
manufacture.

The maximum absorption wavelength of the dye derived fron
acid, dye (74) is 465 nm whereas dye (75) derived from J-acid has
This means that dye (75) is more bathochromic by about 5 nm than
It is observed that the coupling position of acid coupled gamma aci
position, the 8-position is occupied by a hydroxy group. The
position of the J-acid under the same condition is the 4-position,
group maintained its position.

Table 5.1: Yield, melting point and spectroscopic properties of the dyes



(b)

Dye No	R Coupling Component	Yield (%)	M.Pt (°C)	uv spectra λ_{max}	uv spectra ε x 10^4	Characteristics i.r. Peaks [261,262]
(74)		91	240°C Dec.	465	1.8876	3475 -OH....., -NH_2 1036 -SO_3Na 1409 -N=N- 1218 -NH_2 1497 C=C 1340 -SO_2 780 -C-H 700 C=C ; 1168 -SO_3Na
75		97	210	470	1.823	3445 -OH, -NH_2 834, 862, -C-H 1040 -SO_3Na 1493 C=C 1414 -N=N- 1152 -SO_3Na 752 -C-H-NH_2 806 -C-H

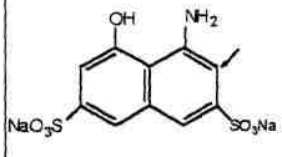
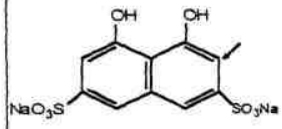
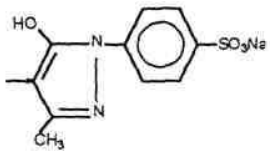
76		83	>320	540	4.449	3448 -OH, $-NH_2$ 1492 C=C 1415 -N=N- 1041 $-SO_3Na$ 1166 $-SO_3Na$ 1338 $-SO_2$ 1440 C=C
77		84	260 Dec	515	6.485	3479 -OH, $-NH_2$ 1497 C=C 1408 -N=N- 1102, 1088 $-SO_3Na$ 826 -C-H
78		75	214-219	435	1.14	3449 -OH, $-NH_2$ 1498 C=C 1013 -N=N- 1063, 1169 $-SO_3Na$ 914, 921, 780, 850, 824, -C-H 1341 $-SO_2$ 1551 C=N

Fig. 5.1: HPLC spectrograph of P-amino toluenesulphon-N-ethylanilide

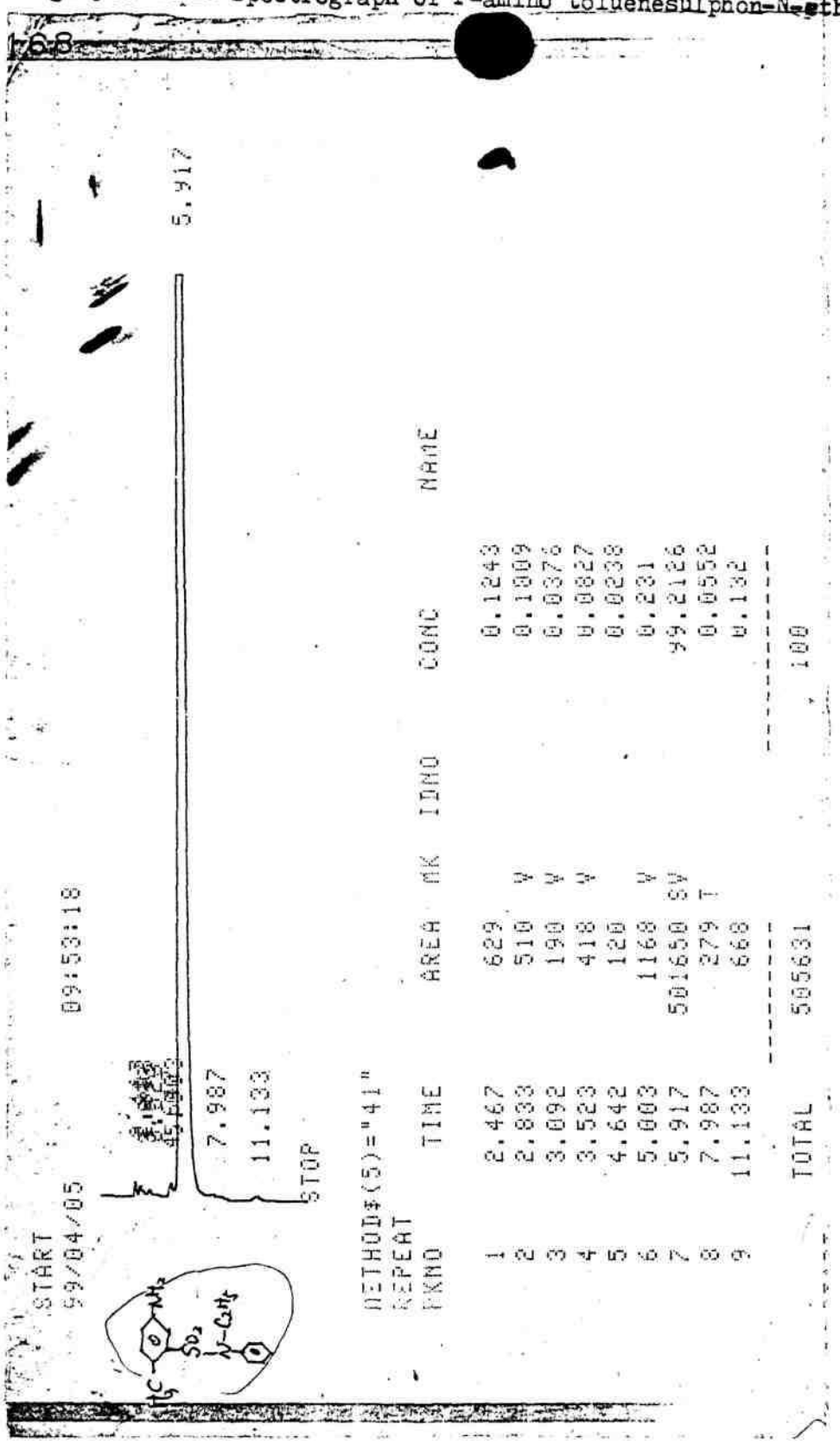
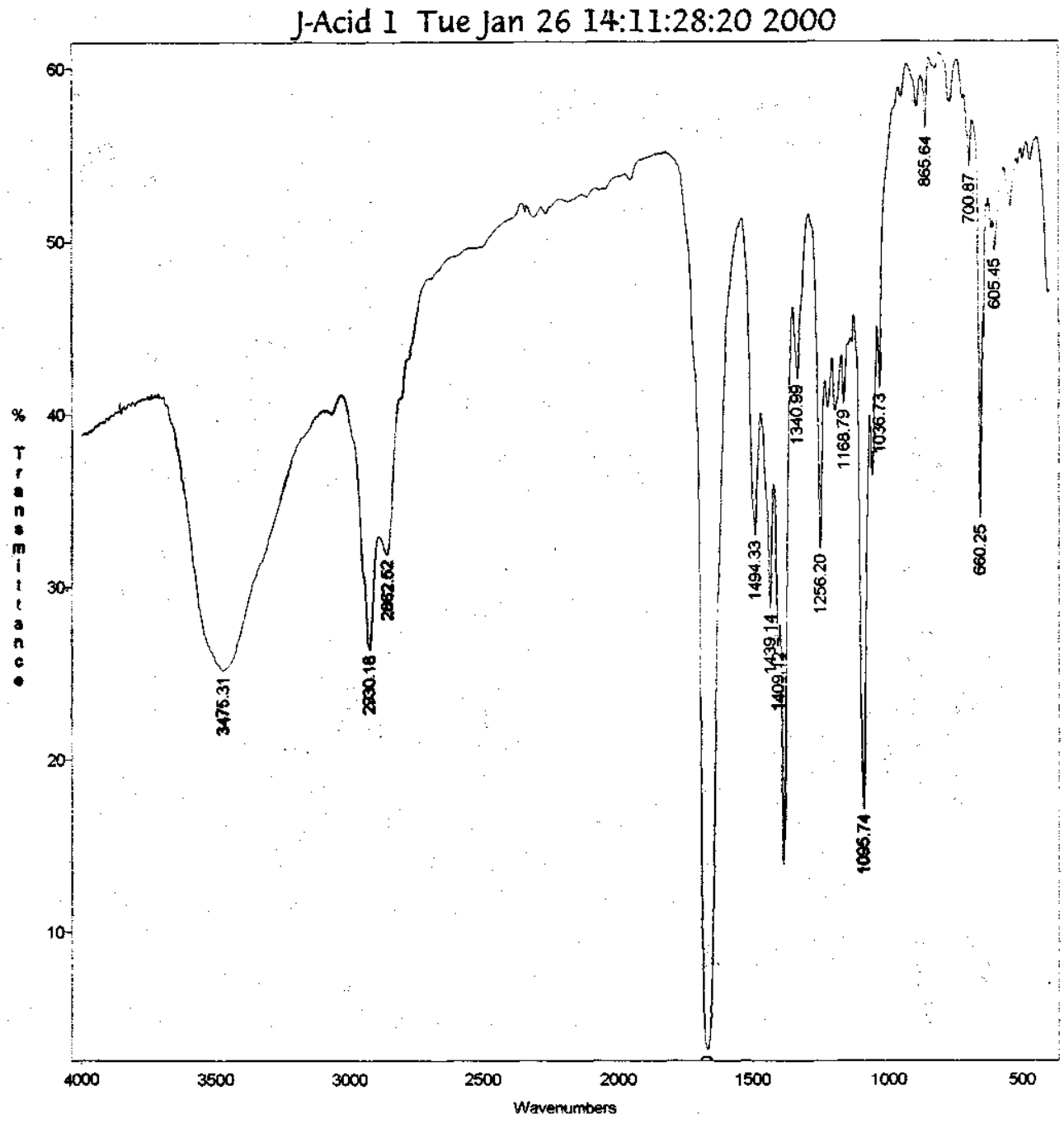


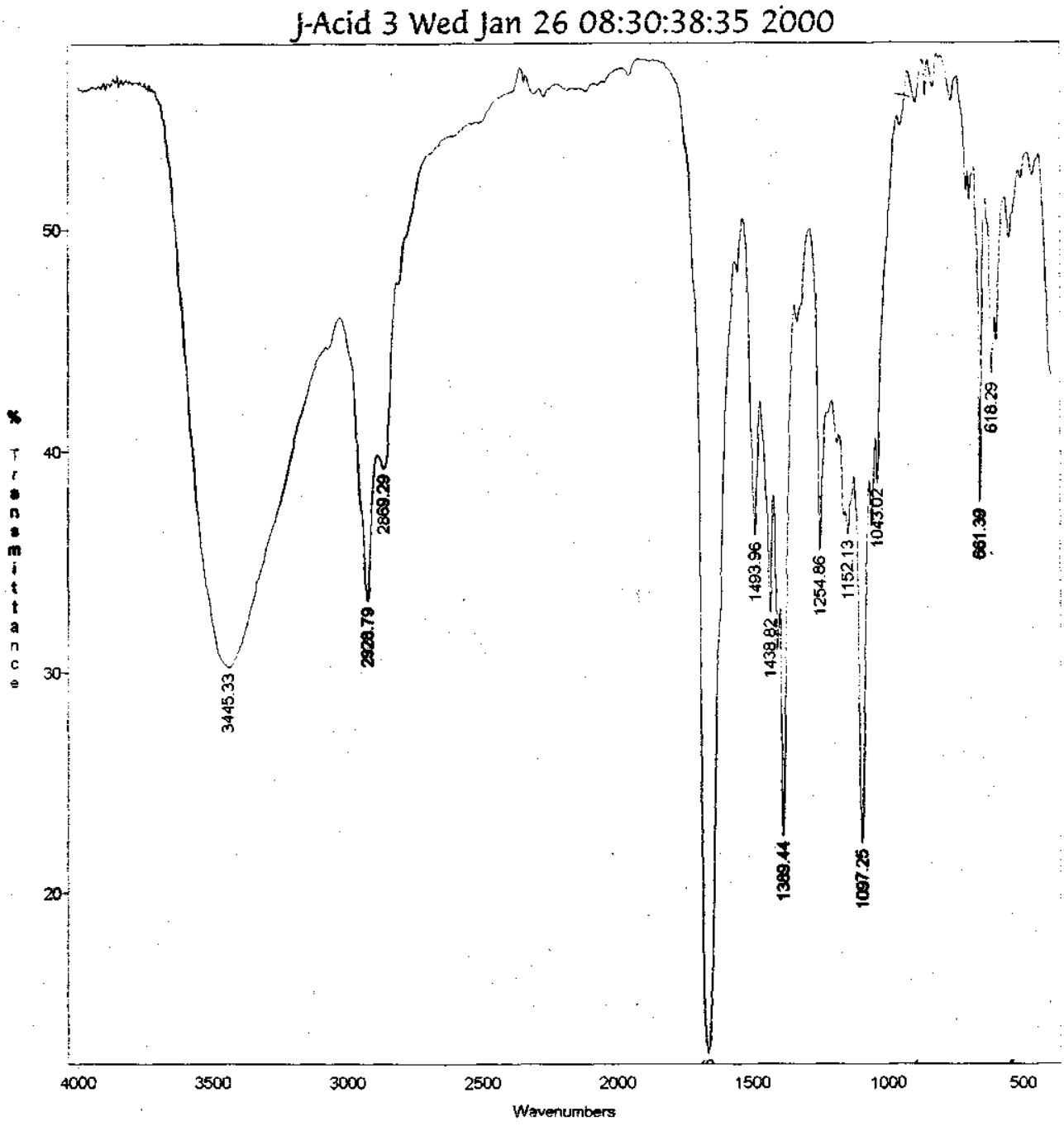
Fig. 5.2: ir-spectrum of dye 74



Peak Report
File: c:\first\data\galaxy\cfir1924.ras
Title: J-Acid 1 Tue Jan 26 14:11:28:20 2000
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
605.45	49.37	660.25	33.94	700.87	54.29
865.64	56.47	1036.73	41.49	1095.74	17.06
1168.79	40.57	1256.20	32.12	1340.99	42.03
1409.12	26.54	1439.14	28.70	1494.33	32.94

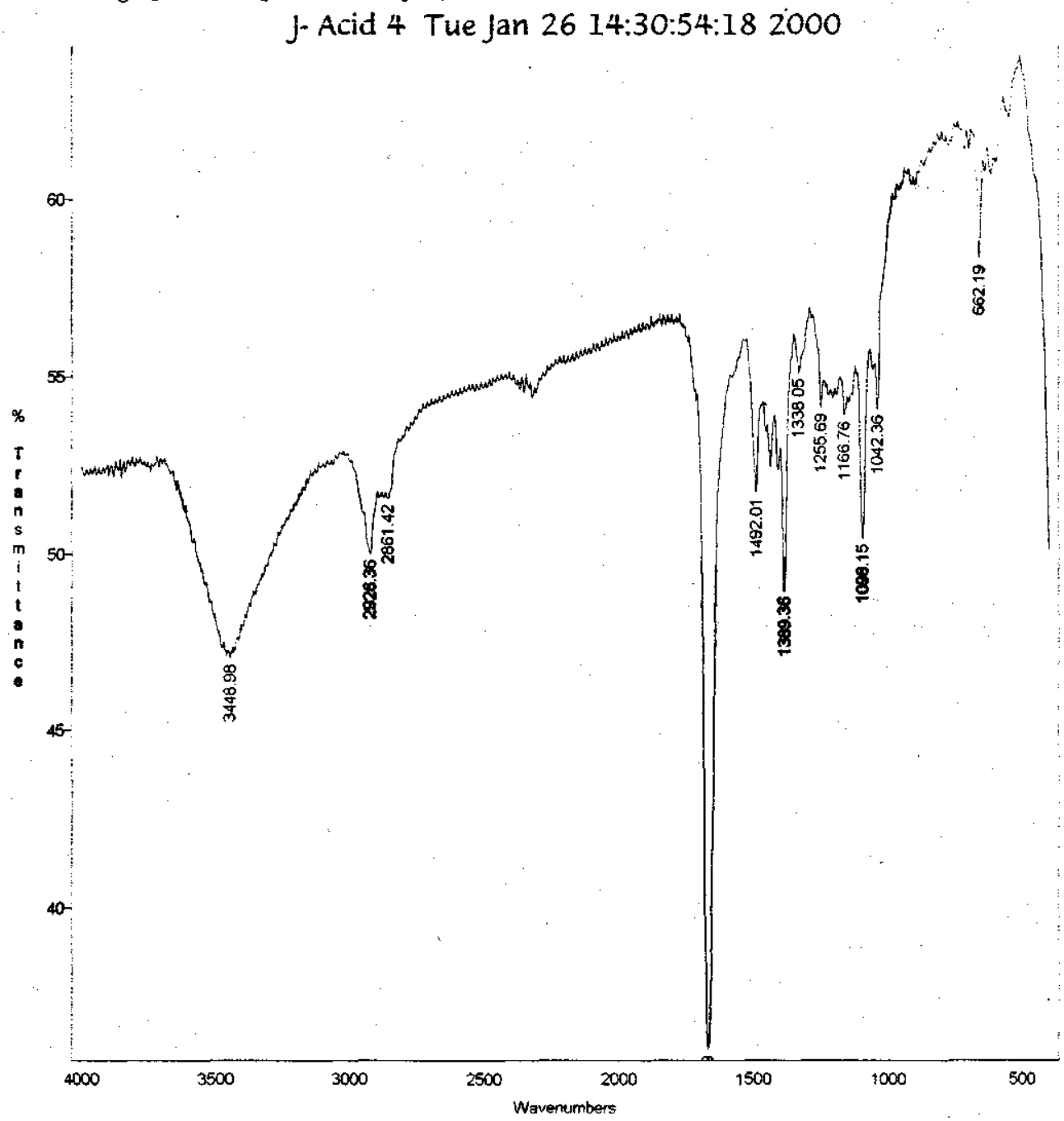
Fig. 5.3: ir-spectrum of dye 75



Peak Report
File: c:\first\data\galaxy\cfir1923.ras
Title: J-Acid 3 Wed Jan 26 08:30:38:35 2000
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
661.39	37.66	618.29	43.39	1097.25	22.20
1043.02	38.53	1152.13	36.16	1254.86	35.44
1389.44	22.56	1438.82	32.66	1493.96	36.07
1667.16	12.74	2869.29	39.19	2928.79	33.20

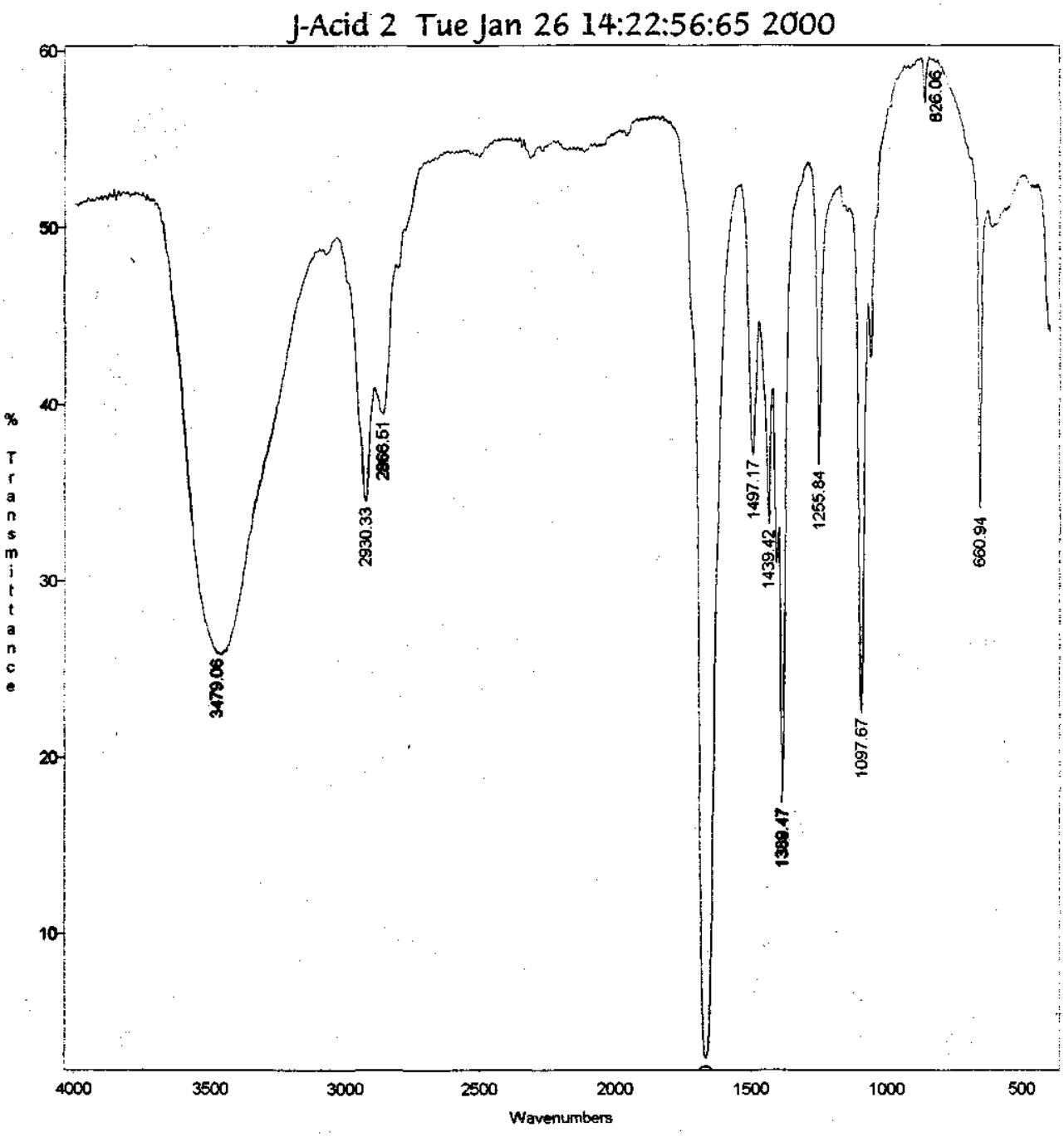
Fig. 5.4: ir-spectrum of dye 76



Peak Report
File: c:\first\data\galaxy\cfir1926.ras
Title: J- Acid 4 Tue Jan 26 14:30:54:18 2000
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
662.19	58.35	1098.15	50.42	1042.36	54.07
1166.76	53.90	1255.69	54.11	1338.05	55.08
1389.36	48.93	1492.01	51.73	1667.79	35.98
2861.42	51.54	2926.36	50.00	3448.98	47.06

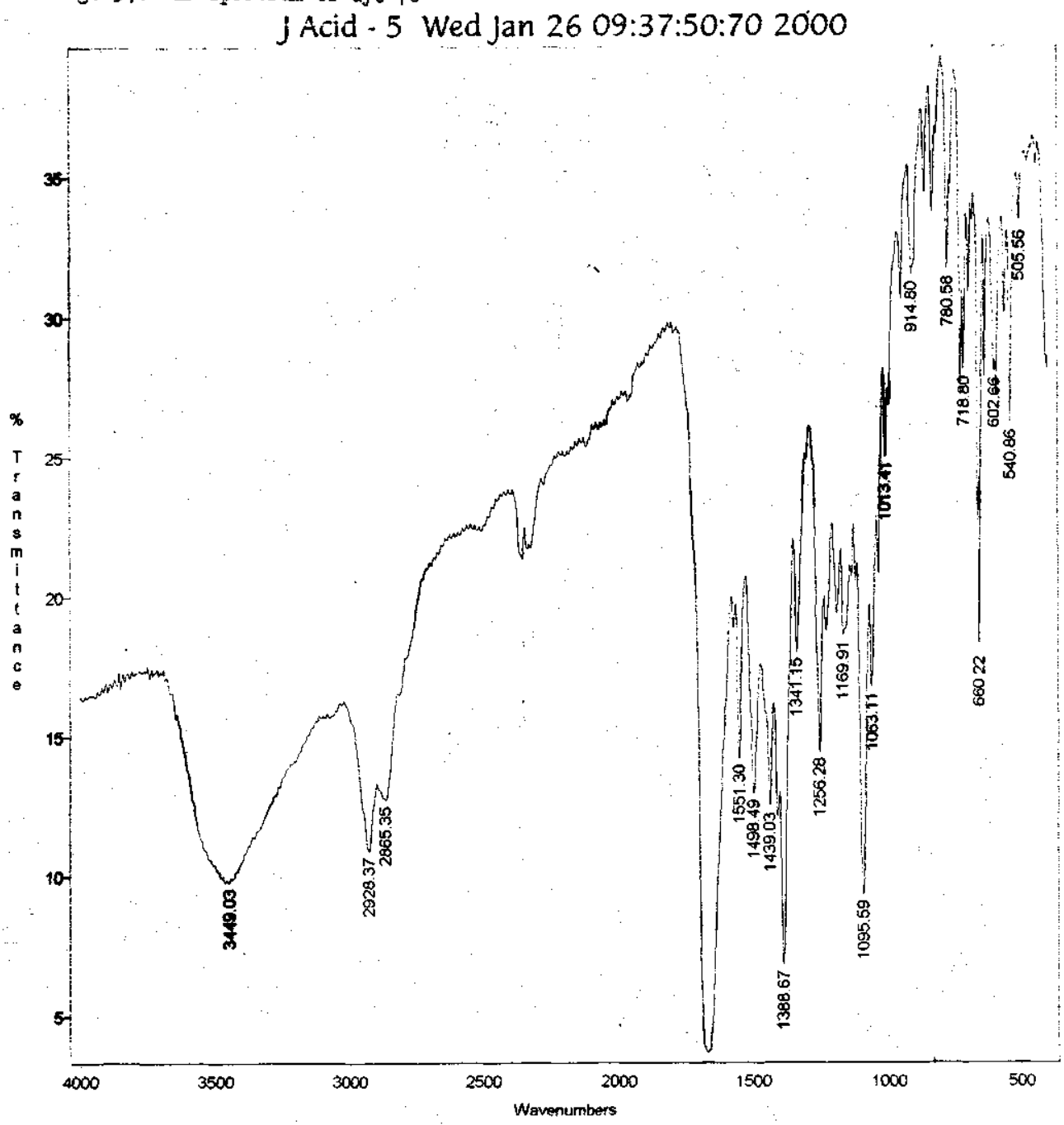
Fig. 5.5: ir-spectrum of dye 77



Peak Report
File: c:\first\data\galaxy\cfir1925.ras
Title: J-Acid 2 Tue Jan 26 14:22:56:65 2000
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
660.94	34.10	1097.67	22.54	1255.84	36.60
1389.47	17.44	1439.42	33.23	1497.17	37.20
1668.00	2.86	2866.51	39.43	3479.06	25.91
2930.33	34.50	826.06	59.30		

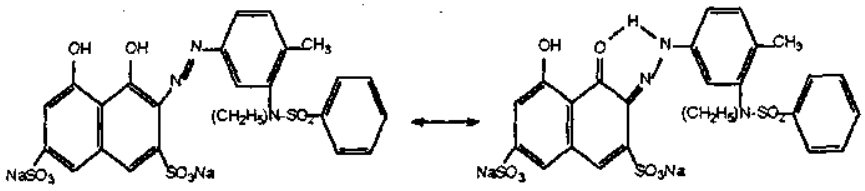
Fig. 5;6: ir-spectrum of dye 78



Peak Report
File: c:\first\data\galaxy\cfir1927.ras
Title: J Acid - 5 Wed Jan 26 09:37:50:70 2000
Filter: Three Point Center of Gravity

cm-1	%T	cm-1	%T	cm-1	%T
3449.03	9.77	2928.37	10.90	2865.35	12.72
1668.81	3.71	1551.30	14.19	1498.49	12.92
1439.03	12.46	1388.67	6.84	1341.15	18.03
1256.28	14.42	1169.91	18.64	1095.59	9.33

The derivative of H-acid, dye (76) has a wavelength of maximum absorption of 540 nm whereas that of chromotropic acid dye (77) is 515 nm.

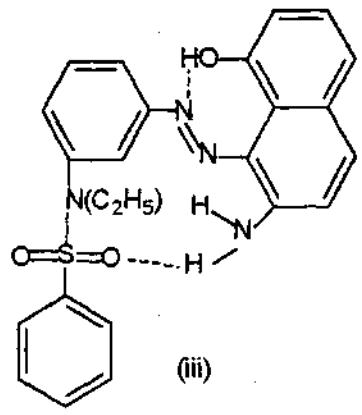


(i) (ii)

Scheme 5.1

The two pairs; (74) and (75) in one group and (76) and (77) in the other, all indicated that it is the dye with the least absorption wavelenth maxima that is least absorbing as seen from the extinction coefficients.

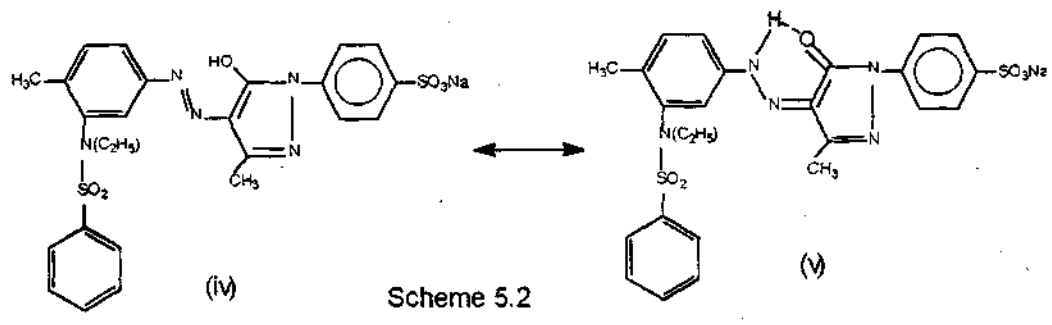
Whereas, the higher wavelength of absorption shown by dye (76) over dye (77) can be attributed to the higher electron donating strength of the amino group over the hydroxy group, the same explanation cannot be made with respect to dye (74) and (75). However, what seemed to be the main similarity between dye (77) and (74) is the increased intramolecular interactions favoured in dye (77) by the azo-hydrazone tautomerism[251-252] illustrated in Scheme 5.1, and intra molecular hydrogen bonding shown in structure (iii) for dye (74). These factors can be imagined to discourage free flow of electrons which would consequently increase the ionization potential.



(iii)

Both dyes (76) and (75) are not as disposed to exhibit the effects as such, they absorb at higher wavelengths on a comparative scale.

The dye derived from 4-sulphophenyl-3-methyl-5-pyrazolone, dye (78) as expected produced a yellow dye, however, it is only disturbing that the yield is poor and the extinction coefficient is the smallest, however, it can also exhibit azo-hydrazone tautomerism as shown in Scheme 5.2.



(iv) (v)

Scheme 5.2

However, the extinction coefficient of all the dyes are very low inexpectedly. This can be attributed to aggregation.

dye aggregation in fibre and aqueous phases. This could be promoted
presence of electrolytes. To reduce the influence of these two, the dy
applied at a uniform pH of 4 in the absence of electrolytes.

Table 5.2: Diffusion Coefficient and Activation Energy of Dye (74) on Wool at 333K and 353K

Time		333K		353K	
T (s)	$\sqrt{t}$	Mt	Mt/M∞	Mt	Mt/M∞
600	24.5	0.075	0.14	0.172	0.34
900	30.0	0.0718	0.17	0.205	0.41
1200	34.6	0.109	0.20	0.28	0.56
1500	38.7	0.124	0.23	0.27	0.54
1800	42.4	0.143	0.26	0.324	0.65
2100	45.0	0.157	0.29	0.324	0.65
2400	48.99	0.161	0.30	0.338	0.68
2700	52.00	0.178	0.33	0.375	0.75
3000	54.77	0.190	0.35	0.400	0.80
3600	60.00	0.211	0.39	0.45	0.90
24 hrs	∞	0.54		0.50	
Slope		7.179×10^{-3}		1.53×10^{-2}	
D/r^2 sec^{-1}		1.01194×10^{-5}		4.5963×10^{-5}	
Activation energy (E) J/mol		73978			

Table 5.3: Diffusion Coefficient and Activation Energy of Dye (75) on Wool at 333K and 353K

Time		333K		353K	
t (s)	$\sqrt{t}$	Mt	Mt/M∞	Mt	Mt/M∞
600	24.5	0.086	0.12	0.206	0.30
900	30.0	0.11	0.15	0.264	0.38
1200	34.6	0.129	0.18	0.306	0.44
1500	38.7	0.15	0.21	0.334	0.48
1800	42.4	0.164	0.23	0.342	0.49
2100	45.0	0.19	0.265	0.404	0.58
2400	48.99	0.195	0.28	0.40	0.57
2700	52.00	0.21	0.30	0.48	0.69
3000	54.77	0.222	0.32	0.528	0.76
3600	60.00	0.25	0.36	0.536	0.77
24 hrs	∞	0.70		0.696	
Slope		7.00×10^{-3}		1.36×10^{-2}	
D/r^2 sec^{-1}		9.6211×10^{-6}		3.6317×10^{-5}	
Activation energy (E) J/mol		64932			

Table 5.4: Diffusion Coefficient and Activation Energy of Dye (76) on Wool at 333K and 353K

Time		333K		353K	
t (s)	√t	Mt	Mt/M∞	Mt	Mt/M∞
600	24.5	0.13	0.0997	0.30	0.21
900	30.0	0.16	0.125	0.39	0.27
1200	34.6	0.18	0.138	0.44	0.30
1500	38.7	0.23	0.178	0.52	0.357
1800	42.4	0.26	0.1994	0.70	0.48
2100	45.0	0.28	0.215	0.62	0.43
2400	48.99	0.30	0.2301	0.788	0.54
2700	52.00	0.34	0.258	0.70	0.48
3000	54.77	0.356	0.273	0.76	0.52
3600	60.00	0.385	0.295	0.84	0.58
24 hrs	∞	1.304		1.452	
Slope		5.6×10^{-3}		1.00×10^{-2}	
D/r^2 sec^{-1}		6.1575×10^{-5}		1.9635×10^{-5}	
Activation energy (E) J/mol		56687			

Table 5.5: Diffusion Coefficient and Activation Energy of Dye (77) on Wool at 333K and 353K

Time		333K		353K	
t (s)	$\sqrt{t}$	Mt	Mt/M∞	Mt	Mt/M∞
600	24.5	0.17	0.15	0.406	0.28
900	30.0	0.21	0.19	0.53	0.37
1200	34.6	0.278	0.25	0.644	0.45
1500	38.7	0.30	0.265	0.68	0.47
1800	42.4	0.326	0.29	0.760	0.53
2100	45.0	0.38	0.335	0.81	0.56
2400	48.99	0.37	0.33	0.88	0.61
2700	52.00	0.42	0.375	0..91	0.63
3000	54.77	0.46	0.41	0.916	0.64
3600	60.00	0.51	0.45	1.04	0.72
24 hrs	∞	1.128		1.44	
Slope		8.67×10^{-3}		1.19×10^{-2}	
D/r^2 sec^{-1}		1.4759×10^{-5}		2.781×10^{-5}	
Activation energy (E) J/mol		30969			

Table 5.6: Diffusion Coefficient and Activation Energy of Dye (78) on Wool at 333K and 353K

Time		333K		353K	
t (s)	$\sqrt{t}$	Mt	Mt/M∞	Mt	Mt/M∞
600	24.5	0.13	0.12	0.368	0.30
900	30.0	0.18	0.16	0.46	0.37
1200	34.6	0.238	0.21	0.56	0.45
1500	38.7	0.27	0.24	0.622	0.50
1800	42.4	0.278	0.25	0.792	0.64
2100	45.0	0.314	0.28	0.750	0.60
2400	48.99	0.26	0.23	0.800	0.64
2700	52.00	0.381	0.34	0.858	0.69
3000	54.77	0.40	0.36	0.920	0.74
3600	60.00	0.46	0.41	1.00	0.81
24 hrs	∞	1.12		1.244	
Slope		8.00×10^{-3}		1.47×10^{-2}	
D/r^2 sec^{-1}		1.2566×10^{-5}		4.2429×10^{-5}	
Activation energy (E) J/mol		59482			

Table 5.7: Diffusion Coefficient and Activation Energy of Dye (74) on Nylon 6.6 at 333K and 353K

Time		333K		353K	
t (s)	$\sqrt{t}$	Mt	Mt/M∞	Mt	Mt/M∞
600	24.5	0.144	0.44	0.18	0.49
900	30.0	0.157	0.475	0.20	0.54
1200	34.6	0.149	0.45	0.22	0.59
1500	38.7	0.168	0.51	0.23	0.61
1800	42.4	0.165	0.50	0.24	0.65
2100	45.0	0.182	0.55	0.247	0.665
2400	48.99	0.19	0.58	0.241	0.65
2700	52.00	0.198	0.60	0.273	0.735
3000	54.77	0.20	0.61	0.275	0.74
3600	60.00	0.208	0.63	0.297	0.80
24 hrs	∞	0.33		0.371	
Slope		5.67×10^{-3}		2.4×10^{-3}	
D^{-}/r^{2} sec^{-1}		6.3124×10^{-6}		1.3854×10^{-5}	
Activation energy (E) J/mol		38425			

Table 5.8: Diffusion Coefficient and Activation Energy of Dye (75) on Nylon 6.6 at 333K and 353K

Time		333K		353K	
t (s)	√t	Mt	Mt/M∞	Mt	Mt/M∞
600	24.5	0.12	0.35	0.14	0.41
900	30.0	0.14	0.40	0.16	0.46
1200	34.6	0.153	0.44	0.21	0.62
1500	38.7	0.16	0.46	0.19	0.55
1800	42.4	0.161	0.47	0.20	0.59
2100	45.0	0.18	0.53	0.21	0.61
2400	48.99	0.205	0.59	0.224	0.66
2700	52.00	0.20	0.565	0.24	0.69
3000	54.77	0.205	0.59	0.24	0.71
3600	60.00	0.22	0.64	0.26	0.75
24 hrs	∞	0.345		0.34	
Slope		8.1×10^{-3}		1.00×10^{-2}	
D'/r^2 sec^{-1}		1.2882×10^{-5}		1.9635×10^{-5}	
Activation energy (E) J/mol		20596			

Table 5.9: Diffusion Coefficient and Activation Energy of Dye (76) on Nylon 6.6 at 333K and 353K

Time		333K		353K	
t (s)	$\sqrt{t}$	Mt	Mt/M∞	Mt	Mt/M∞
600	24.5	0.060	0.29	0.104	0.36
900	30.0	0.060	0.28	0.13	0.44
1200	34.6	0.061	0.29	0.14	0.48
1500	38.7	0.061	0.29	0.15	0.53
1800	42.4	0.065	0.31	0.17	0.59
2100	45.0	0.065	0.31	0.18	0.63
2400	48.99	0.067	0.32	0.210	0.72
2700	52.00	0.067	0.32	0.19	0.67
3000	54.77	0.067	0.32	0.206	0.71
3600	60.00	0.071	0.34	0.233	0.80
24 hrs	∞	0.209		0.291	
Slope		2.143×10^{-3}		1.19×10^{-2}	
D'/r^2 sec^{-1}		9.0173×10^{-7}		2.781×10^{-5}	
Activation energy (E) J/mol		167611			

Table 5.10: Diffusion Coefficient and Activation Energy of Dye (77) on Nylon 6.6 at 333K and 353K

Time		333K		353K	
t (s)	$\sqrt{t}$	Mt	Mt/M∞	Mt	Mt/M∞
600	24.5	0.17	0.50	0.195	0.54
900	30.0	0.18	0.534	0.23	0.64
1200	34.6	0.174	0.51	0.274	0.76
1500	38.7	0.19	0.57	0.260	0.73
1800	42.4	0.202	0.60	0.308	0.86
2100	45.0	0.210	0.62	0.29	0.805
2400	48.99	0.23	0.68	0.305	0.85
2700	52.00	0.22	0.64	0.321	0.89
3000	54.77	0.225	0.66	0.350	0.89
3600	60.00	0.24	0.70	0.350	0.97
24 hrs	∞	0.339		0.360	
Slope		5.33×10^{-3}		1.13×10^{-2}	
D/r^2 sec^{-1}		5.5781×10^{-6}		2.5072×10^{-5}	
Activation energy (E) J/mol		73466			

Table 5.11: Diffusion Coefficient and Activation Energy of Dye (78) on Nylon 6.6 at 333K and 353K

Time		333K		353K	
t (s)	√t	Mt	Mt/M∞	Mt	Mt/M∞
600	24.5	0.113	0.51	0.12	0.46
900	30.0	0.122	0.55	0.164	0.63
1200	34.6	0.129	0.58	0.179	0.69
1500	38.7	0.131	0.595	0.183	0.705
1800	42.4	0.13	0.59	0.193	0.74
2100	45.0	0.144	0.65	0.207	0.795
2400	48.99	0.14	0.63	0.199	0.77
2700	52.00	0.157	0.71	0.217	0.835
3000	54.77	0.16	0.72	0.23	0.88
3600	60.00	0.166	0.75	0.241	0.925
24 hrs	∞	0.221		0.260	
Slope		6.67×10^{-3}		9.78×10^{-3}	
D/r^2 sec^{-1}		8.7354×10^{-6}		1.8781×10^{-5}	
Activation energy (E) J/mol		37418			

Fig 5.8: Rate curves for dye (74) on wool

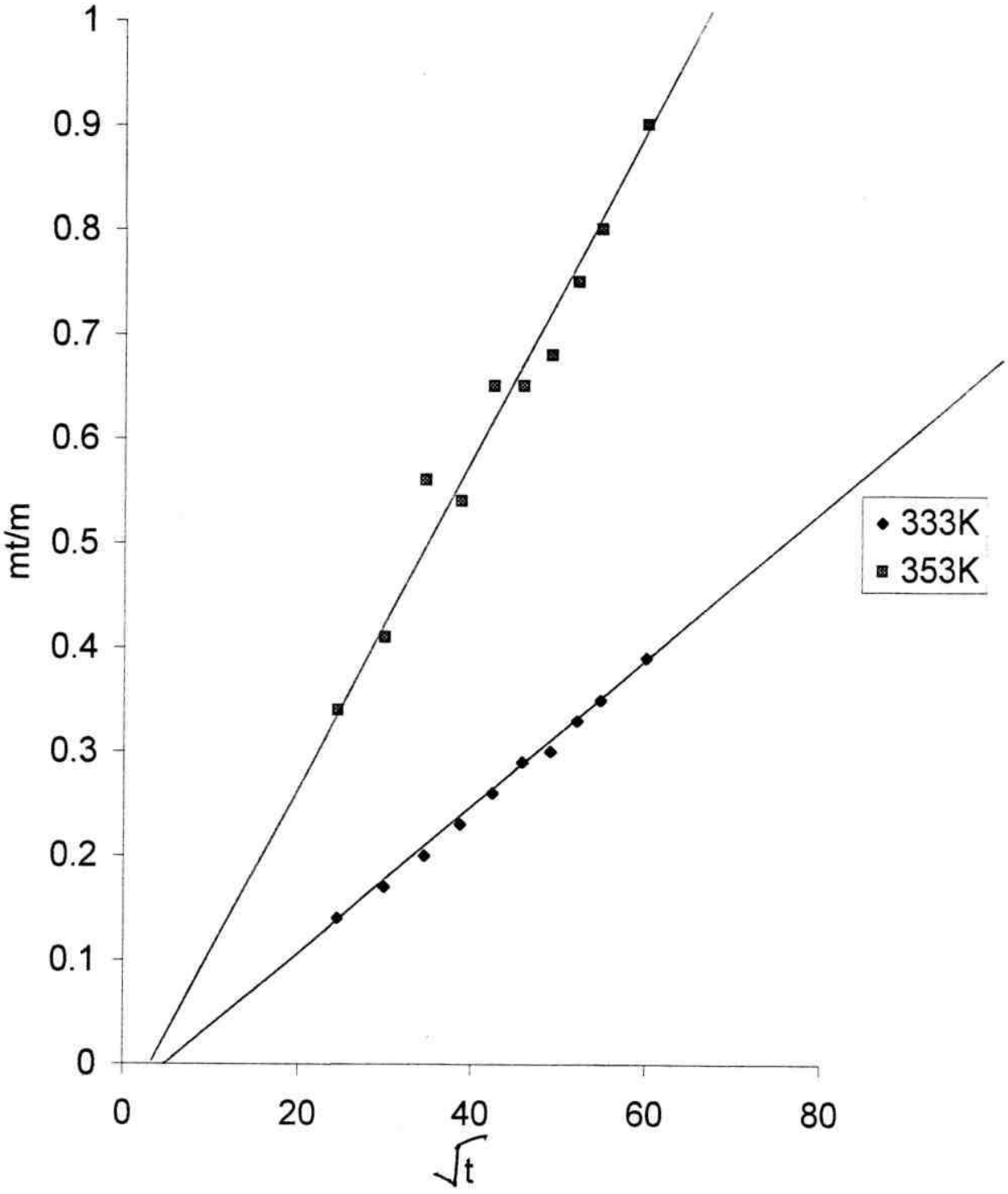


Fig 5.9: Rate curves for dye (75) on wool

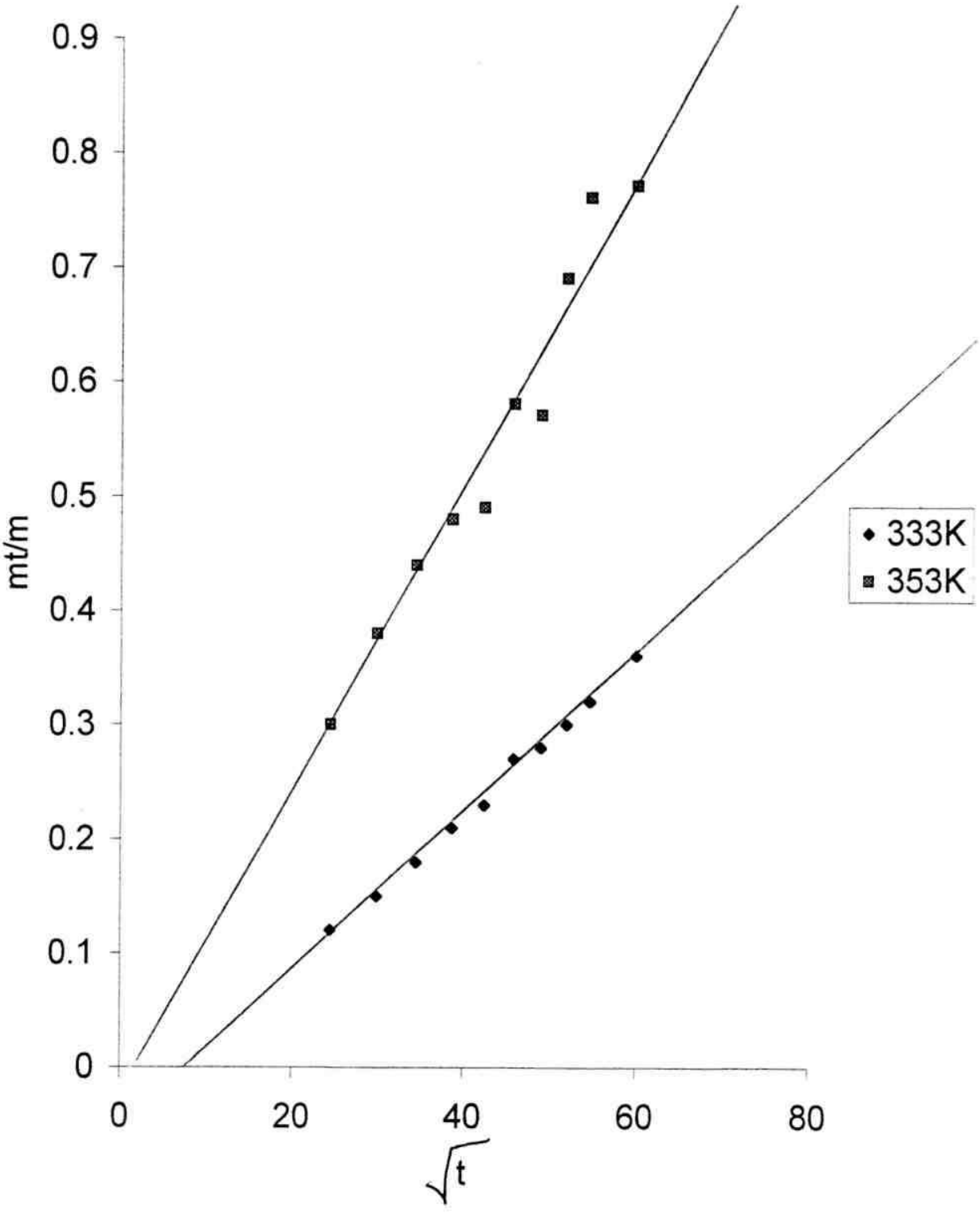


Fig 5.10: Rate curves for dye (76) on wool

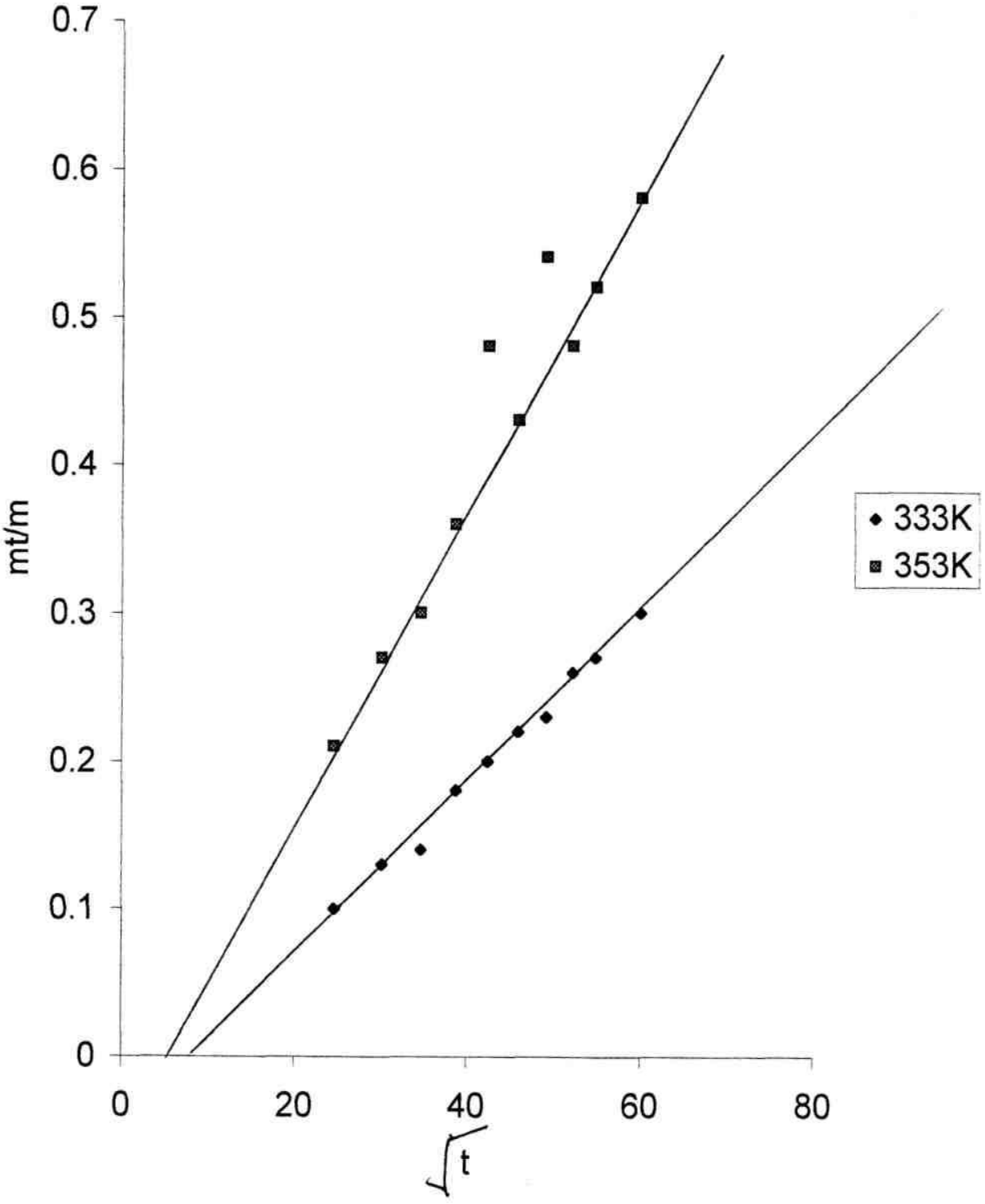


Fig 5.11: Rate curves for dye (77) on wool

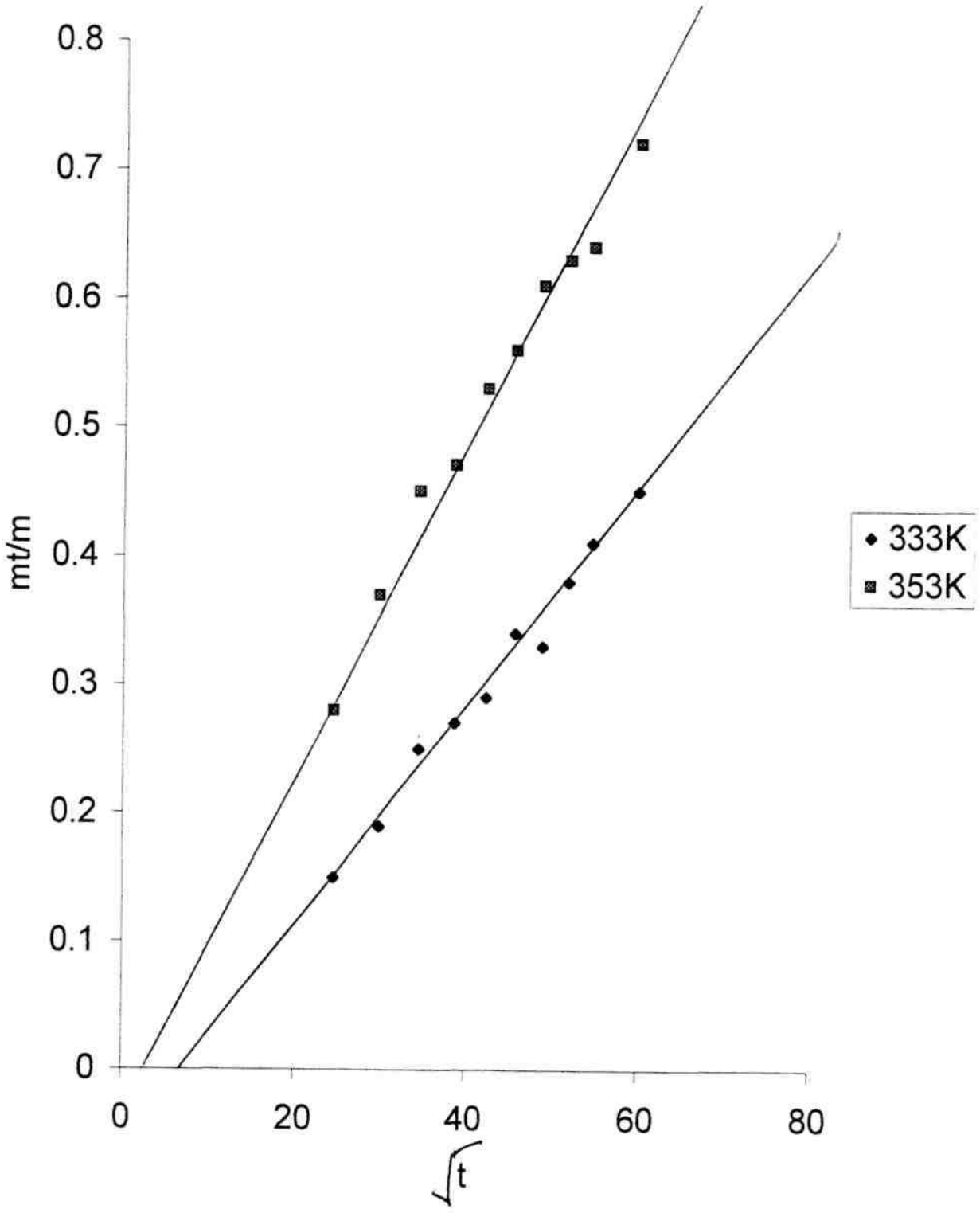


Fig 5.12: Rate curves for dye (78) on wool

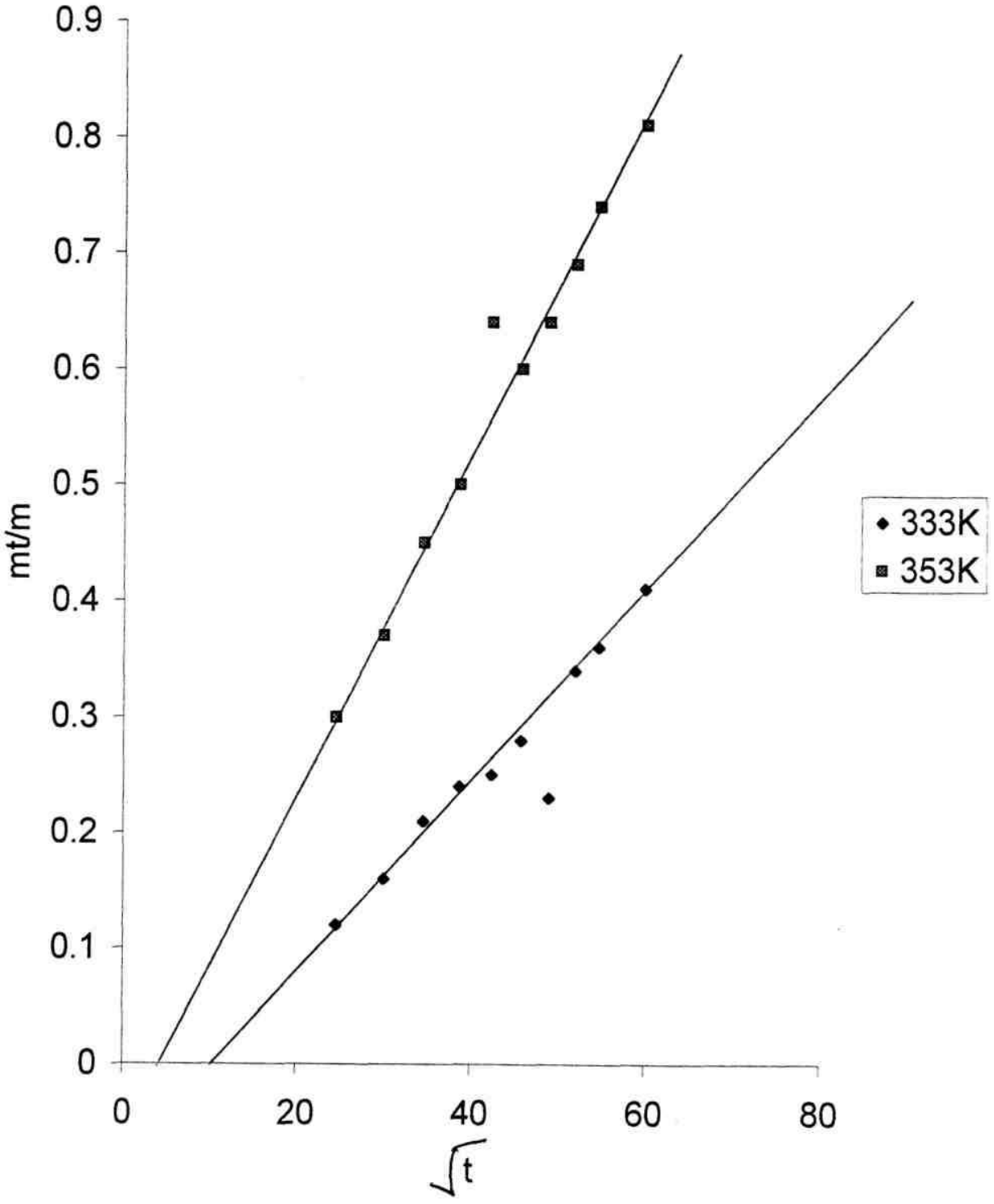


Fig 5.13: Rate curves for dye (74) on nylon 6.6

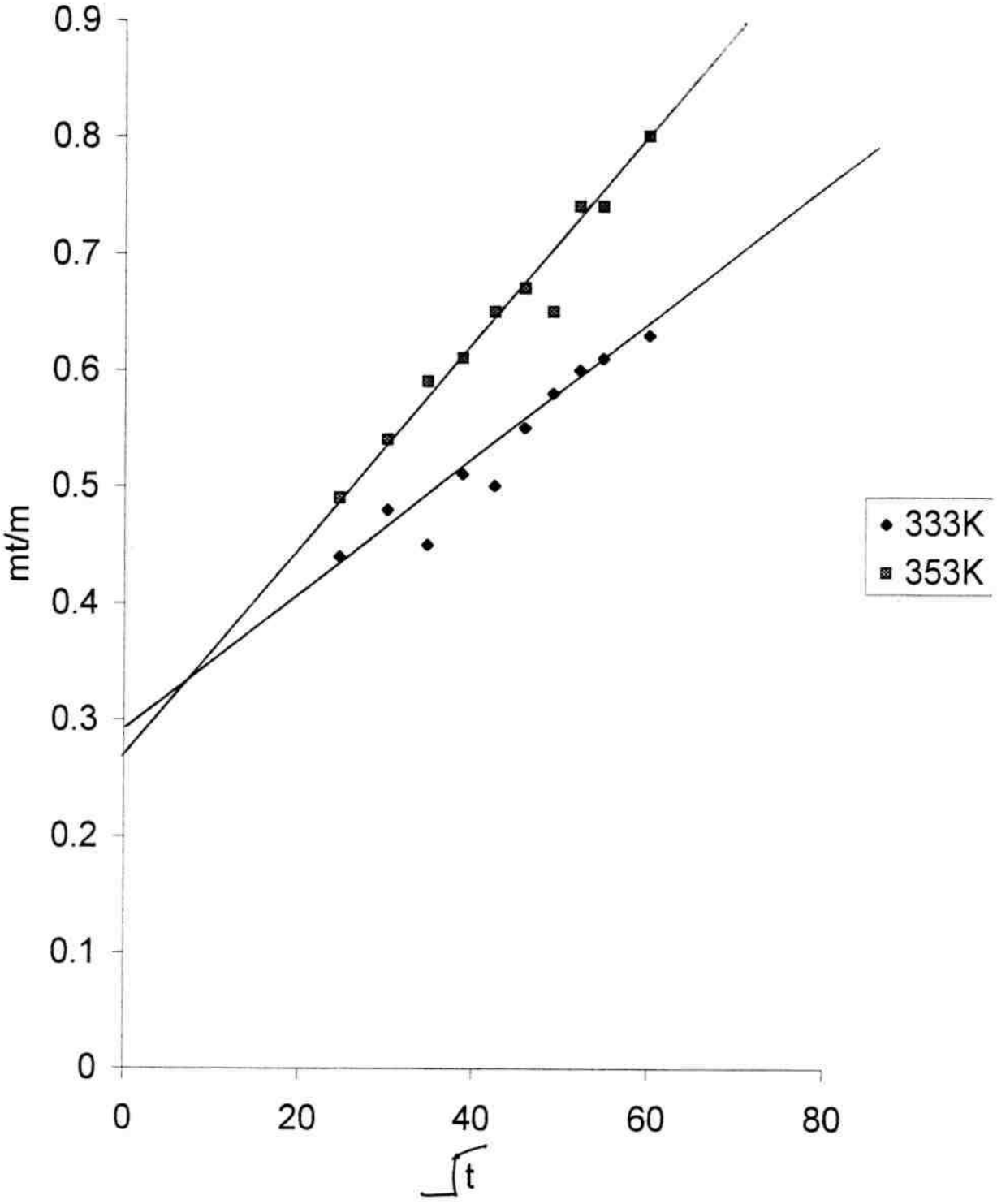


Fig 5.14: Rate curves for dye (75) on nylon 6.6

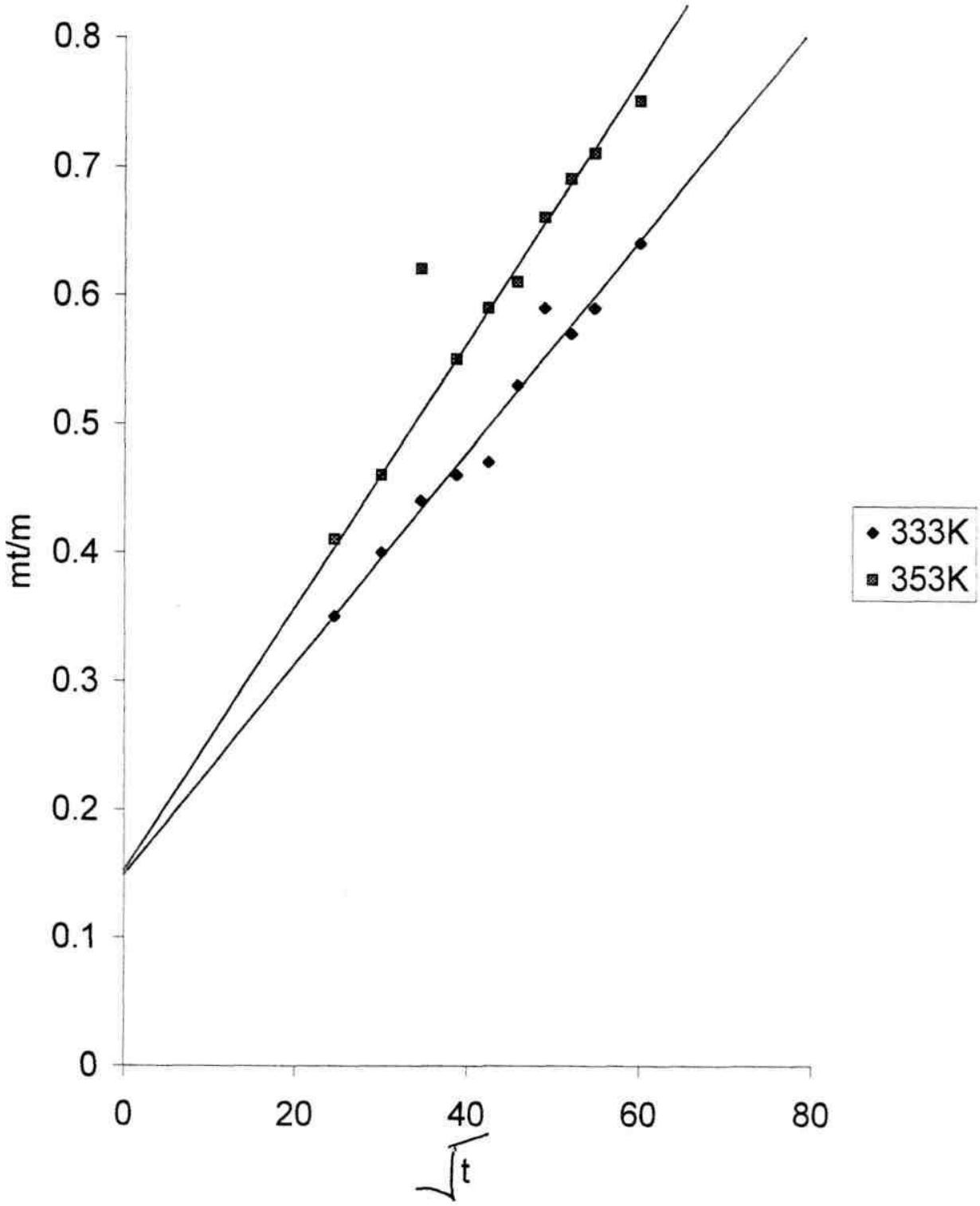


Fig 5.15: Rate curves for dye (76) on nylon 6.6

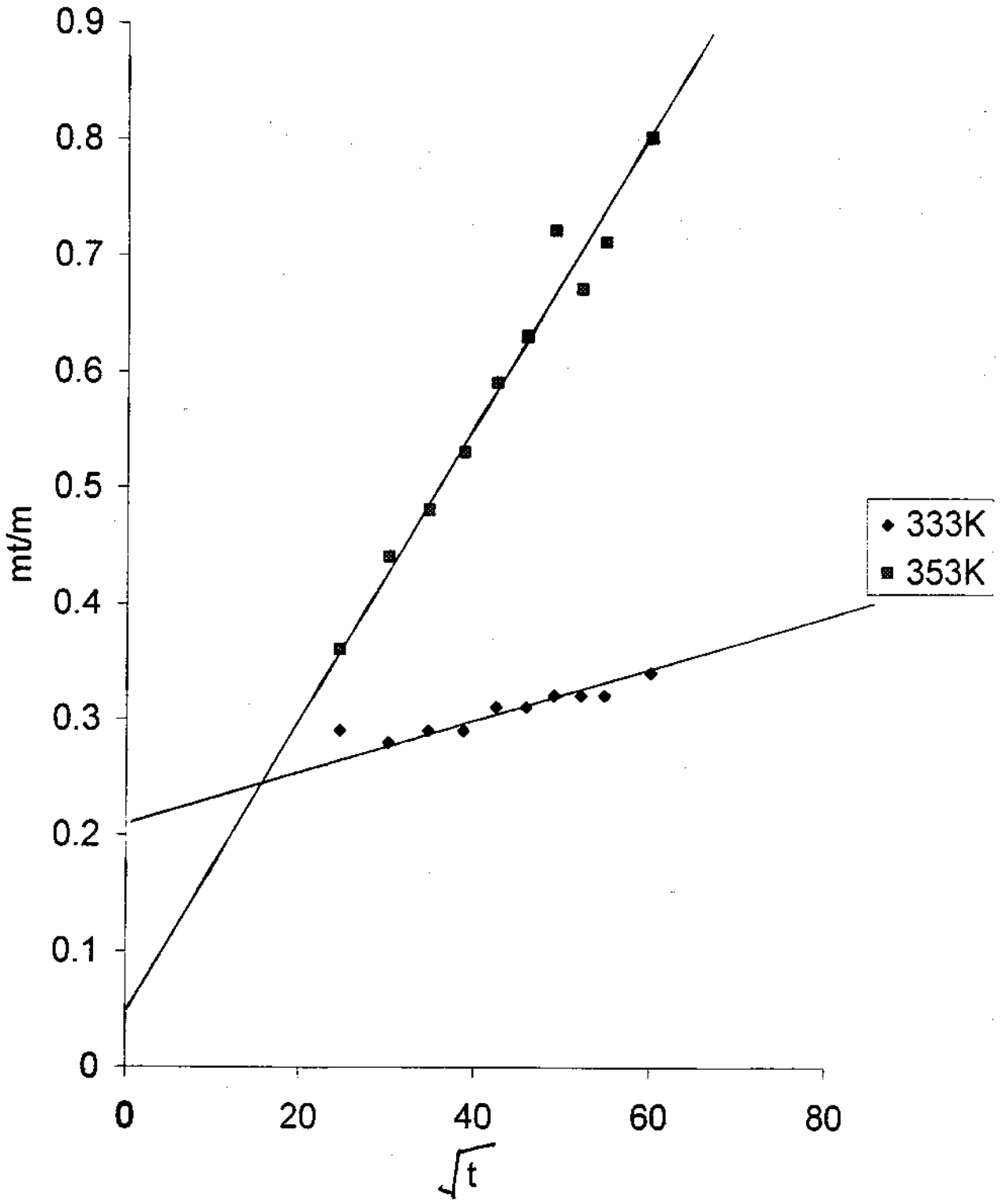


Fig 5.16: Rate curves for dye (77) on nylon 6.6

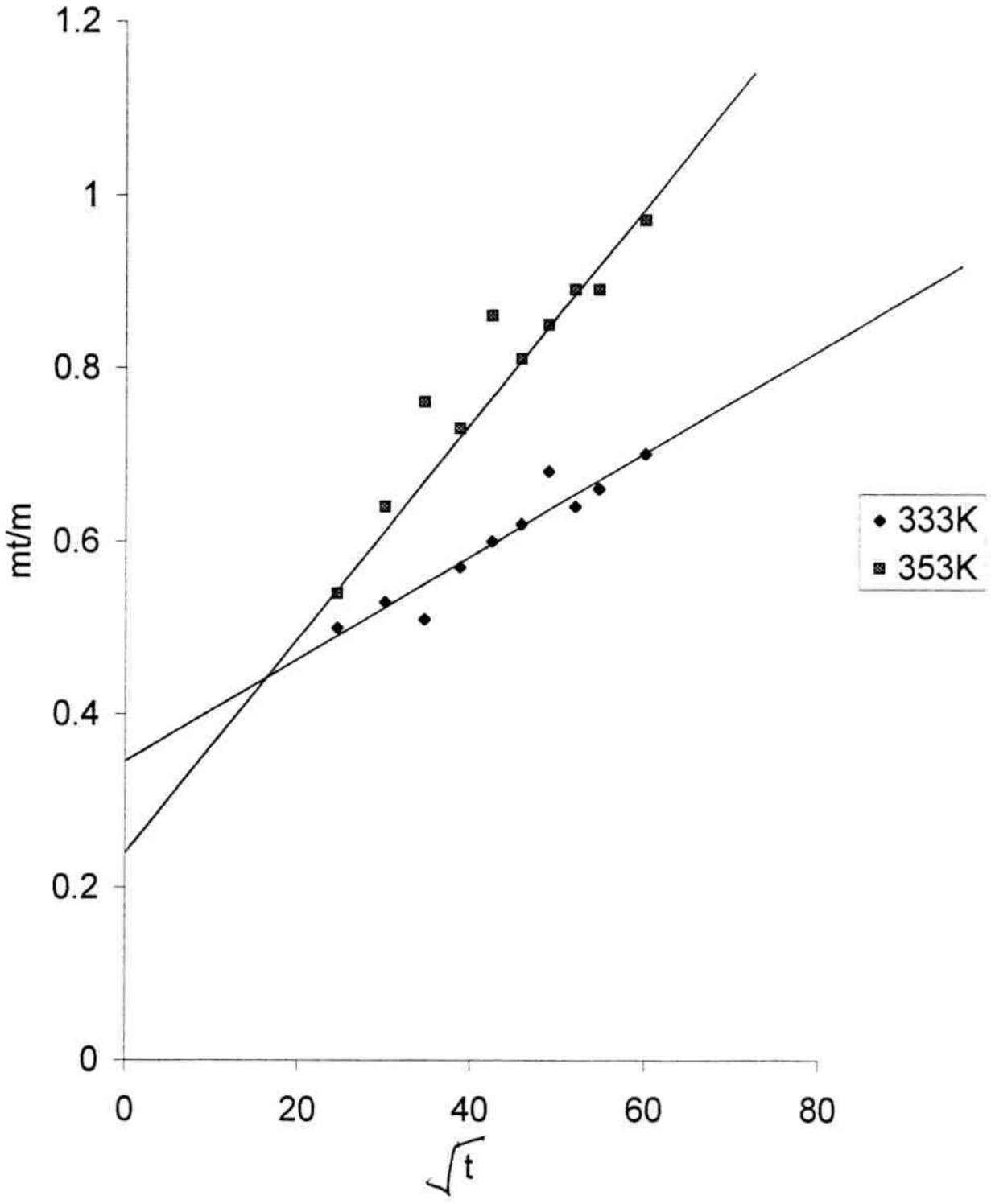
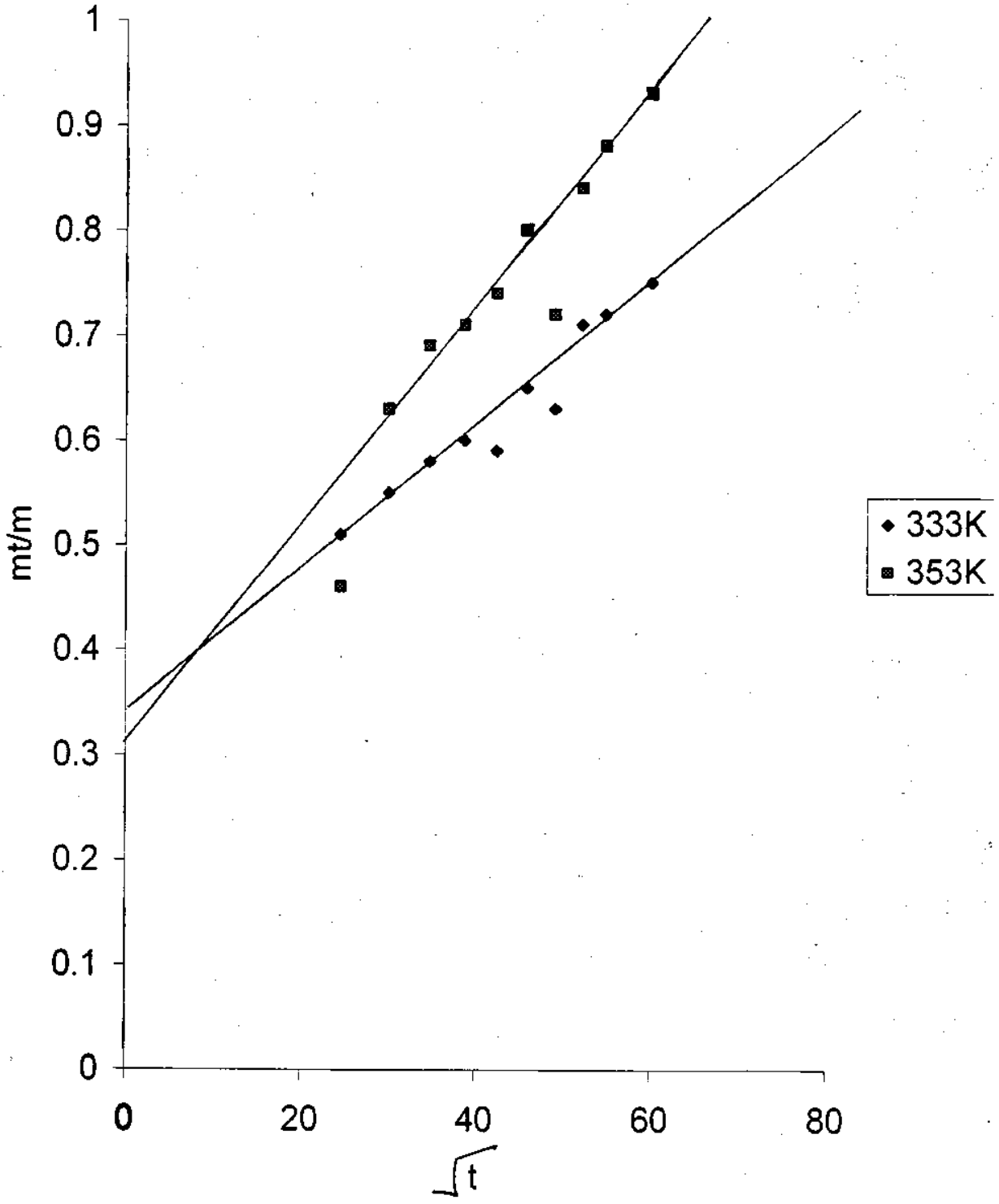


Fig 5.17: Rate curves for dye (78) on nylon 6.6



It can be observed from Tables 5.2 – 5.6 that at all temperatures, the diffusion coefficients of the chromotropic derived dye (77) in wool substrate is higher than the H-acid derived dye (76). For dye (76) the diffusion coefficient is 6.157 x 10^{-6} sec^{-1} at 333K and 1.9635 x 10^{-5} sec^{-1} at 353K whereas it is 1.4759 x 10^{-5} sec^{-1} and 2.781 x 10^{-5} sec^{-1} for dye (77) at the respective temperatures. The activation energy of diffusion for the H-acid derived dye (76) is much higher being 56687 J/mol as compared to 30969 J/mol for the chromotropic acid derived dye (77). Both dyes have virtually the same molecular weights, same ionic charge etc. Their main difference is just that the 1-position of the chromotropic acid coupling component is occupied by an –OH group whereas it is occupied by an $-NH_2$ group in the H-acid coupling component. The difference in the activation energy indicated that it is easier to push a molecule of dye (77) than dye (76). It is indicative of smaller molecular volume for the dye (77) compared to dye (76). Another factor that can influence this difference is the degree of aggregatability.

The atomic radius of a nitrogen atom has been assigned 71 pm whereas that of oxygen as 60 pm. Similarly, the van der Waals radii of the elements are 150 pm and 140 pm respectively.[260] These indicate that the molecular volume of the H-acid derivative dye (76) is bigger than dye (77)

derived from chromotropic acid. This parameter alone can bring about dye (76) to have lower diffusion coeficient and higher activation energy compared to dye (77). The bigger volume associated with $-NH_2$ group can also indicate higher polarisability and higher aggregating power which again can bring about higher activation energy and lower diffusion coefficients. When the dyes derived from J- and gamma-acids, dyes (75) and (74) respectively are compared, it is seen that at all temperatures, dye (74) derived from gamma acid recorded higher diffusion coefficients. It is 1.0119×10^{-5} sec^{-1} at 333K and 4.5963×10^{-5} sec^{-1} for gamma acid dye (74) and 9.6211×10^{-6} sec^{-1} and 3.6317×10^{-5} sec^{-1} for J-acid dye (75) at the two respective temperatures. But dye (74) recorded a higher activation energy being 73978 J/mol compared to 63932 J/mol for dye (75). However, for all practical purposes, this difference in the activation energy is not very critical.

The dye derived from the pyrazolone intermediate dye (78) gave average values for both the diffusion coefficient and activation energy. Being 1.2566×10^{-5} sec^{-1} at 333K and 4.2429×10^{-5} sec^{-1} at 353K. The activation energy being 59482 J/mol. It has only one solubilizing group, it aggregates to a higher extent which can explain why it has higher value than

the dye derived from chromotropic acid dye (77) but being lower than dye (74) and (75) by being slimmer and more flexible.

With respect to nylon 6.6 substrate, the only notable difference is that the dyes derived from J-acid dye (75) and gamma acid, dye (74) are faster at almost all the temperatures over the H-acid derived dye (76) and chromotropic derived dye (77). They therefore show lower activation energies than the latter dyes. For dye (76) the diffusion coefficient are 9.0173×10^{-7} sec^{-1} at 333K and 2.781×10^{-5} sec^{-1} at 353K with an activation energy of 167,611 J/mol. That of the chromotropic acid derived dye (77) are 5.5781×10^{-6} sec^{-1} at 333K and 2.5072×10^{-5} sec^{-1} at 353K for diffusion coefficient with an activation energy of 73466 J/mol. The equivalent values for dye (75) are 1.2882×10^{-5} sec^{-1}, 1.9635×10^{-5} sec^{-1} and 20596 J/mol. for dye (74). They are 6.3124×10^{-6} sec^{-1}, 1.3854×10^{-5} sec^{-1} and 38425 J/mol. In nylon substrate too it can be seen that dye (76) derived from H-acid recorded higher activation energy than dye (77) derived from chromotropic acid. Similarly, the dye derived from gamma acid dye (74) also recorded higher activation energy than the J-acid derived dye (75). It would be anticipated that the intra-molecular hydrogen bonding as would result as shown in structure (iii) should very much reduce the degree of aggregation of the gamma acid dye and also the chromotropic acid dye shown in Figure

(ii) of Scheme 5.1. A closer look at the two structures will reveal that both structures (ii) and (iii) will suffer from loss of flexibility which will seriously impair mobility. This as anticipated should slow down the speed of the dyes, whereas, the loss of association by intrar molecular association should discourage aggregation which effect is expected to speed up the mobility of the dyes through the pores of the fibres. Which of these factors controls the phenomena of diffusion in relative term would therefore have to be a balance of these two effects resulting from the same consequence. It appeared that with respect to the difference between dye (74) and (75) with respect to activation energy, it is the loss of flexibility that is the stronger influence because dye (74) recorded higher activation energies in both substrates.

However, with respect to H-acid derived dye (76) and chromotropic acid derived dye (77) where in both substrates dye (76) is the slower dye and the highest in activation energy. In addition to what was used to explain what could bring about this, the intrar molecular association through the hydrazone form in chromotropic acid dye (77) can bring about less aggregation which can speed up the mobility and reduce the activation energy compared to dye (76) derived from H-acid.

5.2.2 Thermodynamic Parameters of the Dyes on Wool and Nylon 6.6

Direct method of dermination was used. The pH of the dye bath was maintained at 4 for both wool and nylon 6.6 substrates. It involved dyeing 0.05g samples in a dye solution at a liquor to goods ratio of 200:1 using 6% shade at 60°C and 80°C for 24 hours for nylon 6.6 and 96 hours for wool until equilibrium was attained. The dye adsorbed was estimated spectrophotometrically by dissolving the dyed wool sample in 5% NaOH at the boil and stripping the dye from nylon 6.6 with 20% pyridine solution at the boil. The dye remaining in solution was also determined. Five different determinations were made. The results are shown in Tables 5.12 to 5.13.

Table 5.12: Thermodynamic Parameters of the Dyes on Wool

	Dye (74) g/0.05g		Dye (75) g/0.05g		Dye (76) g/0.05g		Dye (77) g/0.05g		Dye (78) g/0.05g	
	369K x 10^{-2}	353K x 10^{-2}	369K x 10^{-3}	353K x 10^{-3}	369K x 10^{-2}	353K x 10^{-2}	369K x 10^{-3}	353K x 10^{-3}	369K x 10^{-3}	353K x 10^{-3}
	1.6	2.6	6.3	8.3	1.8	2.2	3.1	7.3	6.4	1.0
	1.9	2.7	6.3	8.7	1.9	2.3	3.2	7.8	6.9	0.97
	1.7	2.8	6.4	8.8	1.8	2.3	3.5	7.9	7.0	0.99
	2.0	3.0	6.5	8.4	1.7	2.4	3.3	7.6	6.8	1.10
	1.5	2.6	6.7	9.1	2.0	2.5	3.6	8.0	6.7	0.98
Average	1.7	2.7	6.4	8.7	1.8	2.3	3.3	7.7	6.8	1.00
[D]f/kg	340	540	130	170	360	460	66	150	140	200
[D]s/L	1.3	0.30	0.36	0.13	3.2	2.7	3.7	3.2	2.9	2.6
$-\Delta\mu^{\circ}$J /mol	20486	25261	21477	24323	17897	18340	12245	14551	15301	1605
$-\Delta H^{\circ}$ J/mol	130609		87113		28114		65427		31537	
$-\Delta S^{\circ}$ J/mol	298		178		28		144		44	

Table 5.13: Thermodynamic Parameters of the Dyes on Nylon 6.6

	Dye (74) g/0.05g		Dye (75) g/0.05g		Dye (76) g/0.05g		Dye (77) g/0.05g		Dye (78) g/0.05g	
	370K x 10^{-3}	353K x 10^{-3}	370K x 10^{-3}	353K x 10^{-3}	370K x 10^{-3}	353K x 10^{-3}	370K x 10^{-4}	353K x 10^{-4}	370K x 10^{-3}	353K x 10^{-3}
	1.28	1.50	1.05	1.25	1.4	1.52	4.7	6.7	1.40	1.55
	1.32	1.36	1.25	1.32	1.46	1.54	5.1	6.9	1.48	1.64
	1.29	1.43	1.13	1.31	1.47	1.53	4.9	6.5	1.42	1.59
	1.30	1.50	1.09	1.33	1.50	1.49	4.8	7.0	1.45	1.62
	1.33	1.39	1.17	1.29	1.48	1.53	4.7	6.8	1.45	1.60
Average	1.33	1.39	1.14	1.30	1.46	1.52	4.8	6.8	1.45	1.60
[D]f/kg	26.0	28.8	22.8	26.0	29.2	30.4	9.6	13.6	28.8	32.0
[D]s/L	1.12	0.81	0.386	0.170	2.35	1.35	1.95	1.83	1.66	1.24
$-\Delta\mu^{\circ}$ J/mol	21716	21970	24590	26253	19792	20629	16943	17374	20820	21029
$-\Delta H^{\circ}$ J/mol	27244		60785		38009		26324		25369	
$-\Delta S^{\circ}$ J/mol	15		99		49		25		12	

The thermodynamics of dyeing give valuable information on the magnitude of the driving force behind the process, the inter play of forces between all the components in the system resulting from molecular interactions in both the fibre and dyebath and the extent of orientations of the adsorbed dye molecules. Studies on entropy changes also throw light on the extent of hydrophobic bonding that plays an important part in some dye adsorption processes.

The affinity consists of two parts, the heat of dyeing (ΔH°) and the entropy of dyeing (ΔS°) related by the equation:

$$\Delta\mu^\circ = \Delta H^\circ - T\Delta S^\circ$$

The heat of dyeing (ΔH°) is the difference in heat content between that needed to free one mole of dye from the solvent and that required to free the same quantity from the surface or interior of the substrate by thermal agitation.[254] It is thus the heat of sorption or the increase in heat content of the system when dye is sorbed. Large negative values of ΔH° correspond to the idea of high potential affinity. The heat of dyeing has been related to the combination of hydrogen bond, salt-linkages and other polar van der Waals forces of attractions. Such that if it is possible to quantify all these forces of binding they will sum up to the heat of dyeing.[219]

The entropy of dyeing on the other hand is described as the degree of disorder of the system when the dye is sorbed. It was also described as a measure of that part of the affinity which is due to probability i.e. when the molecular motions are sufficiently random. The less the negative is the entropy the higher the entropy gain and the higher will be the contribution of the entropy to the overall affinity. However, if the entropy is positive, as is the case with some dyeing systems, then the higher it is, the greater is the contributions of the entropy gain to the total affinity. Entropy gain due to dye adsorption is related to the increase in entropy due to release of water molecules when salt linkage is formed. Otherwise the entropy term should be negative or loss in entropy as the free moving dye molecules get confined in a fibre. Higher contribution of entropy to affinity has been related to higher hydrophobic and other non polar van der Waals forces of interactions.[221,222,254]

The dyeing process which is the adsorption of a negatively charged dye anions to a surface with a negative surface potential is believed to be driven by the intrinsic affinity of the dye anion. Initially, when the negatively charged dye anions are adsorbed, the increase in the surface potential due to the adsorbed dye would lead to electrostatic repulsion of further anions. But this will lead to a saturation or thermodynamic

equilibrium when the decrease in free energy due to adsorption and the increase in the surface free energy due to the increase in the surface potential.

A survey of the affinities of these dyes under study on both fibres indicate that the dyes derived from H- and chromotropic acids, dyes (76) and (77) being disulphonated gave lower values than J- and gamma acid dyes, (75) and (74) that are monosulphonated, i.e. for wool, at 369K, dye (76) has –17897 J/mol; dye (77), -12245 J/mol; dye (75) has –21477 J/mol; dye (74) has –20,486 J/mol. For nylon 6.6 at 369K, dye (76) has –19792 J/mol, dye (77) has –16943 J/mol; dye (75) has –24,590 J/mol; dye (74) has –21,716 J/mol. These results had followed the anticipated trend. Usually, polysulphonated dyes have larger negative charge than the monosulphonated ones, as such, the increase in surface potential due to adsorption will be more even at lower levels of adsorption such that equilibrium will be attained on a relative term by lower level of exhaustion for the more sulphonated dyes than the mono sulphonated dyes.[216-217]

The dye derived from 4-sulpho-phenyl-3-methyl-5-pyrazolone dye (78) gave values higher than chromotropic acid derivative dye (77) but lower than the H-acid derived dye (76). In wool, at 369K, it recorded –15301 J/mol whereas it gave a value higher than both the disulphonated dyes on

nylon 6.6 but lower than J and gamma acid derivative dyes (75) and (74) being –20820 J/mol at 369K. Though, it is also monosulphonated. A closer look at the structure of the dye showed that it has the least molecular weight, as such, expectedly should have the least affinity, everything being equal.

It can further be seen that with both fibres, H-acid derived dye (76) recorded higher affinity value than the chromotropic acid derived dye (77). Similarly, J-acid derived dye (75) recorded higher affinity value than the gamma acid derived dye (74). The main similarity between chromotropic acid and gamma acid is the ability to display higher intra- molecular association which among other things will reduce the aggregation as seen in section 5.12 and as a consequence reduce the affinity.

When the performance of the dyes are compared on the two substrates, it is seen that at the lower temperatures with the exception of gamma acid dye (74), the dyes have higher affinities on nylon 6.6 than on wool. At the higher temperatures, (369K), without exception, the dyes recorded higher affinities on nylon than on wool. One explanation for this is that the wool substrate contains about 30% water which hydrates the charged site of adsorption, this is quite large compared to just about 3% in a nylon 6.6 substrate. This hydrated sites will reduce the coulumbic driving force of

union with the negatively charged dye anion far more in wool than in nylon 6.6.

With respect to the heat of dyeing, it is observed that with the exception of H-acid derived dye (76), the dyes recorded higher values on wool than on nylon 6.6. For wool, dye (76) recorded –28114 J/mol, dye (77), -65427 J/mol, dye (75) –87,113 J/mol, dye (74) –130609 J/mol, the pyrazolone dye (78) recorded –31537 J/mol. For nylon 6.6, dye (76) recorded –3809 J/mol, dye (77) –26324 J/mol, dye (75) 60,785 J/mol, dye (74) –27244 J/mol and dye (78) –25369 J/mol. This accounted for the higher polar forces of attraction on wool for the dyes. In other words, hydrogen bonding, polar van der Waals forces of attraction are greater with the wool substrates than with nylon 6.6 substrate which is far more crystalline. It is the formation of these polar bonds that further aid the adsorption process by eliminating hydrated water around polar groups on the dye and the substrate. This would enable the dye molecule to come sufficiently close to the fibre so that the dispersion forces can be effectively operative and bind the dye to the surface.

In contrast, the entropy gain is higher in the case of the nylon substrate over the wool substrate with the exception of the H-acid derived dye (76). For wool, the entropy is: dye (76) –28 J/mol, dye (77) –144 J/mol,

dye (75) –178 J/mol, dye (74) –298 J/mol, for the pyrazolone dye (78) it is – 44 J/mol. For nylon substrate, dye (76) recorded –49 J/mol, dye (77) –25 J/mol, dye (75) –99 J/mol, dye (74) –15 J/mol and the pyrazolone dye (78) recorded –12 J/mol. This result can be explained from two points. The release of the more highly ordered hydrated water molecules from the polar sites on wool will rather bring more disorderliness in the system. Since there are more hydrated water molecules on wool than nylon the higher entropy gain for nylon than wool is understandable. Similarly, the higher degree of crystallinity in nylon will make for more prepondence of hydrophobic and other non-polar forces of attraction on it, rather than in wool. Both factors made nylon recorded higher entropy gain over wool. In summary, heat of dyeing contributed more to the observed affinity terms with the wool substrate, whereas it is the entropy component that contributed for the higher affinity observed with respect to the nylon substrate.

5.2.3 Wash and Perspiration Fastness Properties of the Dyes on Wool and Nylon 6.6

Wash fastness properties of the dyes were assessed using ISO 3, 4 and 5. Alkaline and acid perspiration tests were assessed according to standard

methods. The results are shown in Tables 5.14 to 5.16 respectively for wool and nylon 6.6.

Table 5.14: Wash fastness Rating of the dyes on Wool

Dye No	ISO 3		ISO 4		ISO 5	
	Color change	Staining of White	Color Change	Staining of White	Color Change	Staining of White
74	2-3	2	3-4	1-2	4	2
75	3	2	3-4	2	4	2
76	2-3	2	2-3	1-2	1	1
77	1	3	1	3	1	3
78	2	1-2	2	1-2	3-4	1

Table 5.15: Wash fastness Rating of the dyes on Nylon 6.6

Dye No	ISO 3		ISO 4		ISO 5	
	Color change	Staining of White	Color Change	Staining of White	Color Change	Staining of White
74	4-5	4-5	4	5	3-4	3
75	4-5	5	4-5	4	3-4	2
76	5	5	5	5	3-4	2-3
77	4	5	2-3	5	2-3	5
78	5	5	5	5	3	2-3

Table 5.16: Acid and Alkaline Perspiration Ratings for the Dyes

Dye No	Alkaline				Acid			
	Wool		Nylon 6.6		Wool		Nylon 6.6	
	Change in Shade	Staining of White	Change in Shade	Staining of White	Change in Shade	Staining of White	Change in Shade	Staining of White
74	4-5	1-2	4-5	2-3	5	2	5	5
75	4-5	1-2	4-5	5	5	2	5	5
76	4	1-2	5	5	4-5	2	5	5
77	3-4	1	4-5	4-5	3-4	1	5	5
78	4-5	2	4-5	2-3	4-5	2	5	5

A close observation of the wash fastness ratings in terms of the change in shade reveals that to a certain extent the ratings followed the affinity ratings of the dyes especially on wool substrate. The order of decreasing affinity of the dyes on wool at temperature of 369K is J-acid-dye (75) > gamma acid-dye (74) > H-acid-dye (76) > pyrazolone-dye (78) > chromotropic acid-dye (77). The trend in the washing fastness is J-acid-dye (75) > gamma-acid-dye (74) > H-acid-dye (76) > pyrazolone-dye (78) > chromotropic acid-dye (78), especially when ISO 3 and ISO 4 ratings are compared. This is quite in line with the observation that affinity of dye for fibre molecules tends to reduce the rate of transport of dye into or out of the fibre. The strength of the dye-fibre molecules aim to cause the dye molecules to remain attached to fibre molecules rather than to diffuse along the pores of the fibre.[255] It was also found out by Nicholls[256] that with acid dyes of the same basicity, the desorption rate from wool into alkaline buffer solution falls with rise in dye-fibre affinity. He also found that the rate falls with reduction in basicity. Which implies that the fewer sulphonate groups there are in the dye molecule the more slowly it desorbs into alkaline solution and the more of such groups are present, the more rapid is the desorption. This is quite in agreement with the general assessment. To a certain extent too, the observed trend is inversely related to the

recorded diffusion coefficients of the dyes especially at 333K. At H-acid-dye (76) has 6.16 x 10^{-6} sec^{-1}, chromotropic acid-dye (77) 1.48 x 10^{-5} sec^{-1}, J-acid-dye (75) 9.6 x 10^{-6} sec^{-1}, gamma acid-dye (74) 1.0 x 10^{-5} sec^{-1}, pyrazolone-dye (78) 1.3 x 10^{-5} sec^{-1}. It is noticed that the H-acid derived dye (76) is the slower dye than the chromotropic acid dye (77) and H-acid derived dye (76) recorded the better change in shade.

Similarly, at temperature 353K, J-acid-dye (76) has a diffusion coefficient of 3.6 x 10-5 sec-1, whereas gamma acid-dye (74) has 4.6 x 10-5 sec-1. The change in shade rating of J-acid-dye (75) is higher than that of gamma acid derived dye (74) with ISO 3 whereas they have the same rating with ISO 4 and 5.

A general correlation between diffusion coefficient and wash fastness with dyes of same basic structure and basicity as H- and chromotropic acid dyes (76) and (77) and between J- and gamma acid (75) and (74), is that, the wash fastness should be inversely proportional to the diffusion coefficient.

Similar observation made for wool apply to nylon 6.6 as well, with the only exception of the rating for H-acid-dye (76) which is higher than gamma acid-dye (74) and J-acid-dye (75). This is not in consonant with the affinities of the dyes on nylon 6.6. J-acid-dye (75) recorded the highest affinity at the two temperatures considered but is only second best, closely

following the H-acid-dye (76). This may be explained from the lack of sufficient time employed in the wash fastness procedure for true equilibrium to be established. The higher rating in both dyes on nylon 6.6 than on wool is hardly surprising as the higher affinity of the dyes on nylon 6.6 than on wool was recorded.

The results of the perspiration tests both in alkaline and acidic media have followed the general trend observed with the wash fastness assessment. The only additional observation is that the acidic perspiration rating was better than the alkaline rating. For this observation, Nicholls[256] explained that as the result of repulsion between the anionic sulphonate groups and anionic charged sites in the fibre, i.e negative affinity is produced, in alkaline medium as opposed to the acidic medium condition where there is positive affinity of sulphonate groups for cationic sites in the fibre which will by analogy produce superior fastness properties than the alkaline medium condition.

5.2.4 Light Fastness Rating of the Dyes on Nylon 6.6 and Wool

Light fastness ratings of the dyed wool and nylon 6.6 substrates were assessed using a xenon arc artificial fadeometer. The faded substrates were

compared with faded blue printed card obtained from University of Leeds. The results are shown in Table 5.17.

Table 5.17: Light Fastness Rating of the Dyes on Wool and Nylon 6.6

Dye No	Wool	Nylon 6.6
74	6-7	3
75	4	1-2
76	3-4	1-2
77	6	3
78	8	7-8

The light fastness ratings of the dyes on wool indicated that for the disulphonated dyes, chromotropic acid derived dye (77) gave the higher rating, whereas with respect to the mono sulphonated dyes other than the pyrazolone derivative, gamma acid (74) gave the higher rating of 6-7 as compared to 4 shown by J-acid derived dye (75). Here like in the other places, the influence of the intra -molecular hydrogen bonding can be inferred. Both chromotropic acid (77) and gamma acid-dye (74) exclusively

among their respective pairs exhibit this effect, it is very likely that this transformation gives certain photostability to the chromogen.

Sekido et al[257] similarly when investigating the effect of para substitution in the diazo component with respect to para substituted aniline as diazo component coupled to gamma acid clearly manifested the superiority of the alkaline coupled aniline to the acid coupled dyes. Alkaline coupling only will favourably dispose the dye structure towards exhibiting enhanced stability by intra-molecular hydrogen bonding. Another possible evidence of the effect of hydrazone form in photostability is the fact that β-naphthol gives far higher light fastness on wool than α-naphthol[258]. However, the influence of amino group substitution in amino naphthols in terms of light fastness is not so straight forward. It can also be seen that gamma acid derived dye (74) recorded higher light fastness rating over chromotropic acid (77). Similarly the J-acid derived dye (75) recorded higher fastness rating over the H-acid derived dye (76). It is as if the lower the sulphonic acid groups the better the photostability. This had been investigated in details by Giles et al,[230-231] who explained the effect of the number of sulphonic acid from the point of view of surface activity in relation to aggregation states. They indicated that the physical state of a dye in a fibre affected the light fastness of the dyeing. This is because

aggregated dye particles generally faded less rapidly than the dye in a monomolecular dispersed state. Generally everything being equal the lower the number of sulphonic acid groups, the lower the surface activity and consequently, the higher the aggregatability and vice versa. This explains why gamma acid-dye (74) and chromotropic acid dye (77) were better in photostability when compared with their respective partners.

With respect to nylon 6.6 substrate, it is observed that gamma acid-dye (74) and chromotropic acid-dye (77) recorded the same rating of 3, whereas dye (75) and dye (76) recorded the same rating of 1-2. The sighted higher photostability deducted to be due to intramolecular hydrogen bonding interaction can be seen here as well. However, the influence of the number of sulphonic acid groups is not highlighted. Generally, however, the light fastness on nylon 6.6 is far inferior to the ratings on wool substrates. This may be due to among other factors, the degree of exhaustion, the relative aggregate states of the dyes in the two substrates etc.

The dye based on substituted pyrazolone (78) gave the best all round lightfastness rating on both substrates. Stead[259] found out that gamma acid, 2-naphthylaminesulphonic acid and 5-pyrazolone are able to impart photostability to azo dyes. However, photochemical explanation for this observation has not been given.

CHAPTER 6

EXPERIMENTAL

6.1 General Information

6.1.1 Melting Points

Melting points were determined using a Gallenkamp block melting point apparatus and are uncorrected.

6.1.2 Spectra

Infrared spectra were recorded on a ATI Mattson Genesis series FTIR i.r spectrophotometer. The solvent used was DMF using a sodium chloride disc. The visible and ultra violet spectra were recorded on a Unicam SP 800 uv-vis spectrophotometer, a times on a unicam uv-visible spectrophotometer, vision software V 3.32. The absorbance readings were obtained using a cornin colorimeter 253.

6.1.3 Calibration Curves

Calibration curves were obtained for dyes 65 to 73 by dissolving an amount of the dye in 10 cm^3 of 10% NaOH made up to 50 cm^3 with water to give concentration ranging from 1.0 – 9.0 x 10^{-4}gm. Using the cornin colorimeter 253 set at the wavelength of maximum absorption of the various dyes shown in Table 4.1. A predetermined dilution was done and the

absorbances at the known concentration were read from the instrument. Figures 6.10 – 6.14 were obtained. 10% NaOH solution was used for calibration because it can strip the dyes from nylon 6.6 fabrics.

Similarly, the dyes were dissolved in $10cm^3$ of 5% NaOH, after which an oven dried, severally maintained 0.05g wool samples were dissolved in the mixture at 100°C. The calibration curve was obtained by getting the absorbances of predetermined concentrations of the dyes in the mixture using a solution of 0.05g wool in 10 cm^3, 5% NaOH ratio for dilution and as the blank. The calibration curves are as shown in Figures 6.20 – 6.25. These curves are used to extrapolate the amount of dyes adsorbed by 0.05g wool substrate after dissolving the fabric in 10 cm^3, 5% NaOH solution at the boil. In both cases, the dyes obeyed Beers-Lamberts law most especially at the low concentration of the dyes in the various solvents.

Similarly, for the same dyes (65) – (73), 2 cm^3 of 0.2M NaCl with pH adjusted to 4.00 with amount of dyes such that 1.0 – 9.0 x 10^{-5} gm is in solution is used to obtain calibration curves shown in Figures 6.30 – 6.35.

Calibration curves for dyes (74) – (78) were prepared in 20% pyridine solution and 5% NaOH solution. Necessary amount of the dyes to make 1 – 5 x 10^{-3} gm in 10 cm^3 of 20% pyridine made up to $50cm^3$ with distilled water was used to make the calibration curves in Figures 6.40 –

6.44. 10cm3 of 20% pyridine solution was used to strip these dyes from nylon 6.6 fabric after which the solution was diluted to 50cm^3 with distilled water.

For stripping from wool, 10% of 5% NaOH solution at the boil was used to dissolve the whole dyed wool fabric of about 0.05g. The calibration curve was therefore made by dissolving enough quantity of dye to make from 1 – 3 x 10^{-5} g of dye in 10cm^3 of 5% NaOH made up to 50cm^3 with distilled water. Curves 6.50 – 6.54 were plotted.

6.1.4 Determination of the Diffusion Coefficients

Determination of the diffusion coefficient of the dyes in wool and nylon 6.6 fabrics for dyes (65) to (78) was carried out after adjusting the pH to 4.00, no dye assistant was used The wool and the nylon 6.6 samples were cut to 0.025gm. The dyeing was carried out using a shade of 20% on weight of the fabric and a liquor ratio of 400:1, which was 10 cm^3 of the liquor. Enough time was allowed for temperature to stabilize before dyeing commenced. Dyeing temperatures were set at 60 and 80°C for dyeing times of 5 – 50 minutes at 5 minutes intervals. Another sample was allowed to be dyed for 24 hours. At the end of these periods, 10 cm^3 of 20% pyridine was used to strip the dye from the nylon 6.6 fabric at the boil whereas 10 cm^3 of

5% NaOH was used to dissolve the dyed wool. For the two systems, the solution were diluted to the $50cm^3$ mark with distill water. Absorbances of these dyes were read up with a cornin colorimeter 253 at the various wavelength of maximum absorbance of the dyes. These absorbance represents (Mt). The absorbances of the dyes after 24 hrs of dyeing was M∞. These enables Mt/M∞ against t ½ table to be made from where the curves plotted. The method was used according to the approximation of Vickerstaff assuming a non-steady state condition from an infinite solution. The solution of Fick's second equation reduces to:

$$Mt/M\infty = 2\sqrt{Dt}/\pi \quad \ldots\ldots\ldots (1)$$

The slope of the curves is obtained by rearranging equation (1) to be;

$$Mt/M\infty/\sqrt{t} = \sqrt{4D}/\pi = \text{Slope} \quad \ldots\ldots (2)$$

The diffusion coefficient is given by equation (3) from the slopes of the various curves.

$$D = \frac{(\text{Slope})^2 \times \pi}{4} \text{sec-1} \quad \ldots\ldots\ldots (3)$$

When the diffusion coefficient of the two temperatures were computed, the activation energy was calculated using the Arrhenius equation, which for two diffusion coefficients at two temperatures reduced to equation (4).

$$\text{lin}\frac{D_2}{D_1} = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \ldots\ldots\ldots (4)$$

Where D_2 and D_1 are the diffusion coefficients at absolute temperatures T_2 and T_1 respectively. R is the gas constant whereas E is the activation energy in Joules/mole.

6.1.5 Determination of Affinity

The direct method of finding affinity was used for dyes (65) – (78) on nylon 6.6. Displacement method was used for dyes (65) – (73) on wool substrate because of the apparent lengthy time needed to attain true equilibrium. Whereas, the direct method was used for wool with dyes (74) – (78).

For the direct method of determination, 2% and 8% shades were used for nylon 6.6 and wool fabrics respectively, with a liquor to goods ratio of 10:1 and 200:1 respectively at the pH of 4 adjusted with 2% acetic acid. The samples weighing 0.05g was placed in the dyeing liquor when adequate time was given to attain the predetermined temperatures. The dyeing test tubes were secured tightly to discourage evaporation and dyeing was carried out at 80°C and 96°C for 48hours and 24hours respectively on nylon 6.6 and 96 and 48 hours respectively on wool substrates.

The absorbance of the dyeing liquor before dyeing and after dyeing was determined. After dyeing, the dyed samples were cleaned thoroughly

with distilled water until no residual dye could be seen in the washing liquor. The dyes were then stripped by using 10 cm^3 of 10% NaOH at the boil for dyes (65) – (73) on nylon 6.6 and 10 cm^3 of 20% pyridine for dyes (74) – (78) on nylon 6.6. Where necessary a second stripping treatment was repeated to ensure that more than 99% of the dye had been stripped from the substrate. In each case the residual stripped dye was dilluted to 50cm^3 with distilled water after which the absorbances of the various dyes obtained from the colorimeter and the amount of dye on the fabric read off by extrapolation using the appropriate calibration curves. Five different determinations were carried out. Similar stripping procedure was done for the dyed wool samples but in this case, 10cm^3 of 5% NaOH solution was used to dissolve the whole sample. For the direct method of treatment, equation (5) was used:[169]

$$-\Delta\mu^{\circ} = RT\ln\frac{[D]_F}{V[D]_S} \quad \ldots\ldots\ldots (5)$$

Where $[D]_F$ is the amount of dye in gm in 1000g or 1 kg fabric; $[D]_S$ is the amount of dye in gm in 1 litre or 1000 cm^3 solution. V is the internal volume of the substrate assumed to be 0.33 l/kg for wool and 0.02 l/kg for nylon 6.6 fabrics.

The displacement method of determination of affinity carried out with respect to dye (65) – (73) on wool involved applying the dyes about 2%

shade to the wool sample using 1% of acetic acid to adjust the pH and dyeing at a liquor to goods ratio of 50:1 at 96°C for 1 hour. At the end of the dyeing, a thorough washing was given to the fabric. After the fabric was dried at 60°C for 24 hrs, 0.05g samples were cut. $2cm^3$ of 0.2M NaCl solution at pH 4 was used to strip the dye at 60°C for a period of 2 hours even though shorter time was enough to obtain equilibrium. The amount of dye displaced was determined spectrophotometrically and by extrapolation after necessary dillution. The following equation is used to determine the affinity.[167]

$$-(\Delta\mu D^{o} - \Delta\mu Cl^{o}) = RTIn\frac{[D]_F}{[Cl]_F}.\frac{[Cl]}{[D]} \quad \ldots\ldots\ldots (6)$$

$$Cl_F = [S_F] - [D]_F \quad \ldots\ldots\ldots (7)$$

$[D]_F$ is the concentration of the dye in the fibre

$[Cl]_F$ is the concentration of the chloride ions in the fibre

$[S]_F$ is the saturation level of the wool substrate assumed to be 0.9M/Kg

[Cl] is the concentration of the chloride ion in the solution

[D] is the concentration of the dye displaced.

After determining the affinities at the two temperatures stated, the heat of dyeing (ΔH°) and entropy of dyeings (ΔS°) were calculated from equation (8) and (9).

$$\Delta H^\circ = \left(\frac{\Delta\mu^\circ_1}{T_1} - \frac{\Delta\mu^\circ_2}{T_2}\right) \Big/ \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \ldots\ldots (8)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta\mu^\circ}{T} \quad \ldots\ldots (9)$$

6.1.6 Determination of the Wash Fastness

For dyes (1) – (10) and (65) to (73) ISO 3 was used whereas for dyes (74) to (78) ISO 3, 4 and 5 were used. Two adjacent white fabrics each measuring 10cm x 4 cm obtained such that in the case of nylon 6.6, one piece is nylon 6.6, whereas the second one is cotton. In the case of wool, the first piece is wool, whereas the second one is cotton. A piece of the dyed fabric also measuring 10cm x 4cm whose wash fastness is to be determined is cut and placed between the two adjacent fabric above and sides sewn along the four sides to form a composite specimen to be used for the determination.

6.1.6.1 ISO 3 (CO3)

A soap solution is prepared consisting 5g/l of soap and 2g/l of anhydrous sodium carbonate in distilled water. The composite specimen is placed into a container of a linitest wash fastness testing machine containing the pre-requisite amount of the solution to give 50:1 liquor ratio previously heated to 60 ± 2°C. The specimen is treated at this temperature for 30 minutes.

6.1.6.2 ISO 4 (CO4)

As above, but the treatment temperature is 95 ± 2°C for 30 minutes.

6.1.6.3 ISO 5 (CO5)

As in 6.1.6.1, but additionally, ten non-corridible stainless steel balls are added, the treatment temperature is 95 ± 2°C and treatment period being for 4 hours.

The treated composite specimen is rinsed twice in cold distilled water and squeezed. The composite specimen is opened out and dried in air.

The change in colour of the specimen and the staining of the adjacent fabric is assessed with the grey scales.

6.1.7 Determination of the Fastness to Perspiration

Acid and alkaline perspiration fastness testing were done according to EO4:1978 standard.[186]

Two adjacent fabrics measuring 10cm x 4 cm such that for nylon 6.6 fabric, the first fabric is nylon 6.6 and the second one is wool when the sample is wool, the first fabric is wool whereas the second one is cotton. A composite is formed as in 6.1.6. The composite specimens are wetted in the test solution prepared below at a liquor ratio of 50:1 and allowed to remain in the solution at room temperature for 30 min. They are pressed occassionally to ensure good and uniform penetration of the liquor. The solution are poured away and wiped free of the excess liquor between two glass rods. The composite specimens are then placed between two glass plate measuring 12cm x 6cm with 5Kg weight put on the plate. The arrangement is placed in the oven at 37 ± 2°C for 4 hrs.

The composite is then opened and allowed to dry in the air. The change in color and degree of staining are assessed with the grey scales.

6.1.7.1 Alkaline Solution

0.5g/l 1-histidine monohydrochloride mono-hydrate

5g/l sodium chloride

2.5g/l disodium hydrogen orthophosphate

The solution is brought to pH 8 with 0.1N sodium hydroxide solution.

6.1.7.2 Acid Solution

0.5g/l 1-histidine mono hydrochloride mono hydrate

5g/l sodium chloride

2.2g/l sodium dihydrogen orthophosphate

The solution is brought to pH 5.5 with 0.1N acetic acid solution,

6.1.8 Determination of Color Fastness to Light

The light fastness of the dyed fabrics was assessed according to BO2:1978. Xenon arc lamp was used. The specimen and the standard blue printed cards were mounted on holders and then clamped unto the light fastness test equipment, the effective humidity was that provided by saturated solution of NaCl. A cover is placed over the test specimen and the standard blue cards. The assembly is exposed to the xenon arc light. Preodically, the card is lifted to inspect the effect of the light on the standards. When the standard 3 has faded to the same constrast as the grey scale grade 4-5, the specimens were then inspected and rated by comparing them with the change that occurred in standards 1, 2 and 3. The card is then replaced and exposure is continued until a change in standard 4 can just be

perceived equal to grey scale 4-5 at this point an additional cover is placed overlapping the first cover and to about half of the specimens and standards. Exposure is then continued until a change in standard 6 can just be perceived to be equal to grey scale grade 4-5, then a final cover is placed which should cover about three quarters of the whole assembly.

Exposure is then continued until standard 7 had faded equal to grey scale grade 4.

The whole assembly is then dismounted from the instrument and the covers removed. The changes of the specimens were compared with the relevant changes of the standards under the same condition. The light fastness of the specimen is the number of the standard which shows similar changes in color.

6.1.9 Dyeing Properties

This is applicable only to dyes (1) – (12).

6.1.9.1 Dyeing Procedure

Wool and nylon 6.6 fabric samples each weighing (1g) were dyed in a dyemaster laboratory dyeing machine. The liquor ratio was 50:1 at a pH of 3 using 2% acetic acid. The samples were entered at 45°C raised to 100°C

over 15 minutes and maintained at this temperature for 45 minutes. At the end of this time the temperature was lowered and the samples rinsed thoroughly with water and then dried.

6.1.9.2 Measurement of Exhaustion

This was determined by measuring the optical densities of the dye solutions before and after dyeing, after making the necessary dilution with distilled water. Corning colorimeter 253 was used. The instrument was set at the wavelength of maximum absorption of the dyes. However, before taking the absorbance after dyeing, the dye solution was cooled to room temperature. Equation (10) was used to calculate the exhaustion percent.

$$\% \text{ Exhaustion} = \frac{OD_1 - OD_2}{OD_1} \quad \ldots\ldots\ldots (10)$$

OD_1 and OD_2 being the optical densities of the dye solution before and after dyeing respectively.

Duplicate measurements were taken and the average computed for all the readings.

6.2 Synthesis of the Intermediates and Dyes (1-12)

Dyes (1 – 12), involved the use of acetylated H-acid. Acetylation was achieved by using the commercial grade of the sodium salt of H-acid by

reacting it with acetic anhydride as the acetylating agent. 1g (0.0033 moles) of the H-acid was dissolved at 50°C in 7.00cm^3 of water containing 0.2g (0.0019 moles) of soda ash in a three necked round bottom flask fitted with a mechanical stirrer, reflux condenser and thermometer. With vigorous stirring, 0.058g (0.006 moles) of acetic anhydride was added into the flask over a period of 15 minutes. Stirring was continued for at least one hour to ensure complete acetylation of the H-acid. After this, 1.66g (0.02 moles) of soda ash was added to the reaction mixture to hydrolyse off any acetyl group that may have substituted the hydrogen atom in the hydroxyl group of the H-acid. The alkaline solution of acetyl H-acid was used directly in the coupling reaction.

6.2.2 General Methods for Diazotisation of the Amines for Dyes (1-12)

For dyes (1 – 12), five different aromatic amines were used. These are: 4-chloro-2-nitro-aniline, 2-chloro-4-nitroaniline, 2-chloro-4-methylsulphone aniline, p-aminobenzoic acid and 4-nitro-2-cyanoaniline. The general diazotisation involved dispersing 0.01 moles of the amine in 10 mls of water contained in a beaker equipped with a mechanical stirrer and standing in an ice bath. To this was added the equivalent of 0.025 moles of concentrated hydrochloric acid. The temperature of the amine dispersion

was maintained at 0-5°C using an ice-salt mixture. A solution of 0.01 mole of $NaNO_2$ in 5 mls water was then dropped in over a period of 30 minutes. The solution was kept stirred at 0-5°C for a period of 45 minutes to achieve complete diazotisation. Excess nitrous acid was destroyed by adding 0.5g of urea into the mixture and stirred for a further 15 minutes.

6.2.3 General Method of Coupling Dyes (1) – (12)

The coupling reaction was carried out by transferring the solution of the coupling component into a beaker standing in an ice bath and equipped with a mechanical stirrer. The temperature of the solution was cooled down to 0-5°C using the ice-salt mixture. The ice cold diazo solution was then added with vigorous stirring over a period of 15 minutes. Stirring was continued for another 45 minutes. Dyes containing sulphonic acid groups are salted out by adding 20% NaCl solution and in certain times heated up at up to 80°C, if the precipitates are not much, cooled down, filtered and washed with 20% NaCl and then dried at 60°C in the oven over night.

6.3 Synthesis of the Nitroso Dyes (65) – (73)

6.3.1 Procedure for Nitrosation of 1-Naphthol

1-Naphthol, 0.1mol (14.42g) was dissolved in 150cm^3 of distilled water containing 4g of NaOH. While vigorously stirring the solution with a magnetic stirrer, 40cm^3 of acetic acid was added dropwisely. To the fine suspension produced, 6.9g of $NaNO_2$ dissolved in 20cm^3 of distilled water was added over one hour. The reaction was carried out at room temperature. A greenish yellow precipitate was obtained. This was filtered using a suction apparatus and washed severally with distilled water until a clear filtrate was obtained. The residue was dissolved in enough quantity of ethanol and precipitated with distilled water to obtain golden yellow crystals.

6.3.2 Diazotisation of the Amines

Eight different aromatic amines were used for this study. These were aniline, 4-amino benzoic acid, 4-amino phenol, 4-nitroaniline, sulphanilic acid, J-acid, H-acid, 2-cyano-4-nitroaniline. Three methods of diazotisation were used.

6.3.2.1 Diazotisation of Aniline and 4-Amino benzoic Acid

The direct method of diazotisation as described in section 6.2.2 was used.

6.3.2.2 Diazotisation of 2-Cyano-4-nitroaniline and 4-nitroaniline

For these amines, 0.01 mole was dissolved in 0.025ml of hot concentrated HCl, while standing in an ice bath 0.01 mole $NaNO_2$ was added over 30 minutes. The solution was then kept stirred for a further 45 minutes. This method is called the suspension method.

6.3.2.3 Diazotisation of J-, H-, Sulphanilic acids and 4-Aminophenol

0.01moles of the amines were dissolved in 0.6mls of 30% NaOH solution. 0.01 mole of $NaNO_2$ dissolved in $50cm^3$ water was added over 15 minutes while standing in an ice bath. 0.025mole HCl was then added over 30 minutes. The reaction was allowed to continue for a further 30 minutes.

6.3.3 General Procedure for Coupling

0.01moles of the 2-nitroso-1-naphthol prepared in section 6.3.1 were dissolved in 50 mls of distilled water containing 0.4g of NaOH. 50gms of crushed ice were added into the beaker standing in an ice-salt mixture. The diazonium salts, 0.01moles was then added gradually to this well stirred solution over 30 minutes. The reaction was allowed to proceed for 1 hour.

6.4 General Procedure for Premetallization

2-Nitroso-1-naphthol, aniline and 4-aminobenzoic acid azo dyes of 2-nitroso-1-naphthol were used for this study. Two types of complexes of each dye with the various heavy metals were produced. The metallic salts used were $FeSO_4$, $CuCl_2$, $NiCl_2$, $Co(NO_3)_2$, $ZnSO_4$, $Pb(CH_3COO)_2$, $MnCl_2$, $Cr_2(SO_4)_3$ and $FeCl_3$.

6.4.1 The 1:1 Complex

0.02 moles of the nitroso compound was dissolved in $100cm^3$ of distilled water containing 0.8g NaOH. 0.02 mole of the metallic salt was dissolved in 30 cm^3 distilled water and added dropwisely to the solution of the nitroso compound stirred vigorously over one hour. The reaction was continued for a further three hours at room temperature. The crude complexes were purified by dissolving a small quantity in ethanol and then precipitating by the addition of ice water. In some cases, the ethanol solution had to be dropped in ice block where the complex precipitated immediately.

6.5 Synthesis of Dyes (74) – (78)

These dyes were synthesised by diazotising p-amino-toluene sulphon-N-ethylanilide and coupling to five different coupling components. These

are: H-, J-, gamma- and chromotropic acids and 4-sulphonphenyl-3-methyl-5-pyrazolone.

6.5.1 Diazotisation of p-Aminotoluene-N-ethylanilide

2g (6.90×10^{-3} mole) of the amine was dissolved in $3cm^3$ of glacial acetic acid with vigorous stirring for 20 minutes. 1.72×10^{-2} mole of 36% HCl was added to obtain a clear solution. This solution was immediately cooled to 0-5°C to form a thick solution. 0.457g (6.90×10^{-3} mole) $NaNO_2$ dissolved in $3cm^3$ distilled water was then added to the suspension over 30 minutes in a well stirred condition. To the mixture, 0.5g urea was added over 10 minutes to destroy any nitrous acid still remaining.

6.5.2 Coupling

6.90×10^{-3} mole of J-, H-, and gamma acids was added to 20g of crushed ice and well stirred for 30 minutes the temperature being 0-5°C. To this solution was added $6cm^3$ of 5% NaOH, the pH being 8 and kept stirred for a further 30 minutes. This was followed by the addition of $1cm^3$ glacial acetic acid, the pH being 3. Stirring was continued for a further 30 minutes. For chromotropic acid and 4-sulphon-phenyl-3-methyl-5-pyrazolone, addition of the 5% NaOH to make the pH 8 was not preceeded by acidifying

with acetic acid. To the coupling component solutions, the diazo solution prepared in section 6.5.1 was added gradually over 30 minutes, and the mixture kept stirred for a further 30 minutes. For chromotropic acid and the pyrazolone the reaction was continued for 2 hours.

For gamma, J- and H-acids, 20 gm of 10% Na_2CO_3 solution was added over one hour to make pH 4 and stirred for another one hour. This was followed by the addition of 20gm, 20% Na_2CO_3 over one hr to make a pH 7 and the mixture stirred for a further 30 minutes. For both dyes, the crude dyes were heated to about 90°C, cooled down to 40°C and then filtered.

Fig 6.10: Calibration curve for the NaOH solution of dyes (65)-(67)

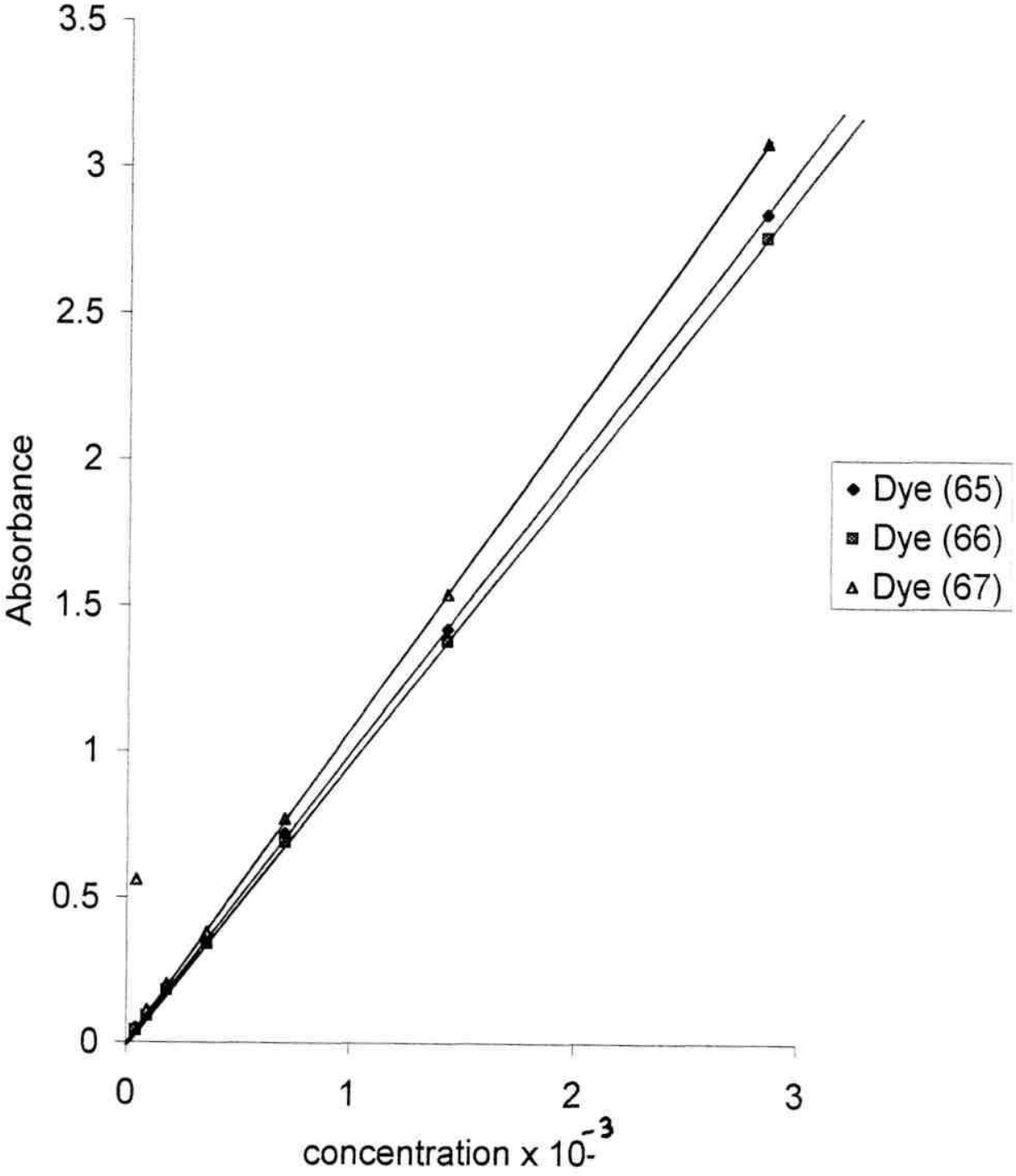


Fig 6.11: Calibration curves for the NaOH solution of dyes (68) - (70)

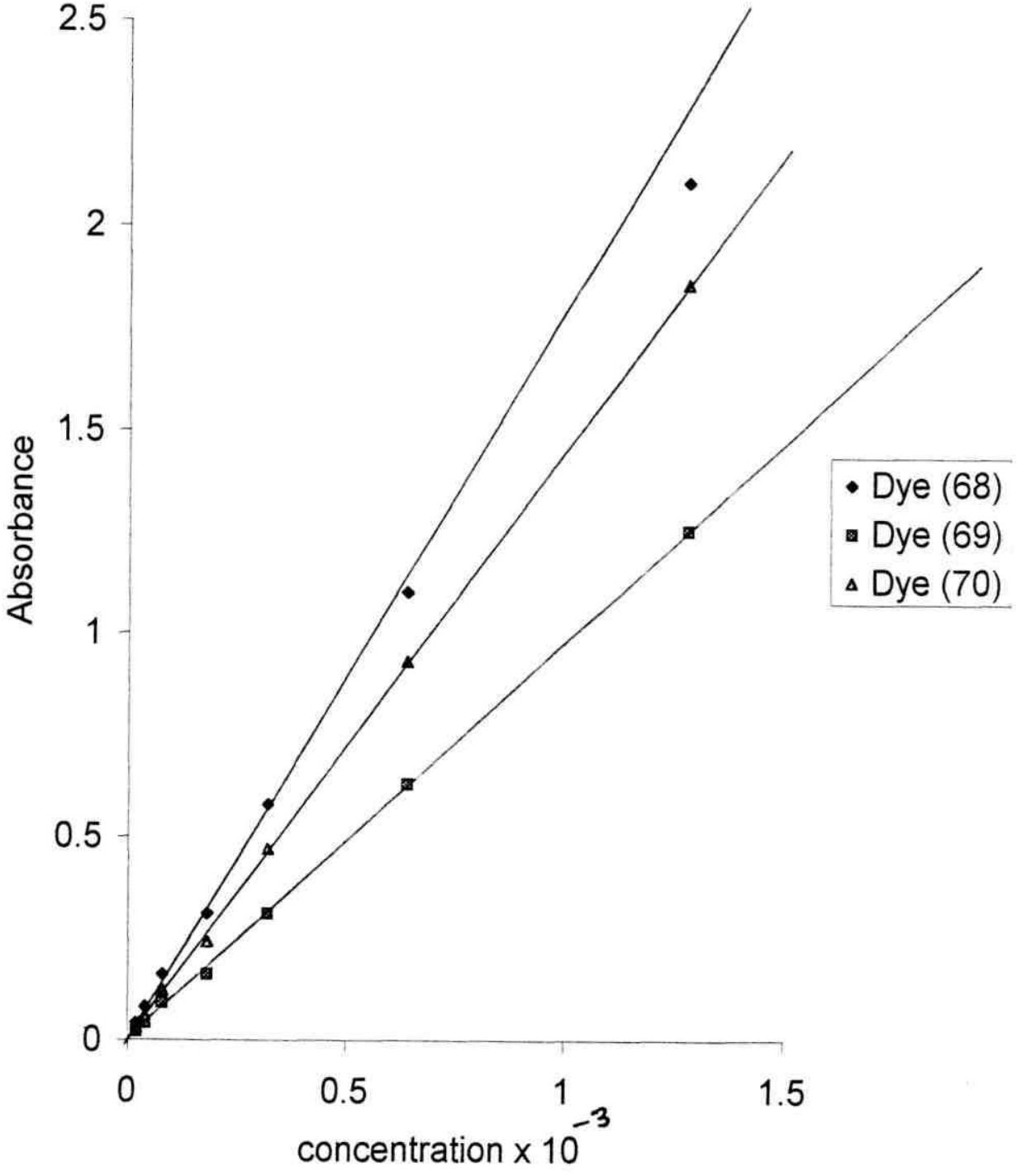


Fig 6 .12: Calibration curve for the NaOH solution of Dye (71)

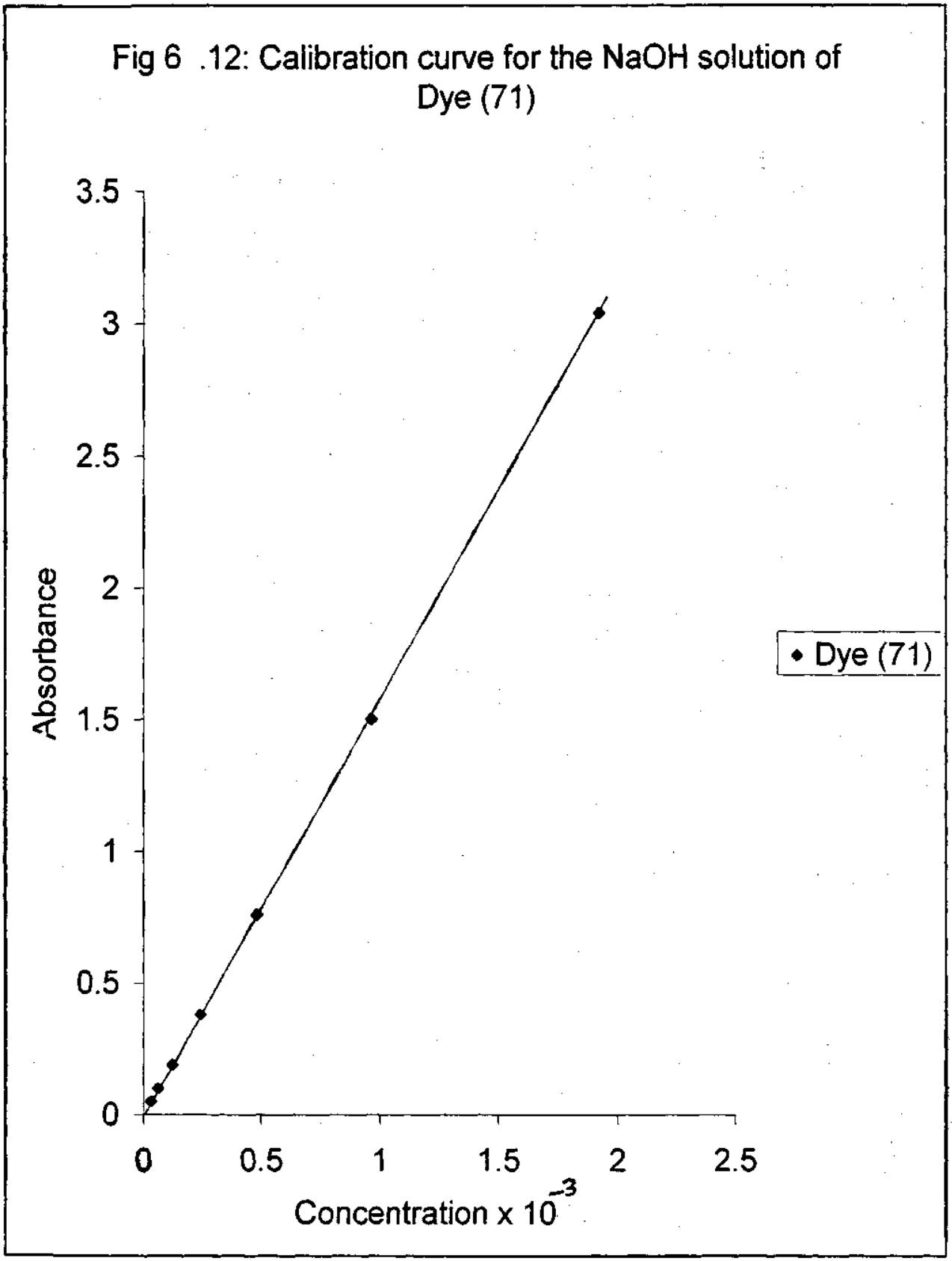


Fig 6.13: Calibration curve for NaOH solution of dye (72)

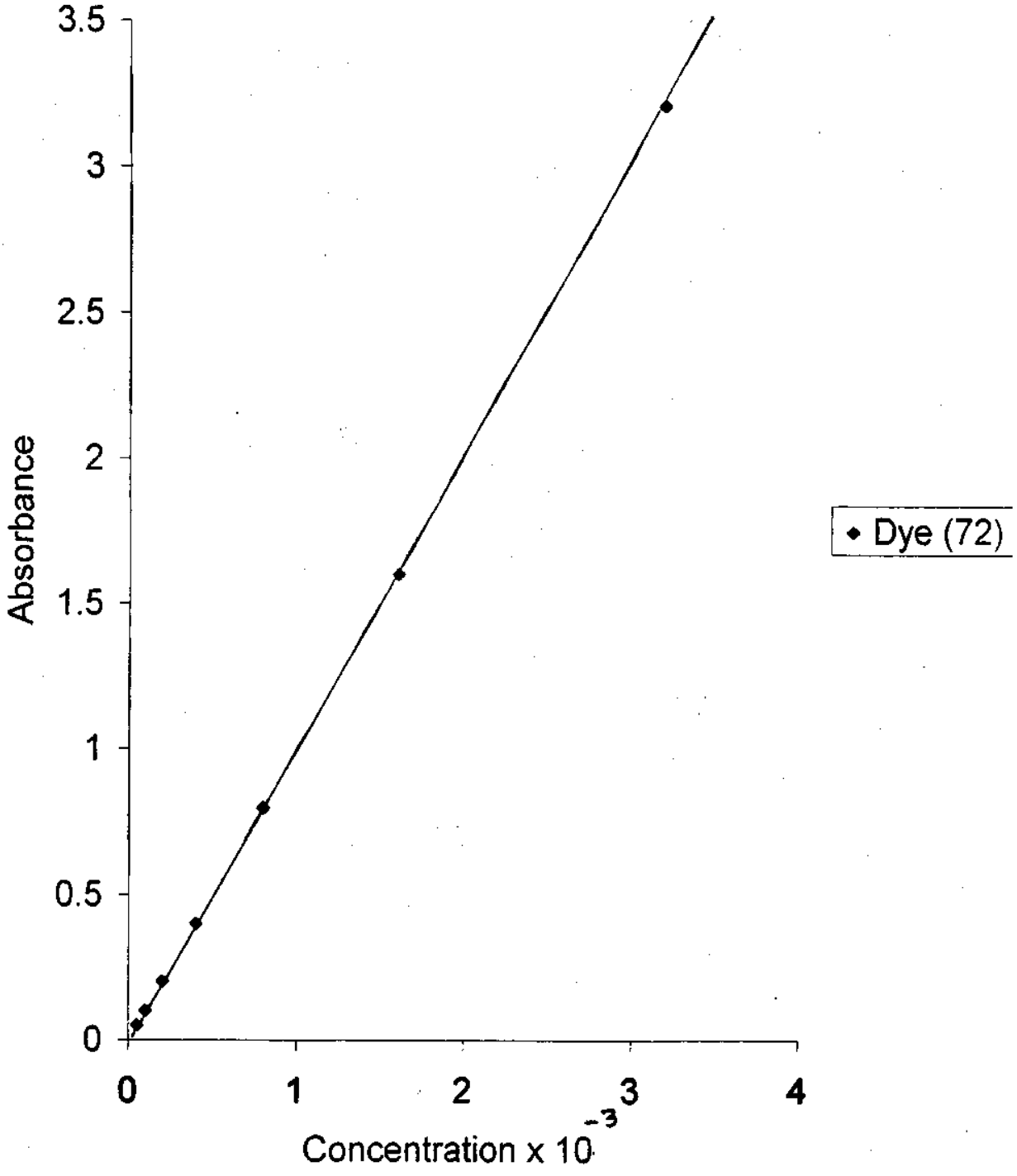


Fig 6.14: Calibration curve for NaOH solution of Dye (73)

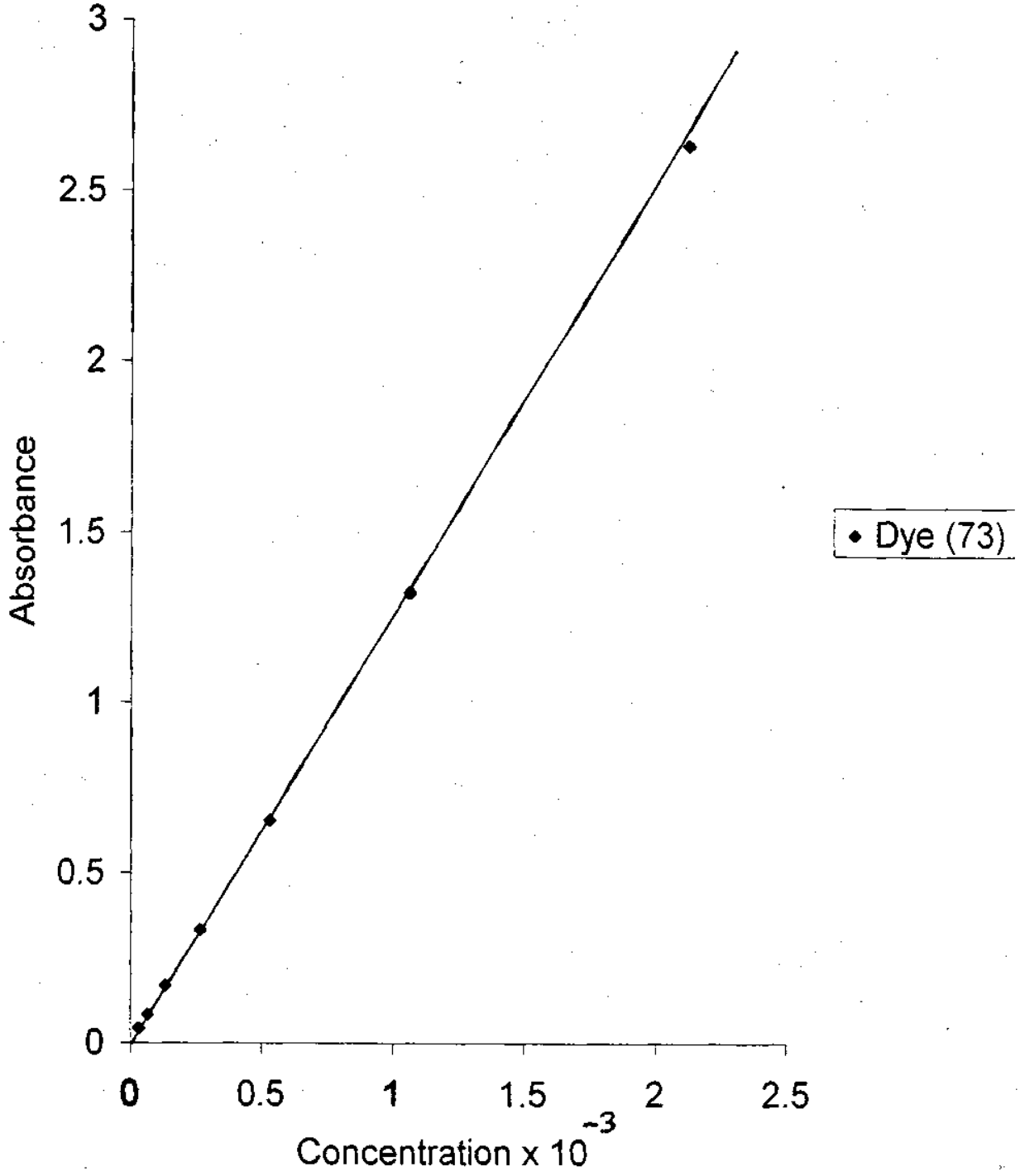


Fig 6.20: Calibration curve for wool/NaOH solution of dyes (65) & (69)

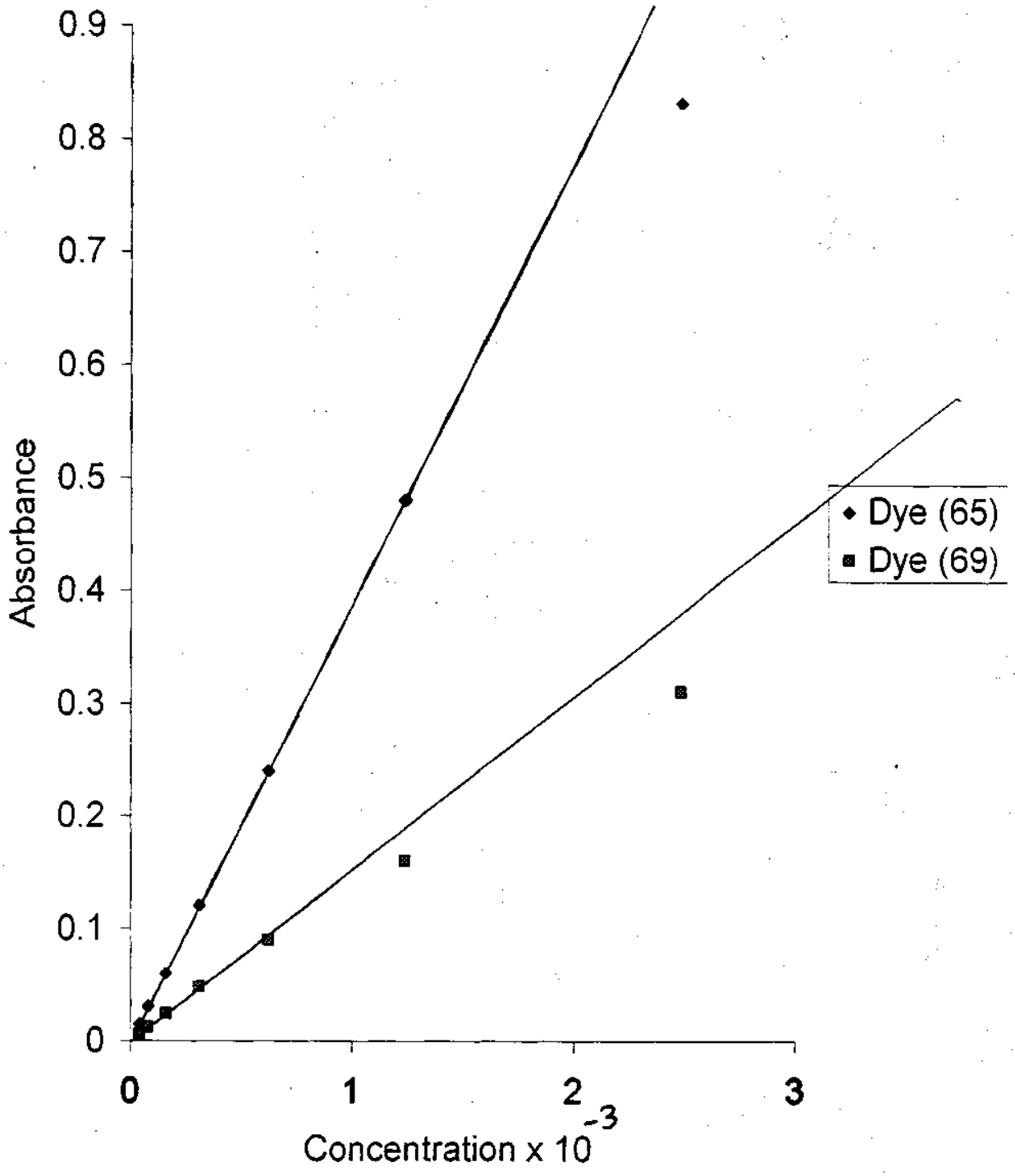


Fig 6.21: Calibration curve for wool/NaOH solution of Dye (66) & (72)

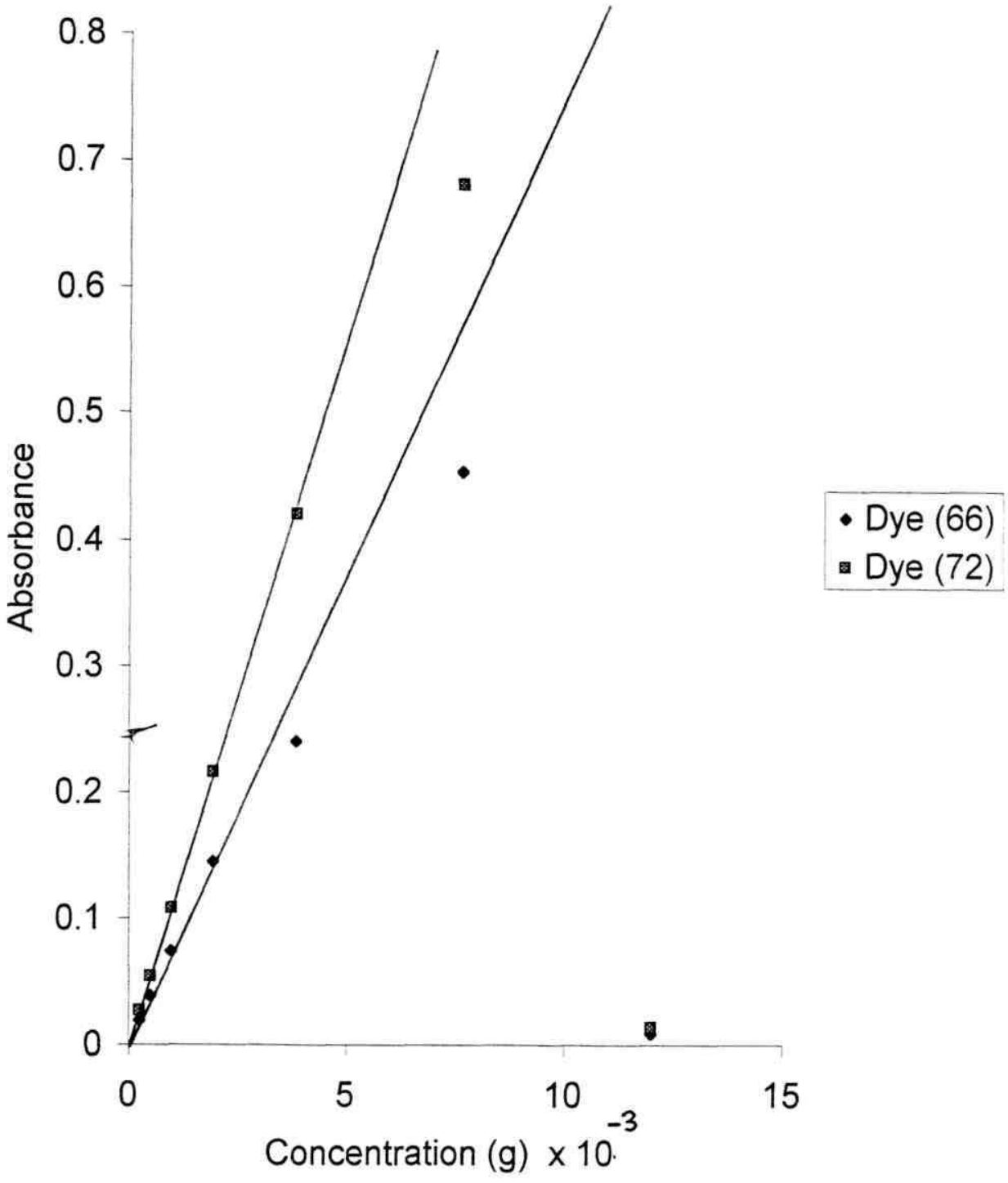


Fig 6.22: Calibration curve for wool/NaOH solution of the dyes (67) & (70)

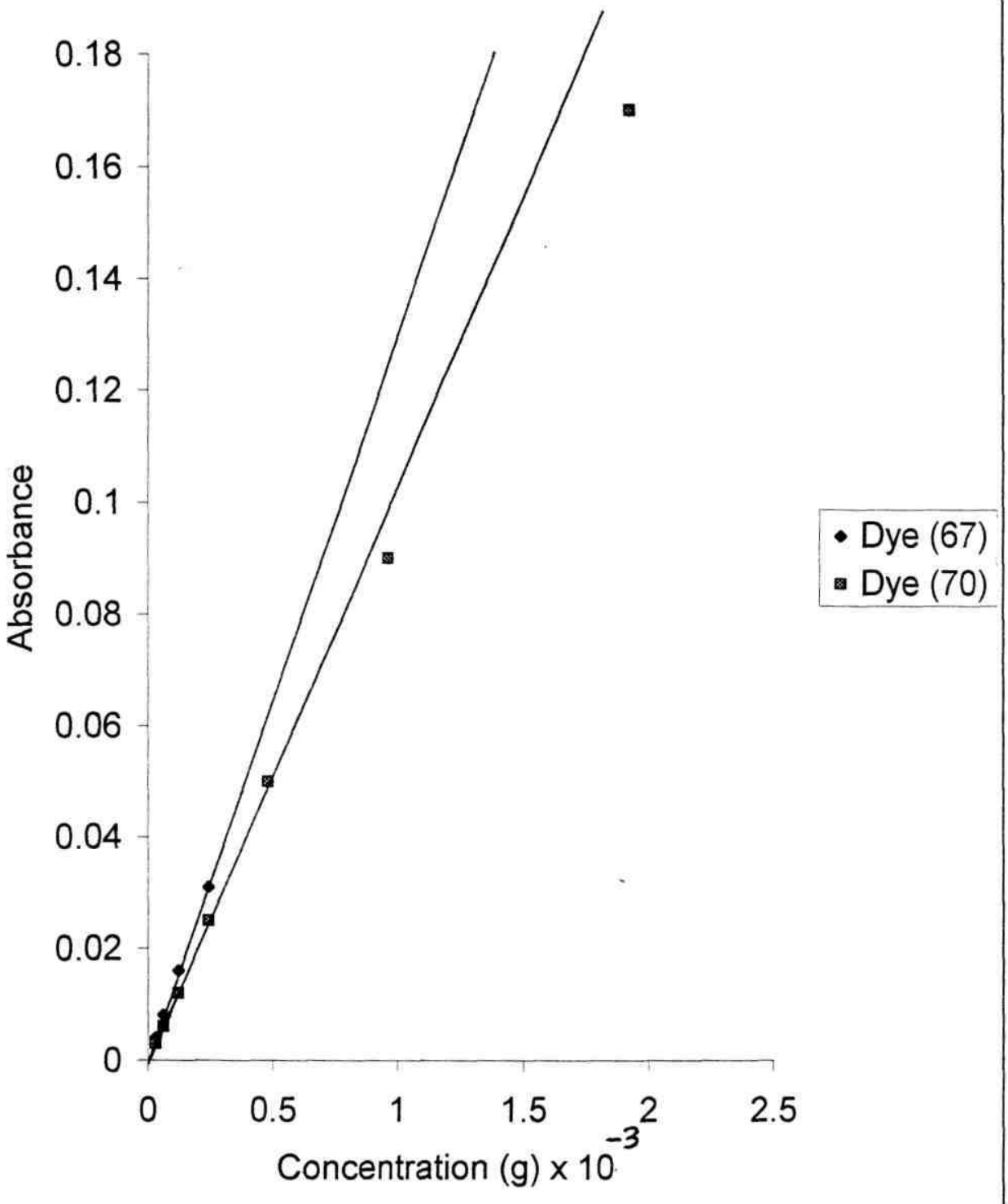


Fig 6.23: Calibration curve for wool/NaOH solution of Dye (68)

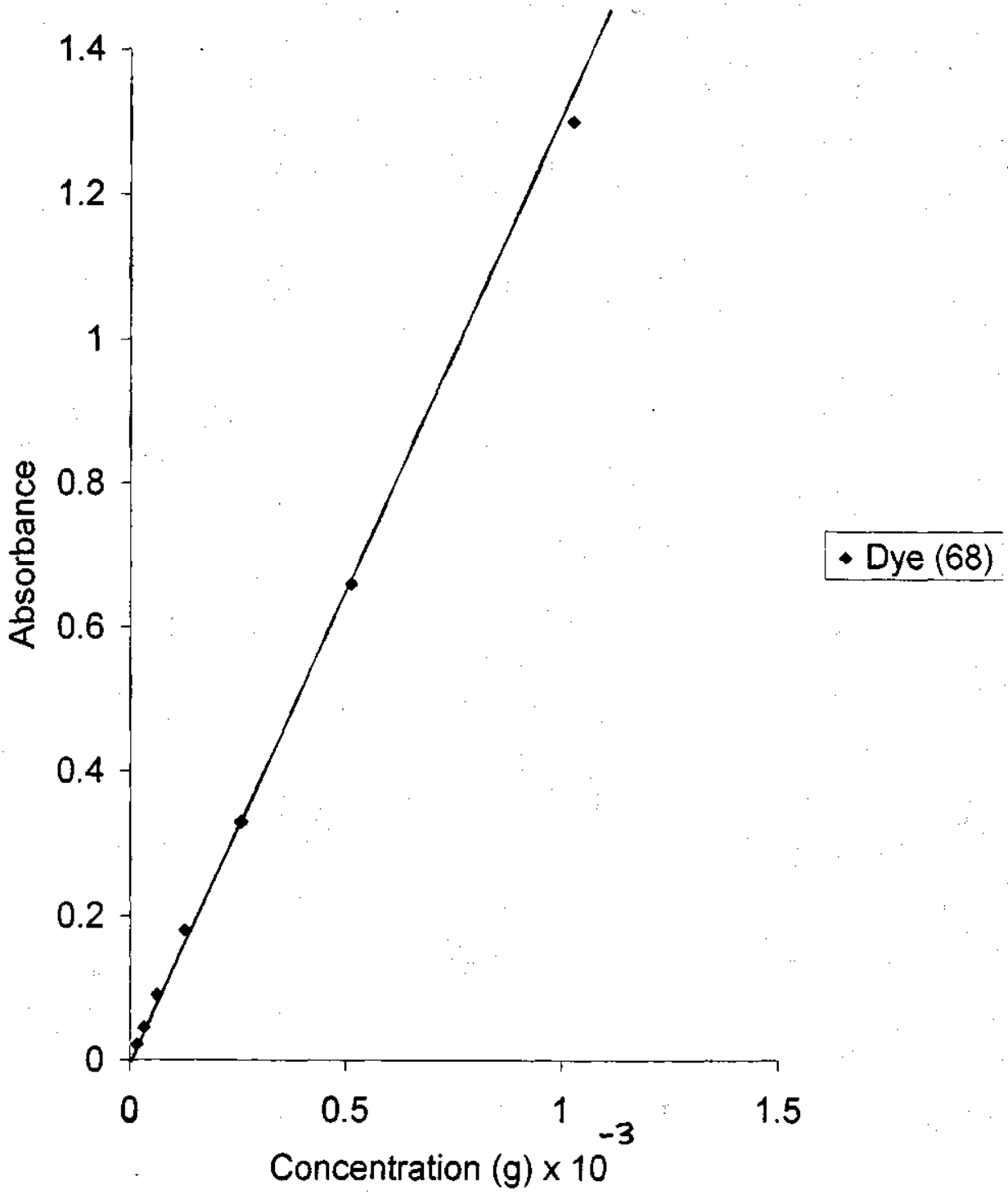


Fig 6.24: Calibration curve for NaOH/wool solution of Dye (71)

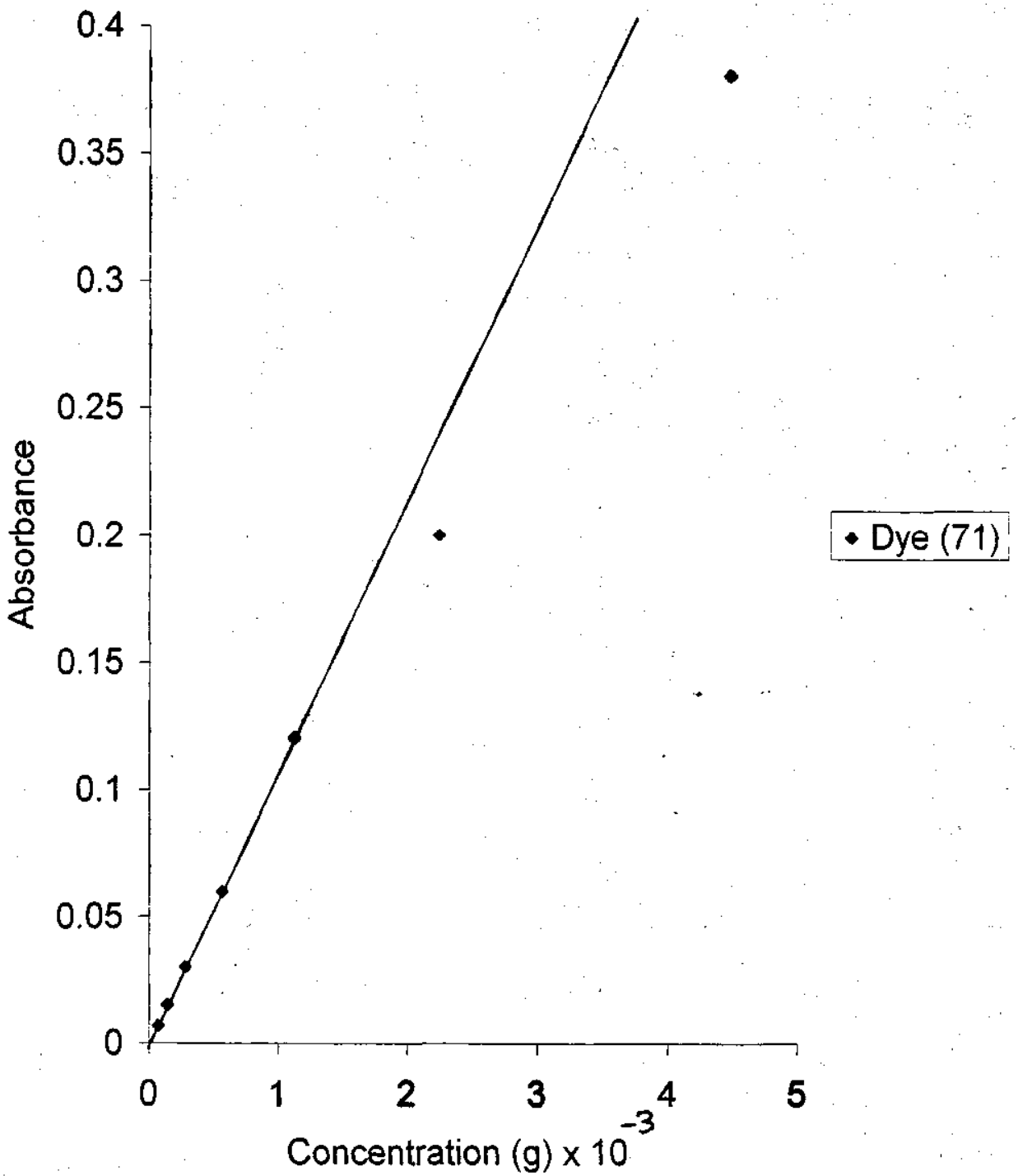


Fig 6.25: Calibration curve for NaOH/wool solution for Dye (73)

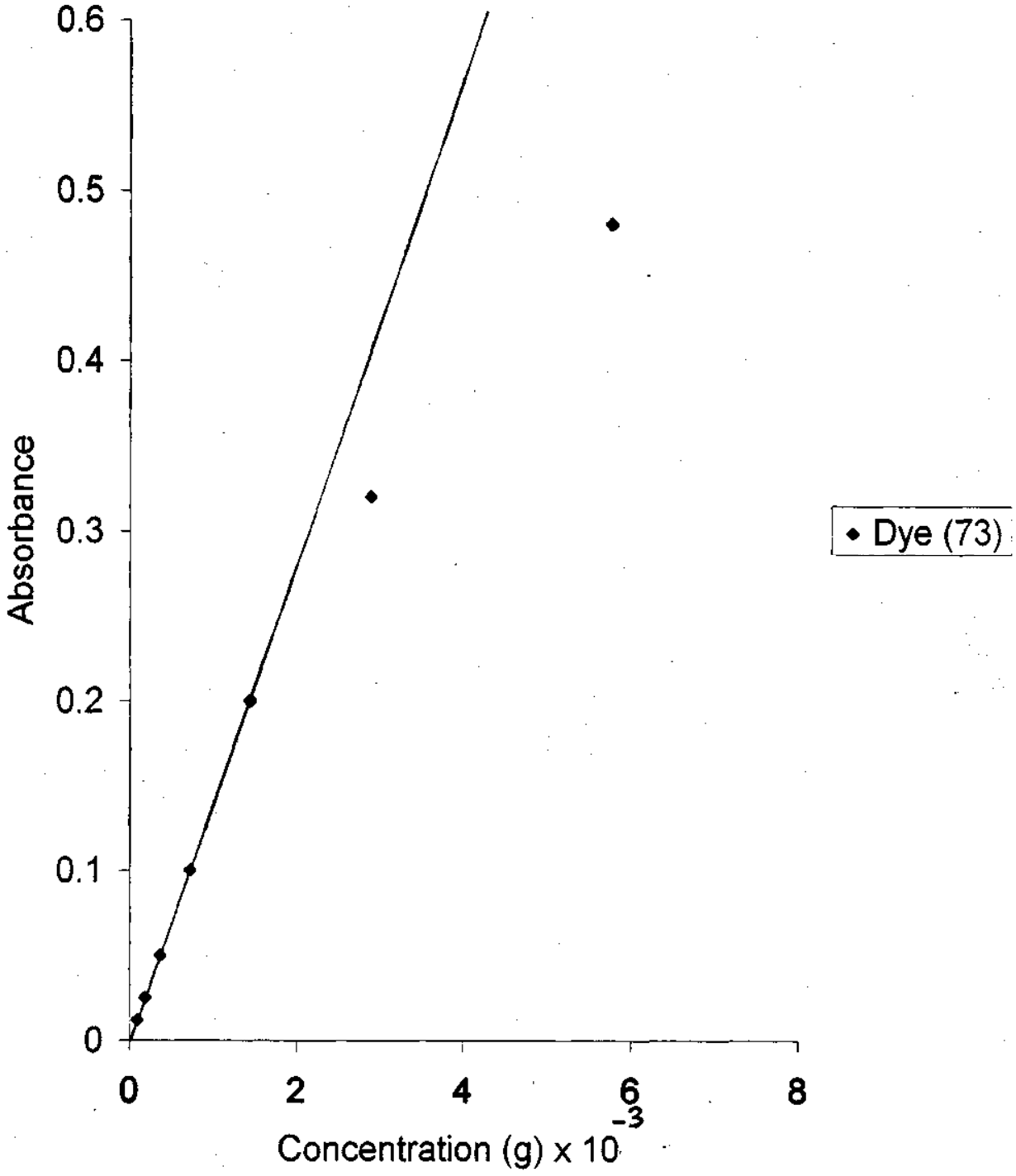


Fig 6.30: Calibration curve for solution of dye (65) & (66) in 2cm3, 0.2M NaCl

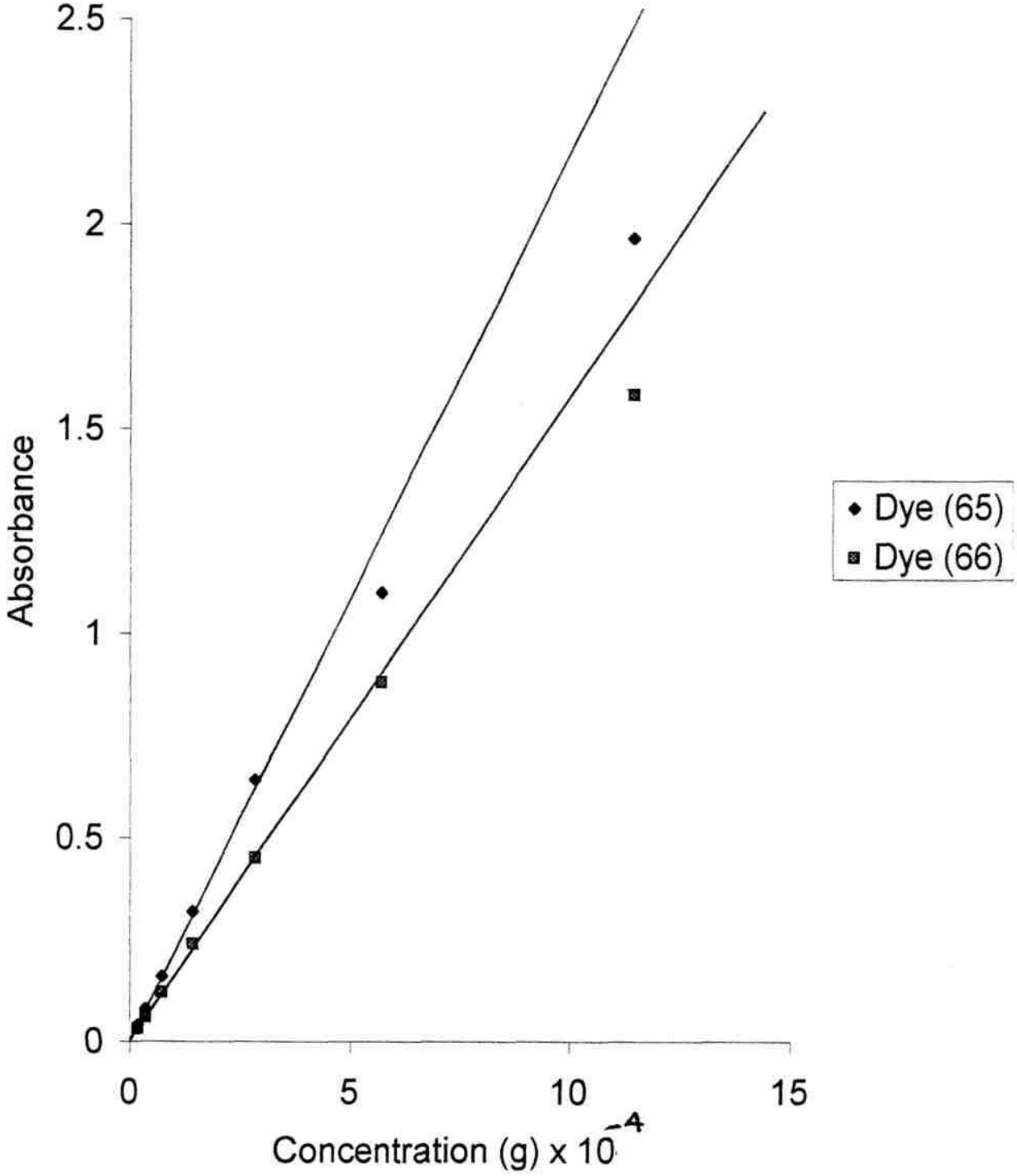


Fig 6.31: Calibration curves for solution of dyes (68) - (70) in 2cm3, 0.2M NaCl

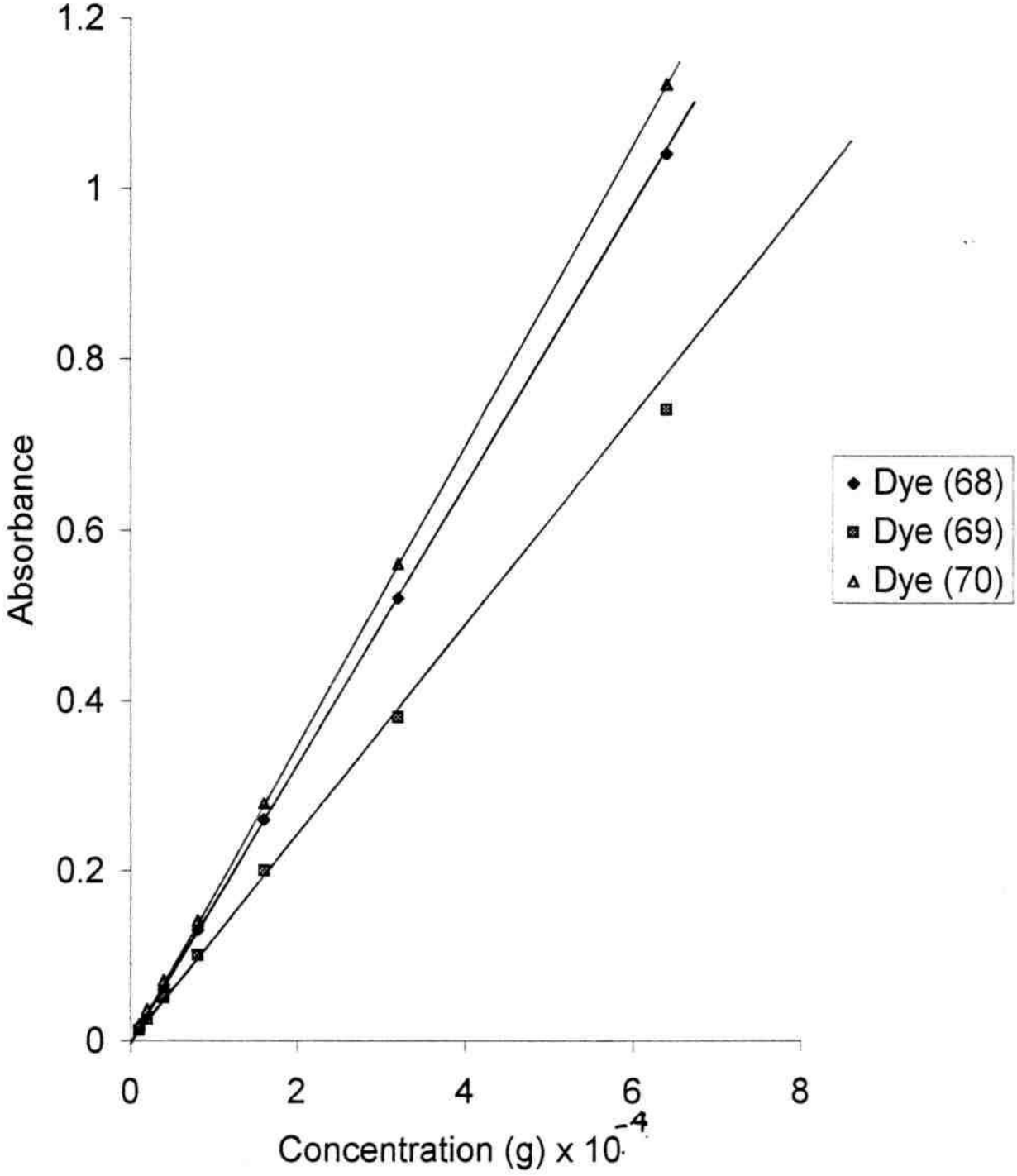


Fig 6.32: Calibration curve for solution of Dye (67) in 2cm3, 0.2M NaCl

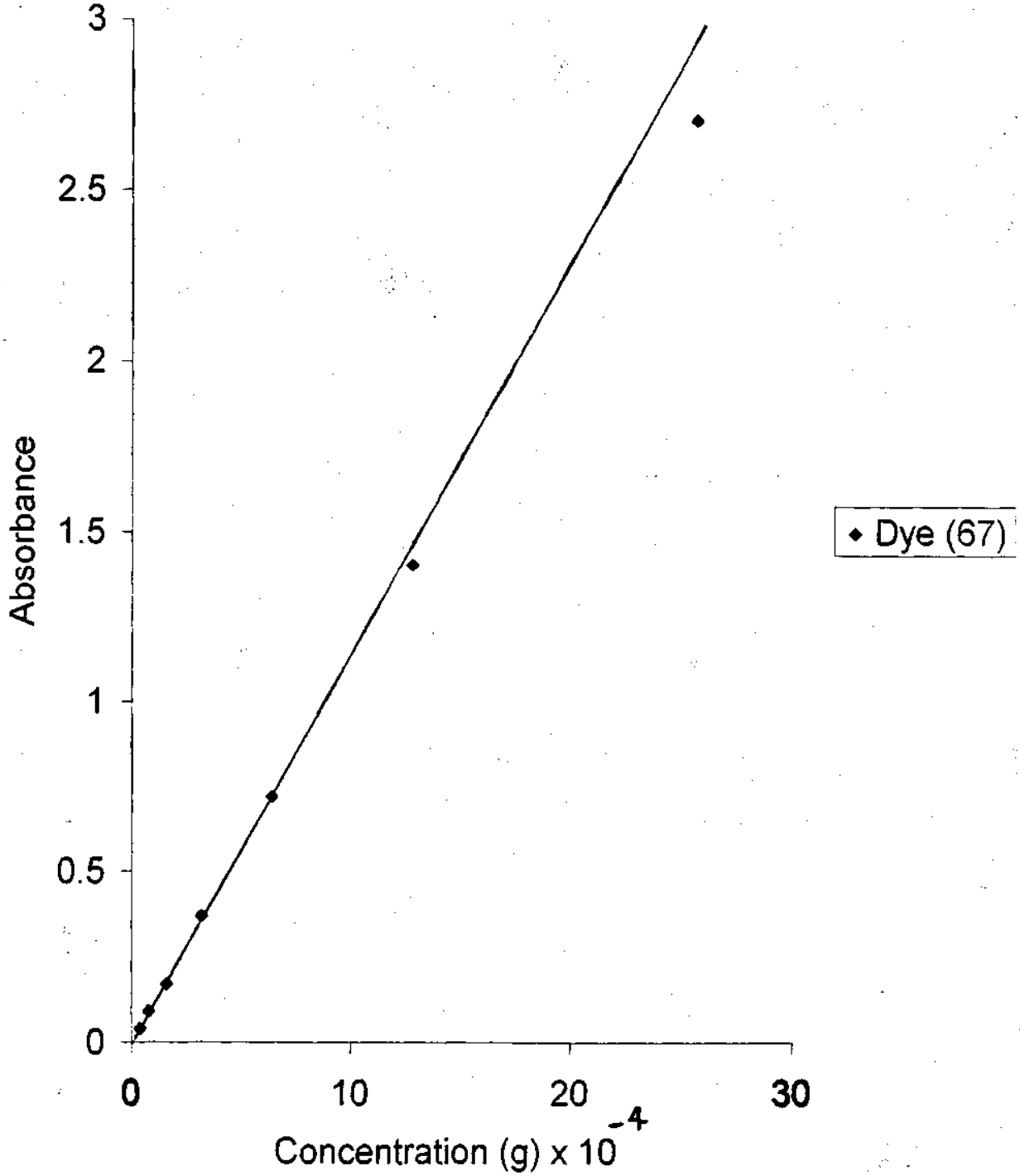


Fig 6.33: Calibration curve for solution of Dye (71) in 2cm3, 0.2M NaCl

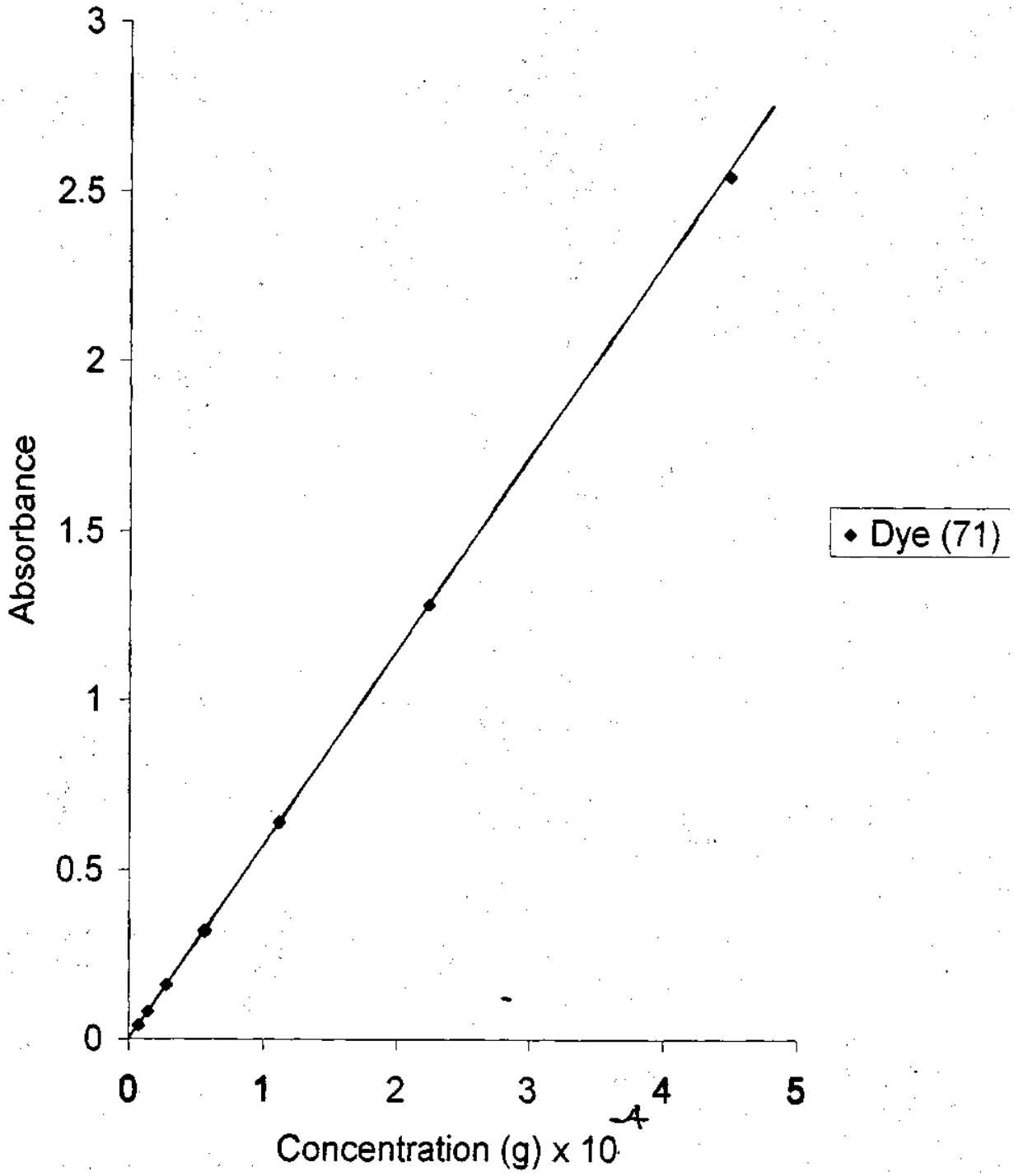


Fig 6.34: Calibration curve for solution of dye (72) in 2cm3, 0.2M NaCl

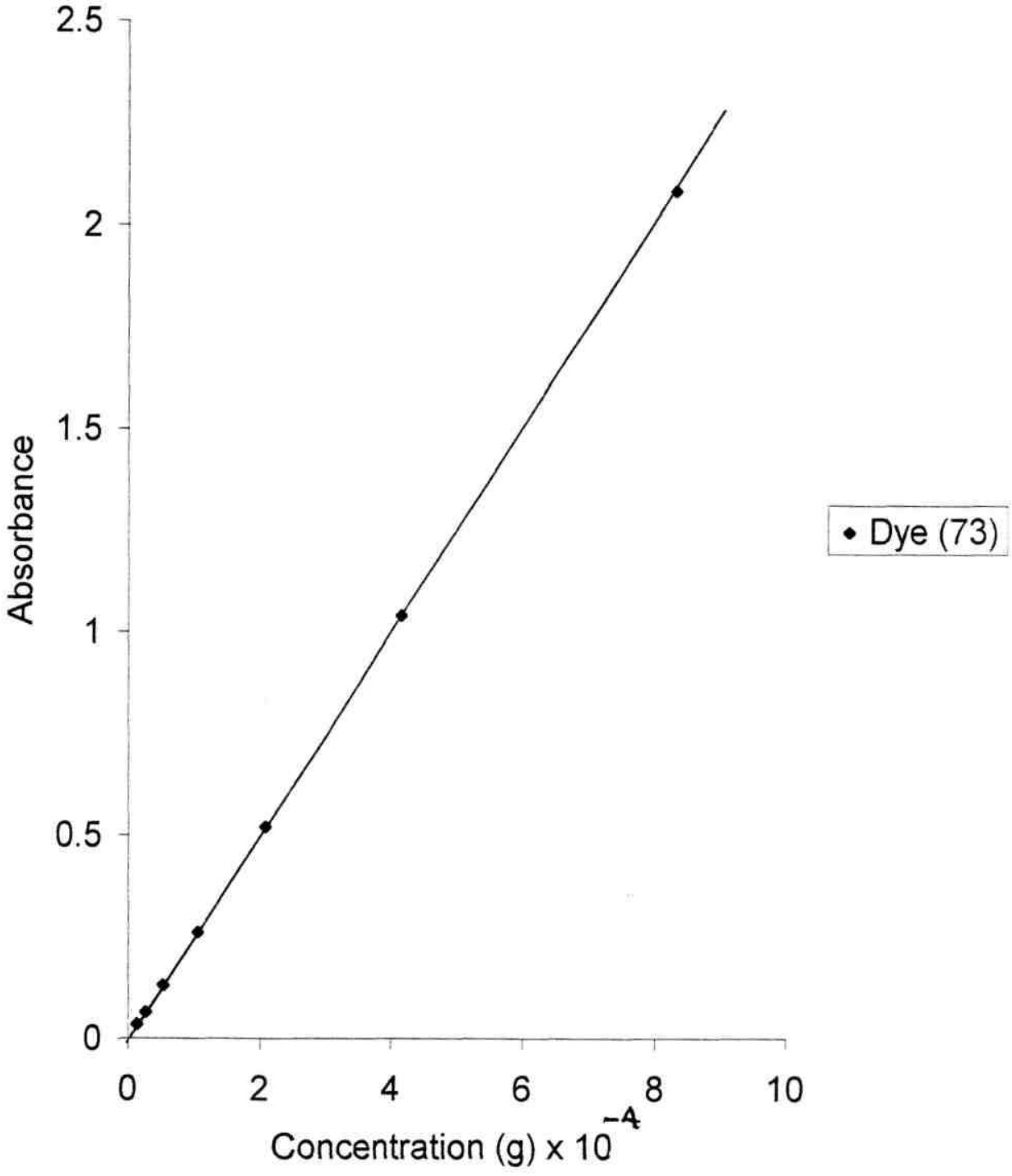


Fig 6.35: Calibration curve for solution of Dye (73) in 2cm3, 0.2M NaCl

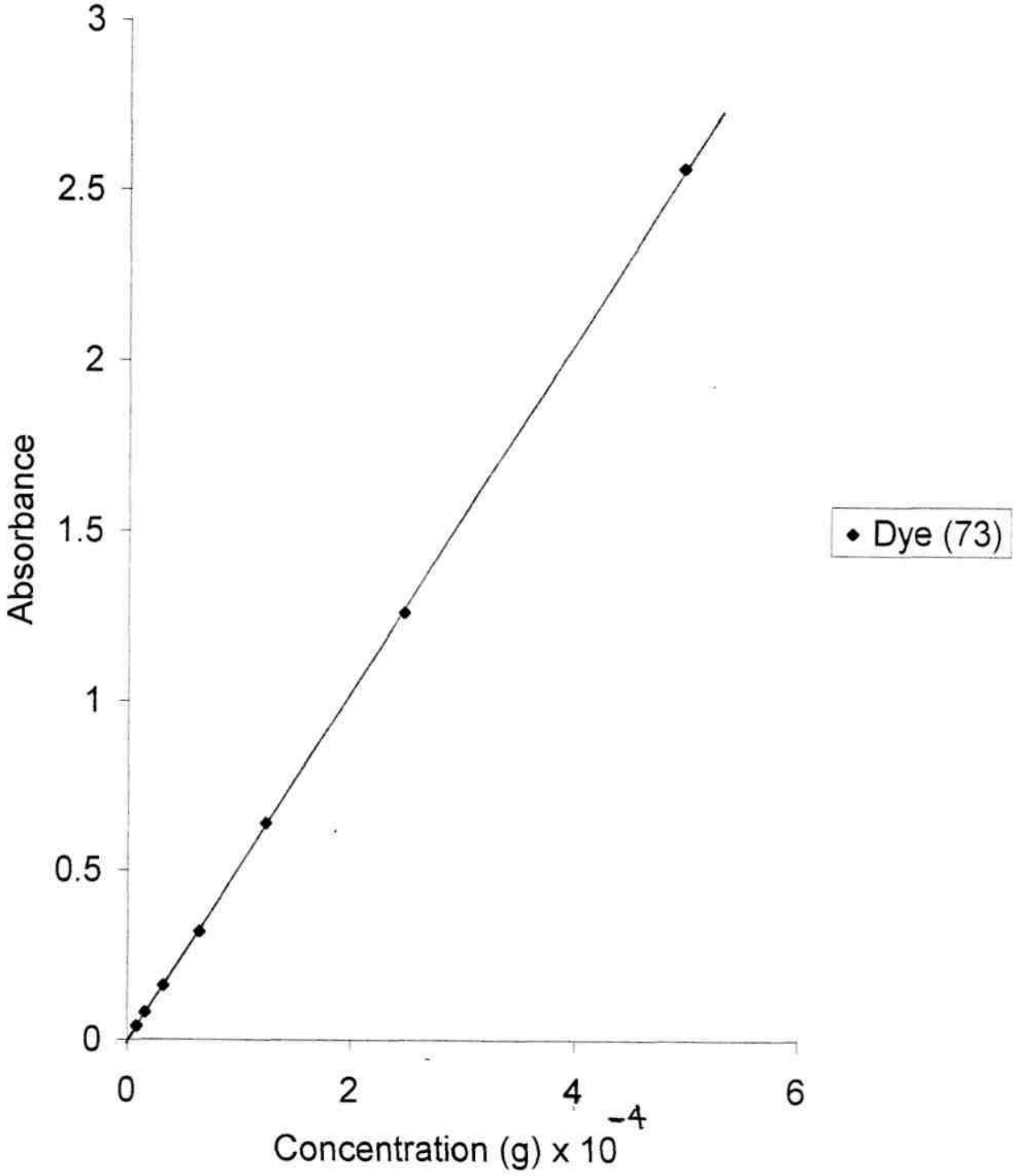


Fig 6.40: Calibration curve for Dye (74) in 20% pyridine solution

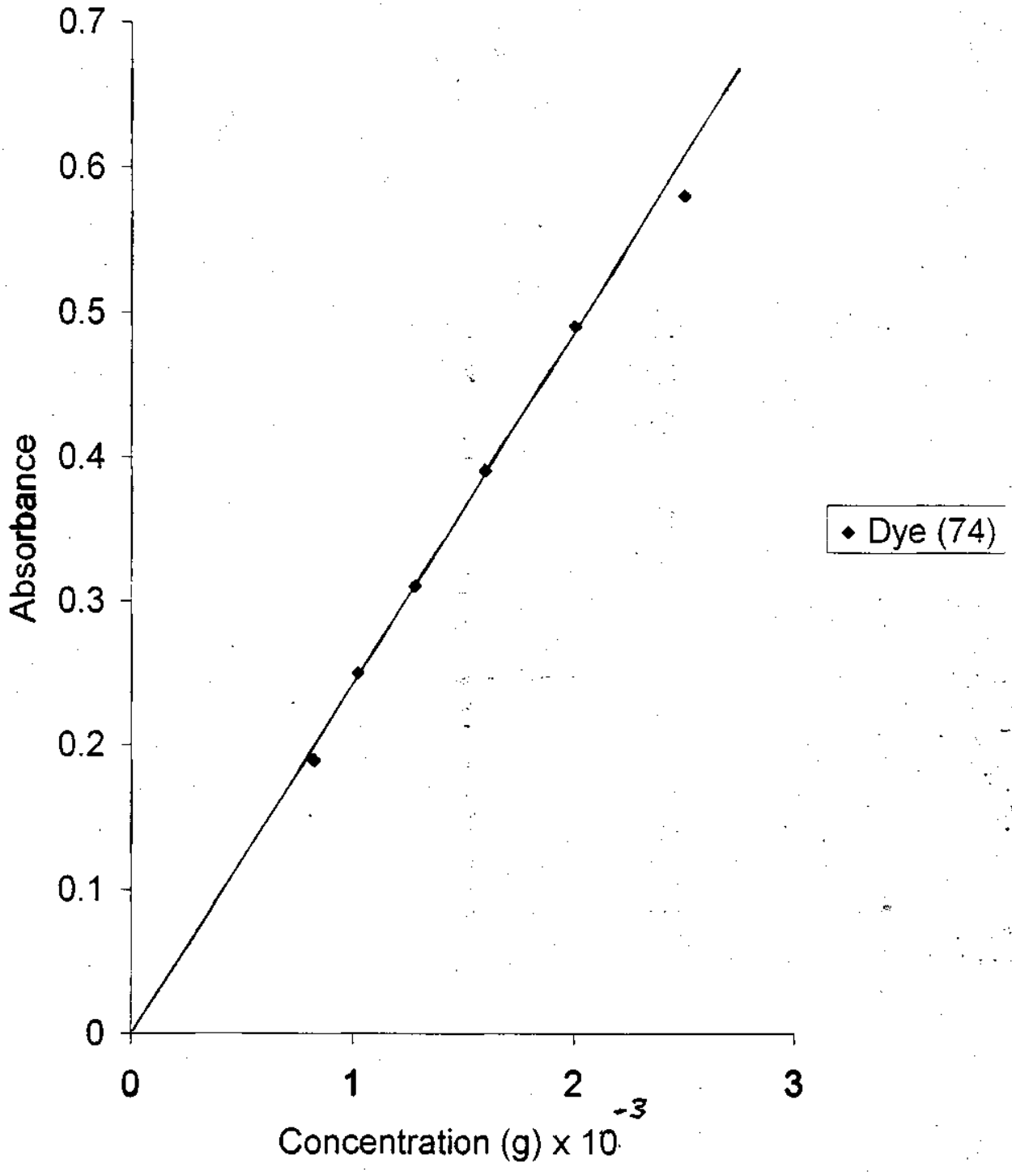


Fig 6.41: Calibration curve for dye (75) in 20% pyridine solution

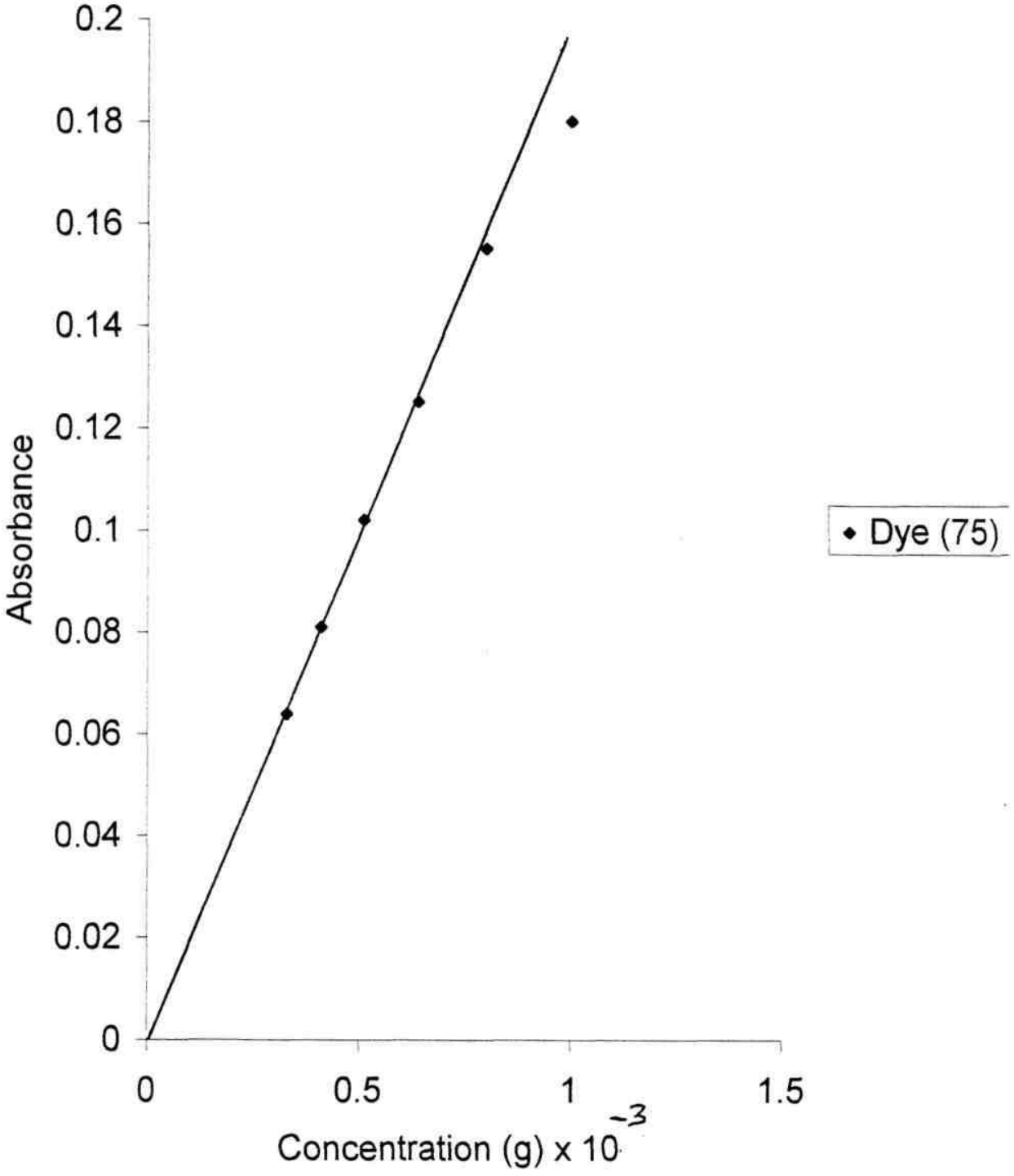


Fig 6.42: Calibration curve for Dye (76) in 20% pyridine solution

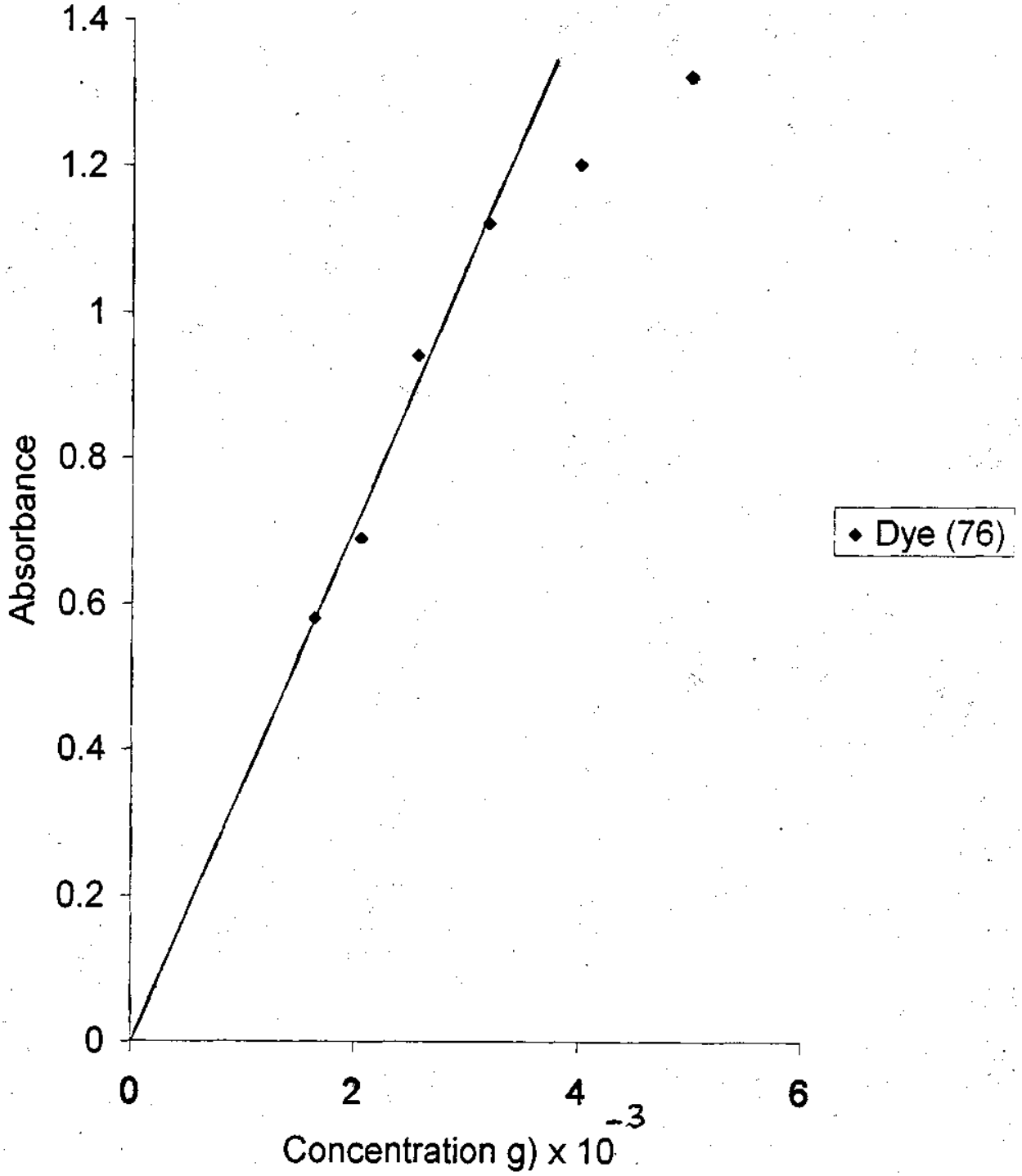


Fig 6.43: Calibration curve for Dye (77) in 20% pyridine solution

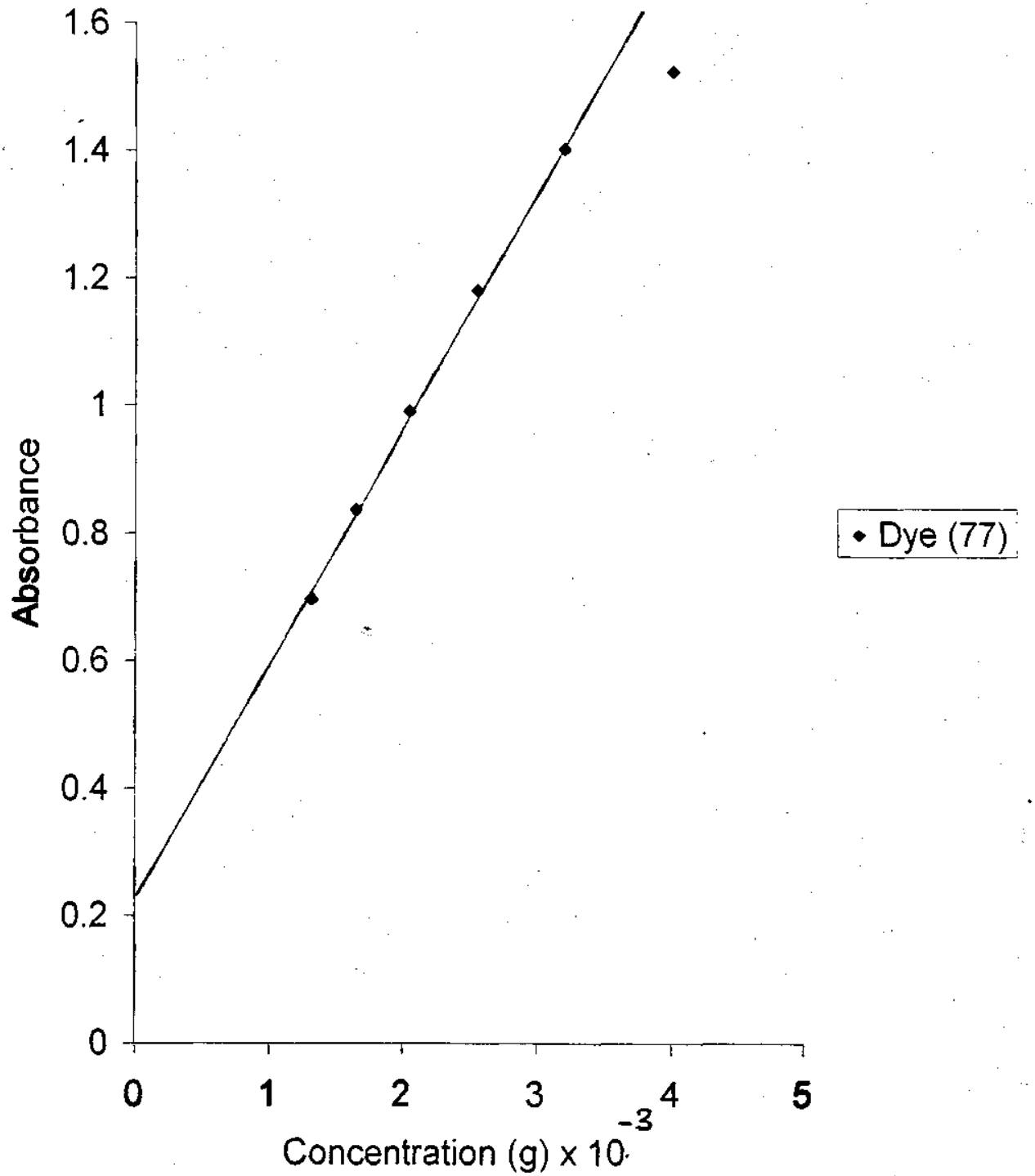


Fig 6.44: Calibration curve for Dye (78) in 20% pyridine solution

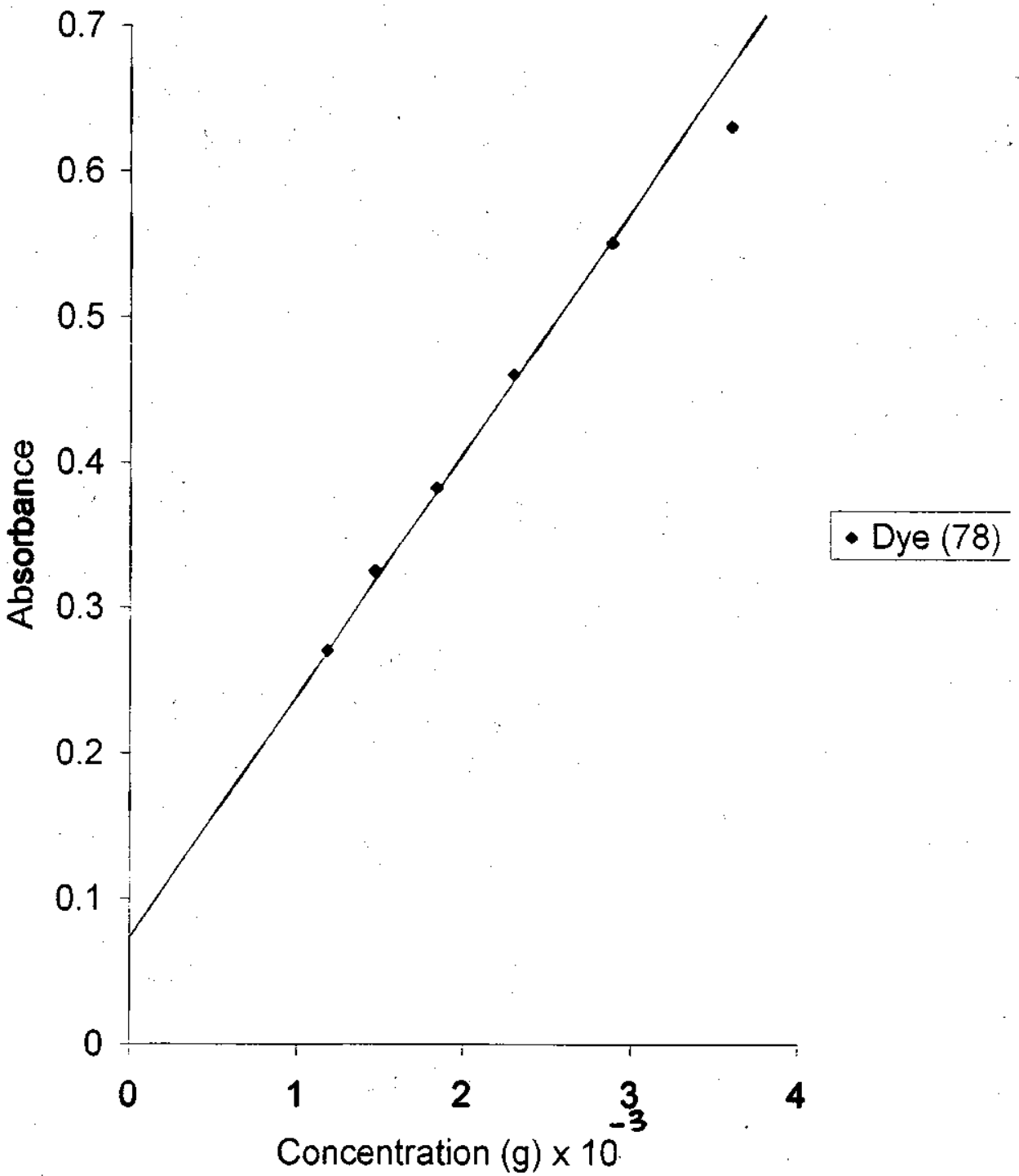


Fig 6.50: Calibration curve for Dye (74) in NaOH/wool solution

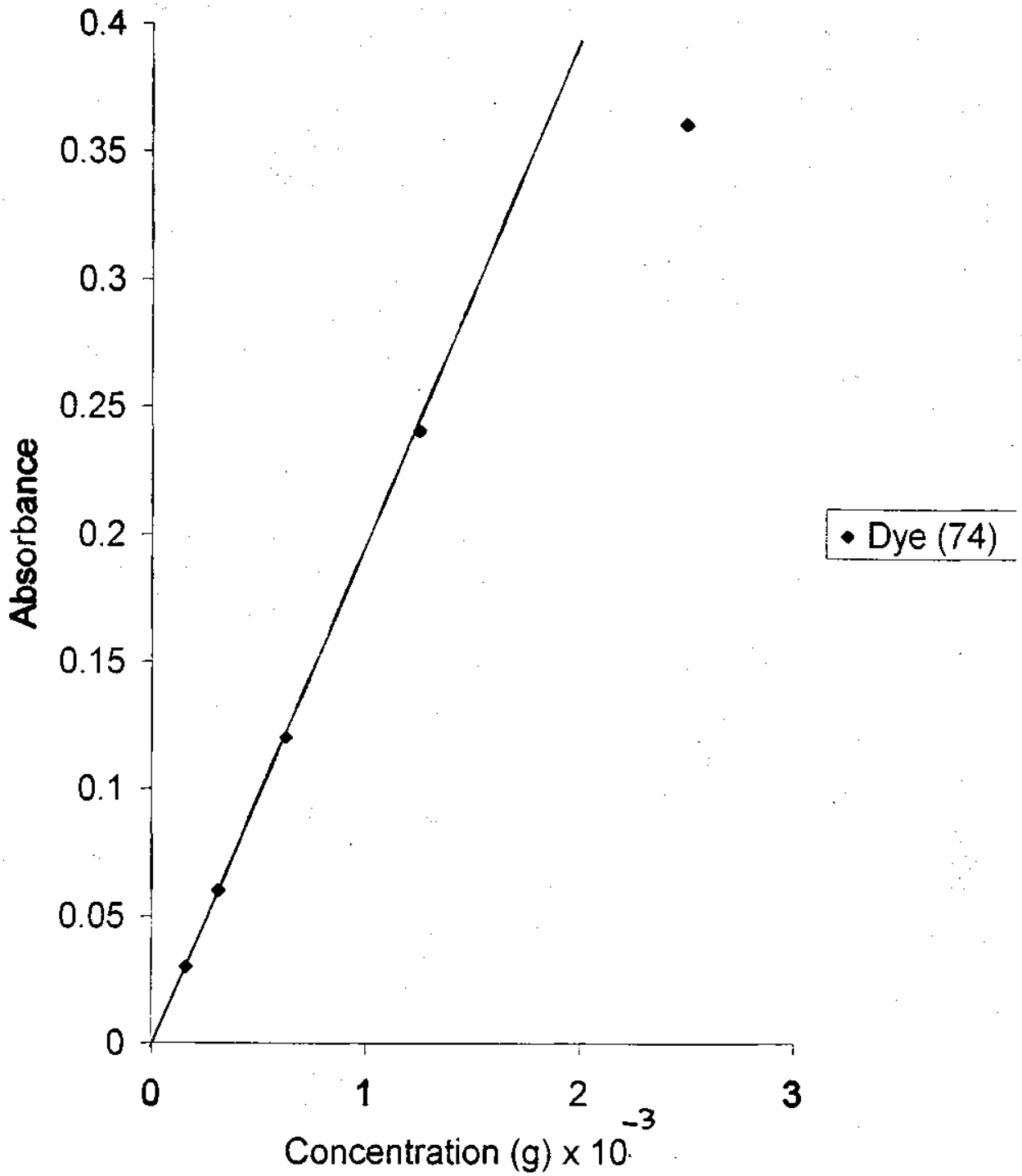


Fig 6.51: Calibration curve for Dye (75) in NaOH/wool solution

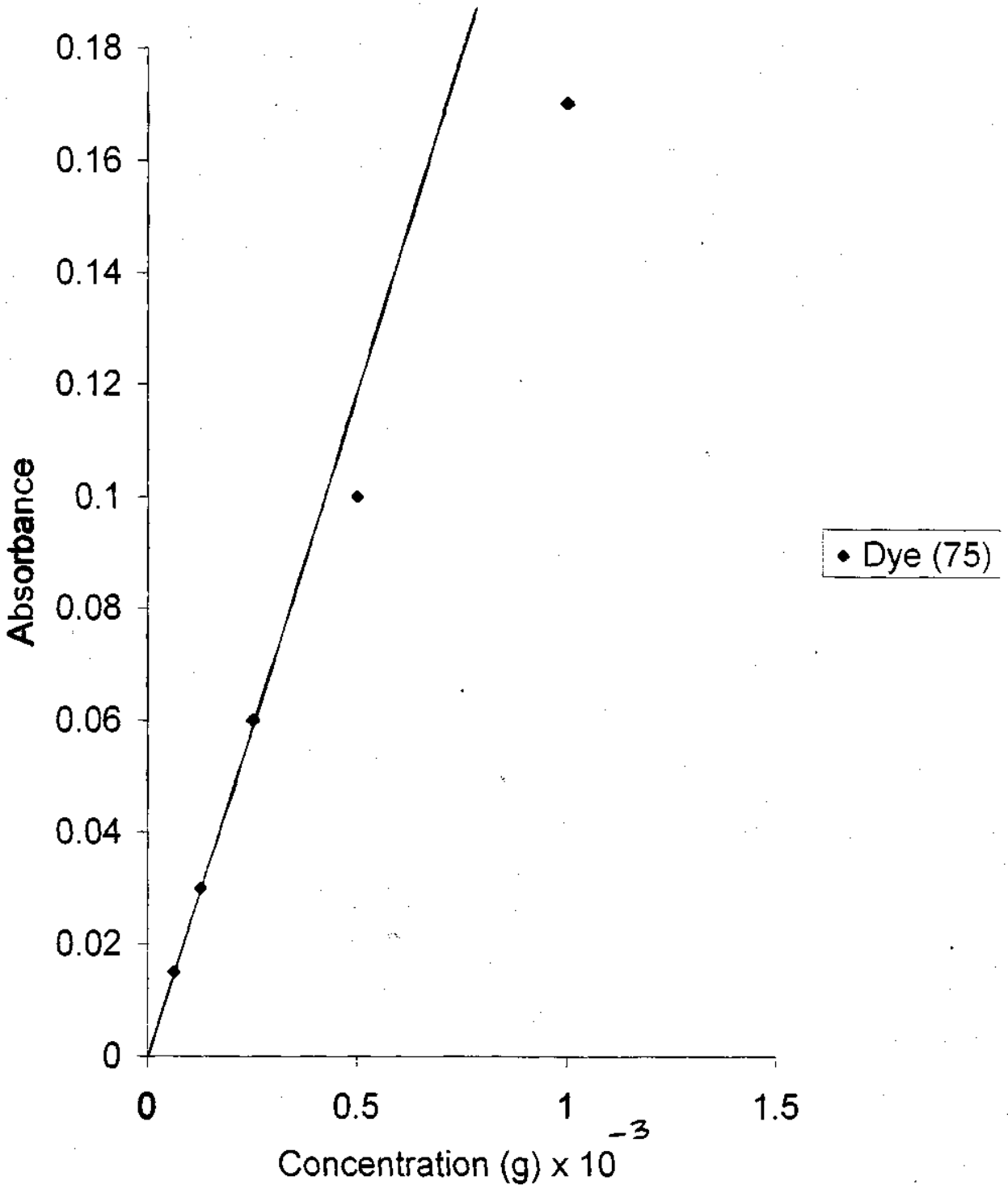


Fig 6.52: Calibration curve for Dye (76) in NaOH/wool solution

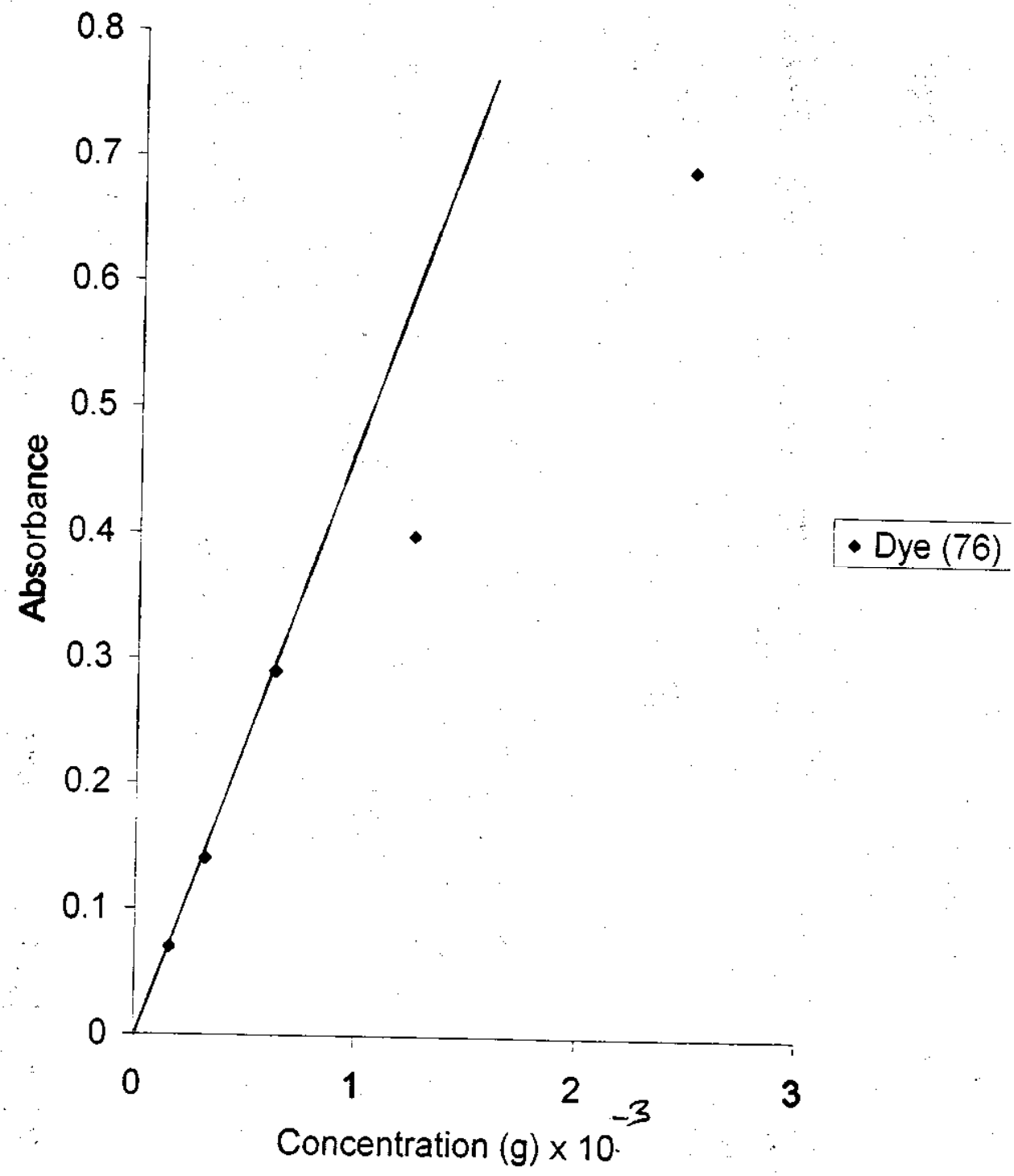


Fig 6.53: Calibration curve for Dye (77) in NaOH/wool solution

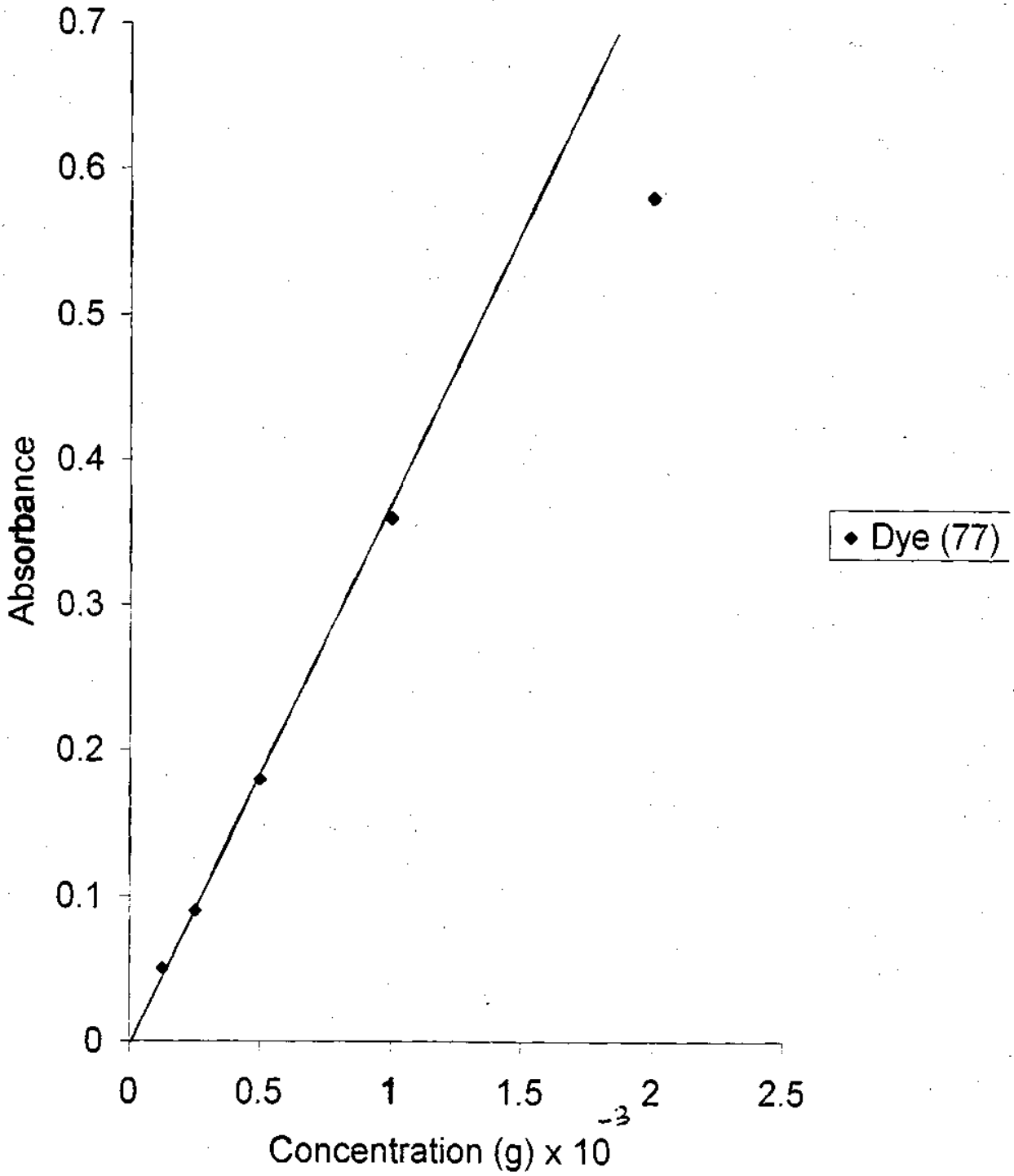
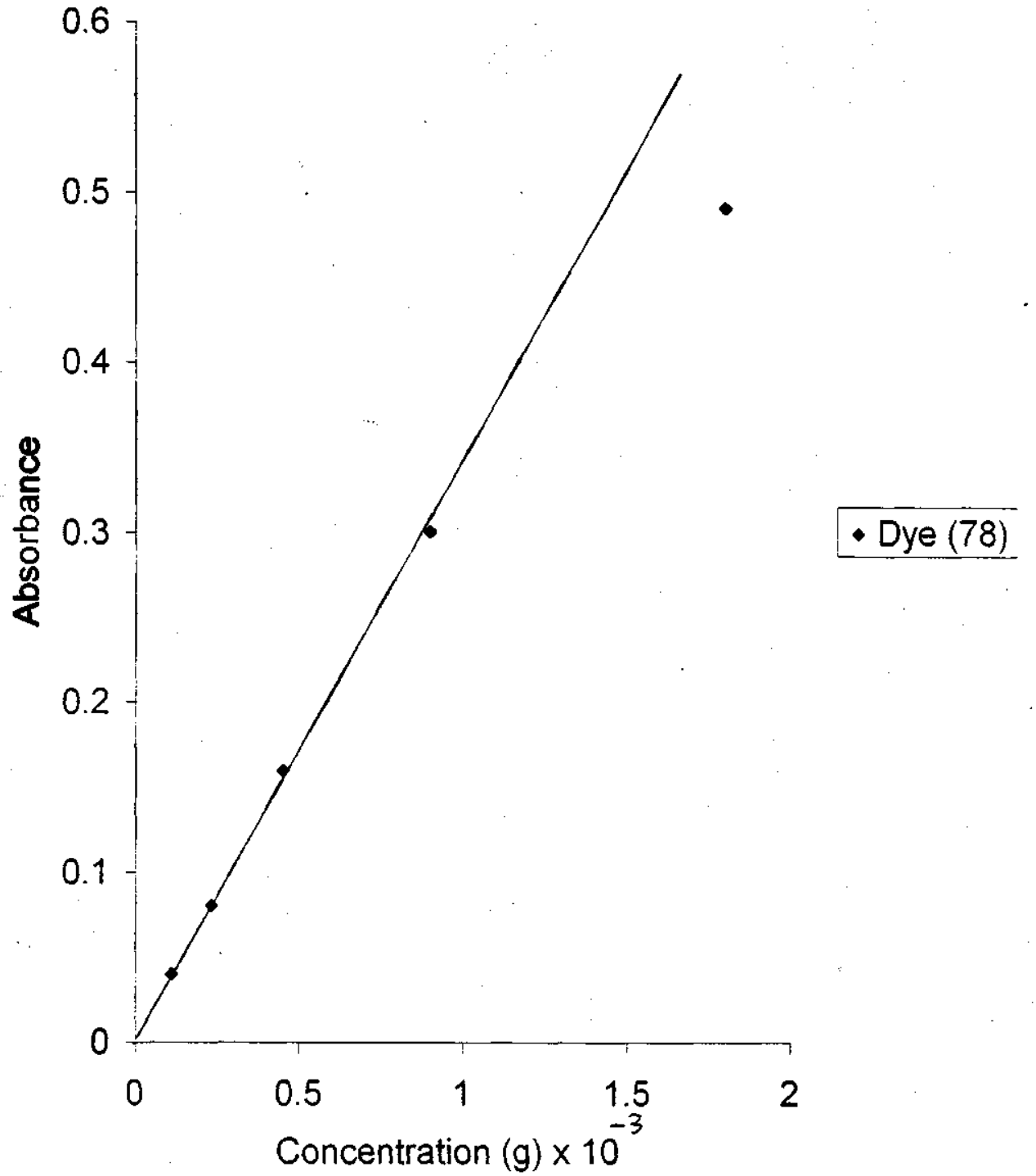


Fig 6.54: Calibration curve for Dye (78) in NaOH/wool solution



CHAPTER 7

CONCLUSION

Acetylation of amino group in H-acid dyes lead to hypsochromism and in most cases hypochromism over the unacetylated dyes. Generally, wet fastness properties were greatly improved however; the light fastness was enhanced only on wool but not on nylon 6.6 substrates.

The results on the metal complex pigments from 2-nitroso-1-naphthol has shown that 2-nitroso-1-naphthol is a very strong ligand. Formation of azo dyes by diazotisation and coupling of primary aromatic amines to the 2-nitroso-1-naphthol do not deactivate the parent system from complex formation. It is also shown that to a larger extent the two different complexes cannot be differentiated by solubility as was observed in the nitrosophenols reported. It was further shown that apart from the shape of the uv-visible spectra of the pigment, there is no major shift in the absorbance maxima between the 1:1 and 1:2 complexes. The nearness of the absorbance maxima for formic acid compared to the other solvents under study indicated that the ligand is so strong that it doesn't break by acidifying as was observed for the nitrosophenols.

These findings are indicative of the facts that these pigments can be used in the paints, vanishes and other such outlets. The quantitative yield

recorded by the pigment has also indicated that the 2-nitroso-1-naphthol can be used in the identification and purification of waste waters polluted for human consumption by the presence of hazardous dosages of heavy metals.

The characterization of the dyes when 2-nitroso-1-naphthol was used as coupling component has shown that 2-nitroso-1-naphthol can couple with diazo component under alkaline medium in a position para to the hydroxyl group. However, the absorption of the derived dyes did not seem to alter very much compared to the unsubstituted nitroso dye. The color quality could be explained by the use of Dewar's postulates and qualitative prediction techniques.

The effect of pH on the adsorption of the dyes by wool and nylon 6.6 substrates confirmed that, acid-dyeing mechanism can be used to explain the exhaustion of the dyes. However, the tautomerism in the dye molecules very much affected the complete compliance of the dyeing mechanism with respect to dyeing polyamide fibre. A dyeing mechanism had been proposed for these types of dyes.

Thermodynamic and kinetic studies didn't however, outline a general trend vis.a.vis the effect of molecular size, molecular volume, the effect of ionizable groups and other such factors to a satisfactory level. Only in certain few cases a minimum correlation was established in both substrates.

The fact that the dyed fabrics could be mordanted by some heavy metals to give distinct shade difference confirmed that the nitroso and the hydroxyl groups are still intact in their relative positions. It also showed that the complex could be formed on the substrate in situ. This has added another post metallizable dye molecules to the already existing ones. Its characteristics is however, very similar to the dyes with salicylic acid residue. The dyeings showed moderate washing fastness on wool whereas, it gave ratings of between good to excellent in both change in color and degree of staining on nylon substrate. The acid and alkali fastness to perspiration is very good on wool whereas it is excellent on nylon 6.6. The only area of concern is the result on light fastness. The rating is not encouraging even after mordanting. This was explained by the exposure of the azo linkage even after coupling.

From the kinetic and thermodynamics of dyeing with p-aminotoluene sulphon-N-ethylanilide as diazo component, it is observed that as the number of sulphonic acid groups are increased, the activation energy of diffusion decreased on the wool substrate, whereas, with nylon 6.6 substrate, the activation energy of diffusion decrease with the increase in the number of sulphonic acid groups. For all the substrates, it is observed that the gamma acid derived dye (74) has higher activation energy than the J-acid

derived dye (75). Similarly, in all cases the H-acid derived dye (76) has higher activation energy than the chromotropic acid derived dye (77). The higher activation energy of the dye (76) over dye (77) was attributed to the higher molecular volume of dye (76) and the reduction in the degree of association due to the hydrazone form of the dye (77). The higher activation energy of dye (74) can also be explained from the intra-molecular hydrogen bonding state of the dye which makes it less flexible. Affinity study shows that the mono sulphonated dyes (74) and (75) have higher values than the disulphonated dyes (76) and (77). They equally have higher heats and entropies of dyeing on wool substrate. In most cases, the same observation can be made with respect to the nylon 6.6 substrate. Explanation of this is attributed to the more increase in the negative surface potential on the substrate by the adsorption of the disulphonated dyes leading to less exhaustion due to repulsion with the result that the mono sulphonated dyes are exhausted to a higher extent leading to higher affinity, enthalpy and entropy. It is noticed also that between the H-acid derived dye (76) and the chromotropic acid dye (77) for both substrates, dye (76) recorded higher values in affinity. Explanation that can explain this is the reduction in the degree of aggregation in dye (77) due to hydrazone tautomeric form. However, J-acid dye (75) recorded higher affinity values in both substrates

attributable to aggregation factor higher in dye (75) due to intra-molecular hydrogen bonding form of dye (74). The pyrazolone dye (78) gave intermediate values of all the attributes in both fibres. Generally, the dyes have higher affinity values in nylon 6.6 than in wool, this is very much in agreement with known cases.

The wash and perspiration tests of the dyed substrates indicate that the monosulphonated dyes (74) and (75) give higher values than the disulphonated ones. It is equally noticed that the rating is in the same trend with the affinity of the dyes in the substrates. Generally, it is seen that the dyes are faster on nylon 6.6 than on wool. The influence of the hydrazone tautomeric form effect also highlight with respect to the light fastness test results. Dye (77) that exhibits this form recorded higher light fastness value. It can be explained from the higher shielding of the nitrogen bond through intra-molecular hydrogen bonding. The pyrazolone dye gave the best dyeings with respect to the wet treatment and light fastness assessment ratings on both substrates.

From the results of the uv-visible spectroscopy, the hydrazone tautomeric form influence lead to the lower wavelength of maximum absorption but higher extinction coefficient to the dyes that exhibit it on comparative basis.

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