CATIONISATION OF COTTON ANDSTUDY OFKINETICS AND THERMODYNAMICS PROPERTIES OF ITS DYEING WITH ANIONIC DYE.

BY

DANLADI ABDU ALHAJI

DEPARTMENT OF TEXTILE SCIENCE AND TECHNOLOGY,
FACULTY OF SCIENCE, AHMADU BELLO UNIVERSITY, ZARIA.

SEPTEMBER, 2014

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BY

DANLADIABDU ALHAJI

(B.Sc. Textile Science & Technology A.B.U. 1987)

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADDUATE STUDIES, AHMADU BELLO UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN COLOUR CHEMISTRY AND TECHNOLOGY.

DEPARTMENT OF TEXTILE SCIENCE AND TECHNOLOGY,
FACULTY OF SCIENCE,
AHMADU BELLO UNIVERSITY, ZARIA.

SEPTEMBER, 2014

DECLARATION

I declare that the work in this thesis entitled KINETIC AND THERMODYNAMIC STUDY OF ANIONIC DYE ON CATIONISED COTTON has been carried out by me in Department of Textile Science and Technology under the supervision of: Prof. P.O. Nkeonye, Prof. M.K. Yakubu and Dr. H. Abba.

The information derived from the literature has been duly acknowledged in the text and a list of references provided. To the best of my knowledge no part of this thesis was previously presented for another degree or diploma at any university.

Abdu Alhaji Danladi ---------- ----------

Signature Date

CERTIFICATION

This thesis KINETIC AND THERMODYNAMIC STUDY OF AN ANIONIC DYE ON CATIONISED COTTON by Abdu Alhaji Danladi meets the regulations governing the award of degree of Master of Science of Ahmadu Bello University, Zaria and is approved for its contributions to knowledge and literary presentation.

Prof. P.O. Nkeonye	----------	----------
Chairman, Supervisory Committee	Signature	Date
Prof. M.K. Yakubu	----------	----------
Member, Supervisory Committee	Signature	Date
Dr. H. Abba.	----------	----------
Member Supervisory Committee	Signature	Date
Dr. A. Danladi	----------	----------
Head of Department	Signature	Date
Prof. A. A. Joshua	----------	----------
Dean, Postgraduate School	Signature	Date

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ABSTRACT

Conventional cotton textiles dyed with direct dyes suffer from the problems of poor exhaustion and moderate to poor washing fastness due to the weak dye-fibre binding forces of hydrogen bonding and Vander Waals attractions. In addition, the dye effluent contains large amounts of dissolved and undissolved electrolytes which are harmful to the aquatic environment. In this work an attempt is made to change the dye-fibre binding force to that of ionic or electrostatic bonding (stronger bond) through cationisation (i.e. imparting positive charge) on the cotton. Cationisation involved the use of CHIPTAC which was converted to its epoxide form called EPTAC which reacted with the fibre to form complexes having two positive heads (dye sites) for formation of ionic bonds with the dye. Cotton cellulose (100%) sliver was purified and cationised prior to dyeing with a direct dye Cupro brilliant blue 2BL (CI Direct Blue158:1). All the dyed samples (cationised and uncationised) were characterised (FTIR), subjected to performance tests (wash and light fastness) as well as kinetics and thermodynamics parameters were studied. Results indicated an improvement in dye exhaustion ranging from 31 to 65% for uncatinised samples (control) to 60 to 85% cationised samples i.e. 51.04% increase. Improvement in wash and light fastness were seen, control samples gave an average rating of 2-3 (colour change) and 3 (staining), cationised samples have 4 (colour change) while 3 to 4 (staining). Light fastness showed percentage increase of 50 to 112.5%. Cationisation resulted in improvement of affinity for the cationised cotton cellulose by the dye ranging from -549.743 to -5253.67 as compared to treated control which showed very low affinity. Activation energy, heat of dyeing, entropy of cationised samples gave more favourable values that enhance dyeing condition than that given by uncatinised samples (control).

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LIST OF SYMBOLS AND ABBREVIATIONS

QUATS	Quaternary ammonium salts
CHIPTAC	3-chloro-2-hydroxy propyl trimethyl ammonium chloride,
EPTAC	2,3 epoxy propyl trimethyl ammonium chloride
$[D]_S^O$	Concentration of dye in original dye bath before dyeing begun
$[D]_S^1$	Concentration of dye in residual dye bath after dyeing
$[D]_f$	Concentration of dye in fabric
$\Delta\mu$	Affinity of dye for the fibre
ΔH	Heat of dyeing
ΔS	Entropy of dyeing
D_T	Diffusion coefficient
$T_{1/2}$	Time of half dyeing
e.g.	For example
etc.	And so forth
Fig.	Figure

CHAPTER ONE

1.0: INTRODUCTION

1.1 Cotton

Cotton fibres grow around seed of cottonplants; it is hydrophilic in nature and dominantly the most abundant source of clothing the world over. Length of cotton fibre ranges from 10-35mm; depending on quality and cotton variety, it has length to width ratio of $3x10^4$μm by 15μm. Generally colour of raw cotton varies from creamy white to grey depending on climatic conditions and the environment it was grown. Native cottonconsists of aggregated fine micro fibrils which are flexible and are attracted to each other by hydrogen bonds. These fibrils crystallize into lamellae (sheets) Adam. (2000), Chavan *et al*.,(1998).

In its raw form cotton contains impurities in the order of 4 to 12%, mainly waxes, protein matter, pectin, vegetable matter, ash etc. These impurities are gotten rid of through processes such as scouring, bleaching etc giving pure cellulose Goli,(2008).Practically pure cotton cellulose(90 to 99%)consist of linear condensation polymer known as poly(1,4-β-D-)anhydroglucopyranose whose repeat unit is a monomer called cellobiose. Cellobiose consist of two glucose units with six carbon atoms joined by glucosidiclinkage. One molecule of glucose contains nearly 6000 to 10000 units of cellobiose. Saowanee*et al*.,(2005). The cross sectional area of cotton fibre strand showing primary wall, lumen, reversal and impurities (pectin, fats, and waxes).

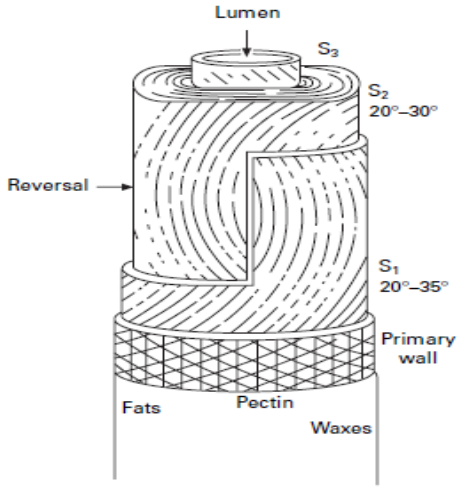


Fig.1.1 Morphological structure of cotton. Adapted fromSundaresan *et al*.,(2006).

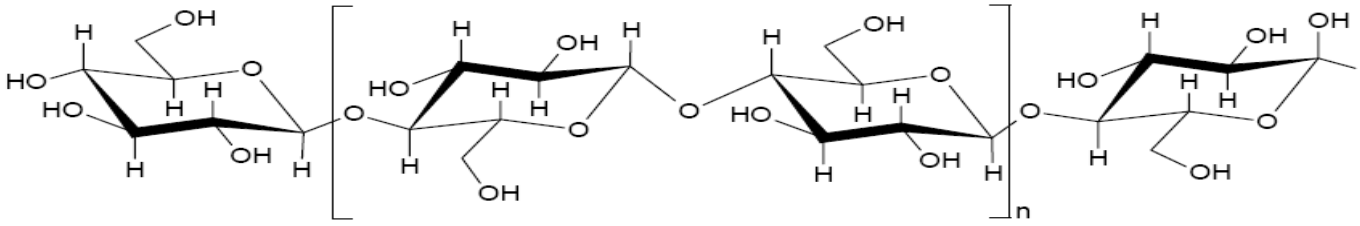


Fig. 1.2 Molecular structure of cotton. Adapted from Sundaresan *et al*.,(2006. Saowanee *et al*.,(2005).

Structurally cotton cellulose consists of one primary and twosecondary hydroxyl groups in each glucose unit. These hydroxyl groups form the reacting sites for substitution reactions such as etherification, esterification and modification such as cationization. Goli , (2008).

Cotton cellulose fibre is not electrically inert, it carries small amount of negative chargesof11mv which is mainly due to presence of carboxylic acid groups formed as a result of oxidation at primary hydroxyl site(-CH_2OH).At pH 8, more hydroxyl groups at hydroxyl-methyl side chains may also be ionized thereby increasing the amount of negative charges significantly. Saowanee *et al*., (2005).

Negative charges on the surfaceof cottoncelluloserepel anionic dyes within dye bath;as a result of this problem efficiency of dye exhaustion and fixation are drastically reduced. To

avert this unwanted situation, many studies were carried out on cotton dyeing, aimed at improving dye uptake as well as fastness properties (Saowanee *et al*., 2005). Majority of the researches in this area centered on introduction of cationic sites into the cotton for interaction with anionic dyes Subramanian *et al*., (2006).

Cotton is suitable to all weather conditions; however it is most suitable to the tropics owing to its high moisture regain of 18%. Furthermore, crystalline structure of cotton cellulose ranges from 65 to 70% with 30 to 35% being amorphous. Bird *et al*., (1975).

In addition 20-41% of space in cotton is not occupied due to lumen and spaces between fibrils. Presence of spacesenhances modification of cotton by giving accessibility tochemical reagents. Subramanian *et al*., (2006).Common dyes used in dyeing cotton fabrics include direct, vat, azoic and reactive dyes. Nkeonye, (1989).

Generally in cotton cellulose structure there are no specific sites for dye attachment; dyes are retainedby means of H-bond, mechanical retention, or physical forces such asVander Waals forcesand dipole-dipole moment.

This short coming explains the reasons for the difficulty in exhaustion and retainingofthe dye molecules in the fibres. Bird *et al*.,(1975. Gile, (1963).

These reasons mentioned above are causesfor low dye exhaustion and poor wash fastness properties associated with most dyes used in cotton dyeing. However, improvements were recorded by making use of salts and other after treatments. Bird*et al*.,(1975), Giles*et al*., (1963), Haruna,(2011).

1.2: Chemistry of Cotton Cellulose

1.2.1:Behaviour of Cotton in Water

Dyeing of cotton fabric, yarn or loose fibres takes place in solution of dye in water either in cold or hot condition. Water molecules do form H-bonds with each other:

Thisbehaviour explains the high boiling point of water. Bird *et al*.,(1975), Giles*et al*., (1963).It is of paramount importance to first and foremost analyze how cotton cellulose materials behave when in contact with water.As water with a formula H_20 dissociates into hydroxyl ions (OH^-) and hydrogen ions (H^+),with cotton cellulose having numerous number of hydroxyl groups distributed all over are in contact, repulsive forces are thus developed which in earnest aggravate the difficulty of dyeing cotton cellulose. Bird *et al*.,(1975).

However presence of intra molecular attractive forces of polarity and H-bond enhance easy wetting of cotton cellulose despite the repulsion. Giles*et al*., (1963), Bird *et al*., (1975), Goli, (2008).

All the mentioned phenomena above result in lowering of surface tension on the water surface which thus ease water absorption and the cotton cellulose gets swollen; this provides more surface area of contact with dye molecules. Chavan *et al*.,(1998).

1.3: Direct Dyes and their Application to Cotton

1.3.1: General

Cotton cellulose in loose fibres, yarn or fabricsis usually dyed with direct, reactive or vat dyes owing to absence of specific sites for dye attachment. Presence of minute negative charges on the surface of cotton cellulose makes its dyeing difficultGiles*et al*., (1963).

Even with direct or reactive dyes, dyeing of cotton exhibits low exhaustion. To improve the situation, large amount of electrolyte has to be employed which could only result in 60-65% dye utilization. Shaukat *et al*.,(2009).

Among the popular dyes for cotton cellulose, reactive dyes are given credit by having better fastness properties than the others due to their ability to form covalent bond with cotton cellulose. Bird *et al*., (1975). Apart from wasting 30-35% of dyes in cotton cellulose dyeing,

large amount of water is employed, this plus large quantity of electrolyte constitutes serious threat to our environment as far as pollution is concerned. Adam, (2000).

In Nigeria, textile effluent is one among the disturbing sources of environmental pollutants. Hazards associated with this waste are contamination of our little available drinking water, killing of aquatic organisms and epidemics such as:

Cholera, typhoid fever and the like. To dye one (1) kilogram of cotton material, an average of 10 kilograms of effluent will be discharged into the environment. Averagely 740grams solute, heat and gases are also discharged into the environment. World statistics has shown that textile industries contribute nearly twenty millions kilograms waste water annually into the sea. Burcu *et al*.,(2011),Haruna, (2011).

Direct dyes are most common known dyes and are the easiest to use, requiring no addition of any chemicals for their application. One of the disadvantages associated with direct dyes is their poor fastness properties to agencies such as washing, light, perspiration etc. However other avenues are currently being exploited in improving these short comings, though at the expense of products production cost. Giles*et al*.,(1963).

1.3.1.1:Dyes

Dyes are organic compounds which have ability of imparting colouring effect on textile substrates, leather, foods etc. In their chemical structure, a dye consist of mainly two parts namely: Chromophore and Auxochrome join together by a linking group. Bird*et al*., (1975)

. Dyes are usually applied in aqueous solution either in molecular or colloidal state of dispersion. Dyes selectively retain some of the wavelength of light that fall upon it, this reason for it natural colour. Oguntona, (1986). Furthermore dyes are classified into various groups based on their chemical composition, mode of application etc. Bird *et al*.,(1975).

1.3.1.2: Colours.

Colour constitute complex phenomena that its theory remain a question of perception and area of view, colour theoreticians, artists, physicians and philosophers view light on different angles, while some view it as pigment, to others its simply ray of light while to some it is mainly waves. Oguntona, (1989).

Colours are classified into primary, secondary and tertiary, it can added, subtracted or mixed to give certain desiring properties at the same time colour have three important dimensions or properties namely: Hue, Value and Intensity. Oguntona, (1989).

1.3.2: Fastness Properties of Direct Dyes.

1.3.2.1: Wash Fastness.

Washfastness of direct dyes on cotton material imply ability of the dye molecules to withstand treatment in soap solution at cold or elevated temperature. This action merely means solubility as well as rate of movement outward of the dye molecules from the fibre in the presence of soap (synthetic detergent). Bird *et al*.,(1975).

These two phenomena rested on fibre-dye attachment. For direct dyes, wash fastness is usually poor in ideal cases, as forces involved are weak and non-ionic linkages. In this work however cationic sites for dye attachment are provided via cationisation to enhance absorption and retention of the anionic direct dye (Haruna (2011).

1.3.2.2: Light Fastness.

When cotton materials dyed with direct dye are exposed to light, fading will result.

The fading process is a complex problem; to explain the phenomena, it is necessary to talk on the basis of absorption of radiant energy in form of photons.

These photons provide excitation energy to the dye molecules which escape resulting in disruption of bonds and rupture of chromophores and auxochromes of dye components and hence colour fading. Nkeonye, (2010).

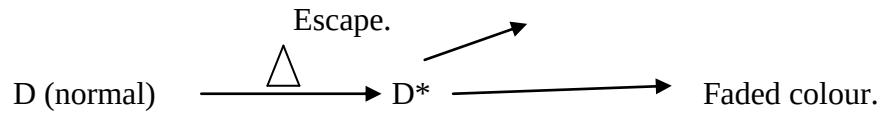


Figure 1.3: Action of photons on dye molecules.

1.4: Modification of Cotton for Better Dyeability.

Environmental research is paving way toward strenuous attention on industries such as cosmetics, leather, plastics, food, paper, textiles and the likes, owing to their high usage of dyes and colorants. Burcu*et al*., (2011). World production of colorants stands at one million metric tons annually; out of this 50% are textile dyes. Though dyes contaminate the environment and affect our health, yet dyes are important to us in clothing, carpets, furnishing, curtains etc. Presently more attention is concentrated on cotton dyeing industries which use nearly 70% of all dyes produced. Invariably most dyes in use are non-toxic yet there are still few that are carcinogenic. Azlan *et al*.,(2008).

Whatever the nature of dyes, its presence in water isundesirable, most of them being recalcitrant organic molecules that are resistant to aerobic activities. Burcu *et al*., (2011),Hauser, (2000).

Many researchesAdam, (2000), Azlan *et al*., (2008), Burcu *et al*.,(2011), Christie, (2006), Haruna, (2011) have been carried out involving modification of cotton to improve its dyeability as well as getting better fastness properties and optimum dye exhaustion without using salts or electrolytes, thereby minimizing the amount of waste water effluent discharges into our environment. Hauser, (2000).

In the past, cotton modification centered on treatment with polyacrylamide or chitosan resulting into conversion of hydroxyl groups in cellulose to amide groups thus making the fibres behave as either wool or nylon. Saowanee *et al*.,(2007); Subramanian *et al*., (2006).Invariably absence of specific sites for dye attachment in cellulose structure is main hindrance for cotton dyeability with anionic dyes; in addition, whenAever cotton material is immersed in water it develops zeta negative potential which repels anionic dyes. These problems led to the low exhaustion as well as poor fastness properties associated with cotton dyeing with either direct or reactive dyes Goli *et al*.,(2008); Haruna, (2011), Karnik, (2002). Cotton modification in recent times involves anchoring the fibre with positive charges in its structure thereby facilitating reactivity with anionic dyes. One of the popular methods in cotton modification is the use of 1,4 bis[2 chloro-4(1-amino-2-hydroxy-3-trimethyl ammonium propane chloride)-S-triazine-6-amino]-benzene dichloride.This treatment confers to cotton two dye reactive sites on its structure Jong, (2007), Karnik, (2002).

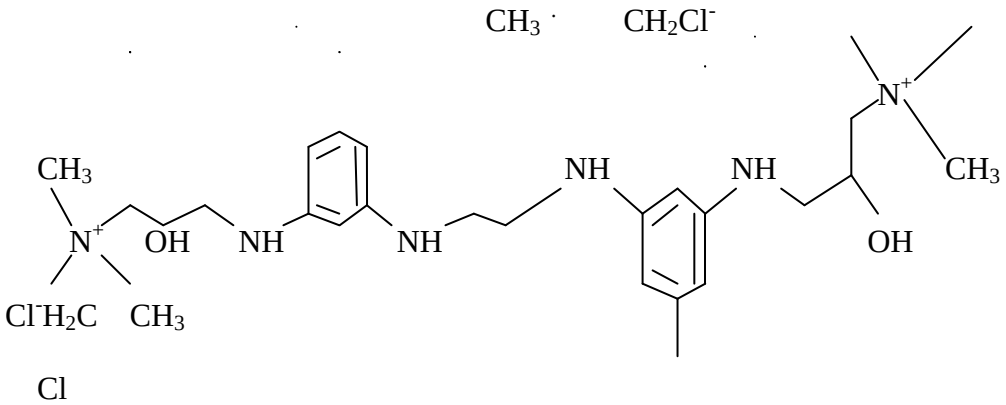


Figure1.4 Structure of 1,4bis[2-chloro-4(1-amino-2-hydroxy-3-trimethyl ammonium propane chloride)-S-triazine-6-amino] benzene dichloride.Adapted fromAdam,T.(2000), Chavan *et al*., (2000), Karnik,(2002).

Previously, 1,2-dichloroethan e was popular in cotton modification Hauser,(2000). In this treatment amide groups are imparted on the cotton structure thereby making it behave as a polyamide fibre.Chitin, a naturally abundant mucus poly saccharide and supporting material of crustaceans insect is another alternative; it is to be chemically converted to chitosan which

is a natural polymer containing large amounts of amino groups. Commonly found in shells of crabs and shrimps, in its chemical structure, chitin consists of 2-acetamido-2-deoxy-β-D-glucose the main functional groups are hydroxyl and amino whichserve for the above treatment.Azlan et *al*., (2009).

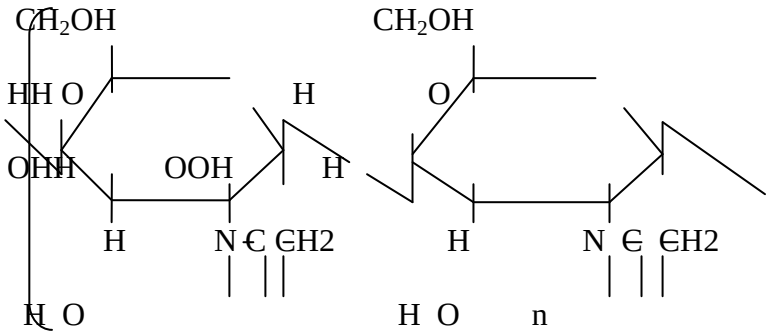


Figure 1.5 Molecular structure of Chitin (Azlan *et al*., 2008, Saowanee *et al*., 2005)

1.4.1: Cotton Modification using Quaternary Ammonium Salt(QUATS).

Quaternary ammonium salt popularly known as QUATS is used to impart permanent positive charges on cellulose structure of cotton; presence of these charges make the cotton fibre dyeable with anionic dyes, with better exhaustion and good fastness properties. Haruna, (2011).

Many researchersAzlan*et al*., (2008), Saowanee*et al*., (2005), Konaghatta*et al*.,(2010) aminated epoxy derivatives to modify cotton cellulose for better dyeability. Others modified cotton by using epoxy dimethyl-3-propane followed by an ethyl iodide quaternization which yielded ions exchanger and acid dyes were successfully applied to the modified cotton cellulose. Goli,(2008).

$$\begin{array}{l} \mathbf{R^2} \\ \quad | \\ \mathbf{R^1 — N^+ — R^3 X^-} \\ \quad | \\ \mathbf{R^4} \end{array}$$

Fig 1.6 General formula for quaternary ammonium salt (QUATS)Haruna,(2011).

Where R_1, R_2, R_3 and R_4 are alkyl groups and X^- is a halide ion (Cl, or Br).

1.4.2: Cationisation of Cotton Cellulose.

The 3-chloro-2-hydroxyl ammonium chloride contains chlorohydroxyl groups which form 2,3- epoxy propyl trimethyl ammonium chloride under alkalineconditions.

This epoxide has two positive heads, one head for dye attachment and the other for permanent bonding with the fibre. The chemical 3-chloro-2hydroxyl propyl trimethyl ammonium chloride is popularly known as CHIPTAC while the epoxide is called EPTAC Subramanian *et al*.,(2006), Karnik, (2002).

The general structure of EPTAC is illustrated in Fig.2.6 below

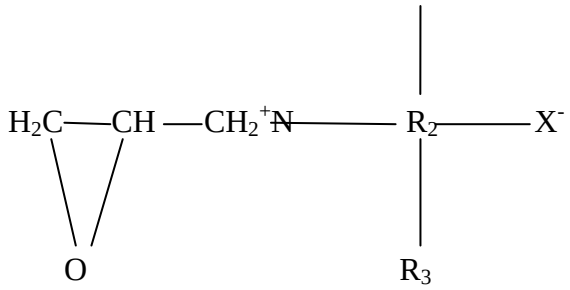


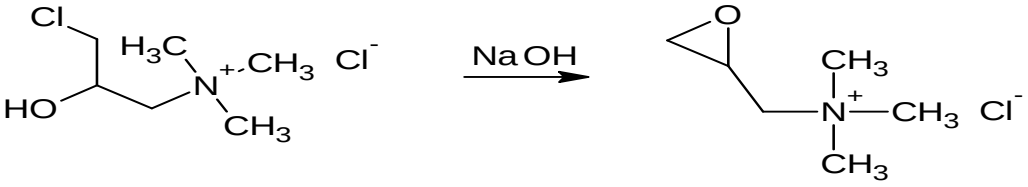
Fig 1.7 shows general chemical structure of EPTAC. Adapted from Adam,(2000), Karnik, (2002), Goli,(2008).

Where R_1, R_2, R_3 and R_4 are alkyl groups and X^- is halide ion (Cl, or Br).

1.4.3: Conversion of CHIPTAC to EPTAC.

A solution of CHIPTAC in the right container is treated with a solution of caustic soda prepared from a standard stock solution. The caustic soda solution is added in drops over a period of 20 minutes. The mixture is then allowed to stand forfurther

30minutes to effect completereaction. Within the time span, CHIPTAC will be converted to the epoxide form(EPTAC). The loose cotton cellulosic fibres are then treated with EPTAC to achieve cationisation.Shaukat *et al*., (2009, Adam, (2000), Chavan et *al*. , (2000). Karnik, (2002).

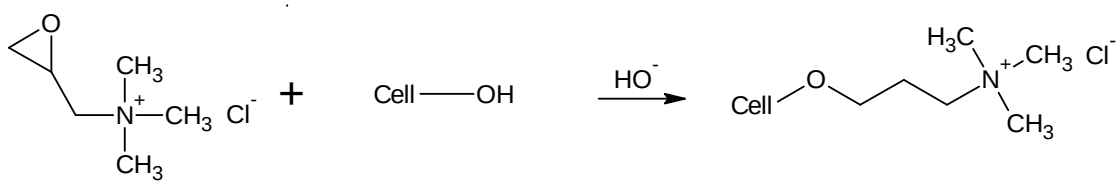


CHIPTAC EPTAC

Fig 1.8 Conversion of CHIPTAC to EPTAC. Adapted from Goli, (2008), Karnik, (2002)

1.4.4: REACTION OF EPTAC WITH CELLULOSE.

By treating cotton in alkalinecondition with EPTAC cationization of cellulose is achieved, thus the fibre acquires positive charges which will now serve as sites for anionic dyes attachment sites. It is worth noting however that there might be a side reaction which will yield unwanted product named 2,3-dihydroxypropyltrimethyl ammoniumchloride, which does not react with cotton cellulose at all (Goli *et al*.,(2008); Haruna,(2011).



EPTAC COTTON EPTAC-COTTON COMPLEX

FIG. 1.9Cationisation of cellulose. Adapted from Karnik, (2002, Haruna, (2011), Goli, (2008).

1.4.5: Hydrolysis of EPTAC.

High solubility of EPTAC in water makes it easy for it to be hydrolyzed forming the unreactive 2, 3-dihydroxypropyltrimethylammoniumchloride which does not

react with cotton cellulose, for this EPTAC has to be applied to thecotton cellulose before dyeing; however, alkalis are used duringtheapplicationasfixing agent.

Potassium hydroxide is given preference because it improves wash fastness of the dyeing; though sodium hydroxide or its carbonate can also be used, but affects brightness as well as colour yield. Goli, (2008).

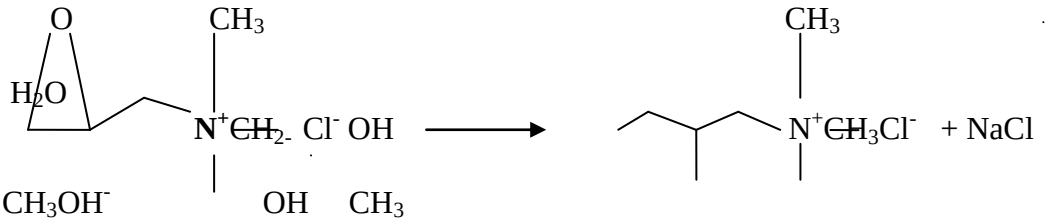


Fig 1.10 Hydrolysis of EPTAC in water. Adapted from Goli, (2008)

1.5: Kinetics and Thermodynamics of Dyeing

Generally all activities encountered during any dyeing process have direct relevance to the dye itself as well as the material (substrate) plus other variables. Montra et al (2006).In this case, which is dyeing cationised cotton with anionic dyes involving no application of salt or electrolyte, there are bound to be a lot of expectations to emanate there from. This unique case in which positive charges are imparted on the cotton cellulose chemical structure by the action of EPTAC poses another challenge. It is therefore important to make good study of the action of anionic dye on uncationised cotton celluloseand compare all the kinetics and thermodynamics parameters of the dyeing, Adam, (2000), Goli, (2008).Whenever cotton cellulosic fibre is immersed in dye solution under suitable condition, the fibre becomes coloured; thus the colour in the solution continuously decreases as long as the fibre is not saturated. In this process, there is diffusion ofthe dye molecules from dye solution to the

interior part of the fibre. Dye affinity for the fibre is the driving force; it determines the rate of the reaction, Goli,(2008).Furthermore, rate or speed of any simple process is a function of temperature. As dyeing involves adsorption, sorption and desorption, temperature plays an important role. From equation for heat of dyeing below it is evidently clear that there is a relationship between temperature and rate of dyeing, Giles et al,(1963), Saowanee et al.,(2007).

$$-\Delta H = R\Delta \ln KT$$

$$\frac{\Delta \ln K}{\Delta(1/T)R} = \frac{-\Delta H}{} \text{---------- (1)}$$

.

Where:

ΔH is heat of dyeing, T is temperature, K is affinity and R is gas constant

Activation energy is given by the equation:

$$\frac{d\ln(k)}{d(1/T)} = \frac{-\Delta E^*}{R} \text{----------(2)}$$

Where:

k is the rate constant and ΔE* is activation energy.

The two equations above paved way for the fact that there is a strong inter- relationship between all the parameters quoted.

1.5.1: Kinetics of Dyeing.

Kinetics is a branch of physical chemistry. It is of prime importance to the practical dyer as valuable information regarding the rate or speed at which dye is absorbed by a given textile material from a dye bath can be obtained.

In talking kinetics of dyeing, it is necessary to explain adsorption curves which are plots of amount of dye adsorbedon- y – axis against time on- x – axis.

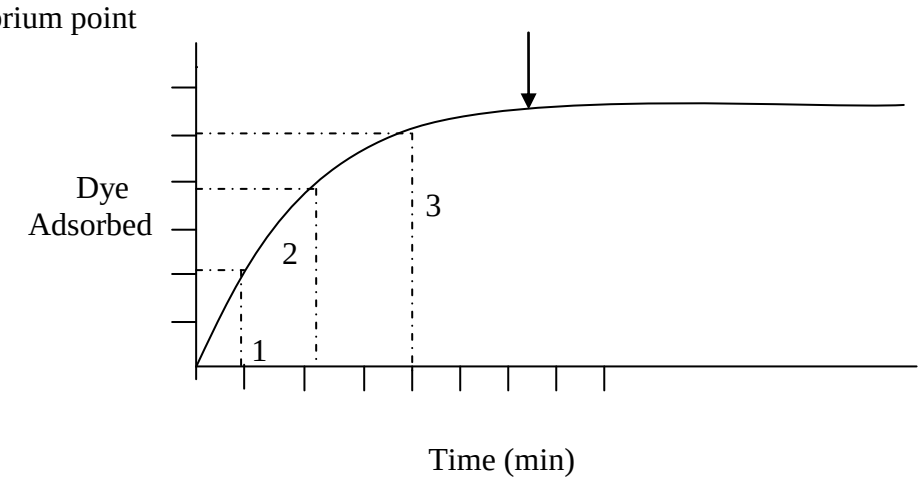


Fig: 1.11 Dye adsorption curve. Adapted from, Bird et al (1975).

Rate of dye adsorption is dependent on many factors apart from the nature of both dye and fibre such as:

(I) Temperature

(II) Agitation (circulation of dye liquor)

(III) Fibre structure

(IV) Dye bath volume (liquor ratio)

(V) pH of the dye bath (acidic, neutral or alkaline)

(VI) Electrolyte content of the dye bath

(VII) Dye affinity

(VIII) Concentration of the dye in the bath

Other parameters are migration, diffusion and dye anchoring (attachment to the fibre), Bird et al, (1975).

1.5.1.1: Dyeing Temperature

Although dyeing can occur at cool or hot condition depending on the nature of dye, temperature change is known to significantly affect the rate of dyeing since the molecules in the bath are in constant random motion, having kinetic energy. Supplying additional heat by increasing temperature means imparting additional kinetic energy which can cause increase in the rate of reaction in endothermic situation or a decrease for exothermic condition, Burcu et al, (2011). Effect of temperature on dyeing is investigated by plotting temperature against time of dyeing(Burcu et al, (2011), Montra et al, (2006, Saowanee et al,(2005).

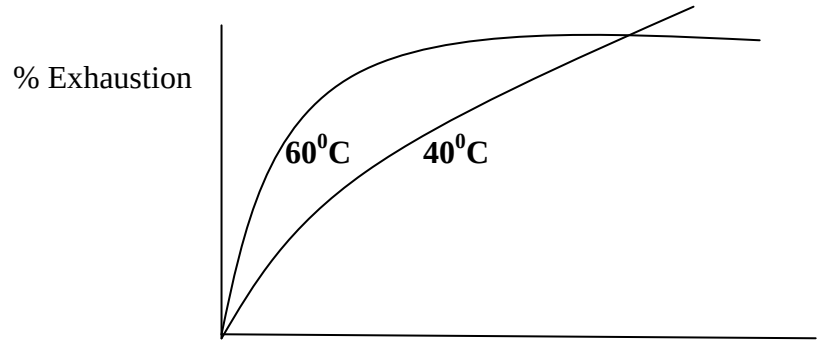


Fig: 1.12 Curve showing effect of temperature on time of dyeing. Adapted fromGiles et al, (1963).

1.5.1.2: Agitation (Dye liquor circulation)

Stirring dye solution is noted to have direct bearing on the rate of dyeing, for in many cases this influences exhaustion rate and reduces the time of dyeing as well as impart an improvement in levelness, Gile et al, (1963).

1.5.1.3: Fibre structure

Substantivity of dye for given substrate is purely dependent on chemical structure of the dye and that of fibre; however, modification of the fibre structure can alter this either positively or otherwise, sometimes this can make a dye which is not substantive to a material to become substantive.Other parameters such as liquor ratio, pH,electrolyte, dye affinity and dye concentration all influence dyeing in their own ways, Giles et al, (1963).

1.5.1.4: Diffusion of Dye into Fibre.

Diffusion is important in any dyeing process. It is the movement of dye molecules from regions of high concentration to those of low concentration, Bird et al, (1975).

Fick's law states that:

Rate of diffusion $= \frac{ds}{dt} = -D\frac{dc}{dx}$

Where

$\frac{ds}{dt}$ = Amount of dye diffusing across unit area per unit time interval

dt = The time interval

$\frac{dc}{dx}$ = change in concentration

dx = change in distance

dc/ dx = concentration gradient

-D = Diffusion coefficient.

To vividly understand diffusion, it is necessary to consider the fibre to be across section of a circular rod made of concentric circles dipped in a dye bath with high concentration of dye molecules initially. Bird et al, (1975).At first a thin layer separating dye molecules in the bath and fibre surface is established; gradually concentration of dye molecules continues to build up. This development results in concentration gradient which then facilitates diffusion of dye molecules into the fibre. Gradually this process continues up to the time when there is an

even distribution of dye molecules all over the entire surface and interior of the fibre. At this point saturation point is reached, hence equilibrium is attained and diffusion will cease. Bird et al, (1975), Giles et al, (1963).

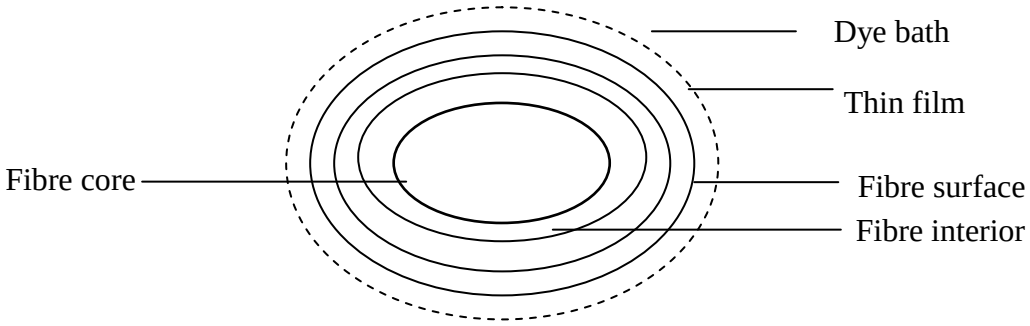


FIG 1.13: Illustration of ring dyeing effect

1.5.1.5: Measurement of Diffusion Coefficient

Dyeing is carried out for an equal time interval say 15, 30, 45, minutes, 1 hour etc. Adsorption of dye is determined by either stripping the dye adsorbed by each piece

for the given time, and then determining the concentration by colorimetric method or simply determining the concentration of dye in solution after dyeing:

Dye adsorbed= initial concentration – concentration in solution after dyeing.

The dye absorbed is plotted against √t (square root of time of dyeing). The slope of graph obtained gives the diffusion coefficient. Bird et al, (1975).

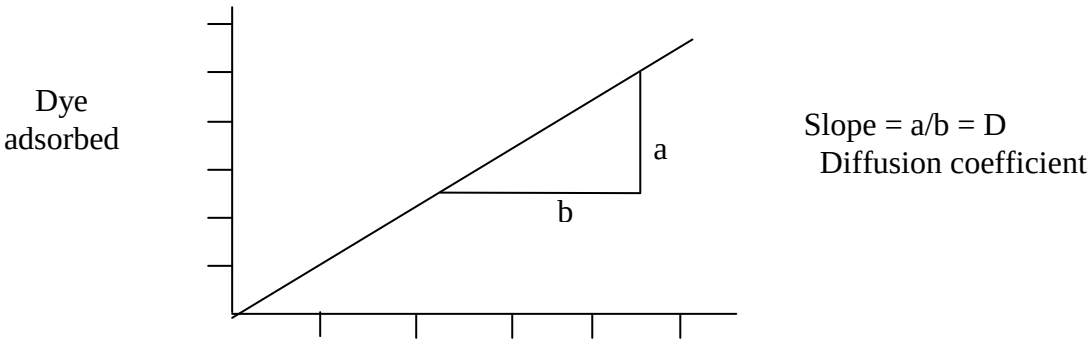


Fig: 1.14 Dye absorbed versus square root of dyeing time (√t). Adapted from (Giles et al, (1963), Bird et al, (1975).

Another indirect way of determining diffusion coefficient is the time of half dyeing.

In this approach, dyeing is carried out at a particular temperature, exhaustion at different times is measured till equilibrium is reached, i.e. time at which the exhaustion remains constant. By plotting % exhaustion against time gives the graph below.

Another alternative way is using infinite dye bath which is a dye bath with constant dye concentration;

in this case dyeing is carried out for a given period oftime andnegligible amount of dye solution is pipetted out over a range of constant time intervals.Absorbencies of all withdrawn dye solutions within the time intervalsare measured. Plot of absorbance against time interval can also be used to obtain diffusion coefficientMontra et al, (2006).

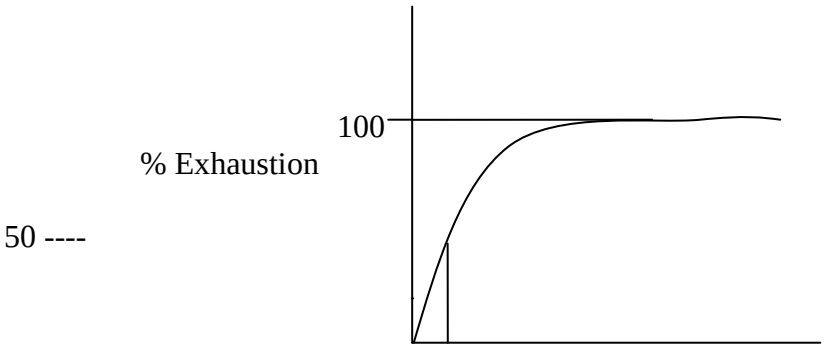


Fig 1:15 exhaustion versus time of dyeing. Bird et al, (1975).

From the y-axis (% exhaustion), point where 50% exhaustion is occurs, a line is extended to cut the curve at the point shown.By means of dotted line a vertical is drawn to cut the x- axis. Time value at this point is the time of half dyeing (t½).

It is worth noting that value of t½ characterizes the dyestuff into fast or slow dyeing. Any dyestuff that exhibited high value of t½ is slow dyeing, while lower value of t½ means fast dyeing. Giles et al, (1963).

1.5.2: Adsorption Isotherms

Isotherms simply imply similar or same temperature. In kinetics of dyeing adsorption isotherms are curves depicting dye adsorbed by the textile material in relation to the amount of dye remaining in solution as functions of the original (initial) dye concentration in the dye bath before dyeing began.

Isotherms are graphical plots, that give information or idea as to which dye can be absorbed by which textile materials. There exists three popular isotherms, with each one named after its founder, Konaghatta et al, (2010),Saowanee et al, (2005), Montra et al, (2006).

(I) Langmuir isotherm

(II) Freundlich isotherm

(III) Nernst isotherm

All these three isotherms are applicable to particular dye-fibre systems. It's therefore important to make choice of the correct isotherm in order to obtain correct results, Bird et al, (1975).

1.5.2.1: Langmuir Isotherm

The fact that cationised cotton acquired positive charges thus giving sites for dye attachment means that this isotherm is applicable.

Langmuirisotherm is established based on the equation:

$$[D]_f = k[D]_s([S]_f - [D]_f)$$

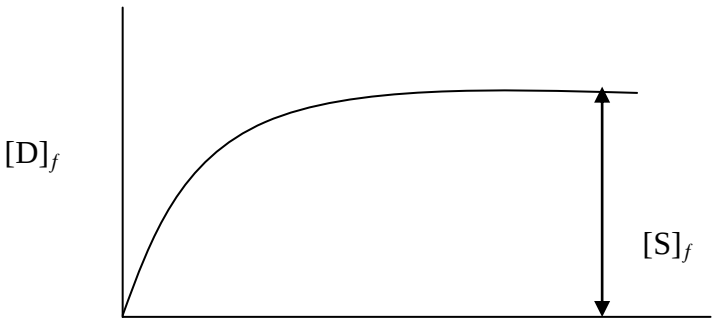
Where

$[D]_f$ = concentration of dye in fibre

$[D]_s$ = concentration of dye in solution after dyeing

$[s]_f$ = maximum amount of dye the fibre can accommodate at equilibrium.

k = a constant



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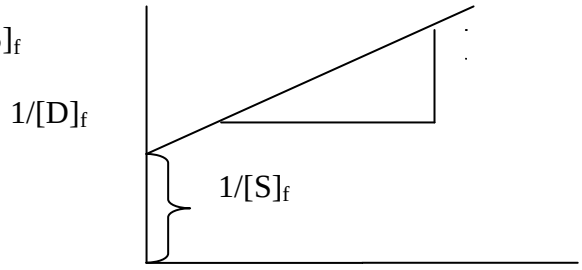
Fig: 1:16Langmuir Isotherm.

Plotting a more appropriate reciprocal relationship of these parameters in Langmuir equation:

$1/[D]_f = 1/k[S]_f [D]_s + 1/[S]_f$

By plotting $1/[D]_f$against $1/[D]_S$, a straight line curve is obtained which cut the y- axis at a point (intercept) representing $1/[S]_f$ and the slope is $1/k[S]_f$.

Slope =$1/k[S]_f$



$1/[D]_s$

Fig. 1.17: Langmuir Reciprocal plot.

1.5.2.2: Freundlich Isotherm.

This Isotherm governs absorption of direct dyes by cotton cellulose material. In this case there are no specific sites for dye attachment. Dye molecules are retained by weak forces such as: H-bond, Van der Waals forces etc. Bird et al, (1975).

Materials under dyeing condition are assumed to be porous solid with large area for absorption of dyes. At equilibrium the concentration of dye in the fibre is proportional to concentration in the dye solution raised to power of "x" (Giles et al, 1963).Equation governing this condition is as shown below:

$$\mathbf{[D]_f = K\,[D]_S^{x}}$$

Where:

$[D]_f$ is dye concentration inside the fibre.

$[D]_S$ is dye concentration inside the solution.

x and K are constants with x usually equals to 0.5.

When $[D]_f$ is plotted against $[D]_S$, the graph obtained is as shown below:

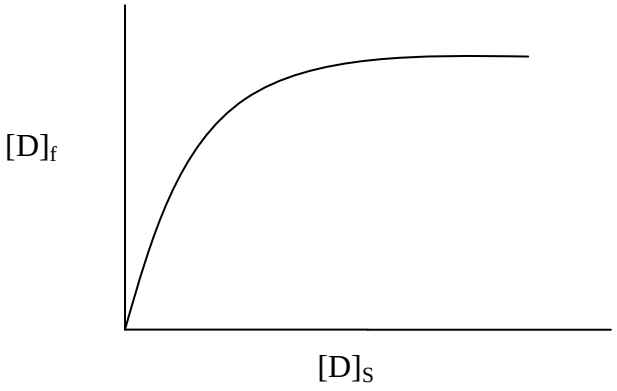


Fig 1:18 Freundlich isotherm.

By plotting log $[D]_f$ against log $[D]_S$ a straight line is obtained which gives better and more useful curve. $\log [D]_f = \log [D]_s + \log k$

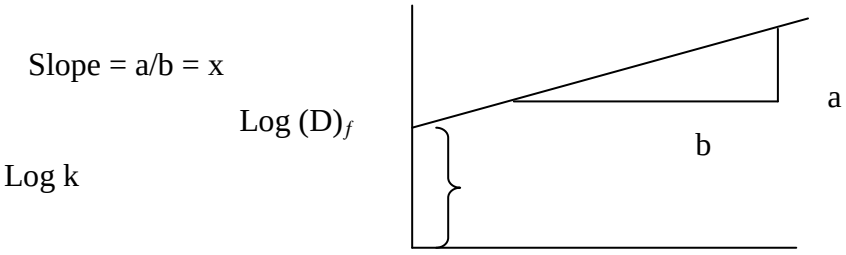


Fig: 1:19 Freundlich isotherm logarithmic plot.

1.5.2.2.3: Nernst Isotherm

This isotherm is strictly based on solution model, dye is assumed to be fully dissolving inside the fibre due to its high affinity as such dyeing is viewed as distribution of solute between two immiscible liquids (solvents) (Bird et al, 1975,Giles et al, 1963).

At equilibrium, this system obeys the equation below:

$$[D]_f = K[D]_S$$

Where

$[D]_f$ = concentration of dye in the fibre.

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

K = partition co-efficient (constant)

By plotting $[D]_f$ against $[D]_s$, a straight line plot is obtained as shown below:

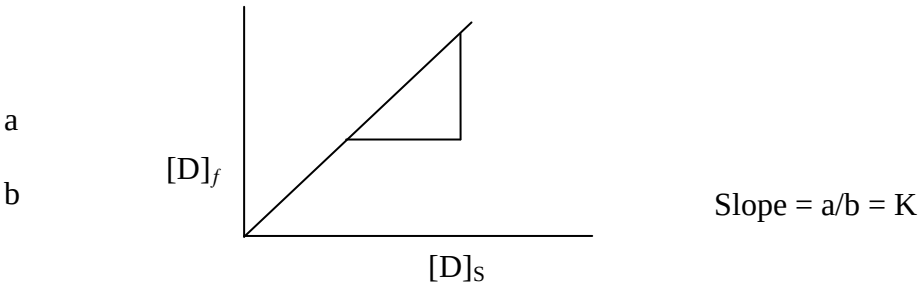


Fig: 1.20 Nernst isotherm

1.5.3: Affinity of Dye for Fibre

Affinity is a measure of how dye molecules have desire to leave dye bath and move into fibre matrix and be retained there in. Affinity is clearly understood when it is explained on the basis of exhaustion which is a ratio between concentrations of dye in material to that in liquor or is related to number of dye molecules distribution between them. When the material has more number of molecules than the dye bath, the dye is thus termed to have higher substantivity for the material.However, affinity is not determinable from single exhaustion data, but on basis of difference in chemical potential of dye molecules in the fibre matrix to that in dye solution.

Any dye that exhibits higher value of chemical potential difference between fibre and dye bath is said to have affinity for the fibre in question (Bird et al, 1975).

Beside the fact that affinity is a quantitative measure of substantivity, it also has direct bearing on the wet fastness property of the dye on the fibre. Higher-affinity simply means good wet fastness properties (Giles et al, 1963).

. Affinity is expressed as:

$$-\Delta U^{o} = RT \ln K.$$

Where:

K is partition co-efficient.

R is gas constant and

T is absolute temperature.

1.5.4: Heat of Dyeing.

From thermodynamics point of view, affinity ΔU^{O}, heat of dyeing (ΔH^{0}) and entropy (ΔS^{0}) have direct relationship as shown by the equation below:

$$\Delta U^0 = \Delta H^0 - T\Delta S^0$$

The heat of dyeing (ΔH^0) when viewed from sorption and desorption of dye molecules, means difference in heat content between that needed to free one mole of dye from the solvent and that required to free same quantity from the surface or interior of the substrate by thermal agitation (Azlan et al, 2006, Bird et al, 1975, Giles et al, 1963).

High negative value of ΔH^o implies high potential affinity which means the dye is substantive. Plotting affinity values at different temperatures against temperature, a straight line graph will be obtained. The straight line will cut y-axis at a point and value of the intercept gives value of ΔH^0 while slope will gives value of ΔS^0.

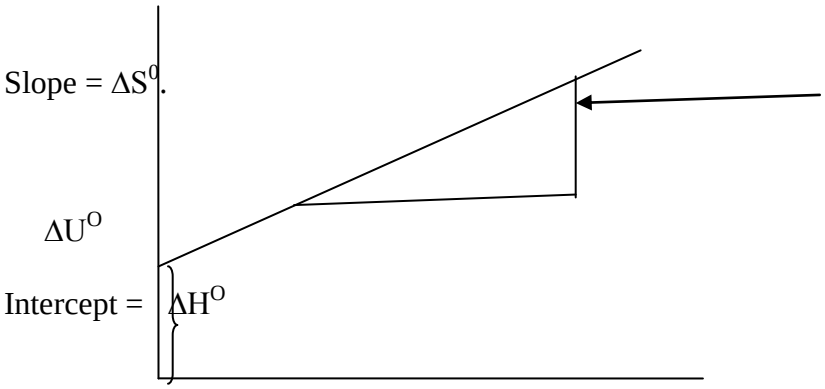


Fig 1:21Heat of dyeing curve (a).

Furthermore, heat of dyeing can also be obtained from the equation below:

$$\Delta H^O = \frac{\sigma (\Delta U^O/T)}{\sigma (1/T)}$$

ΔU^O and ΔH^O are in standard form.

Integrating the equation it becomes:

$$\int \Delta H^O = \int \frac{\sigma (\Delta U^O/T)}{\sigma (1/T)}$$

so the relation becomes:

$$\Delta H^O/T = \Delta U^O/T + C.$$

By plotting $\Delta U^o/T$ against 1/T, value of heat of dyeing can be determined using slope calculated therefrom. Intercept on y- axis represents the constant C which is known as molar entropy.

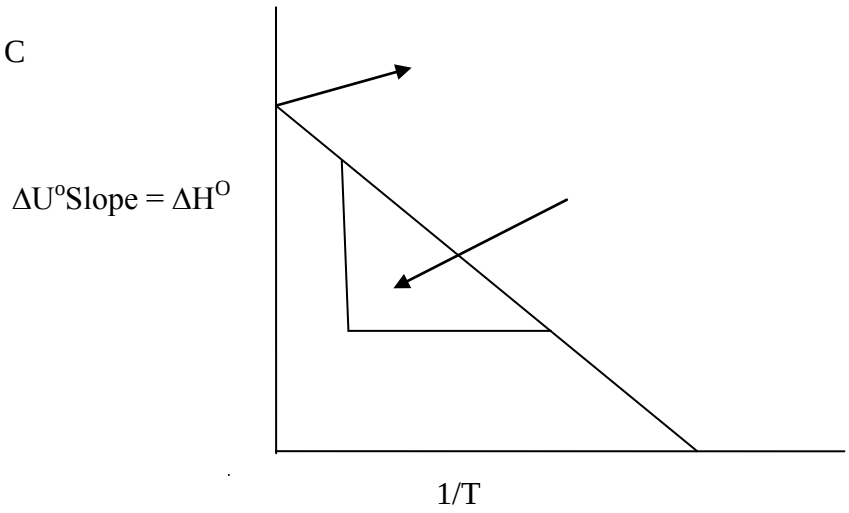


Fig 1.22 Heat of dyeing curve (b)

In situations with only two values of temperatures T_1 and T_2 with corresponding values of affinities ΔU^o_1 and ΔU^o_2, value of heat of dyeing(ΔH^o) can be calculated from the equation below (Bird et al, 1975):

$$\Delta H_o = \frac{T_1\Delta U^o_1 - T_2\Delta U^o_2}{T_1 - T_2}$$

In many cases of dyeing systems, value of ΔH^o is negative which imply exothermic process.

1.5.5: Entropy of Dyeing.

In solution of dye, both molecules of dye and that of solvent are in constant random motion; this situation usually results in a state of high level of disorder or randomness. This level of disorder is what is known as entropy.

The entropy governs the equilibrium state of chemical reaction at high temperature provided that heat of reaction is constant and the system is independent of temperature. At higher temperature, thedye molecules acquire high kinetic energy as such the entropy will be high. The entropy controls the equilibrium state of the system which thus facilitates movement of the dye into the fibre matrix (Burcu et al 2011, Saowanee et al ,2005, Tan, et al 2010),.

Entropy of a given dyeing system denoted by ΔS^O can be obtained from graph of affinity against temperature as could be seen from the equation below:

$$\Delta U^o = \Delta H^o - T\,\Delta S^o$$

Where: ΔU_o is affinity, ΔH^o is heat of dyeing.

T is temperature and ΔS^o is entropy.

1.5.6: Kinetics of Dyeing.

Kinetics of dyeing implies study of rate or speed at which chemical reaction proceeds as well as its mechanism. Kinetics is concerned with various species of molecules type taking part in the reaction and their individual concentrations. Viewing dyeing under this concept, dyeing has numerous kinetic properties such as: exhaustion, rate of dyeing, activation energy etc. (Burcu et al 2011, Konaghatta et al 2010, Montra et al 2006, Tan et al 2010).

1.5.6.1:Activation Energy.

Whenever reactants are brought together in a reacting medium, product will be formed. In other words, the reacting molecules acquire excess kinetic energy which helps in making the reaction to move forward and this condition favours formation of product. The excess energy is what is known as Activation Energy.

Ideally dyeing is considered as mainly diffusion process involving reacting molecules which are in constant random motion from higher concentration point to that of lower concentration (Goli,2008).

Molecules diffusing from solution into fibre matrix are function of total number of molecules present as well as the relation; $e^{-E/RT}$ where R is gas constant,

T is the thermodynamic temperature of reaction and E is the minimum energy value required for the diffusion to occur (Konaghatta et al 2010).

It is a known fact that any rise in temperature will cause a rise in diffusion rate for endothermic reaction only (Haruna 2011). The temperature rise brings about an increase in the activation energy of the diffusing molecules "E" as could be seen from the equation below:

$\mathbf{D_T = D_O - E/RT}$ (D_T is temperature dependent).

Where:

D_o = constant.

R = gas constant.

T = absolute temperature

By taking natural logarithm on both sides, the equation becomes:

$$\mathbf{\ln D_T = \ln D_O - E/RT.}$$

$$\mathbf{2.303 \log D_T = 2.303 \log D_O - E/RT.}$$

$$\mathbf{\log D_T = \log D_O - E/2.303RT.}$$

By plotting a graph of log D_T against 1/T a straight line curve will be obtained; its slope will be –E/2.303R, hence value of E can be calculated.

Intercept on the graph gives log $D_{O.}$

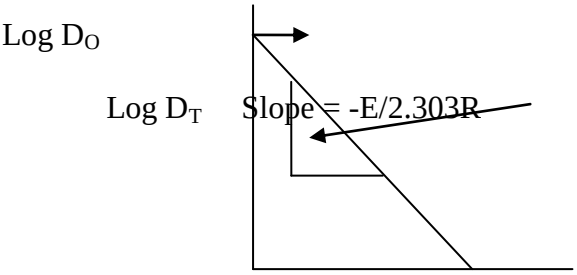


Fig 1:23 Activation energy curve.

When the value of activation energy is high, diffusion rate will be very slow as such dyeing will take longer time and from this it can easily be deduced that affinity of the dye for the fibre is also low. However low activation energy entails faster rate of dyeing and stronger dye-fibre affinity (Subramanian et al, 2006).

1.5.7: Exhaustion Characteristics.

In general all information on characteristics regarding exhaustion of dye in a textile substrate is obtainable from the exhaustion curve. In plotting this curve, percentage exhaustion which is a ratio of concentration of dye inside the fibre to that inside the original dye bath at specified condition of temperature, dye composition and concentration as well as liquor ratio are considered (Bird et al 1975).

$$\% \text{ Dye exhaustion} = \frac{\text{mg of dye in the fibre}}{\text{mg of dye in original dye bath.}} \times 100$$

Exhaustion curves are constructed by making up enough number of dye baths (10-15) with the same conditions (dye assistant, temperature, liquor ratio etc.) and dye concentration.

All the dye baths are placed in the water bath at selected temperatures and are conditioned to the temperature of the water bath. This is followed by dipping of equal mass of material inside each dye bath. These baths are then removed after reaching selected span of time. Dyed substrates are removed and rinsed thoroughly to rid them of any unfixed dye.Residual water used for rinsing should be added to residual dye baths.

Absorbencies for initial dye bath and its corresponding residual bath are measured and recorded using spectrophotometer. From values of each pair of absorbencies, % exhaustion is obtained:

$$\% \text{ Exhaustion} = \frac{\text{Absorbance of original dye bath - absorbance of residual bath} \times 100}{\text{Absorbance of original dye bath}}$$

By plotting % exhaustion against time, exhaustion curve is obtained:

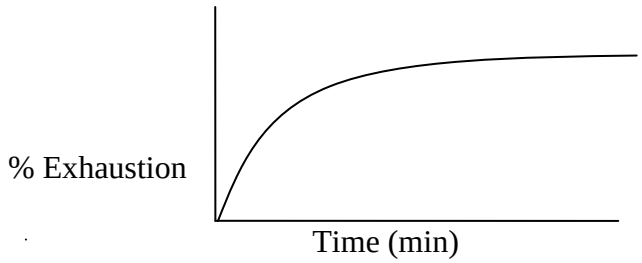


Fig 1:24 Curve of % exhaustion versus time.

It can be seen that dye molecules are rapidly absorbed at first, but gradually reduce up to the time when equilibrium is attained so absorption ceased

This curve can be used to determine time it takes a system to reach 50% exhaustion which is termed as time for half dyeing ($t_{1/2}$).Time of half dyeing ($t_{1/2}$) is obtainable when exhaustions at different temperatures are plotted against time of dyeing. Dotted line is drawn from point of equilibrium to cut y-axis at a point, 50% of this value is extended to cut the curve, this point is extended downward to touch time axis (x-axis), and the value of the time at that point is the $t_{1/2}$.

It is worth noting that dye stuff which exhibits high value of $t_{1/2}$ is slow dyeing, while that with low value of $t_{1/2}$ is fast dyeing type. In addition, $t_{1/2}$ can also shed more light on the substantivity of dye for a given fibre (Bird et al 1975, Giles et al 1963).

1.6: **Statement of the Problem**

Conventional dyeing of cotton is associated with problems of very low dye exhaustion and poor performance properties(i.e. wash and light fastness), which are attributed to lack of dye attachment sites at the same time weaker dye-fibre bonds. These problems call for after treatments processes which thus increase cost. In addition large amount of water, electrolytes, (salt) and electric energy are also usefor comparable fewthousands meters of dyed cotton fabrics.Apart from these problems, another issue is that of excessive discharge of effluents containing dissolved and undissolved salts, which when discharged, affect the natural environment and species in the ecosystem (Haruna, 2011).

1.7: Aims and Objectives ofthe Research.

The aims and objectives of this research are as follows:

i) To cationise 100% cotton cellulose in order to make it susceptible to anionic dyes
ii) To study the kinetics and thermodynamics of dyeing of cationised and uncationised cotton cellulose with anionic dyes (i.e. direct dye).
iii) To reduce environmental pollution.
iv) Reduce cost of dyeing.

1.8: Scope of the Research

This research is limited to studies on cotton sliver using a single commercial direct dye, Cuprophenyl Brilliant Blue

CHAPTER TWO

2.0:LITERATURE REVIEW

The fact that cotton dyeing is associated with peculiar problems such as very low dye exhaustion and poor performance properties particularly wash and light fastness, these problems makes it mandatory for addition of electrolytes and after treatment processes which call for additional cost; in effort to answer these problems, many researches were under taken in search for alternative dyeing methods without using electrolytes and after treatments.

Hauser(2000) is one of the pioneers of Cationisation in which cotton was dyed without the use of both electrolytes as well as after treatments and yet better dye exhaustion and good performance properties were recorded. Another work credited to Hauser is that in Colour Technol No. 5, 282—288 (2001).

The work of Montra et al (2006) involving the use of Lac in dyeing cotton all in search for improved exhaustion and better performance properties. In this work it was found out that remarkable improvement in dye up take was recorded at higher temperatures of dyeing, at the same time activation energy value were noted to increase progressively with rise in temperature.

Adam(2000) carried out a research on Cationisation of cotton using 2,3epoxypropyltrimethylammonium chloride, in this work after characterization, it was found that positive sites for dye anchoring were created. By this it is clear that anionic dye can now be held into the cotton structure with ionic bonds thus an improvement of performance properties is expected.Saowanee et al (2005) in their work cotton was modified by means of pretreatment with chitosan.

In the course of their work, it was established that dye up take is defendant on P^H values, as the dye bath is becoming acidic at lower temperature, dye up take increases. Other dyeing variables were further investigated and the findings were found favourable.

Subramanian et al (2006) tried reactive dyeing on cationised cotton, in this research it was found that dye exhaustion is 99% for cationised samples as against 76% of conventional dyeing, this indicates an increase of 23%.

Another important research carried out in our domain is the work of Haruna (2011),

In this research many mechanical and physical properties were studied and majority of the results obtained showed remarkable influence of Cationisation on the good results so obtained.

The present research differs from most of those carried previously in that Cationisation is to carried from the basic conversion of CHIPTAC to EPTAC, dyeing studying kinetics and thermodynamics of the dyeing as well as the performance properties.

CHAPTER THREE

3.0: MATERIALS AND METHODS

3.1: Materials and Chemicals.

The following materials and reagents were used:

i) Carded cotton sliver from the Departmental Spinning laboratory.

ii) 3-Chloro-2-hydroxy propyl trimethyl ammonium chloride (CHIPTAC)(65%W/V) from Sigma Aldrich Chemie, GmBH – United States (USA).

iii) Potassium Hydroxide (MAY & BAKER Nig. Ltd).

iv) Sodium Hydroxide (MAY & BAKER Nig. Ltd).

v) Cuprous phenyl Brilliant Blue 2BL [C I Direct Blue158:1].

3.2: Equipment and Apparatus.

i) Dual split beam UV Spectrophotometer (UVS- 2700/UVS-2800).

ii) SANFA- DK-420 Electric Thermostatic Water Bath Boiler (SEARCH TECH-INSTRUMENT England).

iii) Sherwood-Colorimeter-257,(Sherwood Scientific Ltd Cambridge, United Kingdom).

3.3: SCOURING OF COTTON SLIVER.

Carded, 100% Cotton sliver obtained from Departmental laboratory was scoured using caustic soda solution, 4% on weight of material (OWM) before modification with EPTAC.

3.3.1: Procedure.

The fibres were boiled in 100ml of 4% w/v caustic soda solution for one hour using 40:1liquor ratio.

3.4.PREPARATION OF EPTAC AND CATIONIZATION OF COTTON

3.4.1: Preparation of EPTAC.

Caustic soda (50%W/V, 12.64g) solution was gradually added to CHIPTAC aqueous solution (65%W/V,45.65g) contained inside a beaker at room temperature within 20 minutes. After the last drop, the content of the beaker was further allowed to stand for another 30 minutes to effect complete reaction.

3.4.2: Cationization of Scoured Cotton Sliver using EPTAC.

Six (6) portions of 40g each scoured sliver were set aside for cationization using 5%, 10%, 15%, 20%, 25% on weight of materials (OWM) and the sixth as control that is uncationised

sample.Five beakers containing the stated percentages of EPTAC were made up to liquor ratio of 20:1 with distilled water and placed in an electric water bath (DK 420) at 30^0C.

The scoured sliver was wetted out and dropped in each beaker. The temperature was rapidly raised to 80^0C in 20-25 minutes and maintained for additional 20 minutes to attain equilibrium.10% (OWM potassium hydroxide solution from 45%W/V stock solution was added to each beaker at 80^0C and maintained for another 45 minutes.

3.5: FTIR CHARACTERISATION.

The raw and chemically treated samples were characterized by FTIR spectrometer at NARICT, Basawa Zaria. The fibres were ground and pressed into the KBr pellets and run through the spectrometer.

3.6:DYEING SCOURED COTTON SLIVER WITH DIRECT DYE.

The thermodynamic and kinetic studies of dyeing of the carded sliver using Cuprophenyl Brilliant Blue 2BL direct dye was done for the purposes of studying the substantivity and diffusion of the dye for the cationized cotton, as well as wash and light fastness properties of the dyed fibre.

3.6.1: Infinite Dyeing of Cationized Cotton to Determine Kinetic Parameters.

Six (6) 250ml beakers were prepared containing 1ml from 2% stock solution of the dye which was diluted to 100:1 liquor ratio were placed in a DK 420 thermostatic bath one at a time for dyeing the cationised and uncationised samples at temperatures of 30^0C, 40^0C, 50^0C and 60^0C repectively.

When a beaker was conditioned to the required temperature, a 5g wetted out sliver was introduced and 0.1ml of dye withdrawn at an interval of 5minutes, starting with 0 minutes

followed by 5, 10, 15, 20, 25, 30, 35, 40 and 45 minutes respectively. Each withdrawn 0.1ml dye was placed and diluted to 5ml in a sample bottle followed by measurement of absorbance using Sherwood colorimeter and recorded. When the tenth 0.1ml of the dye was withdrawn, dyeing was continued up to the end of 4hrs and the last 0.1ml dye was withdrawn representing sample at infinity time of dyeing.

This procedure was carried out for control, 5%, 10%, 15%, 20% and 25% EPTAC concentrations for temperatures of 30^0C, 40^0C, 50^0C and 60^0C.

Absorbancies for 0 up to 45minutes were termed A_t =absorbance at time t, while A_∞=absorbance at infinity (4hrs).

In this dyeing it was assumed that dye concentration in the dye bath did not change.

Furthermore, values of diffusion coefficient for all the samples were determined using the equation (Vickerstaff, 1954):

$$\frac{A_t}{A\infty} = 2\sqrt{\frac{Dt}{\pi}}$$

As there is a direct relation between absorbance and concentration (Beer/Lambert's law), the equation above is applicable.

3.6.2: Dyeing Cationized Cotton to Determine Thermodynamic Parameters.

Similarly for determining thermodynamic parameters, another set of six (6), 25ml beakers were prepared each containing 1ml solution of dye from 2% stock solution and dyeing was at 30^0C, 40^0C, 50^0C and 60^0C.

The 1ml dye in the beakers was diluted to 100ml each, thus making up liquor ratio of 100:1.Before commencement of dyeing, 0.1ml dye each was withdrawn from each beaker using micropipette for absorbance measurement to determine the concentration of dye in solution before dyeing.All the beakers were fully covered using air tight lid supported with polyethylene film to eliminate evaporation and placed in the preset temperature electric

thermostatic water bath. When the beakers were conditioned to the already set temperature, 1g each of cationised cotton sliver was wetted out and dipped inside each beaker.

Dyeing was carried out for 4hrs for all the samples at varying EPTAC concentrations and control. The dyed samples were removed and rinsed thoroughly using cold distilled water. 0.1ml residual dye solution after dyeing was withdrawn from each beaker by means of micropipette and absorbencies were measured to determine concentration of dye inside the fibre $[D]_f$.From values of concentrations of dye before dyeing and that after dyeing, concentration of dye inside the fibre can be determined as well as percentage (%) exhaustion i.e.

$$\%Exhaustion = \frac{[fibre]}{[solution]} x \,\%$$

Where; [fibre] means concentration of dye in fibre
[solution] means concentration of dye in solution before dyeing

3.7: FASTNESS PROPERTIES OF THE DYED SAMPLES.

3.7.1: Wash Fastness.

Wash fastness of dyes on cotton material imply the ability of the dye molecules in the fibre to withstand wet treatment in presence of soap or synthetic detergent solution.

For direct dyes, wash fastness is usually poor due to weaker forces holding the dye inside the fibre; however the situation may be different when cellulose is cationised for attachment of the anionic direct dye (Hauser, 2000).

3.7.1.1: Methodology of wash fastness test.

Wash fastness test was carried out using ISO standard 3.

Dyed sliver was combed and straightened out and from each sample; a piece measuring 10cmx4cm was cut out for the test.

The piece was sandwiched between similar undyed cotton piece and wool fabric piece both measuring 5cmx4cm thus leaving part of the dyed piece exposed.

The washing test was conducted under the following conditions(Nkeonye, 1989) :

Soap ----------5g/l

Soda ash ---------- 2g/l

Liquor ratio ---------- 50:1

Temperature ---------- 60 ± 2^0C

Time ---------- 30 min.

The composite samples were treated under the stated conditions above.

After the test, the samples were removed, rinsed thoroughly and dried at room temperature. The change in colour of the uncovered portion and staining of the adjacent undyed cotton sample were assessed using the Grey scales for assessing change in colour and staining respectively.

3.7.2: Light Fastness.

Dyed samples along with the blue wool standards (1-9)were exposed to natural sun light on templates for up to five (5) days, the level of colour change being recorded daily. The exposure was terminated when the contrast between the exposed and unexposed portions corresponded to Grade3 on the Grey scale for assessing change in colour (Bird et al 1975, Giles et al 1963, Nkeonye,1989). From the results of both cationised and uncationised samples, percentage increase in rating for the cationisesd samples were calculated from the formula:

$$\% \text{ Increase} = \frac{\text{Average rating of treated sampleAverage rating of untreated} * 100}{\text{Average rating of untreated}}$$

3.8: MEASUREMENT OF ABSORBANCE USING COLORIMETER.

Generally many compounds either in solid or solution do absorb ultraviolet or visible light radiation when the light ray passes through them. In the case of dyesolution, these optical phenomena have a direct bearing on the concentration of the dye solute in the solution.

3.8.1: Procedure.

An AVS 2700/ AVS 2800 UV spectrophotometer was used to determine wavelength of maximum absorption of the dye (Cuprophenyl Brilliant Blue 2BL) also referred to as λ_{max}. Initially the instrument was calibrated with distilled water then followed by the dye solution which was diluted and the value of $\lambda_{max}$was determined.Subsequent measurements of absorbance were carried out using Sherwood colorimeter.In measuring the absorbance for a given dye solution, the colorimeter had to be calibrated usin**g distilled water in a plastic cuvette of 1cm thickness. Similar cuvette was also used in taking absorbance of the dye. As a precautionary measure to prevent tendencies of refraction to occur, surface of the cuvette was wiped with soft tissue paper before and after measurement.All values of the absorbancies for the varying concentrations of the solution were recorded in tabular form.**

3.8.2: Determination of concentrations of dye in solution $[D]_S^1$ and fabric $[D]_f$ from measured absorbance values.

Absorption isotherms were constructed using the equilibrium concentrations of dye insolution and in the fabric denoted by $[D]_S^1$ and $[D]_f$. These two variables are linked by the equation:

$$[D]_f = \{[D]_S^O — [D]_S^1\} V/W,$$

Where:

$[D]_S^O$ = original concentration of dye before dyeing.

V = volume of the dye bath and W = mass of fibre dyed in the dye bath.

$[D]_S^O$ is always known, $[D]_S^1$ can be determined from the measured absorbance, and hence $[D]_f$ was obtained from the equation above. However, $[D]_S^1$is better obtained more accurately from the calibration curve which is a plot of absorbance of concentration of dye in fibre against concentration in residual solution.

3.9:CONSTRUCTION OF CALIBRATION CURVE FOR THE DIRECT DYE (C.I DIRECT BLUE 158:1).

Calibration curve for the dye was prepared by setting up the following concentrations of dye from the 2% stock solution: 0.4mg, 0.8mg, 1.2mg, 1.6mg, 2.0mg, 2.4mg, 2.8mg, 3.2mg, 3.6mg; 4.0mg in separate ten conical flasks; content of each flask was diluted with 100ml of distilled water.

Respective absorbance ofeach conical flask was measured and recorded; a curve was plotted of absorbance against concentration. The curve obtained is a straight line passing through the origin (Chapter 4).

3.9.1: Usage of calibration curve.

By Beer /Lambert's law A=K [D]s; where A is absorbance, [D]s is concentration of the dye (solute) in the solution and K a constant. This law has shown that absorbance is directly proportional to concentration (A ∝ [D]s). By plotting A against [D]s, the slope of the curve gives K. [K= A/ [D]s].

Values of corresponding equilibrium concentrations of each conical flask used in calibration above are obtained by multiplying K with the respective

absorbanceSubtracting amount of dye in the fibre $[D]_f$ from concentration of dye before commencement of dyeing $[D]s^o$, the result is amount of dye in solution after dyeing.

To obtain amount of dye in the fibre $[D]_f$,solution, the following is adapted: when 5g of fibre was dyed in 5ml of dye

A 5g cationised fibre (5% EPTAC) was dyed in 5ml of dye solution, initial dye concentration before dyeing was 0.4mg/5ml, absorbance of the dye at equilibrium dyeing was measured to be 0.047. Value of K was determined from the calibration curve for the dye as 5.3582, concentration of dye in solution at equilibrium $[D]_S^1$ is calculated as: Abs. x Constant= 0.047x 5.3582 = 0.25184mg/5ml. Therefore amount of dye in fibre$[D]_f$ =[(0.4— 0.25184)mg/5g] x1000g/kg= 29.63mg/kg

CHAPTER FOUR

4.0: RESULTS AND DISCUSSION

4.1: Cationisation of the cotton cellulose

4.1.1: The results of the Fourier Transform Infrared (FT-IR) Spectroscopy are presented in Table 4:1

Table 4:1 Infrared absorption peaks

Samples	IR- Absorption Peaks cm^{-1}										
	1	2	3	4	5	6	7	8	9	10	11
Control	545.87	1004.95	1329.96	1431.23	1612.44	2128.52	2539.37	2904.89	3285.85	3363.0	4011.11
5%	584.45	651.0	1026.16	1329.96	1426.41	1637.0	2135.27	2535.51	2758.3	2901.04	3304.17
10%	493.79	1011.7	1336.71	1438.94	1644.37	2054.26	2111.16	2312.73	2546.12	2911.64	3311.89
15%	452.32	1003.02	1335.75	1440.87	1528.64	1654.98	1725.38	2038.83	2109.23	2341.66	2534.55
20%	461.0	1014.59	1337.68	1436.05	1505.49	1649.19	2916.47	3342.75	3365.9	3416.05	--------
25%	845.81	990.48	1085.96	1329.96	1418.69	1626.05	2122.73	2223.73	2597.24	2853…78	3130.57

30%	554.55	906.57	1020.38	1333.82	1430.26	1643.41	2135.27	2536.48	2894.28	3355.29	4017.86

It is clear from Table 4:1 that cationization process has been successful consideringthe nature of absorption peaks shown by cationised samples when compared with that of control. For instance, control sample has only twelve (12) peaks showing absorption from 545.87cm^{-1} at peak one (1) to maximum absorption 4266.68cm^{-1} at peak twelve (12). All other cationised samples 5%, 25% and 30% exhibited higher absorptions at peak one (1) of values ranging from 554 to 845cm^{1} while 10%, 15% and 20% clearly showed lower absorptions at peak one (1) with a range of 452 to 493cm^{1}.

In peak twelve (12) all cationised samples apart from sample 30% gave absorptions lower than the contro while in sample 20% no absorption was found.

Furthermore, analysis of the absorptionpeaks identified the following chemical bonds: C-H, C-O, COOH, N H, C=O, O-H and otherswhich were not common either due to stretching, shift or bond vibration.

Table 4.2 Comparison of absorption range and number of peaks.

Sample	Absorption range(minimum to maximum)cm^{-1}	Number of Peaks
Control	545.87 -4266.68	12
5%	584.45 - 4385.31	15
10%	493.79 - 4654.39	17
15%	452.32 - 4268.61	16
20%	461.0 - 3416.05	10
25%	845.81 - 4637.03	19
30%	554.55 - 4395.92	13

4.2 MEASUREMENTS OF FASTNESS PROPERTIES

4.2.1: Wash Fastness.

Wash fastness test based on International Standard Organization Test 3 (ISO test 3) was carried out on both control and cationised samples at the Chemical laboratory of the Textile Department, produced the data shown in Table 4.3

Table 4.3 Wash fastness (ISO 3) results.

Sample	30%		40%		50%		60%	
Control	Change in colour 2-3	Degree of Staining 3	Change in colour 2-3	Degree of Staining 3	Change in colour 2-3	Degree of Staining 3	Change in colour 2-3	Degree of Staining 3
5%	4	3-4	4	3-4	4	3-4	4	3-4
10%	4	3-4	4	3-4	4	3-4	4	3-4
15%	4	3-4	4	3-4	4	3-4	4	3-4
20%	4	3	4	3-4	4	3	4	3
25%	3-4	3	4	3	4	3-4	4	3

From Table 4.3 it is clear that wash fastness ratings for both colour change and colour staining of all cationised samples are better than that of control sample, this stems from the stronger ionic bonds holding theanionic dye on the cationised cotton against the weaker H-bond, Vander Waals and other weak physical forces of attraction in the case of former, control (uncationised) showed an average rating of 2-3 for colour change and 3 for staining while cationised samples have 4 for colour change and 3-4 for staining.

.

4.2.2: Light Fastness

Fastness to light is another important analysis used in determining the performance of a dyed textile material. In this work light fastness test using natural sun light was carried out on all cationised samples and the control. The results are as shown in table 4.4.

Table 4.4 Light fastness of uncationized and cationized dyed cotton

S/No	Dyed Sample	Control	5%	10%	15%	20%25%
1	30°C	2	5	3	3	4	3
2	40°C2		4	3	4	4	4
3	50°C2		4	4	4	4	4
4	60°C2		4	5	5	4	5
5	% Increase---	112.5	87.5	50.0	50.0	50.0	

Light fastness results indicated that all cationised samples have an average increase of between 50-112.5% when compared with the control, thus have better light fastness ratings of 3-5 as shown in the Table 4.4 above. Control sample gave an average rating of 2 irrespective of the dyeing temperatures.

4.3 THERMODYNAMIC PARAMETERS STUDIES.

4.3.1: Calibration curve for the direct dye.

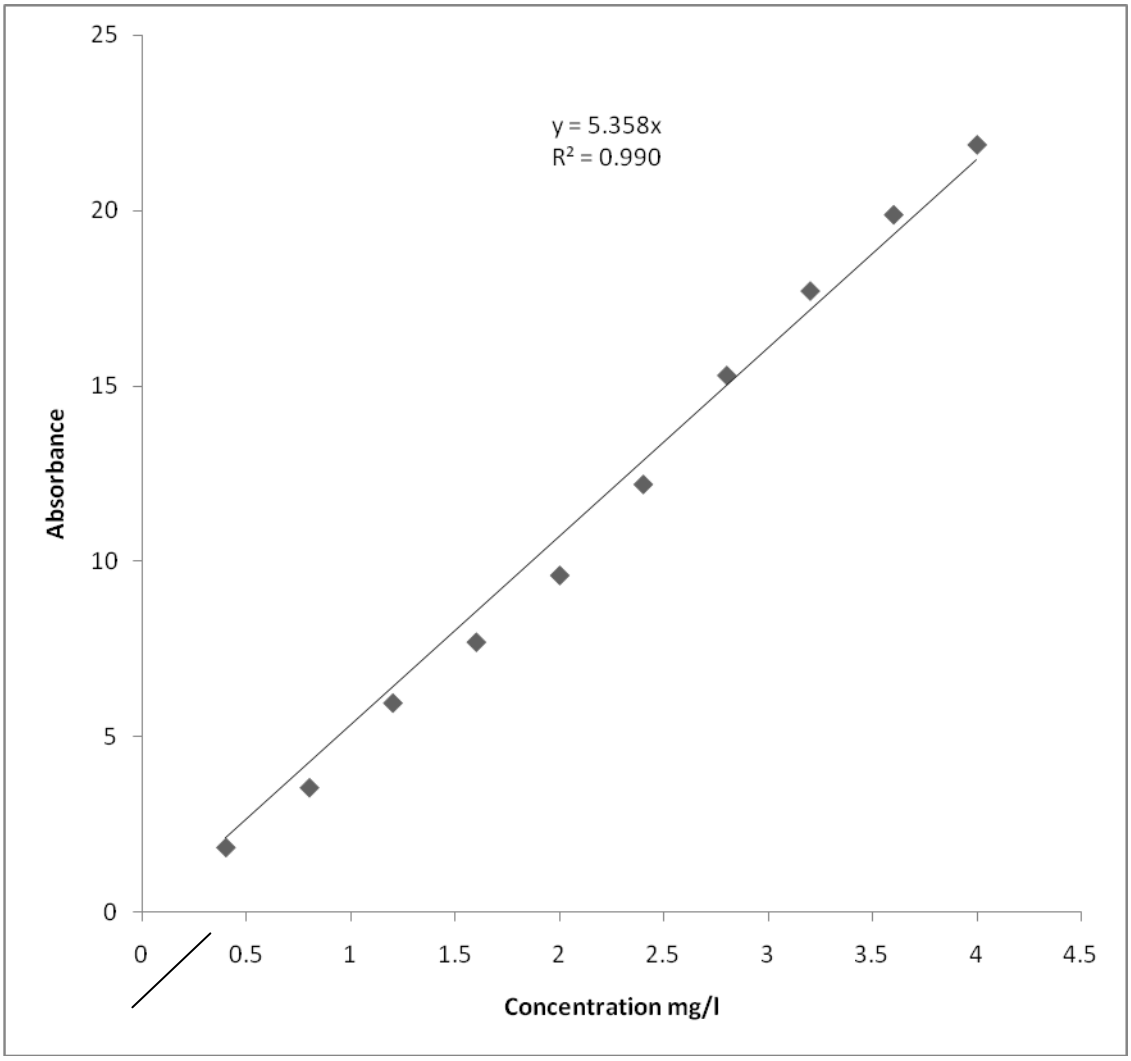


Fig. 4.2 Calibration curve for C.I .Direct Blue 158:1

4.3.2: Available Sites for Dye attachment (Saturation limit).

(sData was obtained from the intercept of Langmuir reciprocal plots of $1/[D]_f$ against $1/[D]_{S)}$

Table 4:6 Available Sites for Dye attachment.

Sample	Available sites/saturation limit(x 10^{-7}mole/kg)			
***	30^0C	40^0C	50^0C	60^0C
Control	….	….	….	……
5%	19.724	25.840	25.381	25.575
10%	21.786	21.882	20.534	21.322
15%	21.552	21.186	25.381	21.186
20%	21.368	22.075	21.413	20.747

It is clear from table 4.6 that there are no sites for dye attachment in the case of control sample, but sites are vividly seen in the case of all cationised samples. Furthermore available sites are observed to be independent of EPTAC concentration, as all the variable concentrations of EPTAC gave same number of sites due to the fact that same amount of fibre was used.

4.3.3: Affinities of control and cationised samples.

(ΔU^O were calculated from the formula - $\Delta U^O = RT \ln K$)

Table 4:7 Affinity values (ΔU^O)

Sample	**Affinity(kjmol^{-1})**

***	30^0C	40^0C	50^0C	60^0C
Control	---------	---------	---------	---------
5%	**-5253.67**	**-3135.51**	**-1780.93**	**-642.72**
10%	-2686.71	-3376.21	-2363.3	-546.743
15%	-3018.72	-1893.62	-1780.93	-549.743
20%	-2934.63	-3659.97	-2401.06	------

When compared with affinities of control samples, cationised samples showed higher affinity values in all the dyeing temperature ranges. This situation has shown remarkable improvement for cotton dye ability with direct dye. In addition, higher affinity value is also a measure of better fastness properties owing to stronger bonds between the fibre and the dye.

4.3.4 Entropy of dyeing.

[Data was obtained from intercepts of affinity (ΔU^O) against temperature (T) plots].

Table 4:8 Entropy values (ΔS)

Sample	Entropy of dyeing ($kJmol^{-1}$)
Control	-
5%	-151.87

10%	-74.337
15%	-75.196
20%	-26.676

Table 4:8 above had shown that entropy value for control is the highest, an indication that there are freer dye molecules in the residual solution which were not attached to the fibre. All cationised samples however have lower entropy values and within appreciable ranges in all cases showing that dye molecules were attracted and attached to available sites with stronger bonds, in this case ionic bonds between positively charged cotton fibres (cations) and negatively charged dye molecules (anions).

4.3.5: Heat of Dyeing (ΔH)

[Data is obtained as slopes of affinity (ΔU^{O}) against temperature (T) plots].

Table 4:9 Heat of dyeing (ΔH)

EPTAC Concentration	Heat of dyeing(ΔH) $kJmol^{-1}$
Control	-4.1
5%	-50999
10%	-25882
15%	-25723
20%	-11349

From the values in the table 4.9, it is seen that the control sample exhibited exothermic reaction meaning that heat is evolved in the process whereas cationised samples portrayed endothermic reaction indicating that heat is absorbed during the dyeing process. This observed trend is associated with the fact that other smaller anions such as hydroxyl, chlorides etc. reacted with the sites; these bonds had to be broken first and energy is required for that.

Values of ΔH for all cationised samples exhibited similar trend thus showing the formation of secondary bonds which have to be broken before the dye entered to form the ionic bond with the cationised cotton fibres.

4.3.6 Kinetic Studies

4.3.6.1 Diffusion coefficient

[Data was obtained as intercept of Log D_T against 1/T plots].

Table 4:10 Diffusion coefficients (s^{-1})

Temp(°K	Control	5%	10%	15%	20%	25%
303	3.929	4.488	2.860	3.951	2.417	1.447
313	3.143	2.245	1.796	3.491	2.213	1.239
323	2.246	2.028	1.143	2.417	2.028	1.011
333	2.074	2.009	1.057	2.246	1.654	0.813

No definite trend was observed as far as diffusion coefficients for all the cationised samples, however, diffusion coefficient appeared to decrease with increase in temperaturefor both control and cationised samples. Since diffusion coefficient is a measure of rate ofdyeing, cationised sample 5% and 15% exhibited the highest rate of dyeing at lower temperature of 303°Kelvin, from this point the rate began to reduce to the lowest values at 333° Kelvin.

4.3.7 Activation Energy

[Data from slopes of Log $D_T$against 1/T plots].

Table 4:11 Activation energy

EPTAC Concentration	Activation Energy ($kJmol^{-1}$)
Control	-15.183
5%	-4.794
10%	-5.066
15%	-5.669
20%	-5.848
25%	-5.951

From the activation energy table, control sample has the highest activation energy valuewhile all cationised samples are having lower values within the range of -4.794to -

5.951.Conclusively, it is clear that dyeing cationised sample is easier than that of control sample requiring little energy.

4.3.8: Dye Exhaustion

Table 4.12 %Exhaustion of the dye by the fibre.

Plot of % exhaustion against temp(T) K

Temp(K)	Control	5%	10%	15%	20%
303	21.51899	85.34483	53.41615	37.14286	61.00629
313	61.78344	60.8	63.33333	51.40845	74.12587
323	65.24064	62.0915	67.64706	34.54545	43.75
333	51.51515	51.85185	81.13208	92.45283	95.65217

From Table 4.12 dye exhaustion appeared to increase with increase in dyeing temperature in the case of uncationised sample and higher EPTAC concentrations for Cationisation but 5% EPTAC being observed to decrease with rise in temperature, with highest values of 85% at 303K.

CHAPTER FIVE

5.0: SUMMARY ,CONCLUSION AND RECOMMENDATION

5.1 SUMMARY

Cotton cellulose (100%) sliver was purified and cationised prior to dyeing with a direct dye Cupro brilliant blue 2BL (CI Direct Blue158:1). All the dyed samples (cationised and uncationised) were characterised (FTIR), subjected to performance tests (wash and light fastness) as well as kinetics and thermodynamics parameters were studied. Results indicated an improvement in dye exhaustion ranging from 31-65% for uncationised samples (control) to 60-85% cationised samples i.e. 51.04% increase. Improvement in wash and light fastness were seen, control samples gave an average rating of 2-3 (colour change) and 3(staining), cationised samples have 4 (colour change) while 3-4(staining). Light fastness showed percentage increase of 50-112.5%.

Cationisation resulted in improvement of affinity for the cationised cotton by the dye ranging from -549.743 to -5253.67 as compared to treated control which showed very low affinity. Activation energy, heat of dyeing, entropy of cationised samples gave a more favourable values that enhance dyeing condition than that given by uncatinised samples (control).

5.2 CONCLUSION

From the studies carried out on the cationised and uncationised cotton cellulose with a directdye (Cuprophenyl Brilliant Blue 2BL (CI Direct Blue 158:1) the following conclusions are made:

i) Cationisation of cotton with EPTAC imparted a surface positive charge to the cotton cellulose which made the cationised cotton susceptible to anionic dye.

ii) The surface positive charge increased the substantivity of the anionic direct dye for the cotton cellulose fibre thus dye exhaustion is seen to increase by 304.76% (21% exhaustion for control and up to 85% exhaustion for cationised samples). At the same time no much heating is required thus power saving advantage.

iii) The direct dye was thus retained on the cotton structure by ionic or electrostatic attraction instead of the usual H-bonding and vander Waals forces for direct dyes on the uncationised cotton fibre as wash fastness rating of 4-5 were recorded for cationised samples as against 2-3 for control, at the same time light fastness increased by 50-112.5%.

iv) The heat of dyeing values confirmed the process is exothermic and values of 11349-50999kJmol^{-1} favour the dyeing of cationised samples.

v) The higher affinity of the dye for cationised cotton celluloseas compared to uncationisedcotton cellulose shown on Table 4.6 is a clear indication that Cationisation has been successfully carried out and sites for dye attachment were provided.

vi) The results of the tests carried out as shown on Tables 4.2, 4.3,4.4,4.5,4.6,4.7,4.8,4.9,4.10 and 4.11 indicated that values given by 5% EPTAC concentration are better in many cases, by this it is evident that this is the optimum concentration of EPTAC for the Cationisation, with cost and pollution in mind beside better performances.

5.3 RECOMMENDATION

- Further research to determine the influence of cationisation on the cotton fabrics and yarn should be investigated
- Further dyeing studies on cationized cotton using other anionic dyes such as vat, acid, reactive and others are recommended
- Industrial assessment of the process to compare level of effluent discharges, power savings, and reduction of colour in residual dye bath as well as volume of water used is recommended.

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APPENDICES

Appendix 1 Thermodynamic Data

Adsorption data for control and cationised samples at different temperatures

Table A1.1: Absorbance for control sample

Time(min)	30^0C	40^0C	50^0C	60^0C
0	0.099	0.092	0.118	0.473
5	0.083	0.083	0.116	0.396
10	0.078	0.078	0.110	0.227
15	0.054	0.070	0.108	0.195
20	0.052	0.061	0.105	0.148
25	0.051	0.059	0.102	0.145
30	0.048	0.057	0.098	0.144
35	0.045	0.054	0.095	0.141
40	0.044	0.049	0.091	0.138
45	0.042	0.046	0.087	0.125
260	0.041	0.036	0.048	0.090

Table A1.2: Absorbance for 5% sample

Time(min)	30^0C	40^0C	50^0C	60^0C
0	0.145	0.073	0.167	0.219
5	0.106	0.063	0.159	0.221

10	0.098	0.059	0.154	0.188
15	0.086	0.055	0.148	0.108
20	0.082	0.052	0.136	0.104
25	0.079	0.048	0.127	0.101
30	0.068	0.043	0.119	0.098
35	0.064	0.037	0.117	0.095
40	0.053	0.035	0.211	0.091
45	0.050	0.032	0.087	0.087
260	0.047	0.029	0.051	0.078

Table A1.3: Absorbance for 10% sample

Time(min)	30^0C	40^0C	50^0C	60^0C
0	0.125	0.080	0.123	0.225
5	0.115	0.078	0.120	0.219
10	0.105	0.074	0.108	0.200
15	0.098	0.070	0.098	0.187
20	0.080	0.067	0.096	0.178
25	0.067	0.064	0.085	0.159
30	0.058	0.062	0.084	0.152

35	0.052	0.058	0.078	0.146
40	0.051	0.053	0.073	0.131
45	0.050	0.045	0.070	0.128
260	0.048	0.041	0.068	0.116

Table A1.4: Absorbance for 15% sample

Time(min)	30^0C	40^0C	50^0C	60^0C
0	0.118	0.168	0.123	0.207
5	0.109	0.159	0.106	0.195
10	0.081	0.148	0.101	0.186
15	0.079	0.135	0.097	0.17
20	0.68	0.119	0.091	0.163
25	0.63	0.116	0.084	0.155
30	0.59	0.11	0.078	0.149

35	0.52	0.096	0.072	0.138
40	0.48	0.087	0.065	0.129
45	0.43	0.071	0.059	0.117
260	0.041	0.068	0.047	0.098

Table A1.5: Absorbance for 20% sample

Time(min)	30^0C	40^0C	50^0C	60^0C
0	0.166	0.106	0.164	0.227
5	0.155	0.096	0.152	0.218
10	0.143	0.087	0.148	0.214
15	0.138	0.074	0.139	0.209
20	0.124	0.069	0.126	0.204
25	0.117	0.062	0.113	0.198
30	0.096	0.057	0.109	0.193
35	0.083	0.048	0.104	0.187

40	0.068	0.039	0.099	0.179
45	0.046	0.033	0.087	0.168
260	0.035	0.024	0.068	0.157

Table A1.6: Absorbance for 25% sample

Time(min)	30^0C	40^0C	50^0C	60^0C
0	0.133	0.555	0.115	0.216
5	0.129	0.405	0.111	0.208
10	0.124	0.309	0.108	0.189
15	0.119	0.206	0.095	0.167
20	0.114	0.109	0.089	0.154
25	0.11	0.103	0.081	0.146
30	0.107	0.097	0.076	0.136
35	0.103	0.085	0.071	0.131
40	0.098	0.079	0.064	0.129

45	0.084	0.074	0.053	0.122
260	0.063	0.069	0.032	0.103

Data for Langmuir plots

Dye concentrations in initial bath, fabric and residual bath [D]so,[D]f, and[D]S1

Table A1.7:Data for Control sample at 30^0C, 40^0C, 50^0C and 60^0C

	300c		400c		500c		600c	
[D]S0 mg/ml	[D]S1 mg/ml	[D]f mg/g	[D]S1 mg/ml	[D]f mg/g	[D]S1 mg/ml	[D]f mg/g	[D]S1 mg/ml	[D]f mg/g
0	0	0	0	0	0	0	0	0
8	0.10819	7.89181	0.004869	7.995131	0.00703	7.992968	0.021638	7.978362
16	0.12334	15.87666	0.004869	15.99513	0.00757	15.99243	0.027048	15.97295
24	0.13957	23.86043	0.005951	23.99405	0.00866	23.99134	0.030294	23.96971
32	0.16067	31.83933	0.007032	31.99297	0.01028	31.98972	0.03408	31.96592
40	0.18771	39.81229	0.008114	39.99189	0.01244	39.98756	0.040031	39.95997
48	0.2272	47.7728	0.010278	47.98972	0.01515	47.98485	0.048145	47.95185
56	0.2813	55.7187	0.011901	55.9881	0.02164	55.97836	0.059506	55.94049
64	0.37326	63.62674	0.016229	63.98377	0.03138	63.96862	0.081144	63.91886
72	0.5626	71.4374	0.024343	71.97566	0.06437	71.93563	0.119011	71.88099

80	1.13602	78.86398	0.047604	79.9524	0.06437	79.93563

Table A1.8 Data for 5% EPTAC samples at 30^0C, 40^0C, 50^0C and 60^0C

	30^0C		40^0C		50^0C		60^0C	
[D]S0	[D]S1	[D]f	[D]S1	[D]f	[D]S1	[D]f	[D]S1	[D]f
mg/ml	mg/ml	mg/g	mg/ml	mg/g	mg/ml	mg/g	mg/ml	mg/g
0	0	0	0	0	0	0	0	0
8	0.064374	1.587125	0.080603	1.583879	0.139568	1.572086	0.208811	1.558238
16	0.069784	3.186043	0.085472	3.182906	0.149607	3.170079	0.230449	3.15391
24	0.080603	4.783879	0.096291	4.780742	0.171484	4.765703	0.241268	4.751746
32	0.090881	6.381824	0.11252	6.377496	0.193123	6.361375	0.300233	6.339953
40	0.101701	7.97966	0.128749	7.97425	0.230449	7.95391	0.348378	7.930324
48	0.123339	9.575332	0.155256	9.568949	0.273185	9.545363	0.418162	9.516368
56	0.155256	11.16895	0.193123	11.16138	0.342969	11.13141	0.481995	11.1036
64	0.208811	12.75824	0.256956	12.74861	0.455488	12.7089	0.697838	12.66043
72	0.311052	14.33779	0.391114	14.32178	0.697838	14.26043	1.044053	14.19119
80	0.643742	15.87125	0.80603	15.83879	1.395677	15.72086	2.088106	15.58238

Table A1.9: Data for 5% EPTAC sample at 30^0C, 40^0C,50C and 60^0C

10% EPTAC

	30^0C		40^0C		50^0C		60^0C	
[D]S0 mg/ml	[D]S1 mg/ml	[D]f mg/g	[D]S1 mg/ml	[D]f mg/g	[D]S1 mg/ml	[D]f mg/g	[D]S1 mg/ml	[D]f mg/g
0	0	0	0	0	0	0	0	0
16	0.146059	3.170788	0.124421	3.175116	0.205565	3.158887	0.340805	3.131839
24	0.162288	4.767542	0.14065	4.77187	0.232613	4.753477	0.389491	4.722102
32	0.183926	6.363215	0.156878	6.368624	0.26507	6.346986	0.443587	6.311283
40	0.216384	7.956723	0.183926	7.963215	0.27048	7.945904	0.519322	7.896136
48	0.259661	9.548068	0.221794	9.555641	0.362443	9.527511	0.643742	9.471252
56	0.319166	11.13617	0.27589	11.14482	0.454406	11.10912	0.80603	11.03879
64	0.427358	12.71453	0.362443	12.72751	0.589646	12.68207	1.017005	12.5966
72	0.643742	14.27125	0.53555	14.29289	0.908813	14.21824	1.552555	14.08949
80	1.287485	15.7425	1.125197	15.77496	1.823035	15.63539	3.10511	15.37898

Table A1.10 Data for 10% EPTAC samples at 30^0C, 40^0C,50C and 60^0C

	30^{0}C		40^{0}C		50^{0}C		60^{0}C	
[D]S0 mg/ml	[D]S1 mg/ml	[D]f mg/g	[D]S1 mg/ml	[D]f mg/g	[D]S1 mg/ml	[D]f mg/g	[D]S1 mg/ml	[D]f mg/g
0	0	0	0	0	0	0	0	0
16	0.128749	3.17425	0.210974	3.157805	0.178517	3.164297	0.346214	3.130757
24	0.144436	4.771113	0.238022	4.752396	0.200155	4.759969	0.389491	4.722102
32	0.166075	6.366785	0.27589	6.344822	0.227203	6.354559	0.448997	6.310201
40	0.193123	7.961375	0.313757	7.937249	0.26507	7.946986	0.524731	7.895054
48	0.232072	9.553586	0.378672	9.524266	0.313757	9.537249	0.643742	9.471252
56	0.289414	11.14212	0.476045	11.10479	0.394901	11.12102	0.80603	11.03879
64	0.385705	12.72286	0.643742	12.67125	0.524731	12.69505	1.071101	12.58578
72	0.589646	14.28207	0.962909	14.20742	0.80603	14.23879	1.552555	14.08949
80	1.179293	15.76414	1.931227	15.61375	1.606651	15.67867	3.159206	15.36816

Table A1.11 Data for 15% EPTAC samples at 30^{0}C, 40^{0}C,50C and 60^{0}C

	300C		400C		500C		600C	

[D]S0	[D]S1	[D]f	[D]S1	[D]f	[D]S1	[D]f	[D]S1	[D]f
mg/ml	mg/ml	mg/g	mg/ml	mg/g	mg/ml	mg/g	mg/ml	mg/g
8	0.124421	1.575116	0.091963	1.581607	0.162288	1.567542	0.448997	1.510201
16	0.14065	3.17187	0.097373	3.180525	0.178517	3.164297	0.497683	3.100463
24	0.156878	4.768624	0.113602	4.77728	0.200155	4.759969	0.589646	4.682071
32	0.178517	6.364297	0.12983	6.374034	0.227203	6.354559	0.643742	6.271252
40	0.205565	7.958887	0.151469	7.969706	0.26507	7.946986	0.751934	7.849613
48	0.248842	9.550232	0.178517	9.564297	0.313757	9.537249	0.908813	9.418237
56	0.281299	11.14374	0.221794	11.15564	0.394901	11.12102	1.125197	10.97496
64	0.41113	12.71777	0.297528	12.74049	0.524731	12.69505	1.498459	12.50031
72	0.638333	14.27233	0.438178	14.31236	0.80603	14.23879	2.250394	13.94992
80	1.233389	15.75332	0.881765	15.82365	1.606651	15.67867	4.500787	15.09984

Table A1.12 Data for 20% EPTAC samples at 30^0C, 40^0C,50C and 60^0C

	300C		400C		500C		600C	
[D]S0	[D]S1	[D]f	[D]S1	[D]f	[D]S1	[D]f	[D]S1	[D]f

mg/ml	mg/ml	mg/g	mg/ml	mg/g	mg/ml	mg/g	mg/ml	mg/g
0	0	0	0	0	0	0	0	0
8	0.124421	1.575116	0.091963	1.581607	0.162288	1.567542	0.448997	1.510201
16	0.14065	3.17187	0.097373	3.180525	0.178517	3.164297	0.497683	3.100463
24	0.156878	4.768624	0.113602	4.77728	0.200155	4.759969	0.589646	4.682071
32	0.178517	6.364297	0.12983	6.374034	0.227203	6.354559	0.643742	6.271252
40	0.205565	7.958887	0.151469	7.969706	0.26507	7.946986	0.751934	7.849613
48	0.248842	9.550232	0.178517	9.564297	0.313757	9.537249	0.908813	9.418237
56	0.281299	11.14374	0.221794	11.15564	0.394901	11.12102	1.125197	10.97496
64	0.41113	12.71777	0.297528	12.74049	0.524731	12.69505	1.498459	12.50031
72	0.638333	14.27233	0.438178	14.31236	0.80603	14.23879	2.250394	13.94992
80	1.233389	15.75332	0.881765	15.82365	1.606651	15.67867	4.500787	15.09984

Data for Langmuir reciprocal plots (1/[D]f against 1/[D]S1)

Table A1.13 Data for control samples

30^0c		40^0c	
1/[D]S1	**1/[D]f**	**1/[D]S1**	**1/[D]f**
9.242998	0.633568	205.3962	0.625381
8.10767	0.314928	205.3962	0.312595
7.164864	0.209552	168.0514	0.208385
6.223937	0.157038	142.1973	0.156284

5.327367	0.125589	123.2377	0.125025
4.401408	0.104662	97.29292	0.104189
3.554924	0.089736	84.02571	0.089305
2.679098	0.078583	61.61885	0.078145
1.777462	0.069991	41.07923	0.069468
0.880266	0.0634	21.00643	0.062537
60^0c		50^0c	
46.21414	0.626695	168.0514	0.625465
36.97131	0.313029	142.1973	0.312637
33.0101	0.208597	132.0404	0.208399
29.34231	0.156417	115.5353	0.156292
24.98062	0.125125	97.29292	0.125032
20.7704	0.104271	80.37241	0.104194
16.80514	0.089381	66.0202	0.08931
12.32377	0.078224	46.21414	0.078151
8.402571	0.069559	31.87182	0.069475
		15.53416	0.06255

Table A1.14 Data for 5% EPTAC samples

	30^0C		40^0C
1/[D]S1	**1/[D]f**	**1/[D]S1**	**1/[D]f**
8.107742	0.104435	8.887333	0.156801
6.440996	0.089534	7.767081	0.125404
4.789029	0.078381	6.440996	0.104505
3.214897	0.069746	5.178055	0.089595

1.553416	0.063007	3.891717	0.07844
		2.556799	0.069824
		1.240648	0.063136

	50^0C		60^0C
5.178055	0.157199	3.330749	0.15773
4.339356	0.125724	2.870443	0.126098
3.660526	0.104763	2.391417	0.105082
2.915718	0.089836	2.074709	0.090061
2.195446	0.078685	1.432997	0.078986
1.432997	0.070124	0.957806	0.070466
0.716498	0.06361	0.478903	0.064175

Table A1.15 Data for 10% EPTAC samples

	30^0c		40^0c
1/[D]S1	**1/[D]f**	**1/[D]S1**	**1/[D]f**
4.621414	0.12568	5.436957	0.125577
3.851178	0.104733	4.508696	0.10465
3.133162	0.089798	3.624638	0.089728
2.339956	0.07865	2.759053	0.07857
1.553416	0.070071	1.867238	0.069965

0.776708	0.063522	0.888733	0.063392
	50^0c		60^0c
3.697131	0.125851	1.925589	0.126644
2.759053	0.104959	1.553416	0.105583
2.200673	0.090016	1.240648	0.09059
1.695932	0.078851	0.98328	0.079387
1.100337	0.070332	0.644099	0.070975
0.548536	0.063957	0.32205	0.065024

Table A1.16 Data for 15%EPTAC samples

	30^0c		40^0c
1/[D]S1	**1/[D]f**	**1/[D]S1**	**1/[D]f**
5.178055	0.125606	3.187182	0.125988
4.309011	0.104673	2.640808	0.104995
3.455263	0.08975	2.100643	0.090051
2.592658	0.078599	1.553416	0.078919
1.695932	0.070018	1.03852	0.070386
0.847966	0.063435	0.517806	0.064046

	50^0c		60^0c
3.772583	0.125834	1.905738	0.126662
3.187182	0.104852	1.553416	0.105583
2.532282	0.08992	1.240648	0.09059
1.905738	0.078771	0.933619	0.079455
1.240648	0.070231	0.644099	0.070975
0.622413	0.063781	0.316535	0.06507

Table A1.17 Data for 20% EPTAC samples

	30^0c		40^0c
1/[D]S1	**1/[D]f**	**1/[D]S1**	**1/[D]f**
4.864646	0.125646	6.60202	0.125475
4.018621	0.10471	5.601714	0.104556
3.554934	0.089736	4.508696	0.089641
2.432323	0.07863	3.361028	0.07849
1.566581	0.070066	2.28218	0.06987
0.810774	0.063479	1.134089	0.063197

	50^0c		60^0c

3.772583	0.125834	1.329903	0.127395
3.187182	0.104852	1.100337	0.106177
2.532282	0.08992	0.888733	0.091116
1.905738	0.078771	0.667352	0.079998
1.240648	0.070231	0.444367	0.071685
0.622413	0.063781	0.222183	0.066226

Kinetics Data

Table A1.41: Data for plot of Log $D_T$against 1/T

CONTROL SAMPLE

T(Kelvin)	(t½) Sec.	DT*10E-3	Log DT	1/T*10E-3
303	12.52	3.929	-2.4057	3.3
313	15.65	3.143	-2.5027	3.195
323	21.9	2.246	-2.6486	3.096
333	16	3.074	-2.7123	3

5%EPTAC

T(Kelvin)	(t½) Sec.	DT*10E-3	LogDT	1/T*10E-3

303	10.91	4.488	-2.3479	3.3
313	21.91	2.245	-2.4573	3.195
323	24.26	2.028	-2.5129	3.096
333	14.09	3.491	-2.5951	3

10%EPTAC

T(Kelvin)	(t½) Sec.	DT*10E-3	Log DT	1/T*10E-3
303	17.2	12.52	-2.2094	3.3
313	27.39	14.09	-2.4672	3.195
323	15.65	20.35	-2.6914	3.096
33	17.22	21.9	-2.9231	3

15%EPTAC

T(Kelvin)	(t½) Sec.	DT*10E-3	Log DT	1/T*10E-3
303	12.52	3.951	-2.4033	3.3
313	14.09	3.491	-2.4571	3.195

323	20.35	2.417	-2.6167	3.096
333	21.9	2.246	-2.7183	3

20%EPTAC

T(Kelvin)	(t½) Sec.	DT*10E-3	Log DT	/T*10E-3
303	20.35	2.417	-2.6167	3.3
313	22.23	2.213	-2.655	3.195
323	24.26	2.028	-2.7364	3.096
333	29.74	1.645	-2.7838	3

25%EPTAC

T(Kelvin)	(t½) Sec.	DT*10E-3	Log DT	1/T*10E-3
303	34	1.447	-2.1089	3.3
313	9.39	5.239	-2.2808	3.195
323	54	0.911	-2.372	3.096
333	10.96	4.513	-2.4563	3

APPENDIX II Graphs and Charts

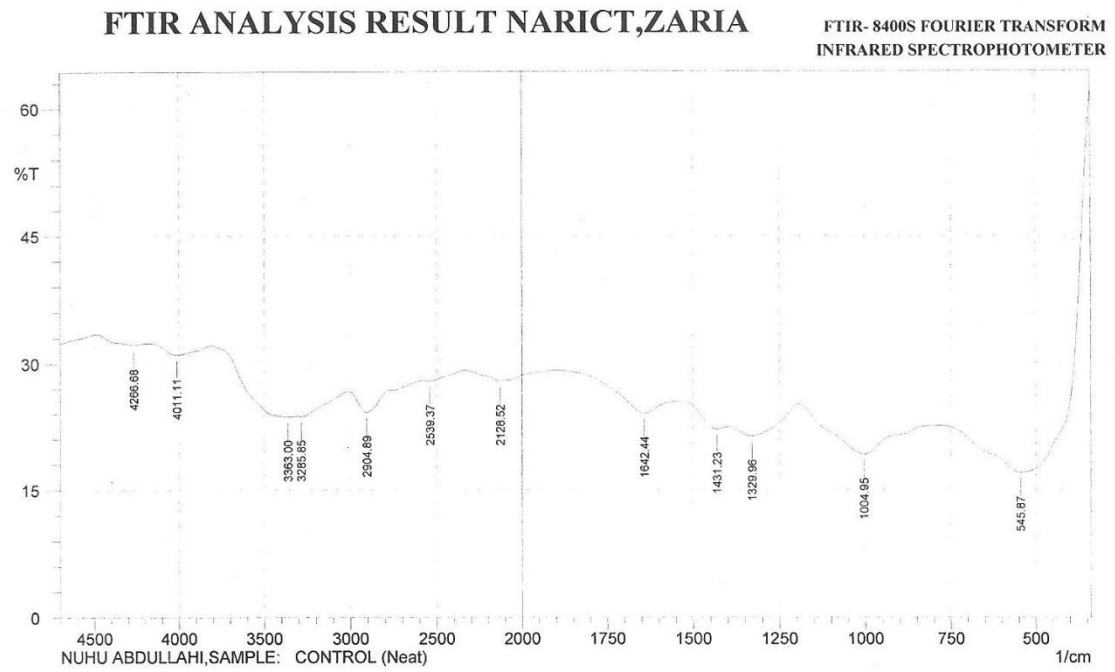


Figure A2.1: FTIR Spectra of the Control Sample

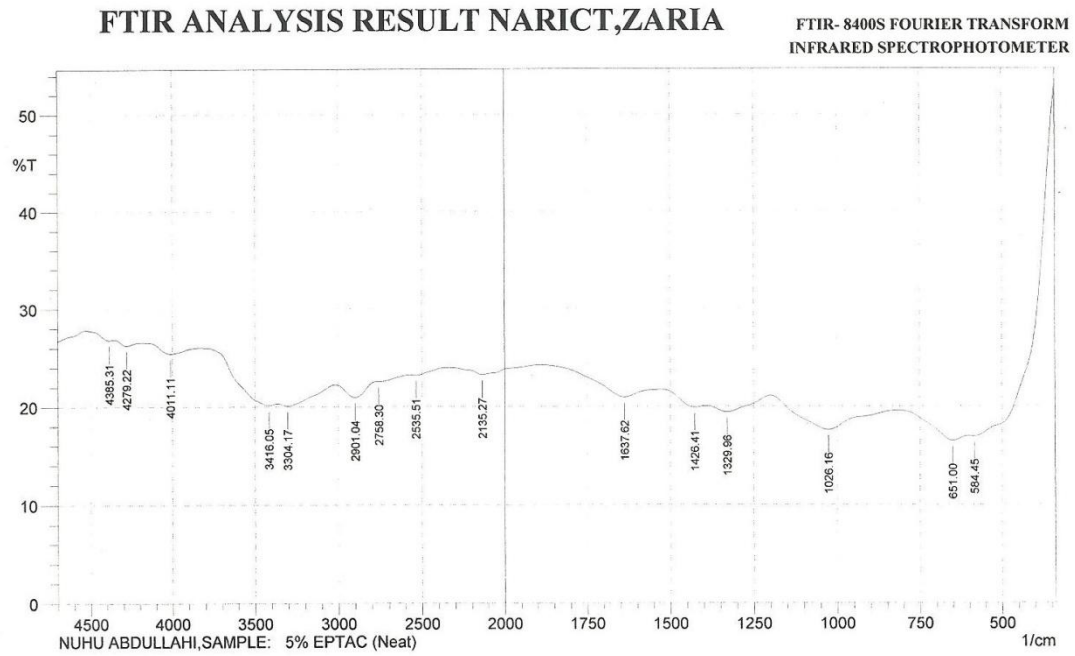


Figure A2: 2 FTIR Spectra of the 5% EPTAC Sample

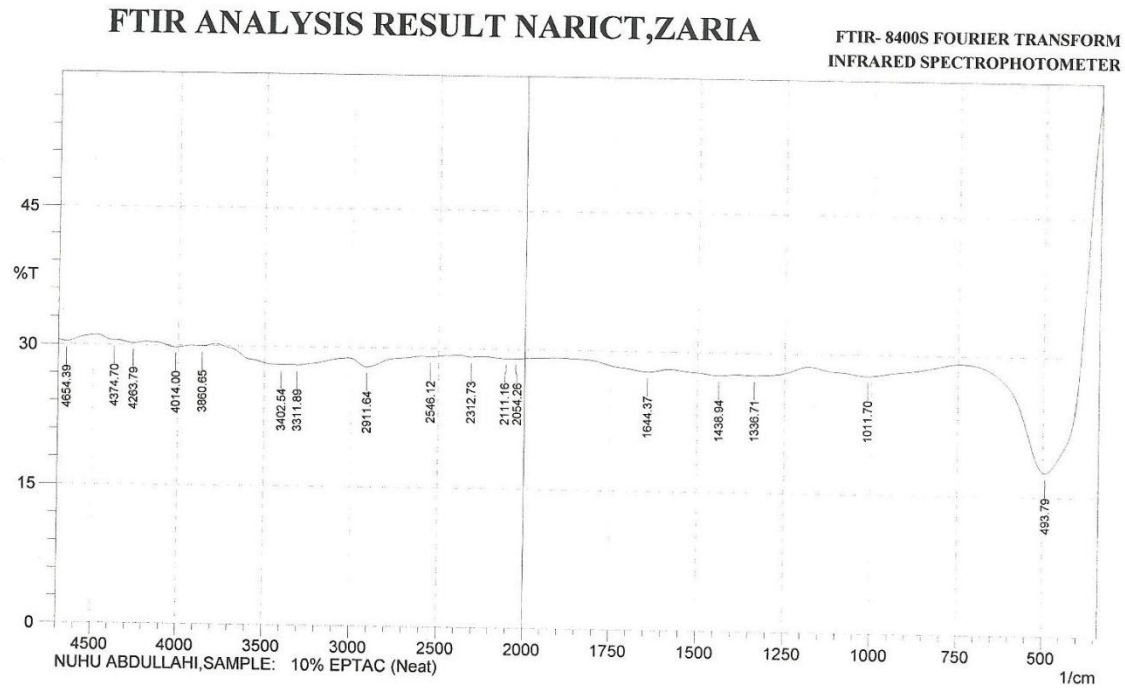


Figure A2.3: FTIR Spectra of the 10% EPTAC Sample

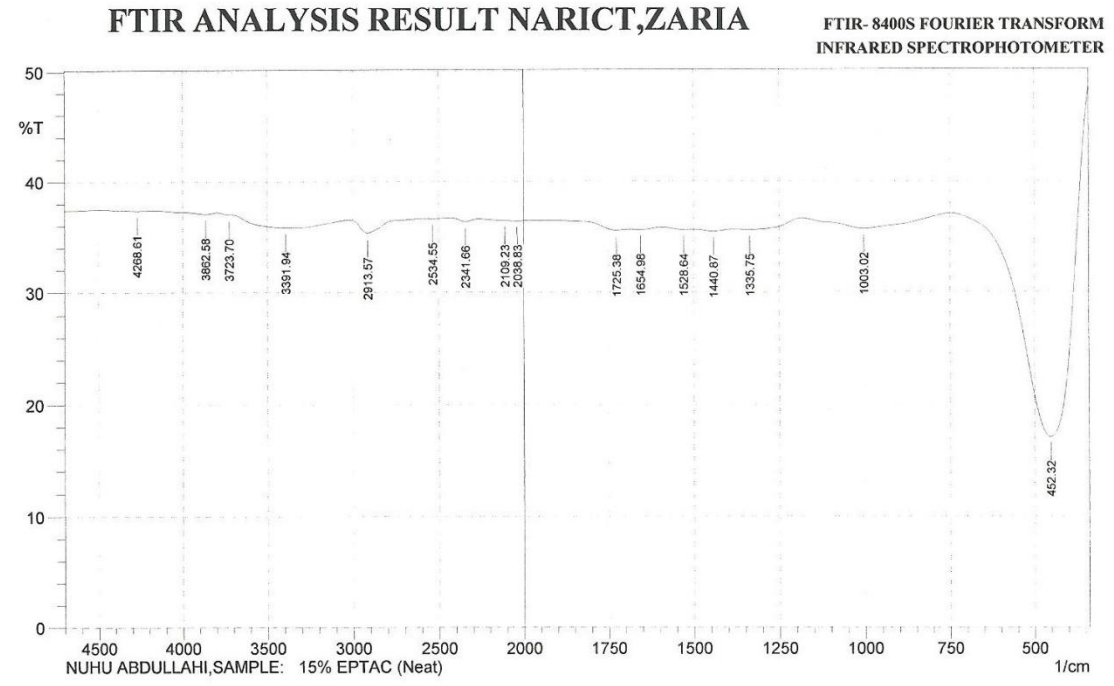


Figure A2.4: FTIR Spectra of the 15% EPTAC Sample.

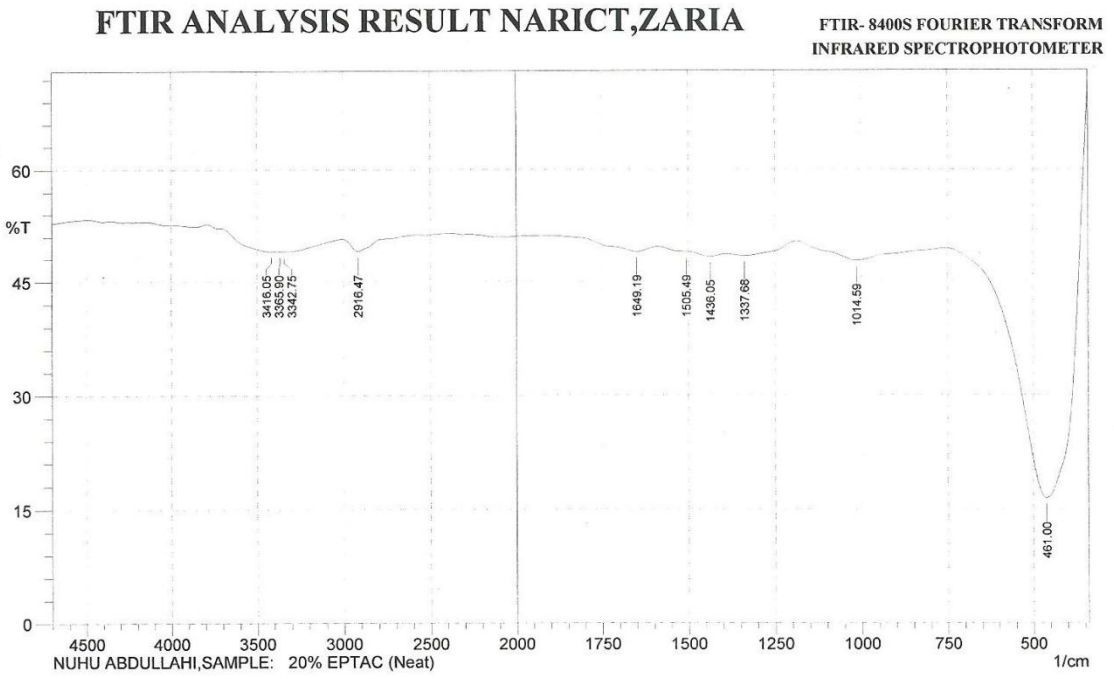


Figure A2.5: FTIR Spectra of 20% EPTAC Sample

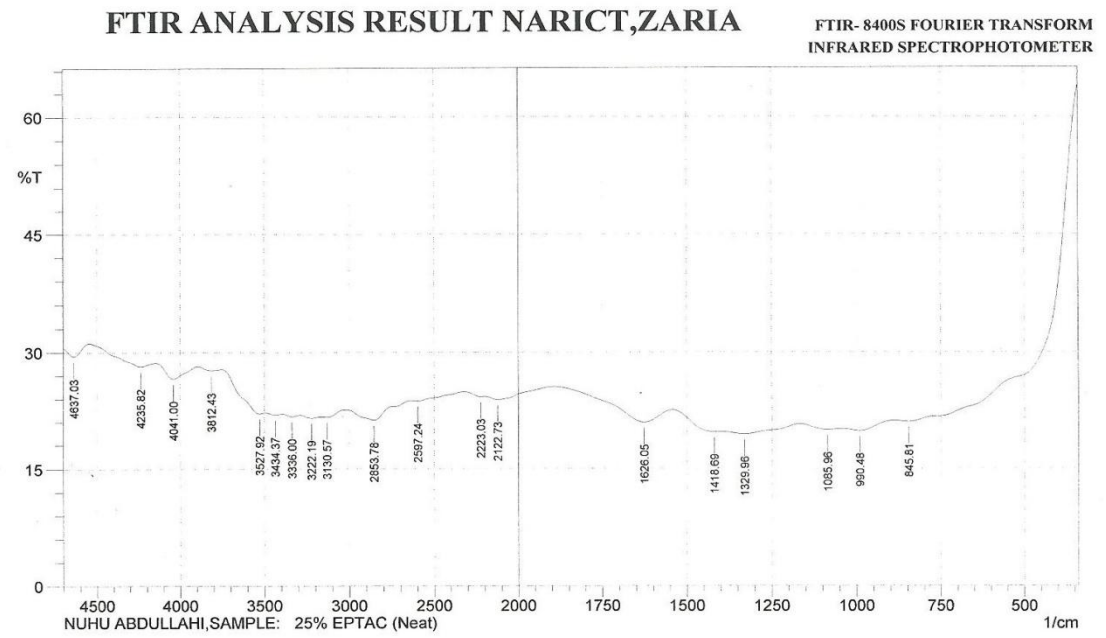


Figure A2.6: FTIR Spectra of the 25% EPTAC Sample

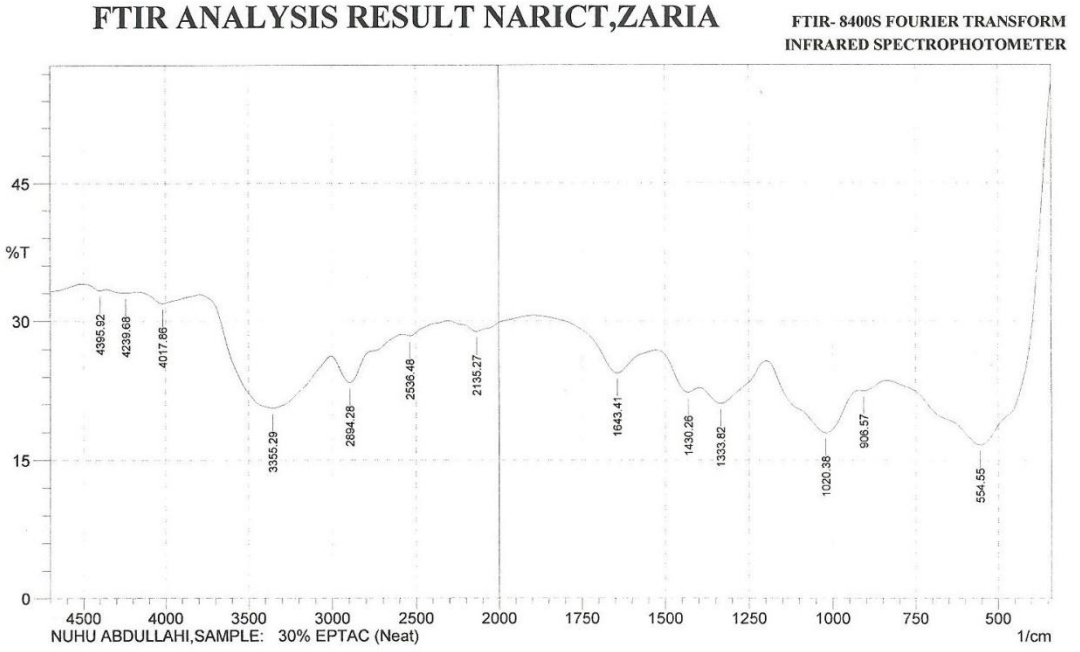


Figure A2.7: FTIR Spectra of the 30% EPTAC Sample

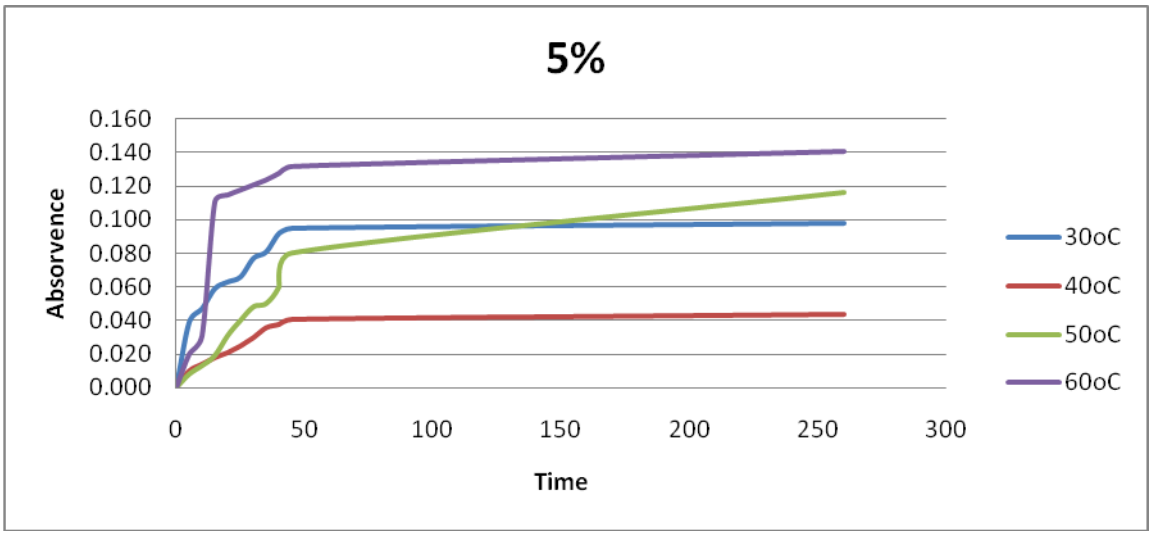


Figure A2.8: Plot of absorbance against time for determining time of half dyeing

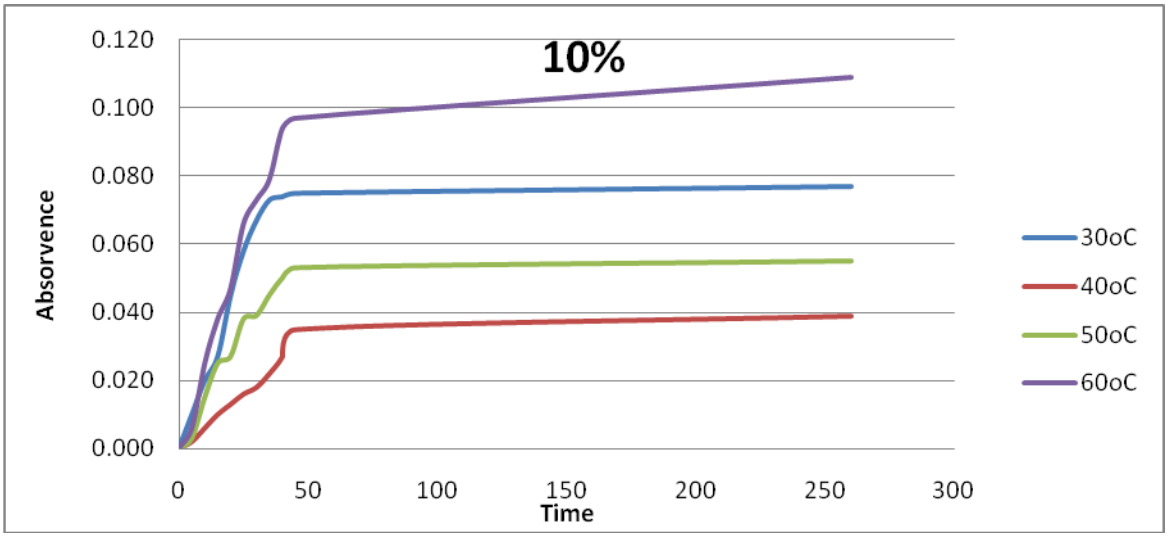


Figure A2.9: Time of half dyeing for 5% EPTAC sample

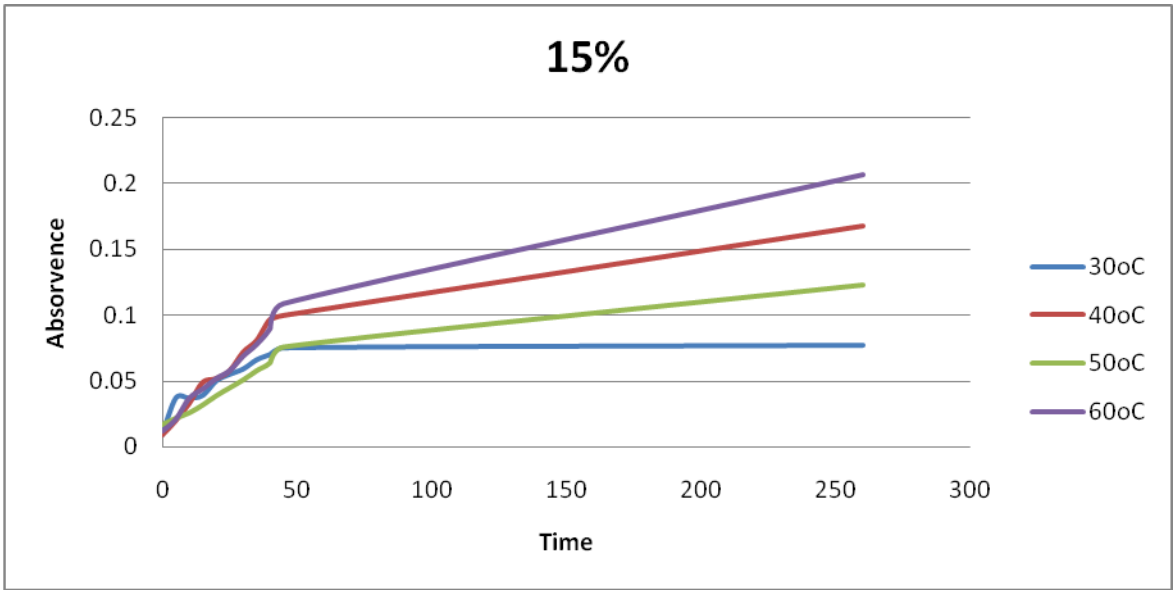


Figure A2.10: Time of half dyeing for 10% EPTAC sample

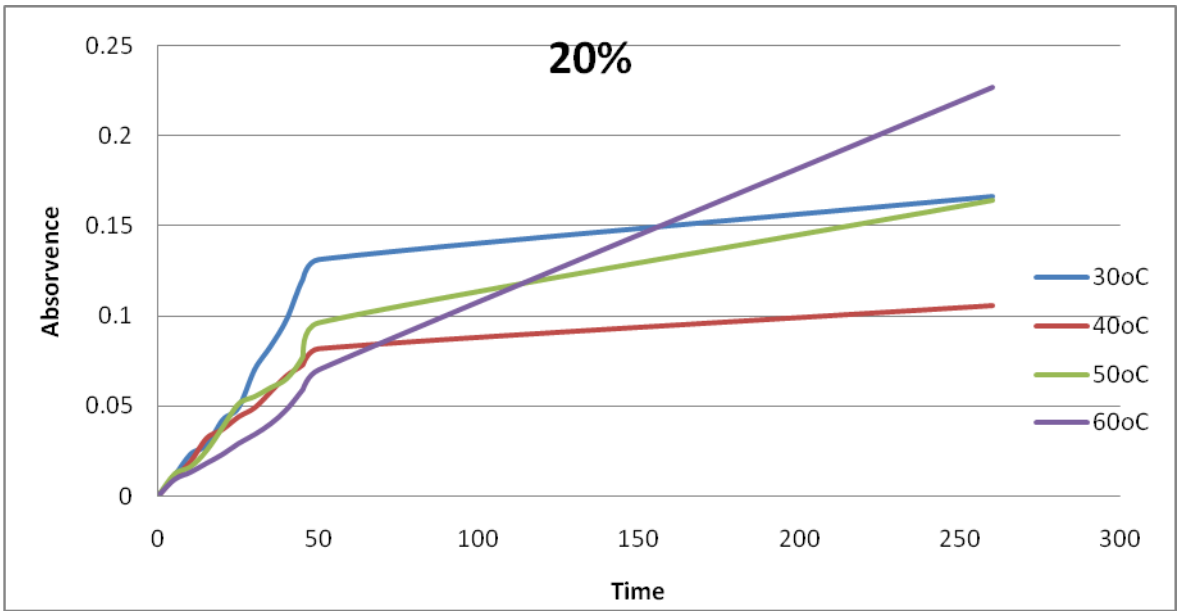


Figure A2.11: Time of half dyeing for 15% EPTAC sample

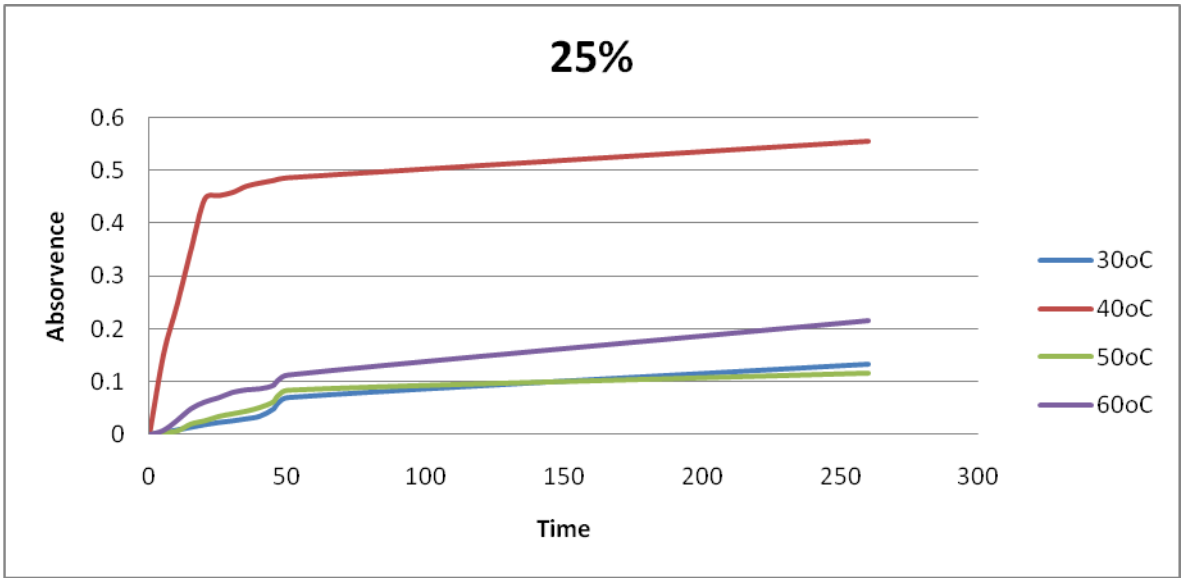


Figure A2.12: Time of half dyeing for 20% EPTAC sample

Langmuir plots of both $[D]_f$ against $[D]s^1$ and $1/[D]_f$against $1/[D]s^1$ for all samples

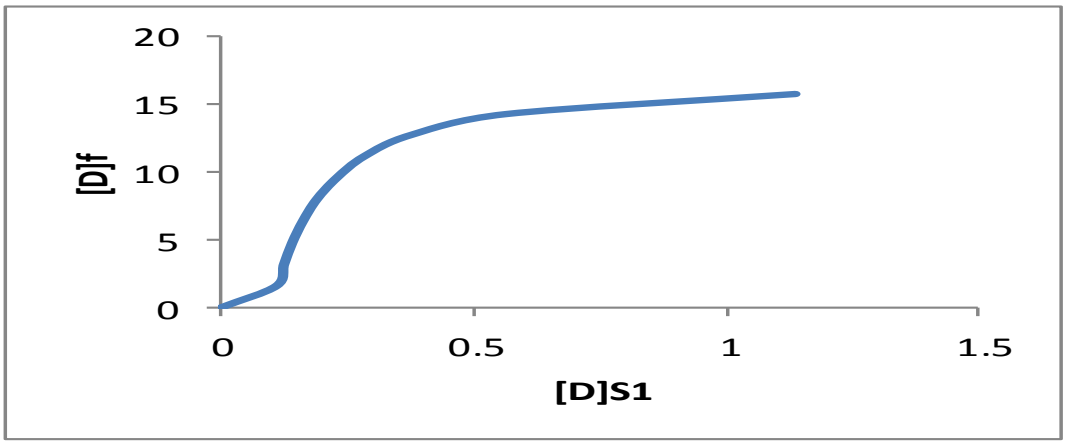


Figure A2.14: Langmuir Isotherm for control at 30^0C

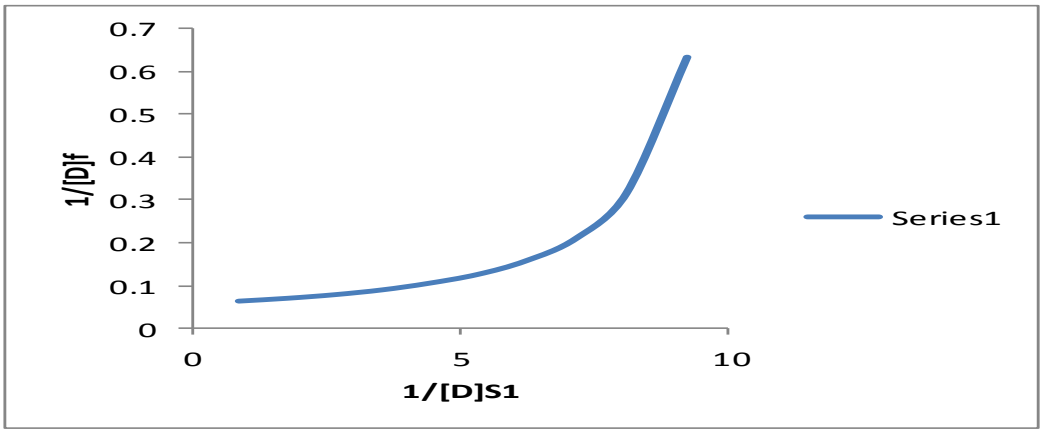


Figure A2.15: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for control sample 30^0C

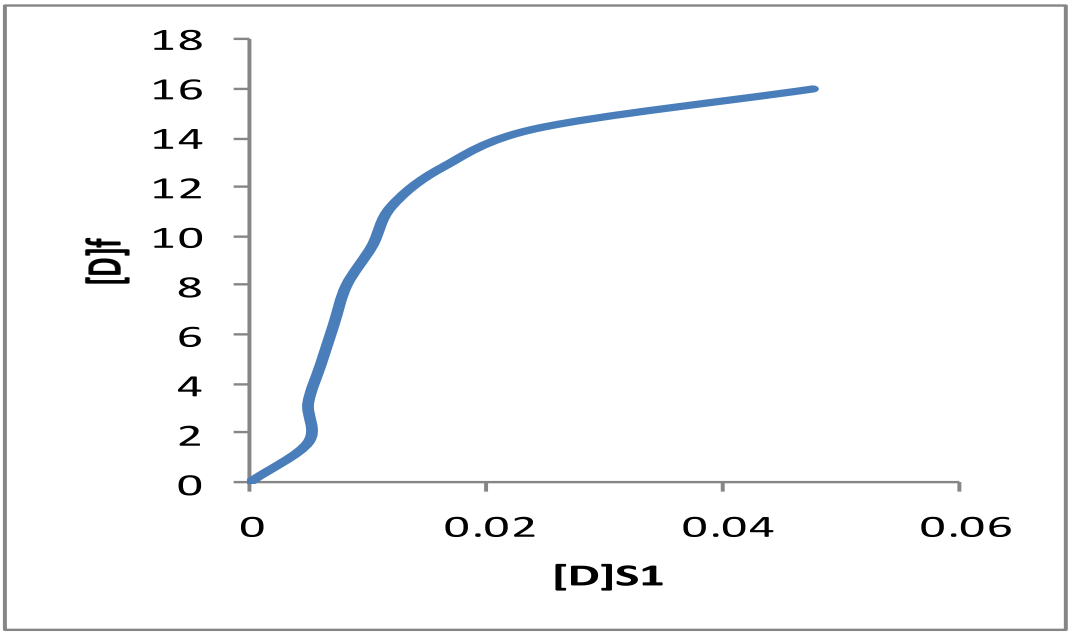


Figure A2.16: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for control sample 40^0C

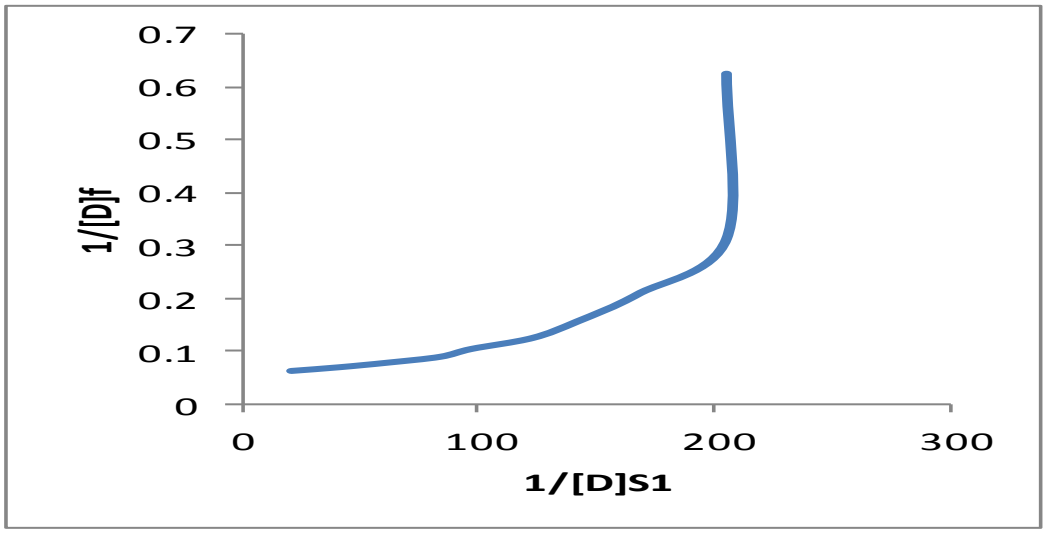


Figure A2.17: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for control sample 40^0

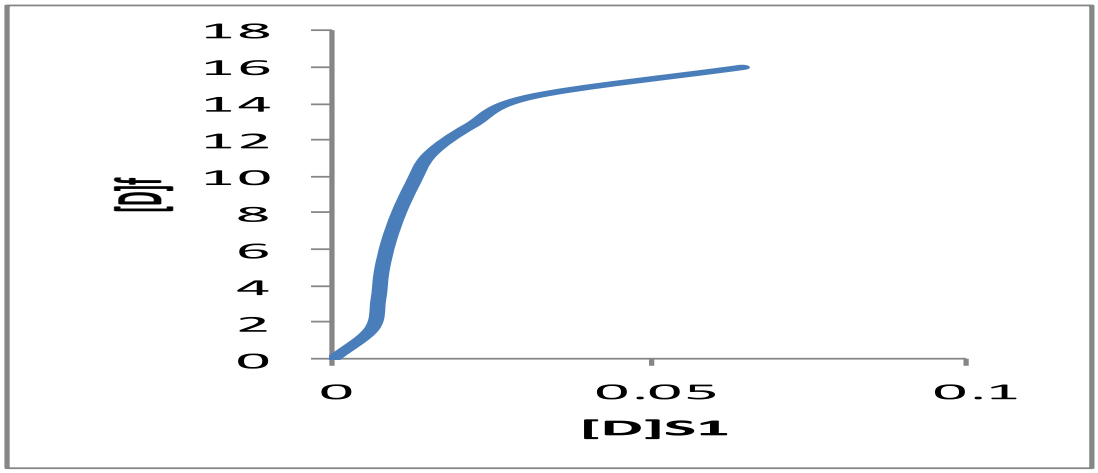


Figure A2.18: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for control sample 50^0C

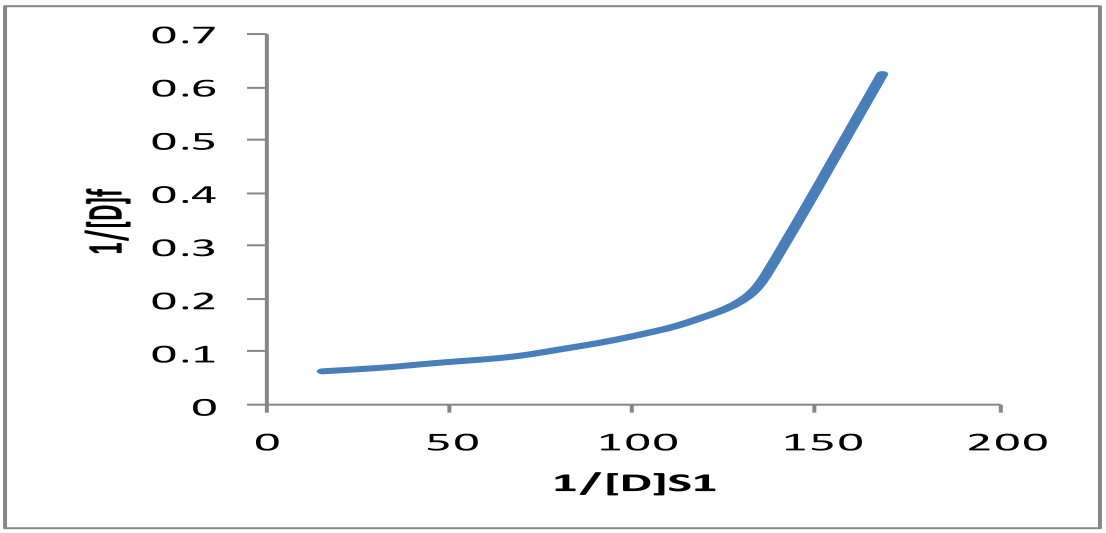


Figure A2.19: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for control sample 50^0C

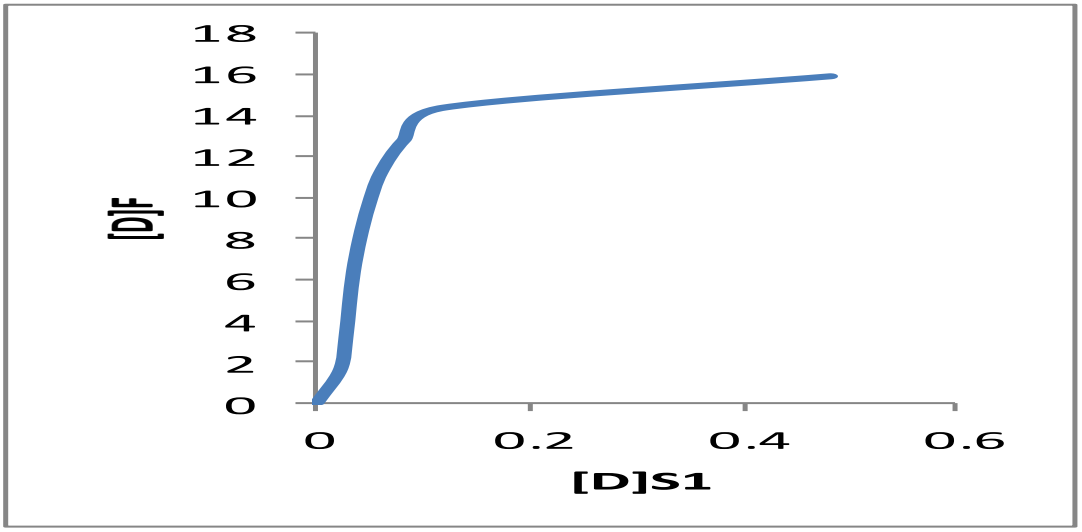


Figure A2.20: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for control sample 60^0C

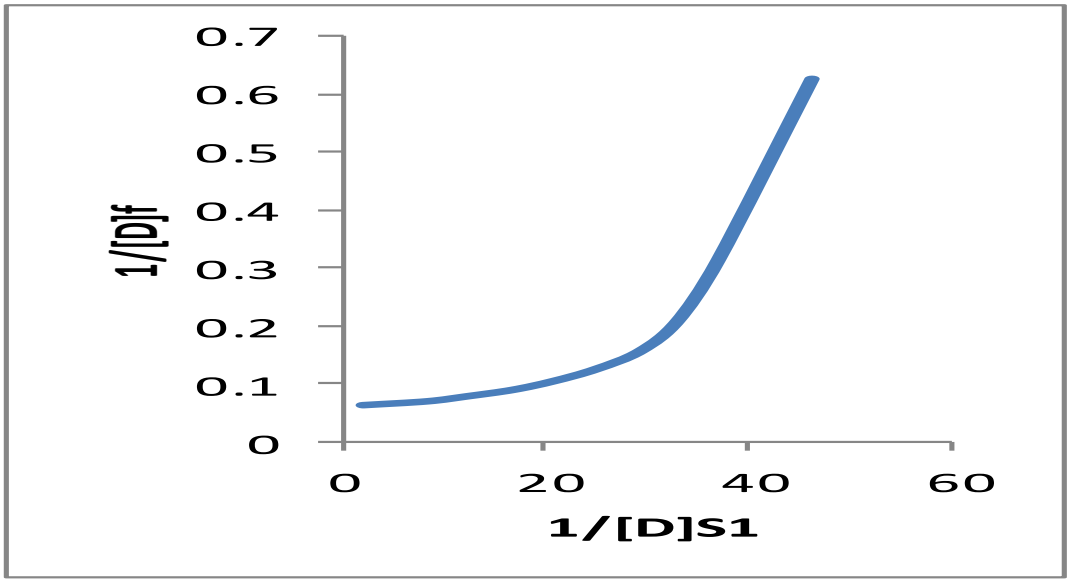


Figure A2.21: Langmuir Isotherm plot of $1/[D]_f$ against $1/[D]s^1$ for control sample 60^0C

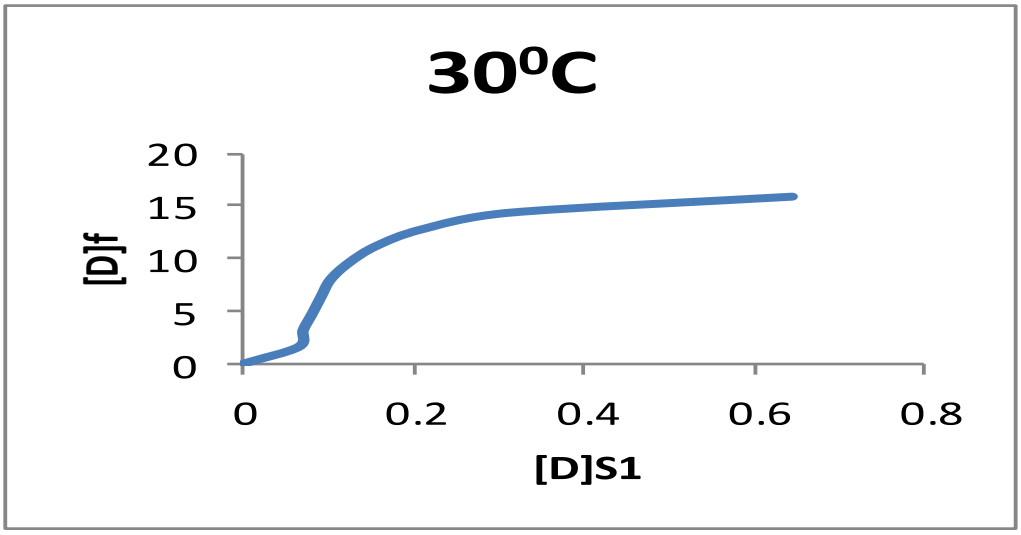


Figure A2.24: Langmuir Isotherm plot of $[D]_f$ against $[D]s^1$ for 5% EPTAC sample 30^0C

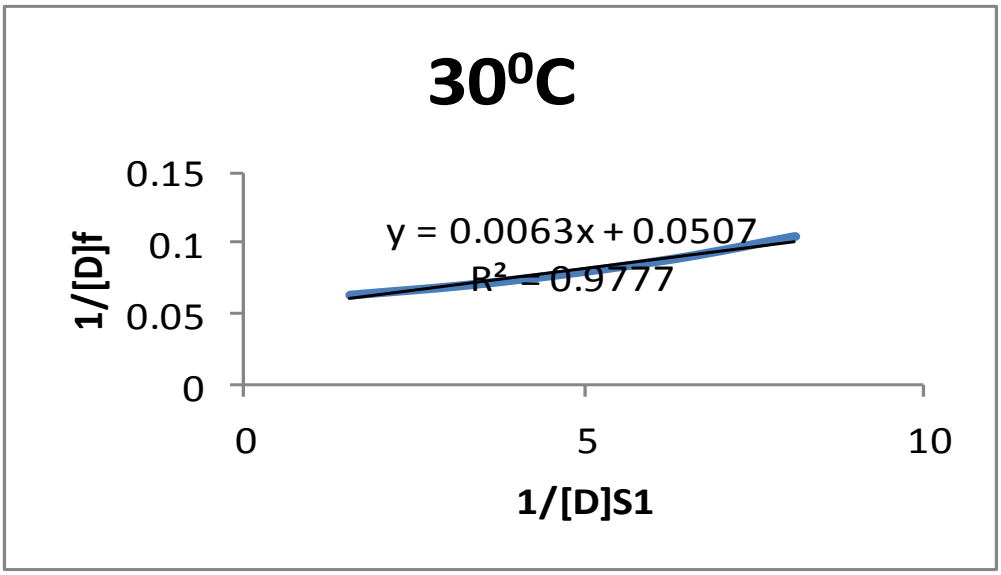


Figure A2.25: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 5% sample 30^0C

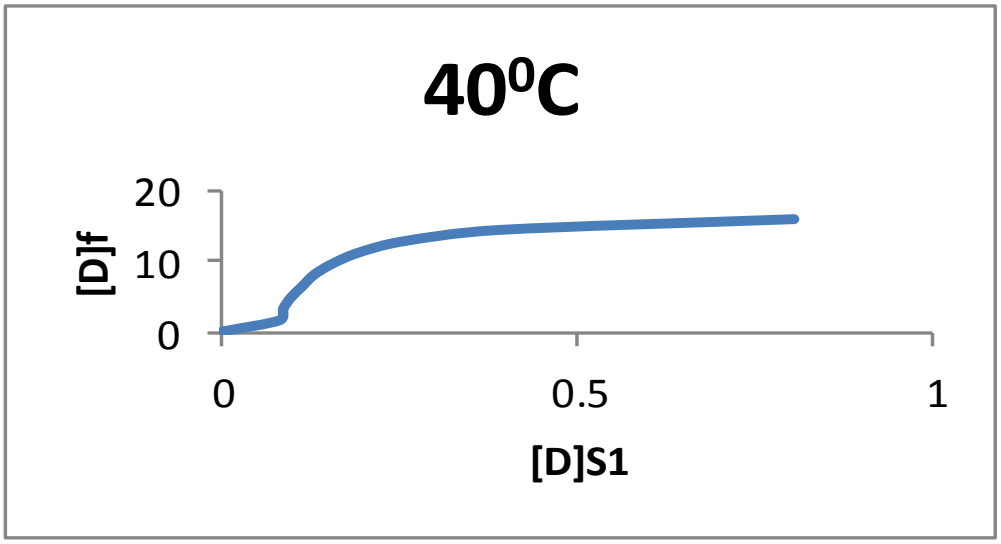


Figure A2.26: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 5% EPTAC sample 40^0C

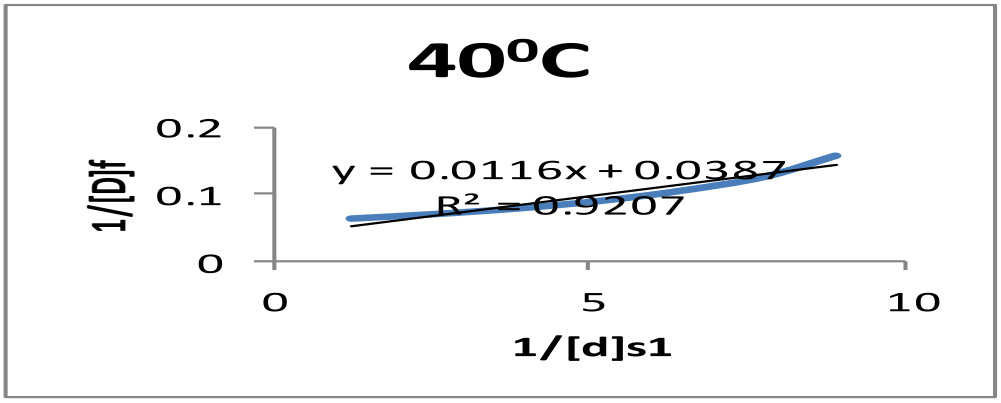


Figure A2.27: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 5% sample 40^0C

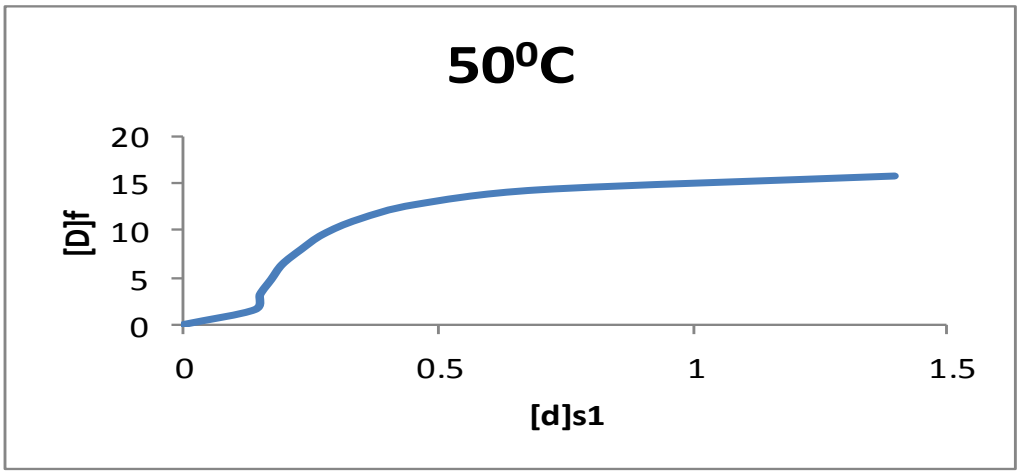


Figure A2.28: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 5% EPTAC sample 50^0C

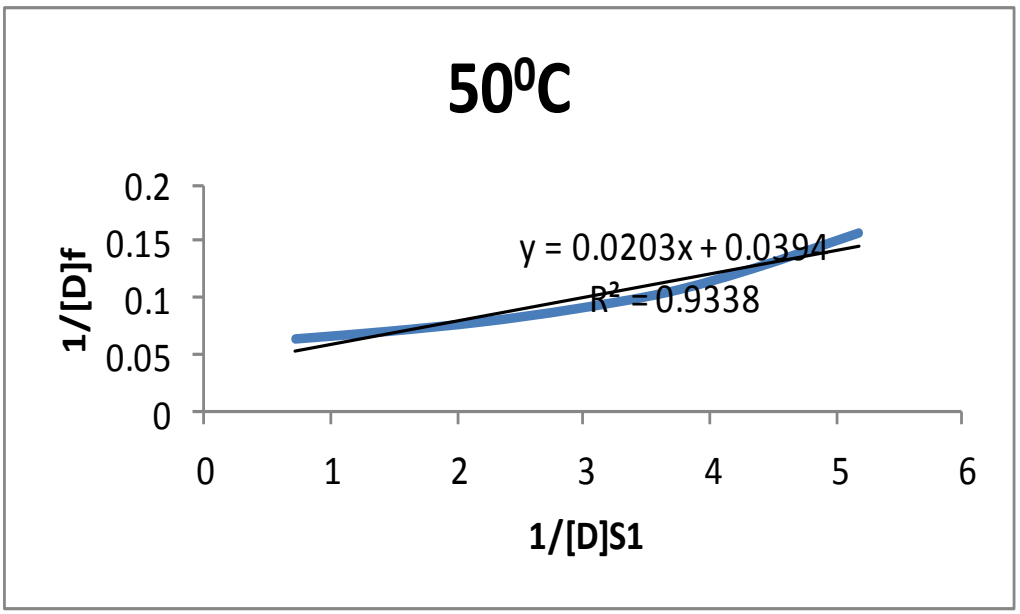


Figure A2.29: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 5% sample 50^0C

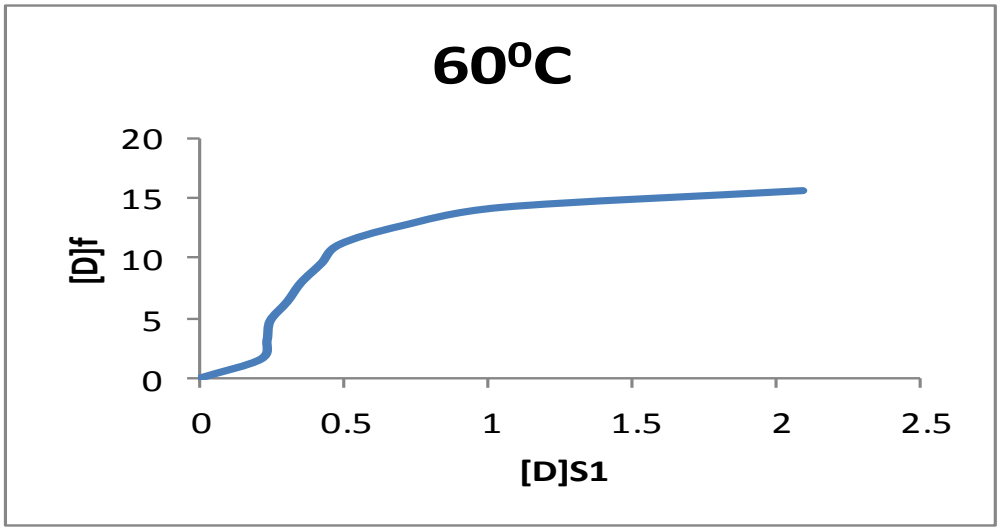


Figure A2.30: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 5% EPTAC sample 60^0C

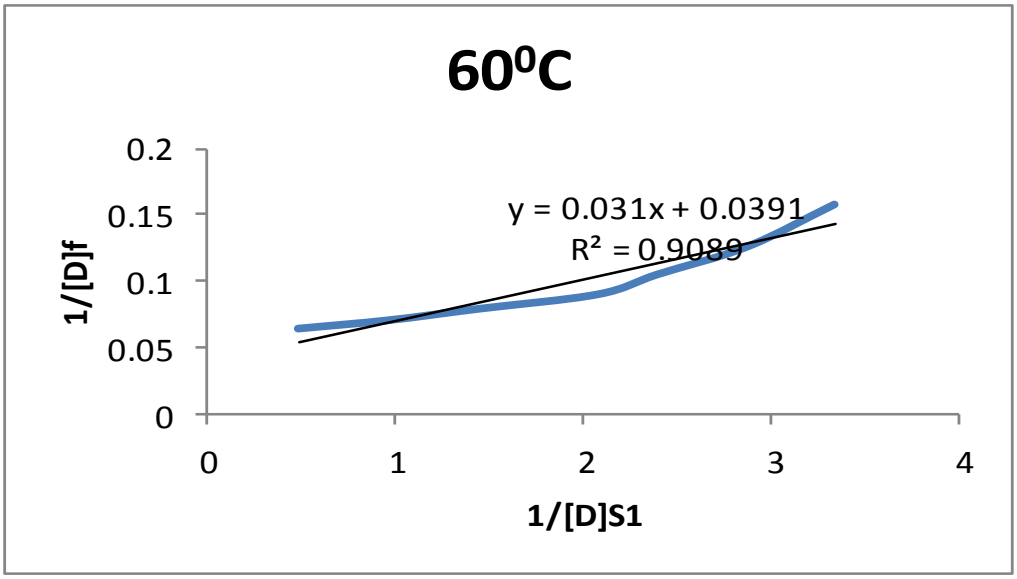


Figure A2.31: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 5% sample 60^0C

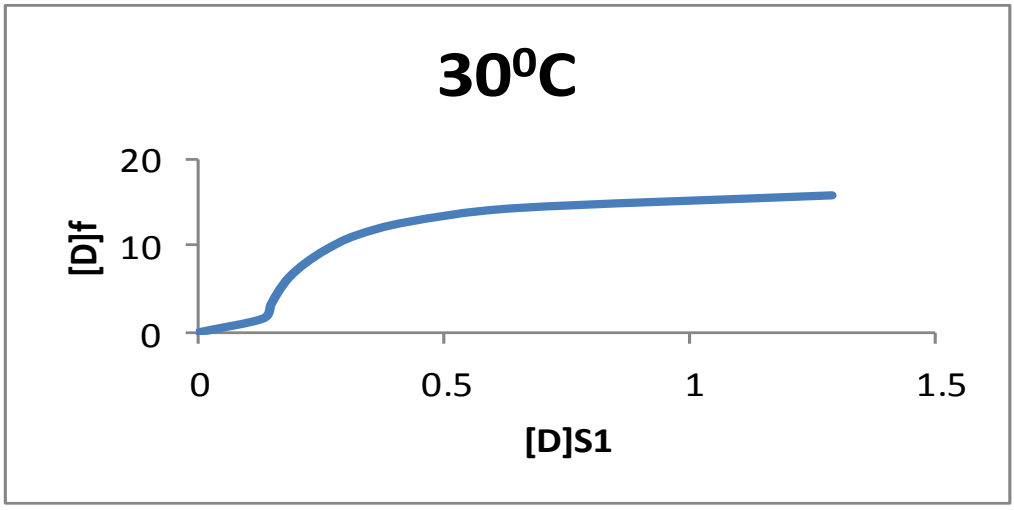


Figure A2.34: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 10% EPTAC sample 30^0C

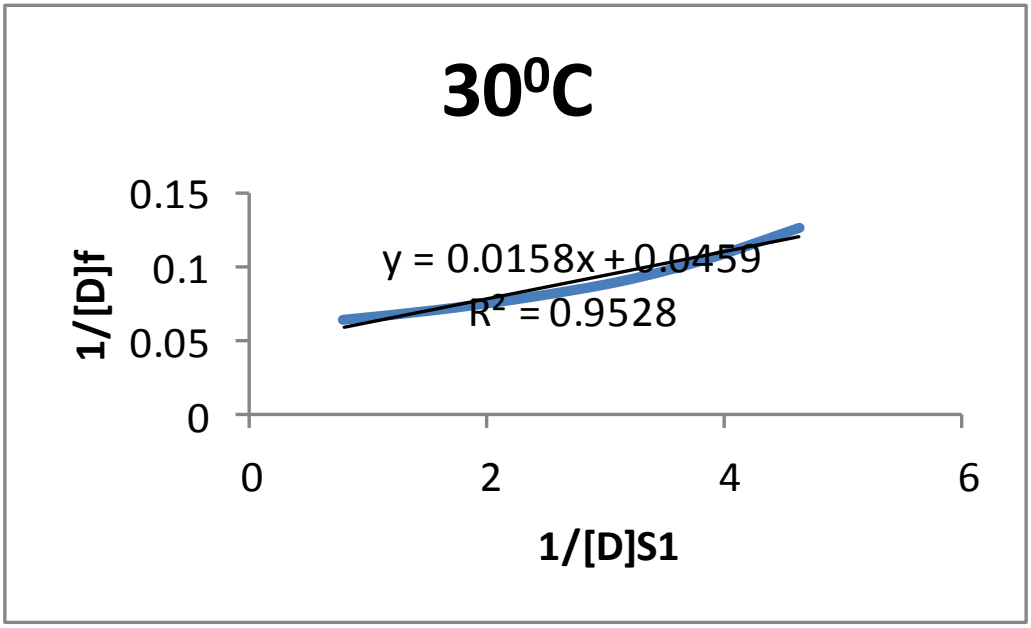


Figure A2.35: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 10% sample 30^0C

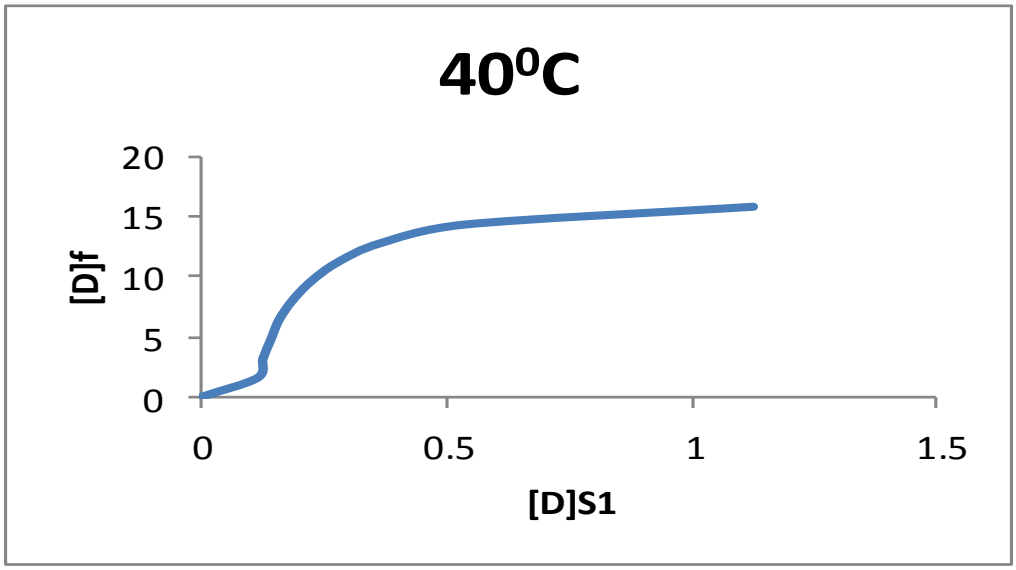


Figure A2.36: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 10% EPTAC sample 40^0C

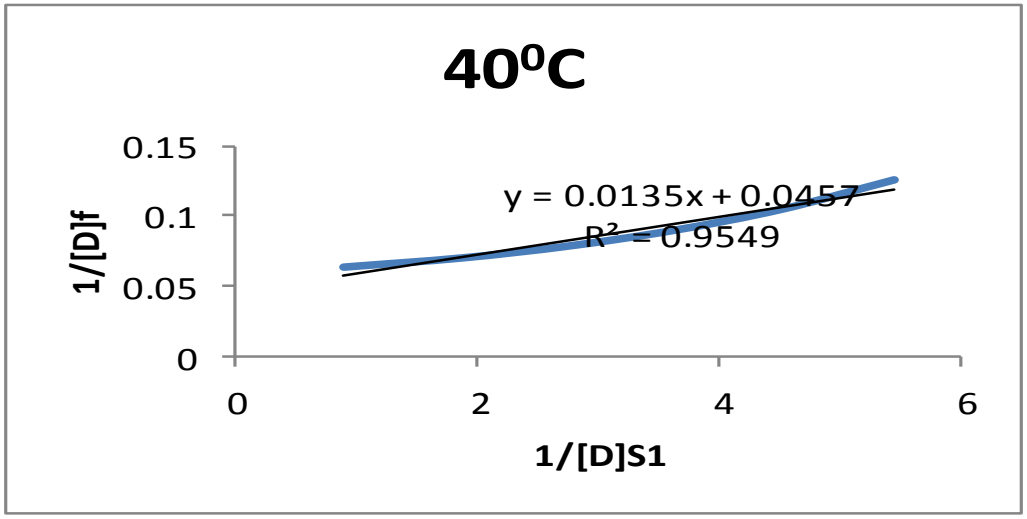


Figure A2.37:Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 10% sample 40^0C

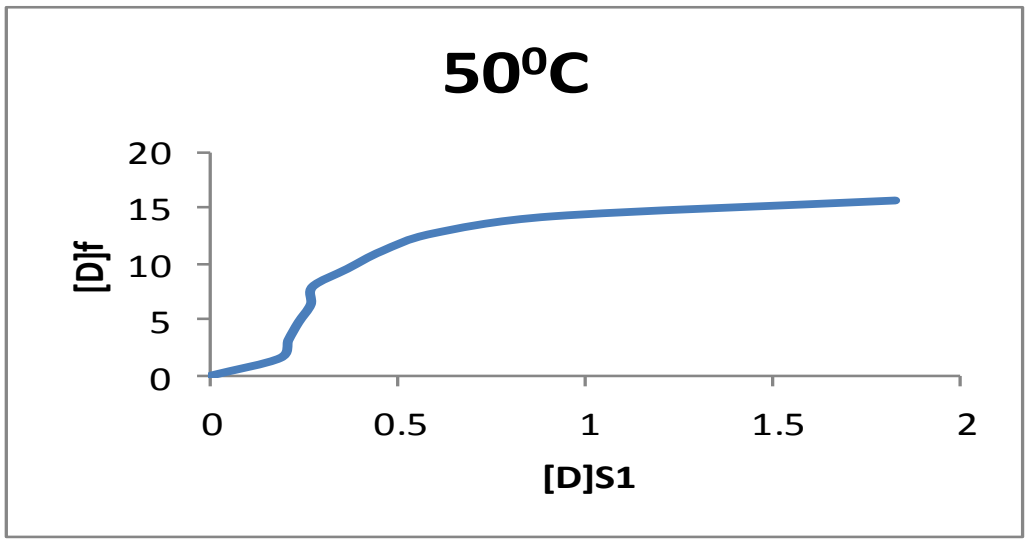


Figure A2.38: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 10% EPTAC sample 50^0C

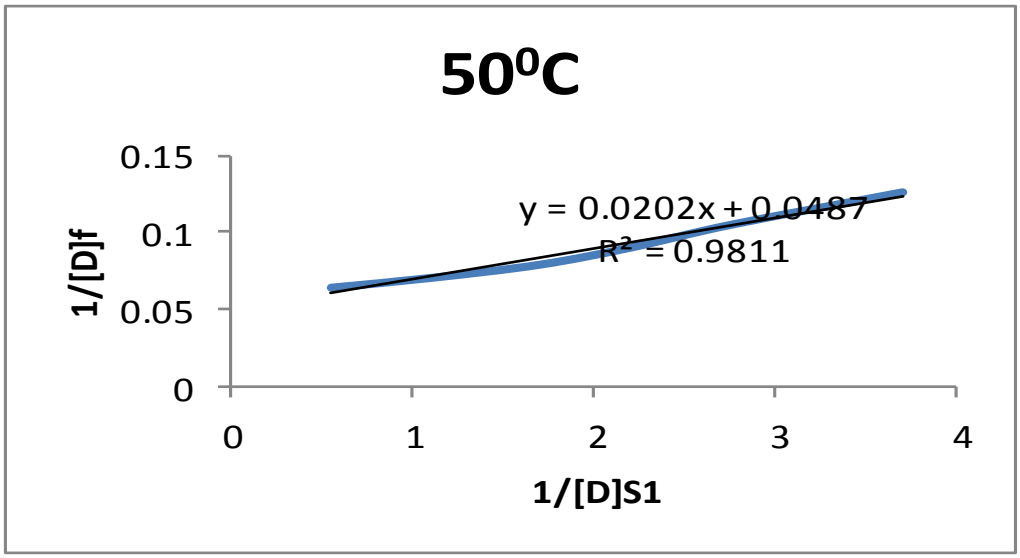


Figure A2.39: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 10% sample 50^0C

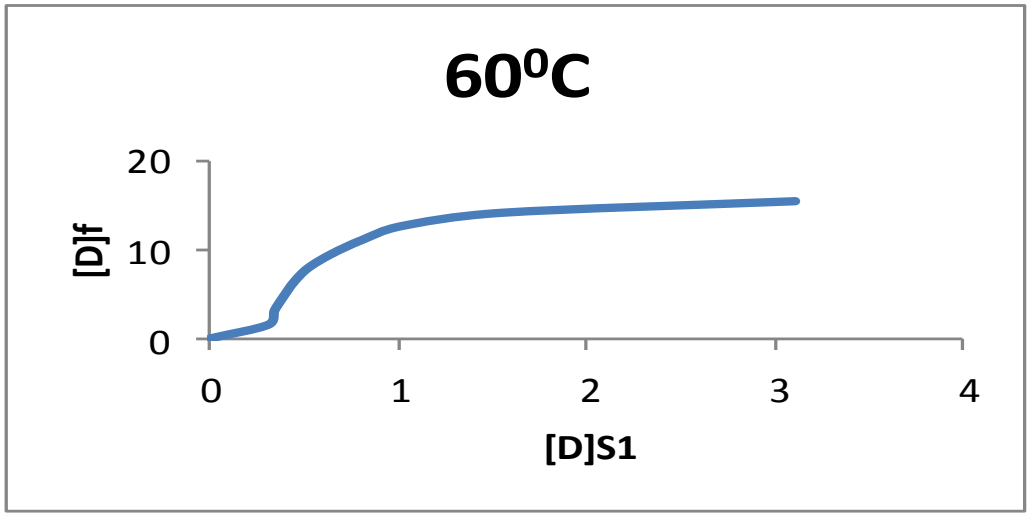


Figure A2.40: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 10% EPTAC sample 60^0C

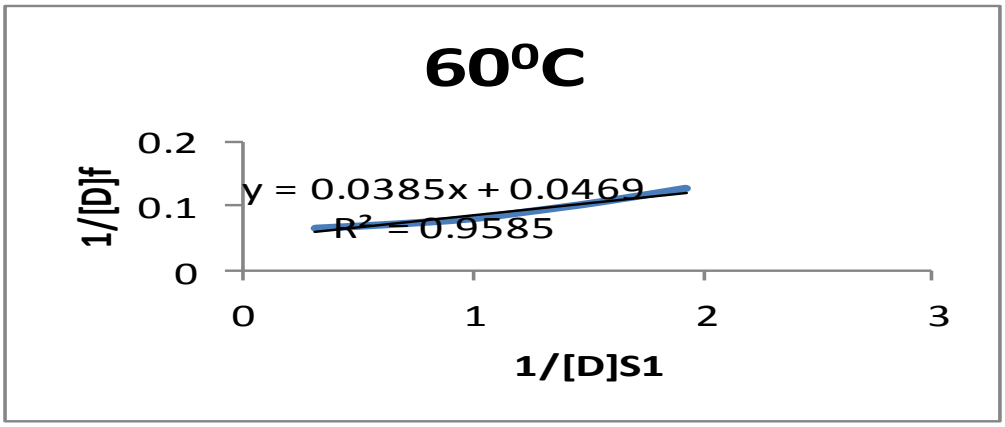


Figure A2.41: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 10% sample 60^0C

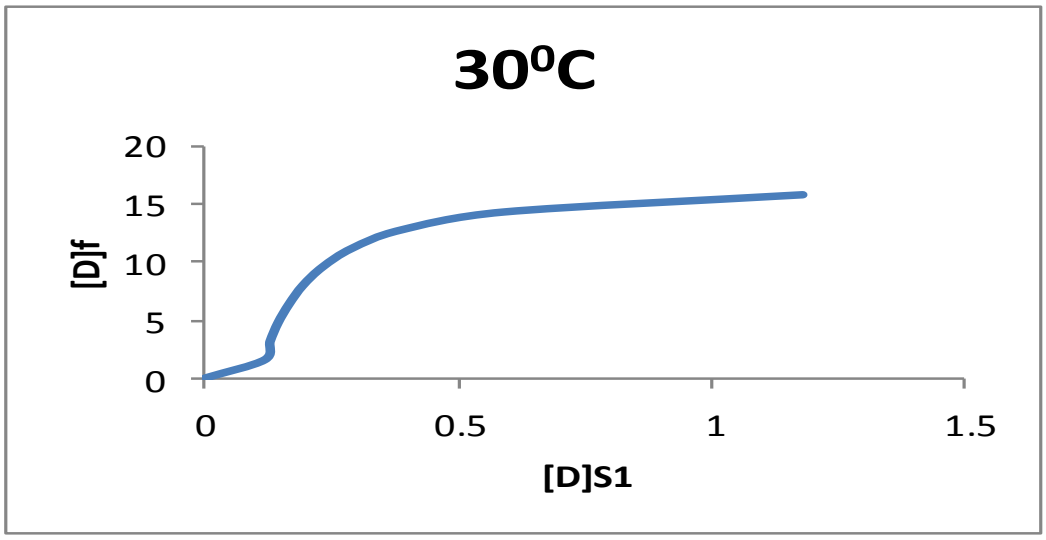


Figure A2.44: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 15% EPTAC sample 30^0C

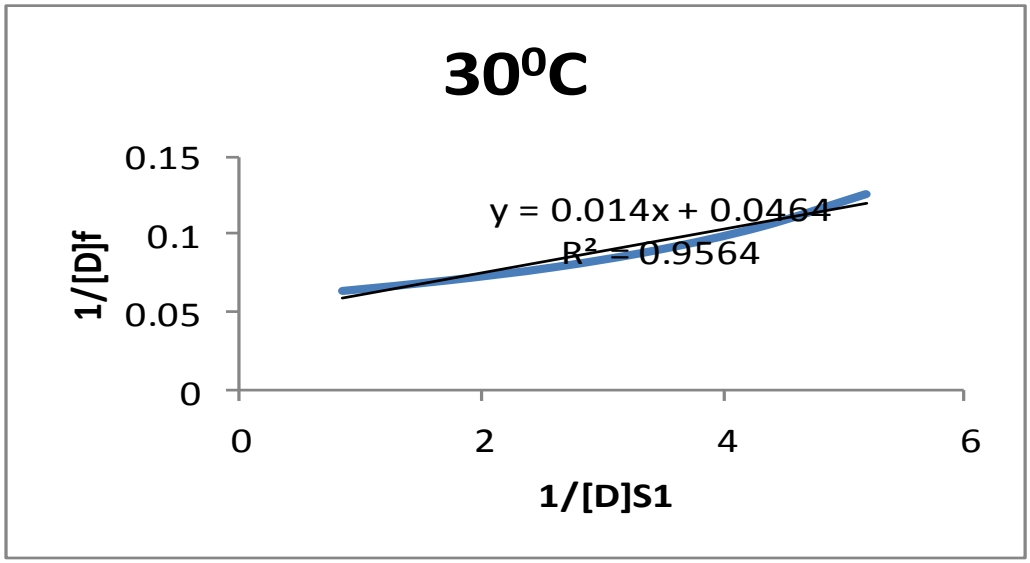


Figure A2.45: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 15% sample 30^0C

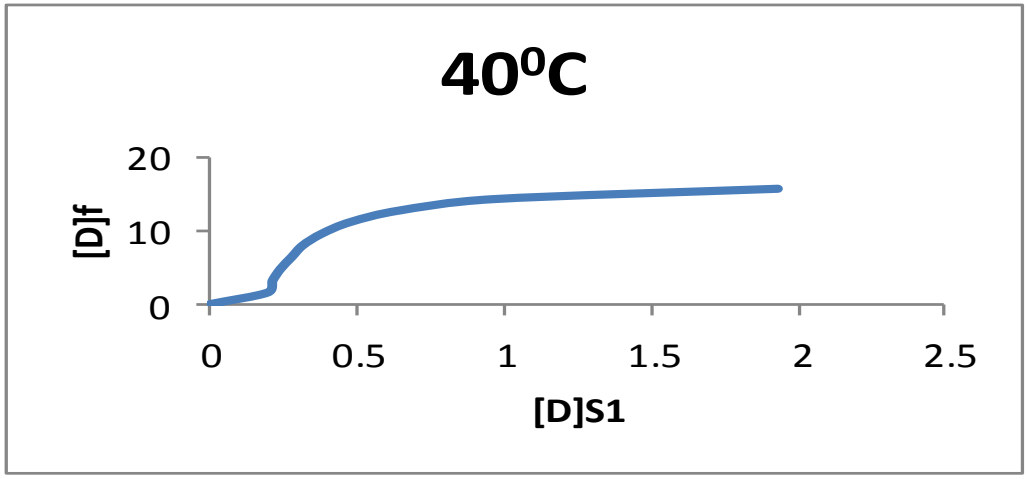


Figure A2.46: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 15% EPTAC sample 40^0C

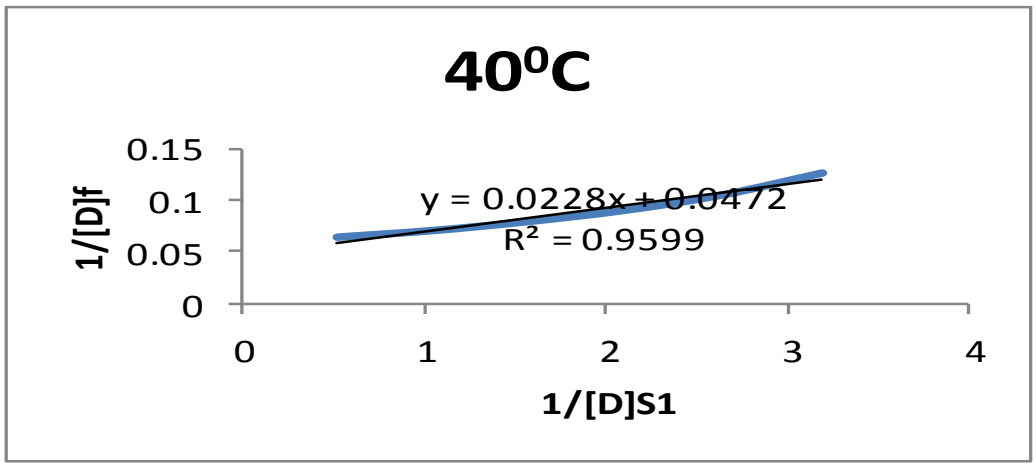


Figure A2.47: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 15% sample 40^0C

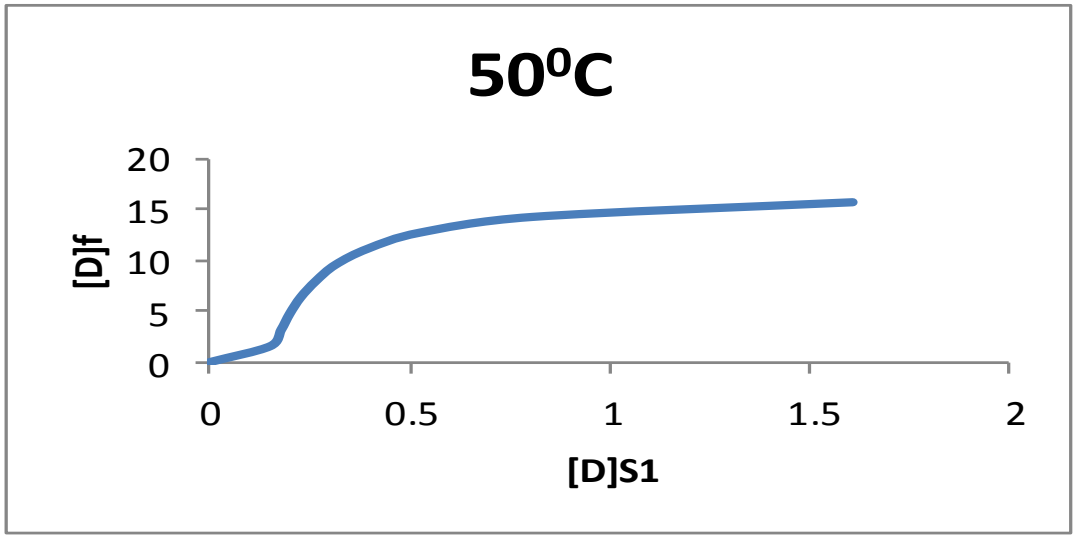


Figure A2.48: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 15% EPTAC sample 50^0C

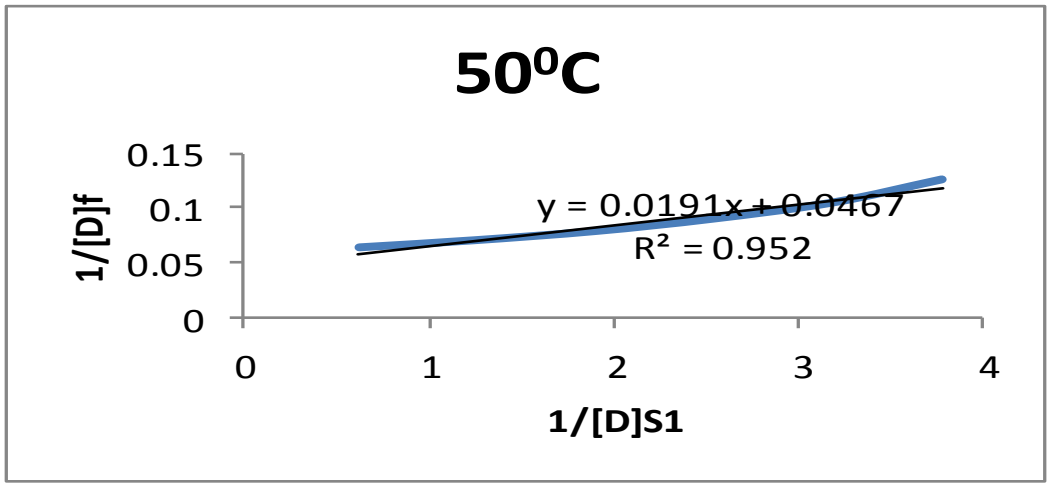


Figure A2.49: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 15% sample 50^0C

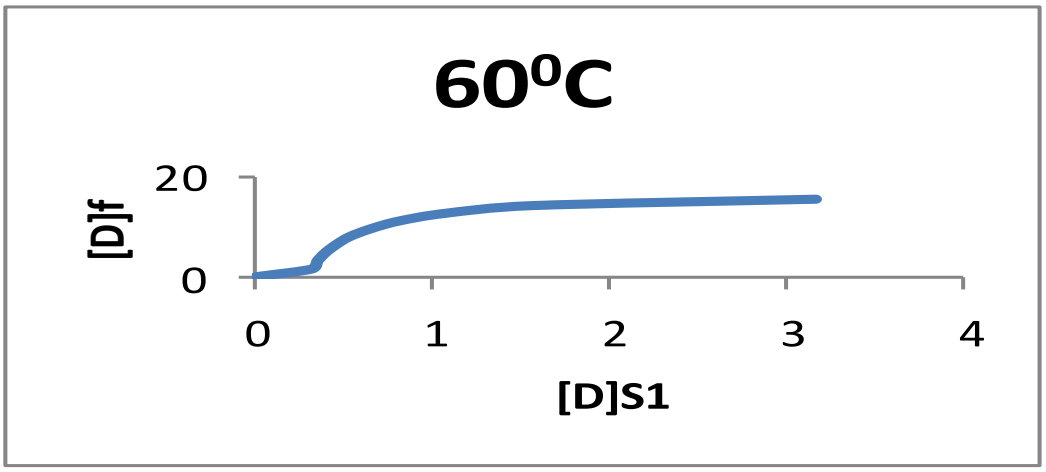


Figure A2.50: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 15% EPTAC sample 60^0C

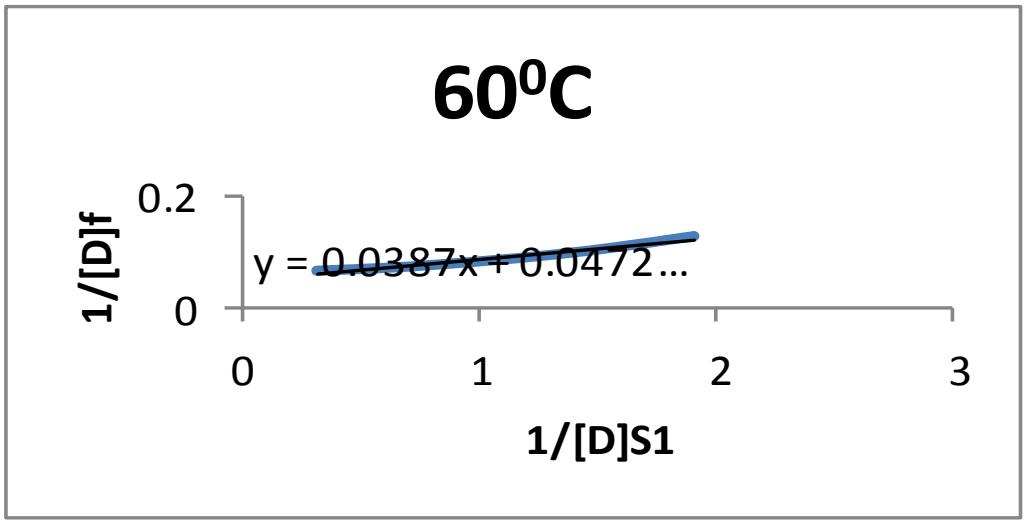


Figure A2.51: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 15% sample 60^0C

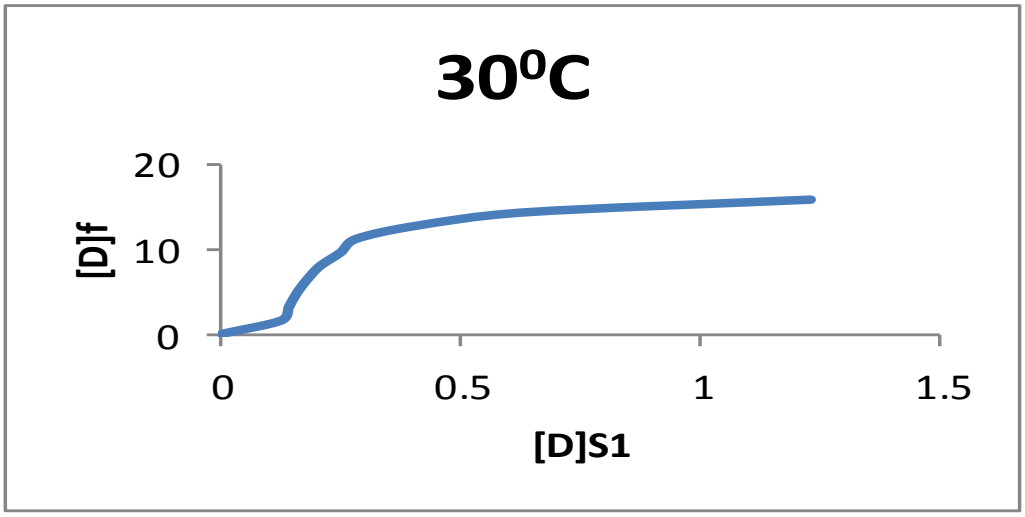


Figure A2.54: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 20% EPTAC sample 30^0C

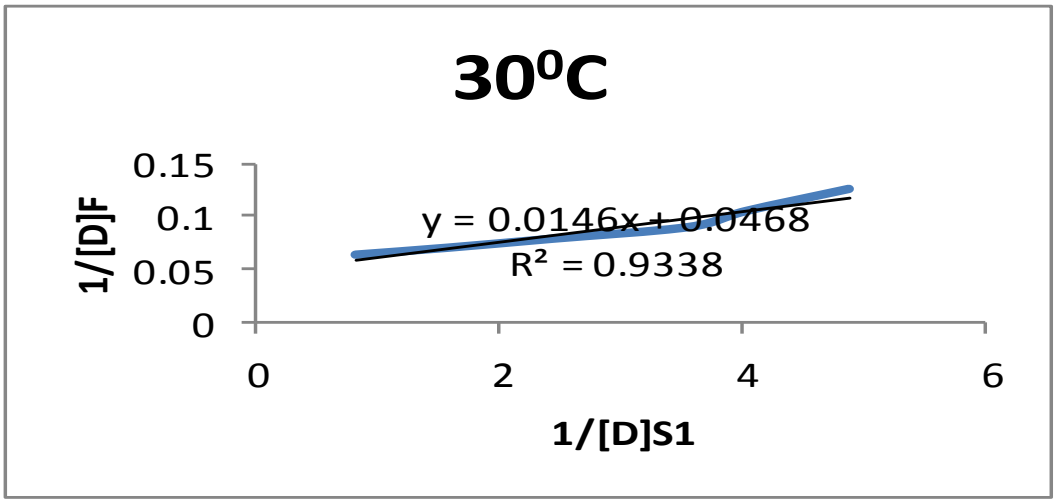


Figure A2.55: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 20% sample 30^0C

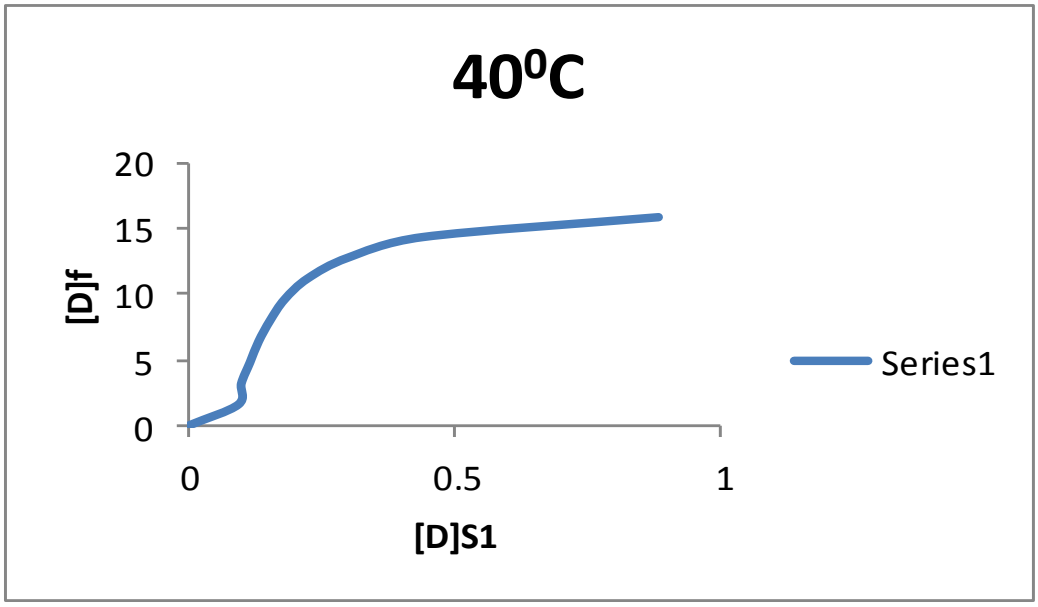


Figure A2.56: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 20% EPTAC sample 40^0C

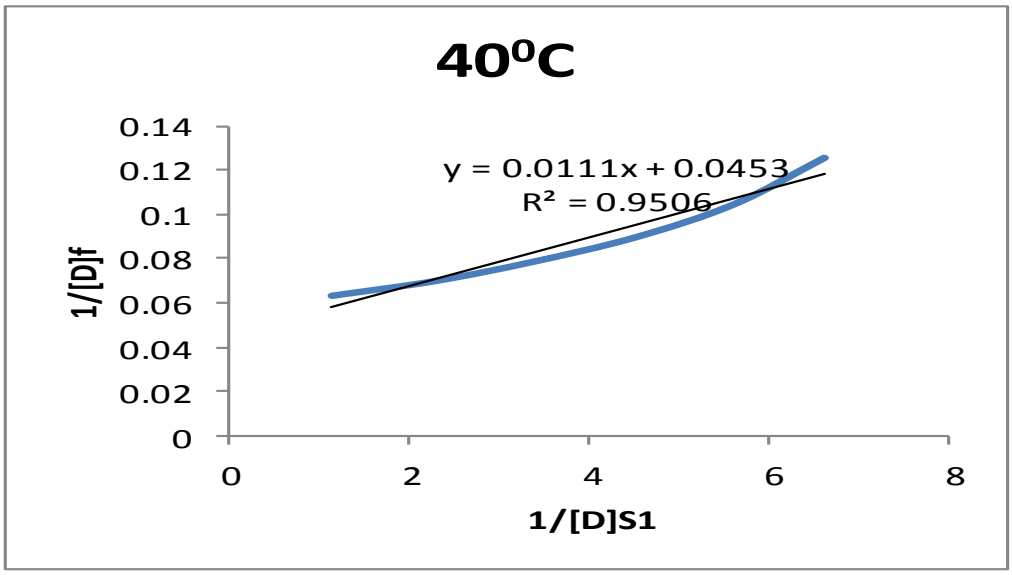


Figure A2.57: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 20% sample 40^0C

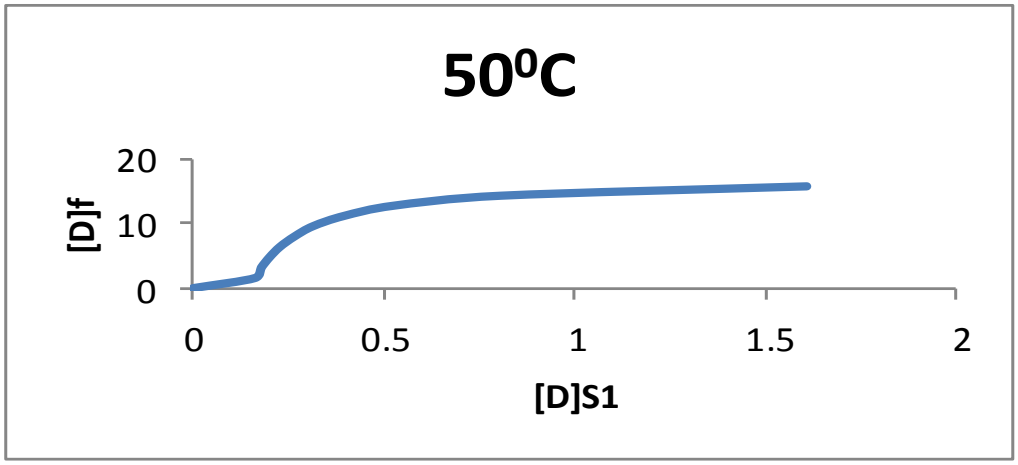


Figure A2.58: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 20% EPTAC sample 50^0C

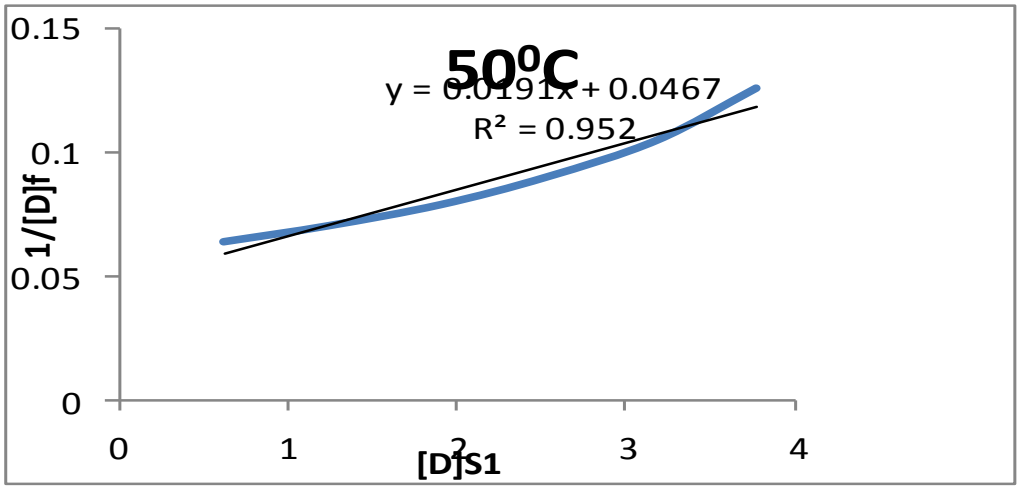


Figure A2.59: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 20% sample 50^0C

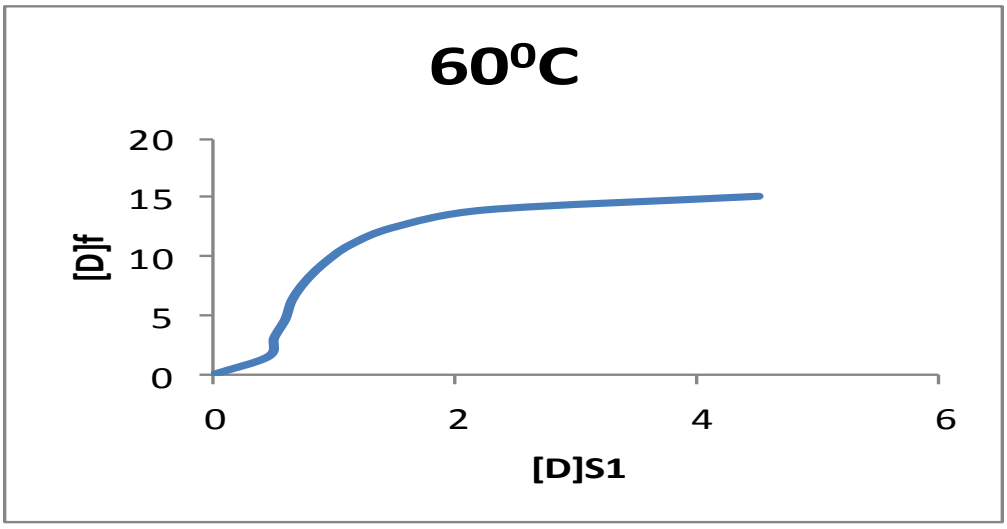


Figure A2.60: Langmuir Isotherm plot of $[D]_f$against $[D]s^1$for 20% EPTAC sample 60^0C

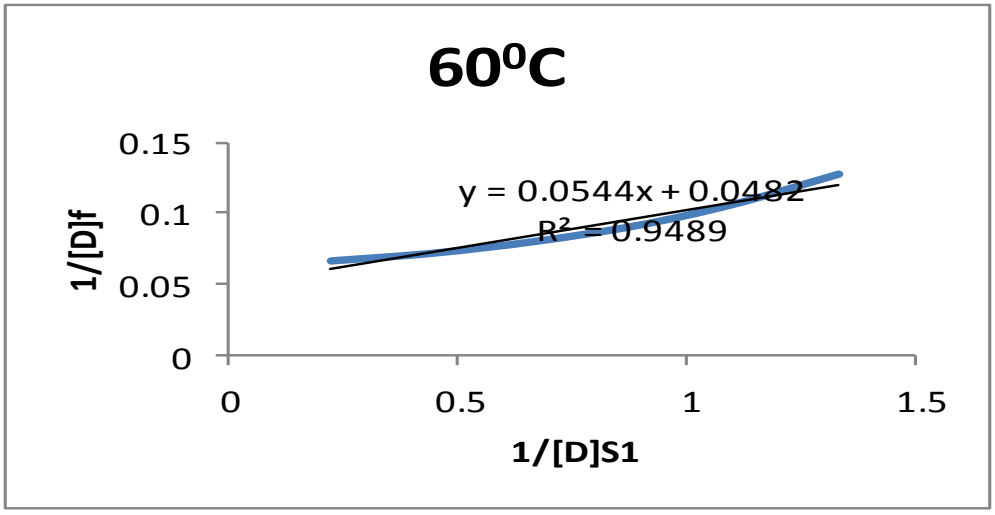


Figure A2.61: Langmuir Isotherm plot of $1/[D]_f$against $1/[D]s^1$for 20% sample 60^0C

Graphs of diffusion coefficient t(Log D_T)against reciprocal of temperature(1/T)

Figure A2.74: Plot of Log $D_T$against 1/T for control sample

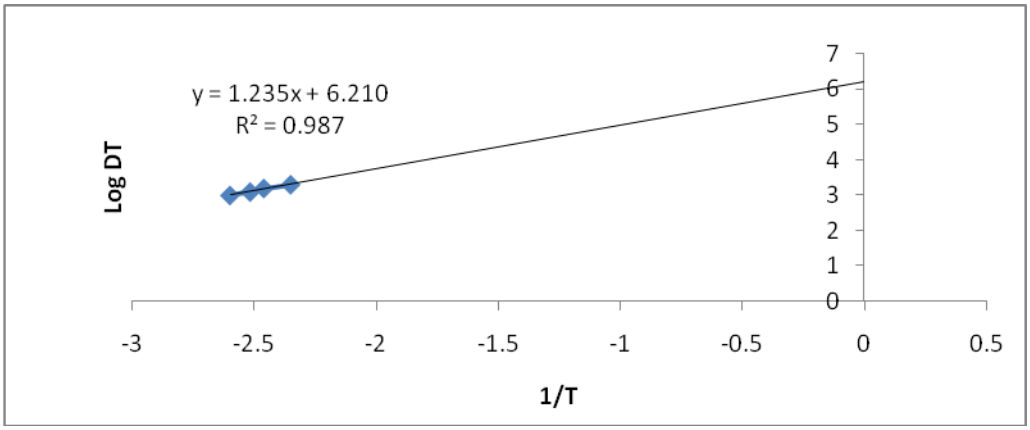


Figure A2.75: Plot of Log $D_T$against 1/T for 5% EPTAC sample

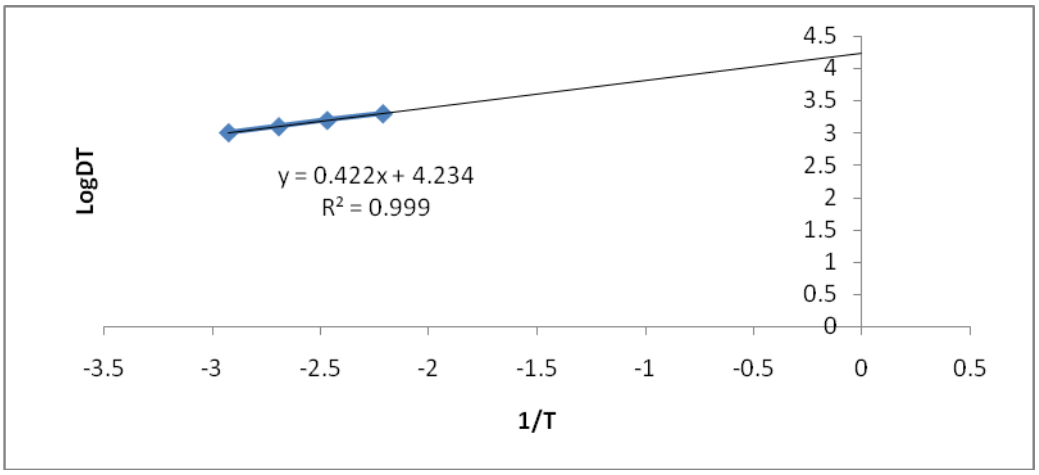


Figure A2.76: Plot of Log $D_T$against 1/T for 10% EPTAC sample

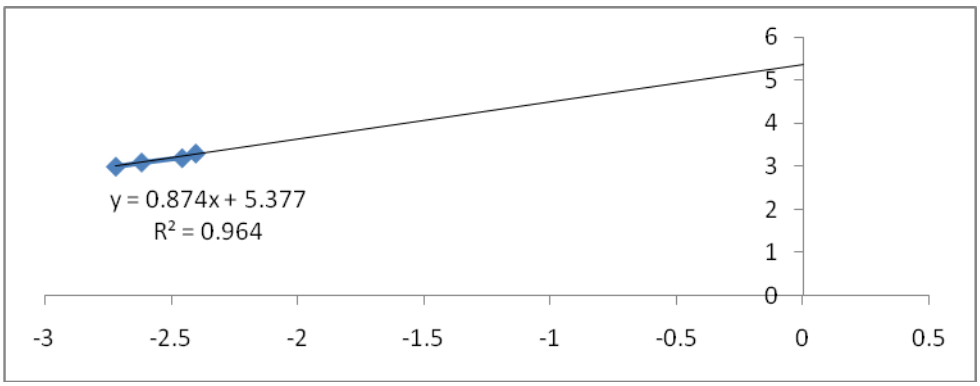


Figure A2.77: Plot of Log $D_T$against 1/T for 15% EPTAC sample

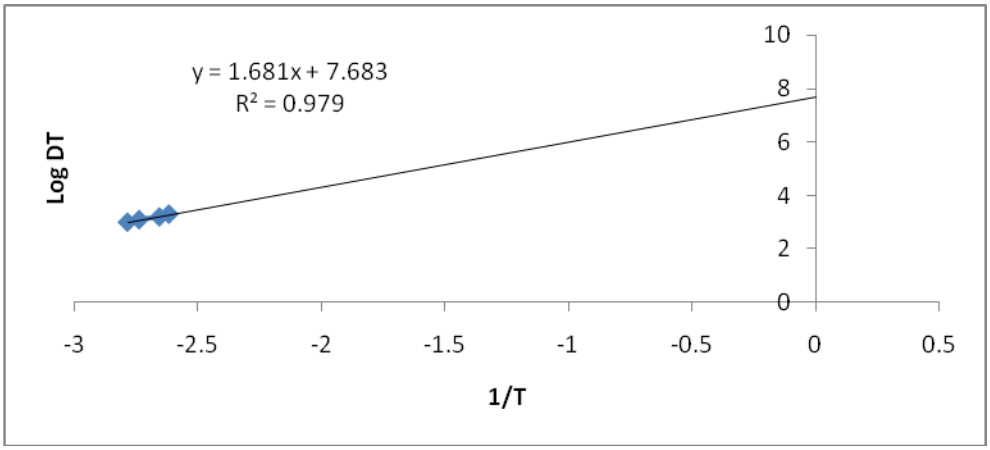


Figure A2.77: Plot of Log $D_T$against 1/T for 20% EPTAC sample

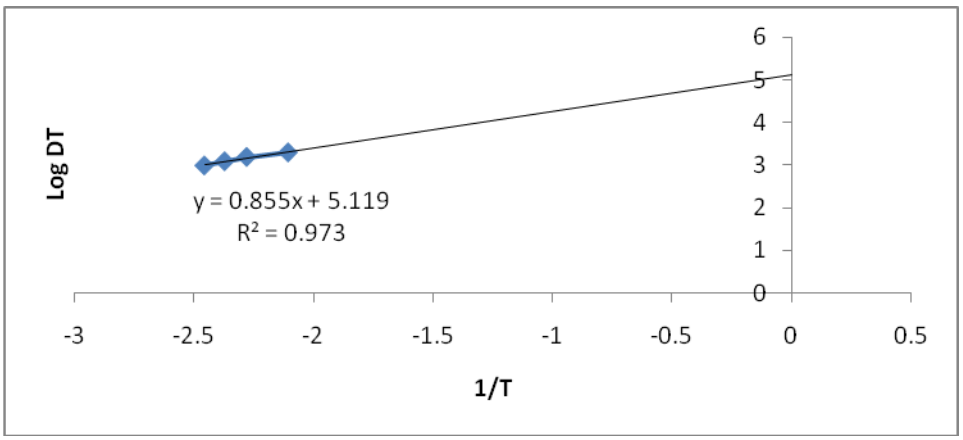


Figure A2.78: Plot of Log $D_T$against 1/T for 25% EPTAC sample

Figure A2.80: Plot of affinity (Δμ) against temperature (T) for control sample

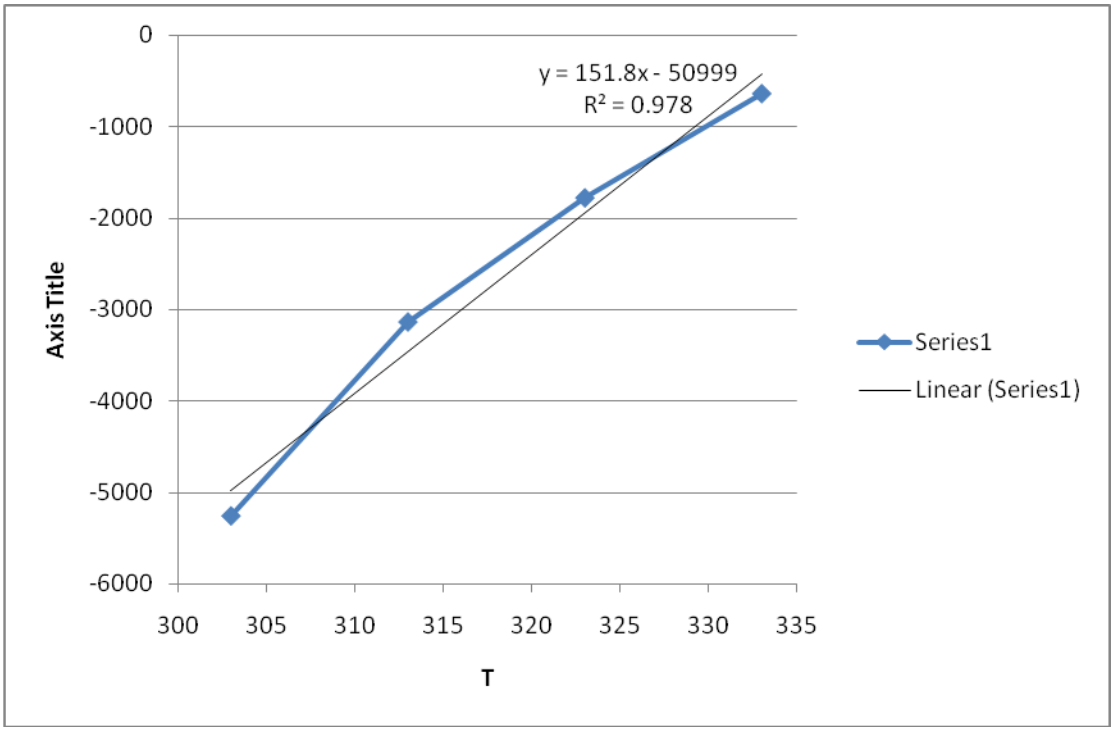
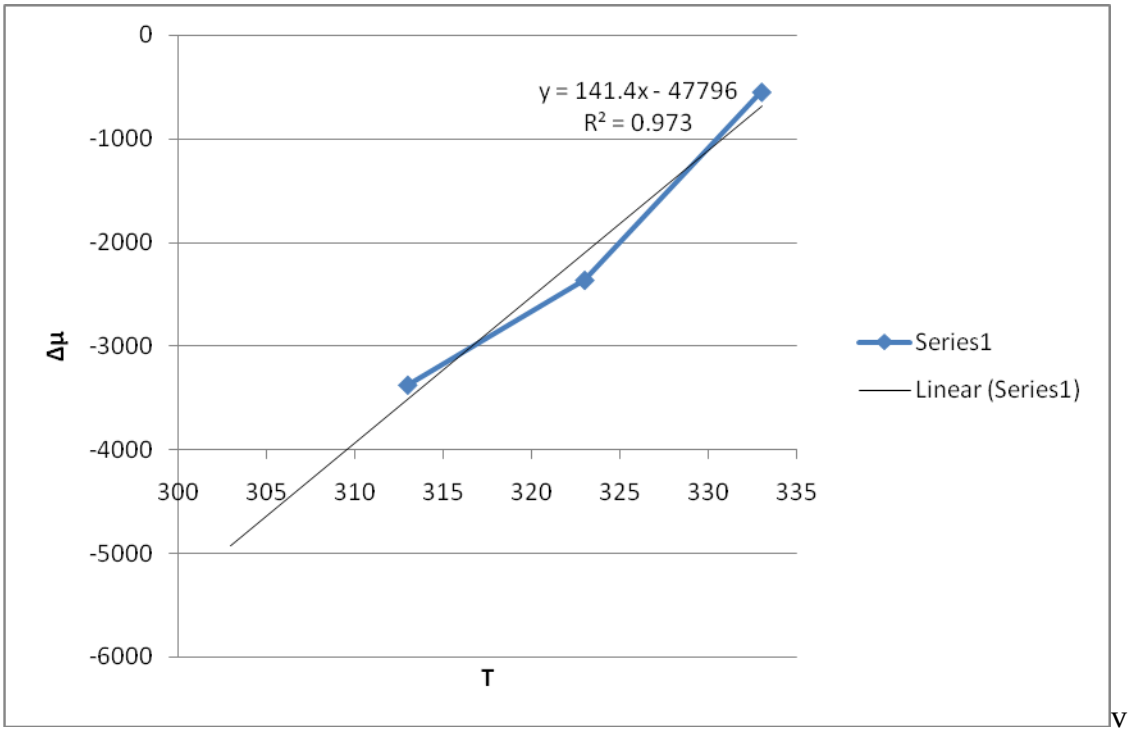


Figure A2.81: Plot of affinity (Δμ) against temperature (T) for 5% EPTAC sample



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Figure A2.82: Plot of affinity (Δμ) against temperature (T) for 10% EPTAC sample

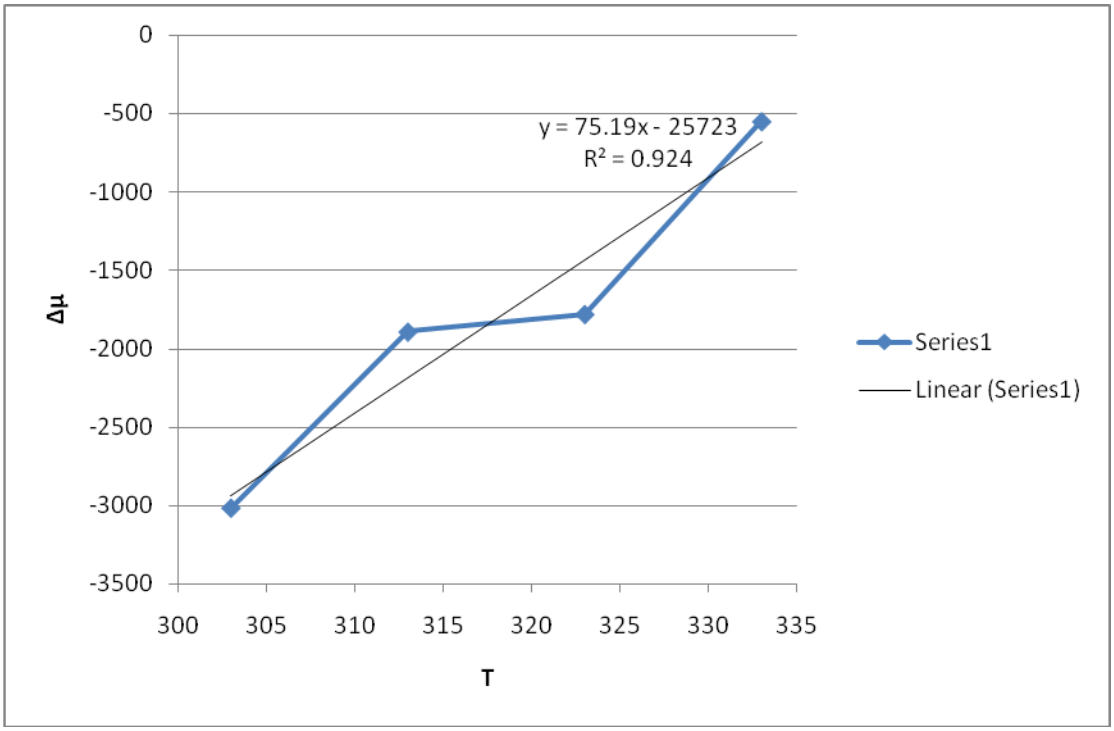


Figure A2.83: Plot of affinity (Δμ) against temperature (T) for 15% EPTAC sample

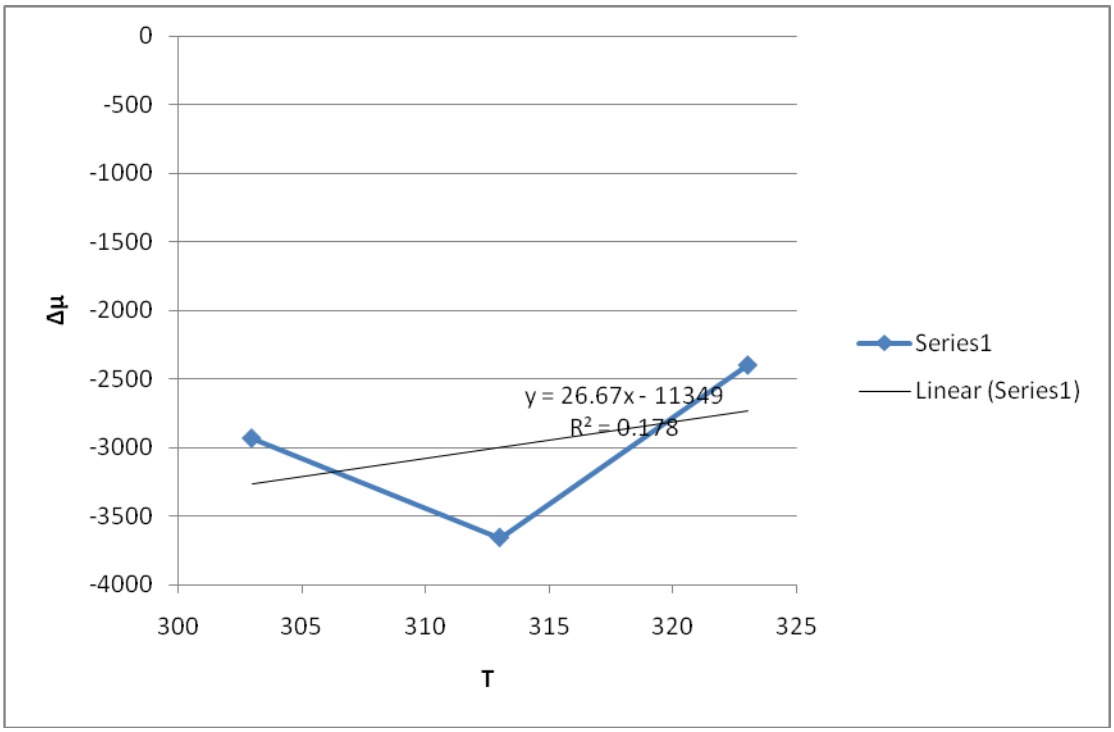


Figure A2.84: Plot of affinity (Δμ) against temperature (T) for 20% EPTAC sample

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PLATES: Photographs of equipment



Plate 1: Polymer laboratory Department of Textile Science & Technology A.B.U. Zaria where the research was conducted.



Plate 2: Beakers containing dye solution which was used for the dyeing.



Plate .3:-**Dual split** beam UV spectrophotometer (UVS- 2700/UVS-2800).

This equipment was used for dye calibration and determination of λ_{max}



Plate .4:-**Sherwood-**Colorimeter-257 absorbance were carried using this equipment.



Plate .5:**SANFA**- DK-420 Electric Thermostatic Water Bath Boiler

Processes involving heating were performed with this equipment



Plate .6:Sample bottles containing dye solution



Plate .7:Dyed fibre samples on display in this picture.