Thesis

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by

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THE ABSORPTION OF NAPHTHOL DERIVATIVES BY CELLULOSIC FIBRES.

ABSTRACT

The azoic dyes are obtained by coupling between, a naphthalene derivative end a diazotized amine The naphthalene derivative is referred to variously as a coupling component, arylamide or by its commercial name e.g. Breathol, Naphthol, etc. It is first adsorbed onto the textile material and the desired colour developed by immersing the fibre or fabric in a solution of the appropriate diazotized amine. The depth of the shade depends mainly on the amount of coupling component adsorbed on the fibre, prior to colour development.

The scope of the present work was to study the uptake of these compounds by cellulosic fibres under various conditions e.g. different alkali, salt and naphthol concentrations; temperature; and the effect of modifying the cellulose structure on absorption. It was also thought that a possible mechanism for the combination of naphthol with cellulose could be worked out and an attempt made to see if the general laws of sorption of solids from solution could be applied to the cellulose naphthol system.

As an introduction to the thesis an account is first given of the structure of cellulosic fibres, describing in outline the early theories of fine structure and the concept of crystallinity and accessibility and their relation to the absorption of dyes and other molecules by cellulosio fibres. An account is also given of the principal results of previous studies on the absorption of arylamides and direct dyes

by cellulose.

The abaorption of free alkali (the solvent for the Naphthols) was first studied, followed by napthol absorption under various conditions by the different cellulose samples. The sain results of the present investigations indicate that:

1) the hydroxyl groups of the cellulose chain are mainly responsible for naphthol absorption as shown by the reduction in absorption when these are oonverted to carbosyl groups.
2) primary hydroxyl groups account for higher equilibrium absorption than secondary ones.
3l oxidation of the hydroxyl groups reduces absorption.
4) opening up the cellulose structure by mereerization increases considerably the absorptive capacity of cellulose.

The absorption of two naphthols by standard cellulose at different starting concentrations was also studied and the results used to test several adsorption theories. Agreement was obtained for the treatment of Saruwalla and Kulkarni leading to the suggested mechanism that only the dye anions are adsorbed on specifio sites, while the sodium ions are diffusely adsorbed. The treatment adopting Hill's statistical approach also yielded a positive agreement. The concurrence of the theories tested lies in the fact that their formulation depends on the basic assumption of an initial monolayer absorption on which is superimposed a diffuse layer.

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CHAPTER ONE

1.0 FIBRE STRUCTURE

1.1 Introduction

The study of sorption by cellulosic fibres can be divided into two parts a) sorption kinetics b) sorption under equilibrium conditions. Studies of the absorption of water vapour, alkali, dyes and dye components, and other molecules have received a great deal of attention for two main reasons. First, it is important for the textile technologist to know how the amount of substance taken up is related to the different variables that control it. Second, the sorption of different molecules by a fibre provides a means of studying its structure.

1.2 Levels of Organisation in fibres

The structure of a fibre can be defined with reference to three levels of organisation[1]. These are the organochemical structure, the macromolecular structure, and the supermolecular structure. The organochemical structure refers to the chemical structure of the basic repeating unit in the polymer from which the fibre is built e.g. the glucose unit in the case of cellulose fibres. The macromolecular structure describes the entire polymer molecule or family of polymer molecules in terms of chain length, chain length distribution, chain conformation and chain stiffness. This, like the organochemical structure, is not uniquely characteristic of fibres, as it could be the same for a

fibre, a film, a powder, or a liquid.

In its native form, cellulose is a carbolydrate (empirical formula $C_6 H_{10} O_5$) in which the basic repeating unit is the D - glucose molecule joined through hemiacetal linkages in the 1,4 position. The anhydroglucose residues have a β - configuration. However, the difficulty of preparing pure samples of cellulose uncontaminated by polymers arising from sugars other than glucose has led to the conception of native cellulose as a family of polysaccharides rather than a single molecular species. It is a mixture of α-, β-, and γ- celluloses with different proportions of these in different celluloses. α - cellulose is insoluble after treatment with caustic soda of mercerizing strength. The alkali-soluble fraction which is reprecipitated on acidification is referred to as β - cellulose, whereas γ - cellulose is completely soluble in such alkali.

The length of the α - cellulose chain i.e. its degree of polymerisation (DP) has been determined using the techniques of osmometry[2], viscometry[3], ultracentrifugation[4] and light scattering[5], but the DP obtained cannot be said to correspond to that present in native cellulose as degradation during purification is inevitable. For native cellulose a DP of at least 3000 has been reported while for regenerated celluloses the DP varies between 300 and 600. The method of ultracentrifugation yields different values for the DP of cellulose

from different sources ranging from 36,000 for flax, 10,800 for cotton to 2 - 3000 for sulphite pulp and 460 for viscose rayon. Thus the molecular weight and its distribution depends largely on the source and purity of the cellulose and to some extent on the method by which it is determined.

The molecular formula of native cellulose may be represented as shown in fig. 1.

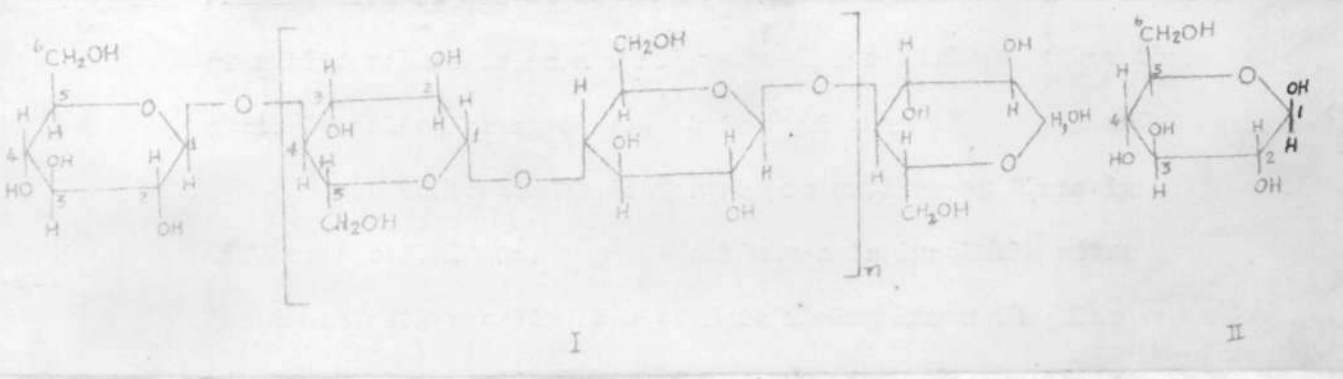


Fig. 1. (I) The cellulose formula,(II) A glucose unit.

Though different samples of celluloses may have the same organochemical structure, the same DP and chain length, they may have different properties, mainly physical ones, which are due to differences in the arrangement of the molecules in the fibres, i.e. due to the difference in the degree and relative amounts of crystallinity and non-crystallinity.

The three-dimensional regularity of the crystalline regions is conferred by the spatial distribution of the hydroxyl groups which makes it possible for the chains to

associate laterally by hydrogen-bonding. X-ray diffraction studies have revealed a monoclinic unit cell (fig.2.) with four anhydroglucose residues arranged parallel to the vertical or 'b' axis with cellubiose units at each corner and the glucose units firmly held together at the 1, 4 positions. Along the 'a' axis the adjacent chains point in alternate directions and are held together by hydrogen-bonding, while along the 'c' axis the lattice is held by weaker van der Waal's forces.

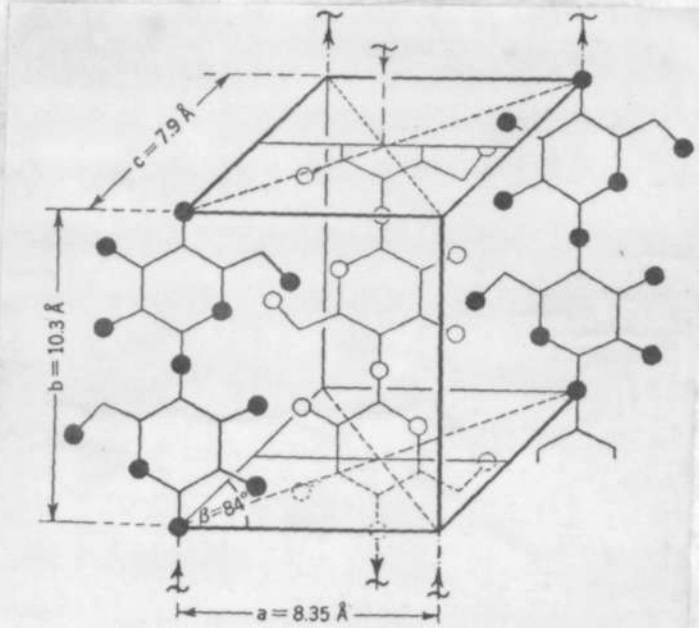


Fig. 2. Cellulose model (Meyer and Misch).[6]

From fig. 1, it can be seen that each anhydroglucose unit of the cellulose molecule (except the end groups) contains three free hydroxyl groups, one primary and two secondary. All the hydroxyl groups contribute to the three-dimensional network of hydrogen bonds, with the C - O.....O angle between 100° and 135°. Except $(OH)_1$, which is hydrogen bonded to a ring oxygen, O_5, each hydroxyl is involved in both donation and

acceptance of protons.

Four crystalline forms of cellulose designated as cellulose I, II, III and IV have been recognised [7]. Cellulose I is the form found in the native cellulose of plants whereas Cellulose II occurs in regenerated cellulose (Viscose, cellulose sheets) or when cellulose esters are hydrolysed. Cellulose II may also be obtained from native cellulose by vigorous swelling treatments, e.g. mercerization or cellulose precipitated from its solution [8]. Cellulose III is obtained by decomposition of an addition compound of cellulose with ammonia [9] whilst cellulose IV is obtained when cellulose has been heated in polar liquids such as formamide, glycol or glycerol under stress [10 - 12].

The β- glucose residues in the crystalline regions are arranged strictly parallel to each other and regularly spaced in a lattice corresponding to the unit cell given by Table I [13].

Table I Unit cell dimensions of different types of cellulose

Axis	Cellulose I	Cellulose II	Cellulose III	Cellulose IV
a	8.35A°	8.10A°	7.74A°	8.11A°
b	10.30A°	10.30A°	10.30A°	10.30A°
c	7.90A°	9.10A°	9.90A°	7.90A°
Angle β	84°	62°	58°	90°

1.3 Degree of crystallinity and accessibility and its determination

Two general methods are used for determining the degree and amount of crystallinity in cellulose materials. These are a) physical, b) chemical methods. The chemical methods are of two types (i) Kinetic studies, depending on two stages of chemical reaction - an initially rapid rate representing reaction in the amorphous regions, and a slower one occuring in the crystalline regions; (ii) reactions depending on reagents which react with

a limited percentage of the total number of hydroxyl groups present. Here the assumption is that the reagent is unable to penetrate the crystalline regions and the extent of reaction is a measure of the accessible fraction in cellulose. It is important to emphasise here that accessibility and amorphousness are not synonymous. The latter refers to a low order of packing whereas the accessible regions include, in addition to the amorphous regions, also the surfaces of the crystalline regions exposed to attack by reagents. The relationship between the crystallinity and accessibility of a cellulose sample may be expressed by [14]

$$A = \sigma\alpha + (100 - \alpha)$$

where A is % accessibility, α is % crystallinity, and σ is the fraction of crystallites accessible to the reagent.

The usual chemical methods employed for determining the degree of crystallinity and accessibility include heterogeneous acid hydrolysis [15], deuterium exchange [16] and formylation [17]. These methods assume an initially very rapid reaction followed by a tailing off or a virtually non-measurable rate of reaction. The extent of the initial reaction represents the amount of accessible material.

Non-kinetic chemical methods of accessibility determination include the measurements of the equilibrium absorption of molecules of different sizes e.g. iodine, dyes and dye

components, etc.

The physical methods of density measurements[18, 19], X-ray diffraction[20] and infrared spectroscopy[21] have also been used to determine degrees of crystallinity. These methods assume that the crystalline and amorphous regions exist as discrete and uniform regions.

1.4 Theories of Fine Structure

Early studies of high polymers were carried out on natural cellulosic fibres and during the last half century various theories of fibre structure have been advanced to explain the many chemical, physical, and mechanical properties of this class of compounds. Notable contributors were Frey-Wyssling[22], Hermans[23], Staudinger[24], Preston[25], Carothers[26], Mark and Meyer[27], and Leadermann[28].

The earliest of these theories known as the micellar theory[29] was originated in the 19th century by Nageli who considered starch grains and plant cell membranes as consisting of "sub-microscopic crystalline particles, called micelles, in between which is embedded some indeterminate intermicellar substance. Solutions of this substance consist of colloidal dispersions of the micelles." The discovery by Mark and Meyer[27] that fibres and other plant materials were able to diffract X-rays lent support to the micellar concept. However, basing his deductions on viscosity measurements of

polymer solutions Staudinger[30] gave the view that the molecules were much longer than could be accomodated in the Nageli micelles. He therefore postulated the continuous theory in which he considered high polymers as made up of a large continuous imperfect crystal with the end groups appearing as local distortions. By this structure an amorphous high polymer consisted of a random network of molecules lacking in three-dimensional order and structural regularity.

As better chemical and physical methods for measuring molecular dimensions became available it was shown that the polymer molecules were about ten times as long as the micelles. The micellar theory had, therefore, to be abandoned, but rather than accept the continuous theory its exponents took up the idea of the fringed micelle by which it was assumed that the same molecule must pass through more than one micelle and the intermicellar substance was a region of non-crystalline material linking the structure together in a continuous molecular network. Thus the crystalline micelles and the amorphous regions occur alternately while the former are held together by primary molecular forces. This was therefore a combination of the two former views - the micellar and the continuous theories.

The new fringed-micellar theory has proved very successful, being capable of explaining many physical, chemical and mechanical properties; thus variations in moisture absorption, uptake of dyes and reactions with other chemicals may be explained by

assuming that the non-crystalline regions were more accessible to penetration by foreign molecules while the crystalline regions are largely unaffected. The stability of the crystalline regions would cause limited swelling in water while differences in density would be due to the closer packing in the crystalline regions as compared with the non-crystalline regions. Mechanical, electrical, optical (birefringence) properties as well as X-ray diffraction were all explained by the theory. IR and NMR studies have confirmed the division between crystalline and non-crystalline regions.

But more important, the theory pointed out that the passage from one region to another did not occur at a discrete boundary. Thus the transition from the crystalline to the amorphous regions occurs in a gradually decreasing manner until there is complete lack of structural regularity, which is identified as the amorphous region. This gave rise to the concept of lateral order distribution whereby regions of varying order or degree of structural regularity exist in a continuous gradation as shown in fig. 3. The truth of this concept has been indicated by the results of several investigators.[31, 32]

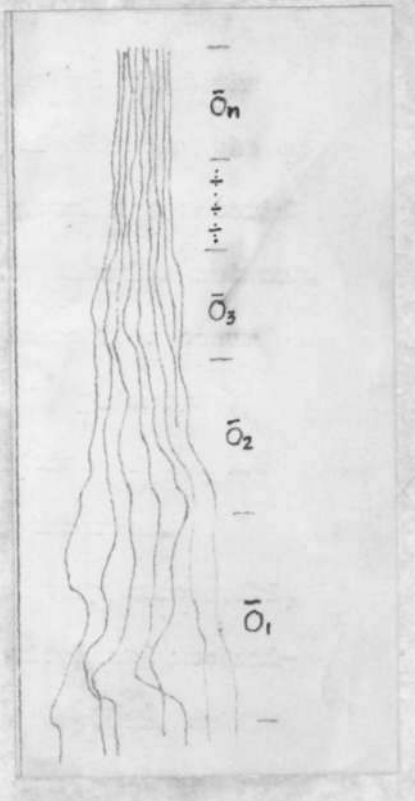


Fig. 3. Lateral order distribution in cellulose.

It would appear that a versatile theory such as this seems, capable of explaining most, if not all, the physical properties of fibres had been discovered. However, the observation of very fine fibrils with the electron microscope raised new problems and ideas. These fibrils of geometrically regular shape (usually ellipsoidal) have well-defined cross-sectional shape and area, and are of varying lengths. It was therefore necessary to include the fringed micelle structure within the fibrils. However, this introduces complications. For example the electron microscope shows fibrils with diameters as small as 100A° whereas X-ray diffraction and other studies indicate that in some fibres the thickness of the crystalline regions are at least 50A° i.e. about ten molecules across the width. It would thus be impossible to fit an orthodox fringed-micelle structure into fibrils that are no more than twice as wide as the crystallites.

The present position with respect to the theories of fibre structure is based on the fringed-fibrillar concept of Hearle[33]. This seeks to remove the underlying assumption of the fringed-micelle theory that all molecules in the crystalline region diverge from the same point, which appears to have no justification whatsoever. The new theory regards the crystalline regions as continuous fringed fibrils made up of molecules diverging from the fibrils at different positions along their length. Branching of the crystalline fibrils could also occur in which a molecule diverges from its original fibril, passes through a non-crystalline region and further on gets incorporated into

another crystalline fibril. A termination of the fibrils could occur by all the components breaking away while formation could be due to a chance approach of two molecules in positions appropriate to crystallization. Branching of the fibrils is also responsible for the formation of spherulites which are seen as circular birefringent areas in the field of view of a polarising microscope.

Thus the fringed-fibrillar theory represents a continuous crystalline fibrillar skeleton joined in a network by fibril branching and by individual molecules passing from one fibril to another. It is therefore basically a combination of the ideas of the continuous structure of Staudinger and the major features of the fringed-micelle theory and also takes into account the experimentally verified occurence of fibrils in cellulose.

The various theories referred to above are represented in fig.4.

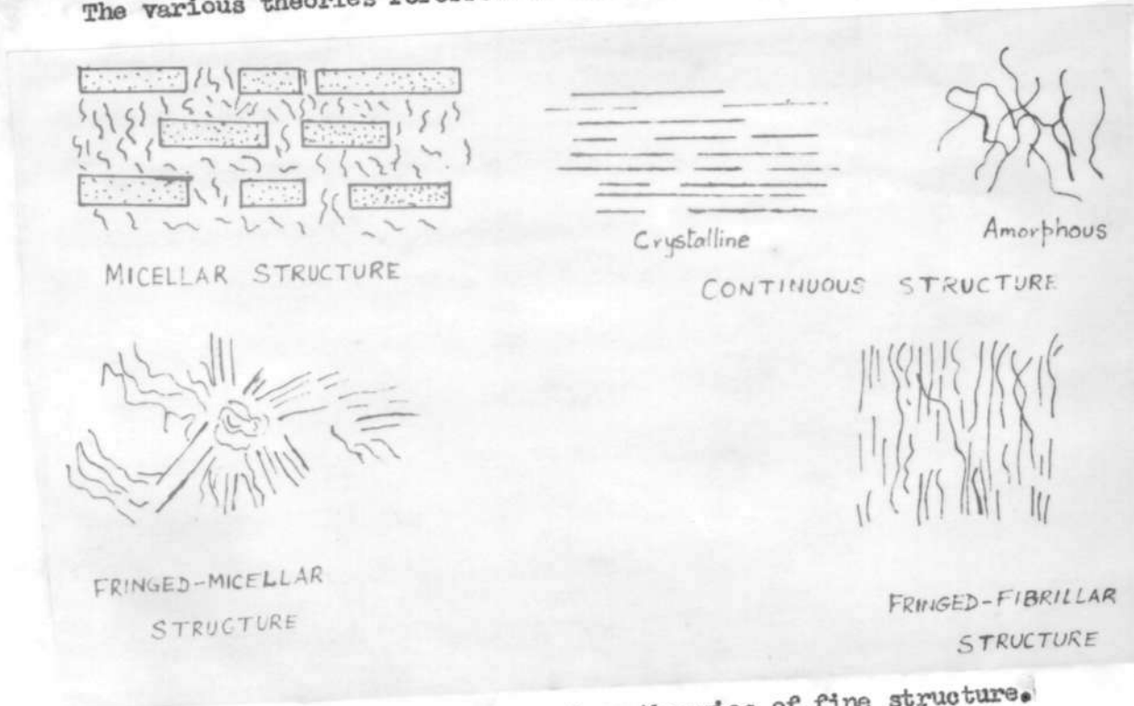


Fig.4. Models representing the various theories of fine structure.

1.5 Cotton

The Cotton plant belongs to the genus Gossypium, with

several variations and a wide geographical distribution.[34] The growth of the fibre is of great importance as it is at this stage that the major structural features are deposited in the cell walls. There are several distinct growth stages accounting for the complex, heterogeneous structure of the fibre. In the first 13 - 20 days there is a lengthening of an epidermal cell as a thin membrane (0.2 μ) called the primary wall. This is followed by the deposition of cellulose on the inner surface of the primary wall over a period of 25 - 40 days. This secondary wall does not fill the cell but leaves a central canal called the lumen. The final stage occurs when the boll opens, attended by drying and loss of water, leading to a collapse of the lumen and yielding a characteristic flat, ribbon-like shape with many twists and convolutions.

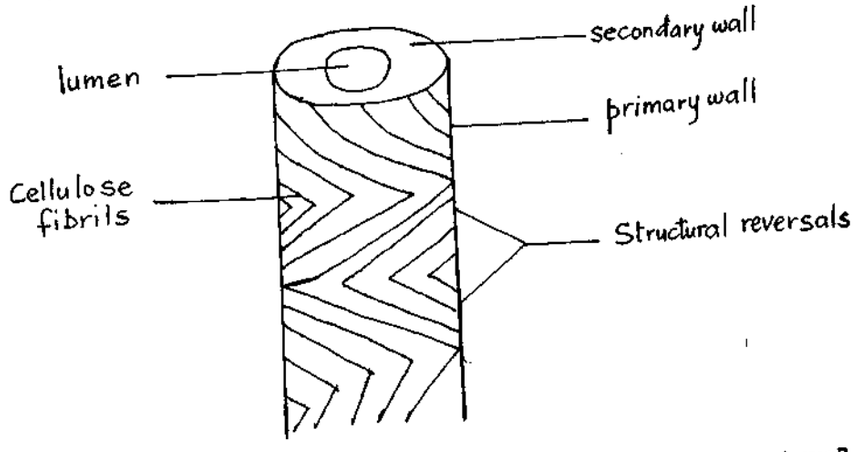


Fig.5. The cotton plant cell showing the structural reversals.

During the secondary wall development fibrils are deposited in a helical manner, with a constant helical angle with respect

to the length and cross-section of the fibre. The presence of these fibrils has been demonstrated by means of the electron microscope. A light microscopic examination of a highly swollen fibre has also revealed a lamellated arrangement of these fibrils in the secondary wall. The lamellate structure occurs throughout the whole length of the fibre. The angle of the helix which the fibrils make with the fibre axis is referred to as fibrillar orientation. For commercial cottons this is about 35°, though they may vary from $20 - 45^{\circ}$.

Many properties of the cotton fibre, especially the mechanical properties e.g. deformation, tenacity, are due to fibrillar orientation. A high degree of fibrillar orientation means a high elastic modulus, and low extensions at break. The reverse is also true. Such other mechanical properties as tensile strength and work recovery as well as some chemical and physical properties are also related to the orientation. Though the direction of the helix remains constant in all layers at a given point along the fibre length, its sense reverses some 30 - 100 times along the entire length of the fibre and this may be responsible for the numerous convolutions observed and for the extensibility of cotton (see fig. 4). At the reversal point the fibrils are oriented almost parallel to the fibre axis.

The effect of mercerization (treatment by NaoH of about 15 - 20% strength) on the fine structure of cotton has been studied. It was shown that the orientation of the crystallites

increase after they have been penetrated by caustic soda. This cannot be due entirely to the deconvolution[35] which accompanies swelling as it would otherwise have been effectively counteracted by the simultaneous shrinkage that occurs. The effect is also due to the large lateral expansion which results from the breaking of the primary wall during swelling. This gives rise to a considerable pressure being exerted on the secondary wall, leading to the ultimate improvement in orientation.

1.6 Fibre properties

While it is true that properties of fibres are a consequence of their fine structure it is also true that the fine structure has been deduced from the properties displayed by these materials. A study of the properties of cellulose fibres may thus be divided into two:

a) properties depending on the amorphous regions, and
b) those depending on the degree of crystallinity and orientation.

The former are exemplified by such processes as moisture sorption, dyeing, swelling, etc. The absorption of dyes is believed to take place in the amorphous region and on the surfaces of the crystalline regions. This is because the molecule of dye is too large to penetrate the close-packed crystalline region. Substantive dyes are believed to be held to the cellulose by hydrogen-bonding effects only.

Moisture regain is dependent on the temperature and relative

humidity of the surroundings, its relationship with either parameter being sigmoid in shape. It also shows the hysteresis effect by which different amounts of water vapour are sorbed, depending on whether the fibre is taken from a lower to a higher relative humidity (absorption) or vice versa (desorption).

The water molecule is able to penetrate the amorphous regions quite readily and because the chain molecules are oriented in the direction of the fibre axis, swelling of the fibre occurs mainly in the lateral direction. The degree of swelling depends on the amount of amorphous material, the size of the crystallites and on the presence of polar groups.

Mechanical, optical and electrical properties of fibres depend on the degree of crystallinity and orientation. These properties include fibre strength, durability, extensibility, crease-recovery, dielectric constant and optical birefringence.

CHAPTER TWO

2.0 SORPTION BY CELLULOSIC FIBRES

2.1 General Theories of absorption of solutes from solution

Whereas the absorption of gases and vapours has received intensive investigation by many workers, the absorption of solutes from solution into solid surfaces has been given much less attention. This might be due to the difficulty introduced by the presence of solvent molecules in the solution and the difficulty in accounting for solute-solvent, solute-solute interactions. However, the applications of such absorption can be seen in chromatographic adsorption analysis[36] used for separating natural products like amino acids, peptides and plant pigments, in biochemical enzymatic reactions[37] occuring by virtue of an adsorption from solution onto the enzyme surface, and the dyeing of fibres[38].

In general the absorption of solutes from solution leads to the formation of a monomolecular layer. Experimental data have been found to fit fairly well into the Freundlich type of isotherm[39] given by

$$\frac{x}{m} = k_1 \, c^{1/n}$$

where x and m are the masses of substance adsorbed and of adsorbent respectively; c is the concentration of the solution after equilibrium has been attained; and n is a constant usually greater than unity. A plot of $\log \frac{x}{m}$ against log c should therefore yield a straight line of slope 1/n.

i.e. $\log \frac{x}{m} = \log k_1 + \frac{1}{n} \log c$

The Freundlich isotherm is similar to the Langmuir isotherm for gases[40], given by

$$\frac{\theta}{1-\theta} = k_A p_A$$

where θ represents the fraction of sites occupied, p_A is the external pressure and k_A is a constant related to the heat of absorption and the surface area of the solid.

For a solution, this can be written as

$$\frac{\theta}{1-\theta} = k_s c_s$$

where c_s is the concentration of the external solution. However the basic assumption of the Langmuir theory must be taken into account for the relationship to hold. These are that

1. The solid surface contains a fixed number of adsorption sites i.e. at equilibrium at any temperature and concentration a fraction θ of the sites is occupied by adsorbed molecules, and a fraction $1-\theta$ is not.

2. Each site can hold only one adsorbed molecule i.e. the maximum adsorption possible corresponds to a complete monomolecular layer.

3. The heat of adsorption ΔH is the same for all the sites and independent of the covered fraction. Using the van't Hoff equation $\partial(\Delta F/T)/\partial T = -\Delta H/T^2$, where ΔF, the change in free energy, is given by

$$\Delta F = - RT \ln p.$$

Hence $\frac{\partial \ln p}{\partial T} = \Delta H/RT^2$

or $\frac{\partial \ln c}{\partial T} = \Delta H/RT^2$

4. There is no interaction between molecules on different sites. The chance that a molecule condenses at an unoccupied site or leaves an occupied site does not depend on whether or not neighbouring sites are occupied. This implies that the external entropy S_A of the adsorbate be given by the equation

$$S_A = - R \ln \frac{\theta}{1 - \theta}$$ where R is the gas constant

There are two limiting cases of the Langmuir isotherm:

a) at low concentrations i.e. when little adsorption has occured, the expression reduces to

$$\theta = k^1 c_s$$

b) at high concentrations when all the available sites are virtually saturated and increasing the concentration has little effect on the amount of solute adsorbed - the flat portion of the isotherm when θ is approximately unity,

$$1 - \theta = \frac{1}{k^1 c_s}$$

2.2 DYE SORPTION

The sorption of dyes by cellulosic fibres is known to occur in several distinct stages.[41] The first is the diffusion of the dye from the solution onto the surface of the fibre. For direct acid dyes the diffusion of the dye anions from the dyebath to the surface of the fibre when the solution is agitated is instantaneous. The rate determining step is however the diffusion of the dye from the surface of the fibre into the interior of the water-swollen cellulose. Neale has suggested a quantitative explanation of the absorption of dyes by cellulose in terms of a Donnan membrane equilibrium and regards direct dyeing as a process of diffusion in which an ultimate equilibrium between cellulose and dyebath is obtained, depending on the condition of dyeing. Factors such as the chemical constitution and fine structure of the fibre, the concentration and substantivity of the dye, the influence of added salt, the temperature, and surface active agents greatly affect the process of diffusion and the overall absorption of dyes by fibres.

2.3 Cellulose Structure

This has already been described. It only requires restatement here that the factors responsible for the chemical reactivity of cellulose are the three hydroxyl groups - one primary and two secondary - and the relative amounts of crystalline and non-crystalline or accessible regions of the fibre.

Absorption occurs mainly in the non-crystalline amorphous regions where the pores and channels (C.20 - 100 A° in diameter)

are large enough to permit the entry of dye molecules which then diffuse along the channels and are absorbed by the cellulose molecules.

The principal chemical forces responsible for the absorption of dyes by cellulosic fibres are the general van der Waal's forces (electronic dispersion forces), hydrogen-bond forces, and the electrostatic forces between charged groups.

2.4 Effect of swelling treatment on absorption

The best known of the swelling treatments to which cellulose may be subjected is mercerization. Mercerization is the treatment of cotton yarns and fabrics with concentrated alkali. Its purpose in industry is to induce greater lustre, greater dye affinity and greater tensile strength in the material. During mercerization a large lateral swelling and longitudinal shrinkage occur causing a very great opening up of the cellulose structure and making available a large number of hydroxyl groups for combination. Since mercerization decreases the amount of crystalline material and increases the separation of the cellulose chains, the resulting fibres have a greater absorptive capacity and are more reactive e.g. moisture regain, absorption of alkali or dyes from dilute solutions are greatly increased.

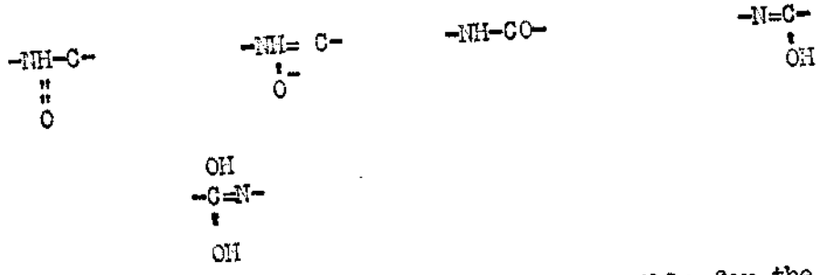
2.5 DYE CONSTITUTION AND SUBSTANTIVITY

For the positive adsorption of a dye from an aqueous solution a greater attraction for the cellulose phase than for the water phase is a prerequisite. By formation of aggregates of colloidal micelles the dye molecules displace the water

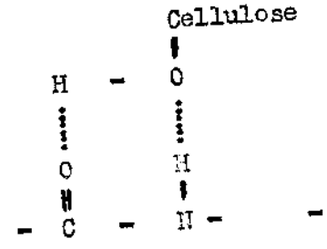
molecules in the intercrystalline regions of cellulose and attach themselves to the cellulose molecules, through the formation of hydrogen-bonds between the dye and cellulose.

The relation between chemical constitution and substantivity of azoic coupling components has been investigated by several workers. Rath[42] has suggested that substantivity was associated with the colloidal character of alkaline solutions of these compounds and was favoured by increase in molecular weight of azoic coupling component.

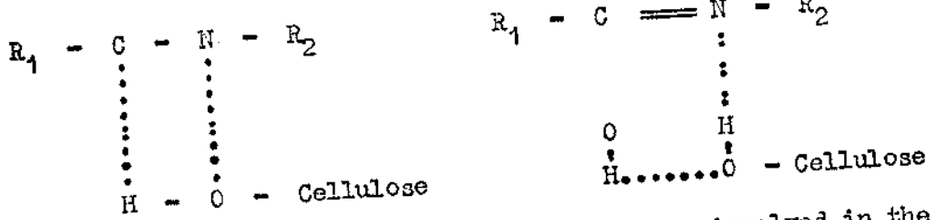
The requirement of hydrogen-bonding between dye and cellulose means that the presence of such groups as azo, amino, hydroxyl, and amide groups in the dye molecule is an essential requirement. Ruggli[43] has suggested that the main grouping responsible for the substantivity of these compounds for cotton was the acid amide (-CONH-) group. Krzikalla and Eistert[44] have attributed the substantivity of these azoic coupling components to the residual affinity of the amide group brought about by enolisation. This is evidenced by the loss of substantivity by the introduction of suitable substituents in the molecule which prevent enolisation. In addition, Schirm[45] has shown that the presence of a conjugated system of double bounds favoured substantivity as a result of the residual valency in conjugation with the auxochrome present e.g. bixin



However, the fundamental factor responsible for the substantivity of 'naphthols' is the hydroxyl group adjacent to the -CONH-group, which takes part in the attachment to cellulose. Groups capable of accepting or donating electrons aid substantivity provided that the position of the substituent is conducive to substantivity. This permits the formation of hydrogen bonds with the hydroxyl group of cellulose.



This is capable of resonating as follows:



That the hydroxyl groups of cellulose are involved in the bonding is shown by the fact that

1) on esterification of the cellulose its capacity for absorbing direct dyes is inhibited.[46]

2) The heat of dyeing for direct dyes have been shown to be about 7Kcals - same order as required for H-bond formation[47].

3) For linear dye molecules the most stable arrangement between dye molecule and cellulose occurs when the substantive groups in the dye occur alternately at a distance of 10.3 - 10.8 A° or multiples thereof, which corresponds to the periodicity of the cellobiose unit of the cellulose chain[48].

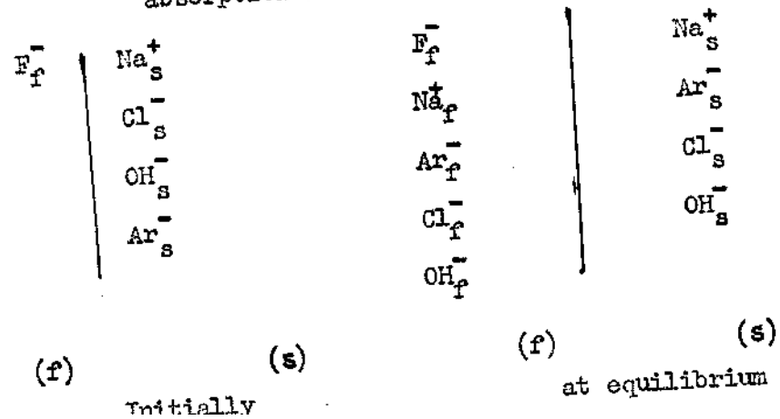
2.6 Effect of added electrolyte on absorption

The theory[49], which applies strictly only to carboxyl - free cellulose (the nearest approximation of which is cotton) predicts that as salt/dye ratio, p, is increased the substantivity ratio q (Dye absorbed/Dye in solution) approaches a finite upper limit. However, the experimental plots of log q against log p are linear for large p, and give no indication of a finite upper limit. The theory of direct dyeing of cellulose makes use of 3 postulates concerning the system at equilibrium.

1. electrical neutrality of the cellulose phase and of the dyebath. Cellulose has a negative charge with respect to water. This charge in oxycellulose increases with the degree of oxidation and with the build-up of dye on the fibre. In aqueous solution also the anionic dye molecule ionises, acquiring a negative charge. Hence an electrostatic repulsive force i s set up between the dye anion and cellulose surface. The effect of this

zeta potential is to oppose the absorption of the anion. Added electrolyte has the effect of shielding the like charges and thereby overcoming the repulsion between the ionized dye and the surface of the cellulose, and thus facilitating absorption.

2. Donnan relations between the concentrations of the free ions in the two phases. This takes into account the distribution of freely diffusible ions between two phases separated by a membrane . In this case we have the cellulose surface and the solution as the two phases and the interface between them as the membrane. The cellulose contains some fixed charges F^- which are unable to permeate the membrane . In the solution, in the presence of alkali solvent and electrolyte, say sodium chloride, the diffusible ions are Na^+, Cl^-, OH^-, Ar^-. The distribution of ions in the cellulose phase (f) and the solution phase (s) initially and after equilibrium absorption is:



It has been shown that at equilibrium the product of the concentrations of the diffusible ions on one side of a membrane is the same as that of the same ions on the other side.

i.e. $(Na_f^+) \cdot (Ar_f^-) \cdot (Cl_f^-) \cdot (OH_f^-) = (Na_s^+) \cdot (Ar_s^-) \cdot (Cl_s^-) \cdot (OH_s^-)$

Applying the condition for electrical neutrality

$$Na_f^+ = Ar_f^- + Cl_f^- + OH_f^- + F_f^-$$

Assuming that at high NaCl concentration

$$Cl_s^- = Cl_f^-$$

$$OH_f^- = Na_f^+ - F_f^- - Ar_f^-$$

Therefore the Donnan relation may be expressed as

$$\frac{Na_s^+ \times OH_s^- \times Ar_s^-}{Ar_f^- \times Na_f^+ \times (Na_f^+ - F_f^- - Ar_f^-)} = 1$$

3. Proportionality between dye absorbed and the concentration of free dye ion in the cellulose phase.

Added electrolyte has a further effect in causing a reduction in the solubility of the dye and thereby aiding aggregation of the dye molecules which is necessary if a strong dye-cellulose complex is to be formed.

The effect of added salt has been extensively investigated.[50] Neale[51] has also shown that the basic dyes Janus Red B (CI 266) and Victoria Blue B (CI 729) have a strong affinity for bleached cotton even from neutral solution containing no added electrolyte. The behaviour of these dyes which ionise in

solution to give positively charged dye ion is in favour of the electrostatic theory of the salt effect.

2.7 Energy Considerations

The energetics of dye sorption by cellulose can be described by reference to three parameters viz. the change in standard free energy of the system (also known as the affinity ΔG°); the heat of reaction (absorption) ΔH°, and the entropy change ΔS.

2.7.1 Dye Affinity[52]

ΔG°, the affinity of the dye - cellulose complex is given by

$$-\Delta G^{\circ} = RT \ln \frac{A_f}{A_s} \qquad (1)$$

where A_f and A_s are the activities of the dye in the fibre and in solution respectively; R is the gas constant and T the temperature in degrees absolute.

For a non-aggregating dye $Na_z Ar$ the activity of the dye in solution is given by

$$A_s = (Na_s^+)^z (Ar_s) \qquad (2)$$

assuming the activity coefficient of unity, while the activity of dye in the fibre is given by

$$A_f = \frac{(Na_f^+)^z (Ar_f)}{V^{(z+1)}} \qquad (3)$$

(Na_s^+) and (Na_f^+) are the concentrations of sodium ions in solution and in the fibre, expressed as g. ions per litre of

solution and g. ions per kg. dry fibre respectively. Ar_s and Ar_f are the concentrations of arylamide in solution and on fibre expressed in similar units as above respectively.

Re-arranging, equation (1) above becomes

$$\log A_f = \log A_s - \frac{\Delta G^\circ}{2.303\ RT}$$

Hence a plot of $\log A_f$ against $\log A_s$ at constant temperature should give a straight line of unit slope. ΔG° may be calculated from the intercept on the $\log A_f$ axis.

2.7.2 Heat of Reaction[53]

The heat of dyeing represents the energy of bond formation between cellulose and dye. If ΔG_1 and ΔG_2 are the affinities at two different temperatures T_1 and T_2, the heat of reaction ΔH° is given by the equation

$$\Delta H^\circ = \frac{\left(\frac{\Delta G_1}{T_1} - \frac{\Delta G_2}{T_2}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

If ΔH° is constant, a plot of $\frac{\Delta G}{T}$ against $\frac{1}{T}$ should give a straight line of slope ΔH°

The heats of dyeing (ΔH) and entropy change (ΔS) of several direct dyes on cellulosic fibres for a mean temperature of 350°K as determined by Marshall and Peters[54]

are shown in Table II

Table II Heat of reaction $-\Delta H$ and change in entropy $-\Delta S$ for some direct cotton dyes determined at a mean temperature of 350°K

Dye	$-\Delta H$ kcal/mole	$-\Delta S$ gcal./°Cmole	No. of points of attachment
Chrysophenine G	14	31	2
Durazol Red 2B	11	21	2
Durazol Grey RG	15	31	2
Chlorazol Violet N	12	21	2
Chlorazol Sky Blue FF	20	43	3

From the heat of formation of a hydrogen-bond (7kcal/mole) Marshall and Peters have concluded that at least two hydrogen bonds are involved in the attachment of a direct dye to cellulose. However it must not be assumed that hydrogen bonds are the sole factors in the values of the heat of reaction.

2.7.3 Entropy of Reaction[55] ΔS

This represents the restriction in the mobility of the molecules of the arylamide as a result of its attachment to the cellulose molecule. It can be evaluated from a knowledge of the affinity and the heat of reaction using the equation

$$-\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S$$

CHAPTER THREE

3.0 EXPERIMENTAL PROCEDURE AND RESULTS

3.1 MATERIALS AND CHEMICALS

3.1.1 MATERIALS

1. Preparation of Fibre Substances

a. Standard Cellulose

A 30's single yarn spun from Northern Nigeria cotton and obtained from the Nortex Limited, Kaduna was used. It was carefully purified according to standard procedure:[56]

(i) Scouring. This treatment which was employed to remove oils, waxes and fatty acid impurities in cotton depends on the use of alkali which may either form a soap with the free fatty acids or decompose fats to form a soap. The soap then emulsifies the oils and waxes which can be removed by rinsing.

The yarn in lee form was scoured under steam pressure of 35 lbs/in^2 for seven hours. The scouring liquid was made up of 0.1N sodium hydroxide, 1% sodium silicate and 1% Lissapol NDB. The material to liquor ratio was kept at 1:8. The scouring was carried out in a Pyrex beaker which was placed in an autoclave. Care was taken to see that all the air was expelled from the autoclave before the pressure was raised. At the end of the scouring treatment the autoclave was allowed to cool down sufficiently so as to avoid any degrading action of

atmospheric oxygen on the alkali-soaked cellulose. The scoured sample was then thoroughly rinsed, first with tap water, followed by distilled water.

(ii) Bleaching. The purpose of the bleaching process was to produce a pure, white absorbent material. The reagents usually employed are either oxidising agents (hypochlorites, peroxides, etc.) or reducing agents (stannous chloride, sodium bisulphite, etc.)

The scoured yarn was treated with bleaching powder solution containing 3 gm available chlorine/litre for four hours at a pH of about 10.5. The yarn was turned from time to time. It was then thoroughly washed with distilled water.

(iii) Souring. To decompose any residual bleaching reagent and any insoluble calcium salts which may have been deposited on the fibres the bleached yarn was treated with 1% hydrochloric acid solution for thirty minutes. This was followed by repeated washing with distilled water for three days till the pH of the wash was neutral.

Conditioning of the fibre

The fibre substance was conditioned by placing it in an atmosphere of 65% relative humidity at 30°C provided by a saturated solution of sodium nitrite in a vacuum dessicator. 1 g. samples were also placed in the same dessicator and removed and weighed from time to time until they showed no further change in weight. The fibre substance was maintained in this compartment so that all subsequent samples

removed for experiment could be easily comparable.

At the end of the purification processes the fibre substance was found to have the following specifications:

Carboxyl content (iodimetric method)[57] 0.612 meq/100g.

b. Mercerized cellulose[58]

Standard cellulose prepared as above was treated with 17.5% sodium hydroxide solution at 20°C for one hour. The purpose of this treatment was to remove the β and γ celluloses present in the sample and to bring about a swelling of the yarn. The sample was washed many times with distilled water and steeped in 1% acetic acid for 10 - 15 minutes. The yarn was then kept in contact with 0.01 N hydrochloric acid overnight, washed free of acid, dried and stored in an atmosphere of 65% relative humidity at room temperature of 30°C.

c. Nitrogen dioxide oxycellulose[59]

A solution of nitrogen dioxide in carbon tetrachloride in the ratio of one of the former to eight of the latter was used. Standard cellulose, cut into small pieces of 1 - 2 mm length to allow for as uniform penetration of the oxidant as possible, was treated with the solution of nitrogen dioxide in carbon tetrachloride in a 2 - litre Quickfit flash. The material to liquor ratio was 1:15. The stoppered flask was mechanically shaken at room temperature (30°C) during the oxidation.

The oxidised product was separated from the oxidising mixture, blown with air to remove any volatiles present, washed with carbon

tetrachloride and then soaked in frequent changes of distilled water until the wash water was neutral to bromthymol blue indicator. The samples were air-dried and then conditioned at 65% relative humidity at 30°C.

Carboxyl content 45.0meq/100g.

d. Periodate oxycellulose [60,61]

Standard cellulose cut into 1 - 2 mm pieces was treated with a 0.05M solution of sodium metaperiodate for 24 hours at 30°C. The pH of the solution was kept between 5.3 to 5.6. At the end of the reaction the oxycellulose obtained was washed with distilled water till free from acid, vacuum - sucked and air-dried. It was conditioned at 65% relative humidity at 30°C.

Determination of Oxygen consumption of periodate oxycellulose [62]

The periodate solution was neutralised with sodium bicarbonate solution and treated with excess standard sodium arsenite solution. 10% aqueous potassium iodide solution was added and after being kept at room temperature for 10 - 15 minutes the excess arsenite solution was titrated against standard iodine solution. The determinations were carried out before and after the oxidation and the amount of periodate consumed calculated from the difference in the titres.

1cc of 0.10N sodium arsenite solution ≡ 0.0095965g. HIO_4

≡ 0.010696g. $NaIO_4$

On this basis, the periodate oxycellulose prepared for this study consumed 146 mg. $NaIO_4$ per g. of sample.

e. Reduction of periodate oxycellulose with borohydride[63]

30 g. of the periodate oxycellulose were treated with a 0.10 M aqueous solution of sodium borohydride in a 2-litre Quickfit flask for 48-72 hours keeping a material to liquor ratio of 1:50.

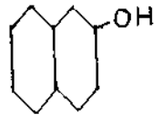
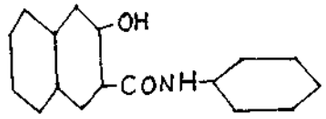
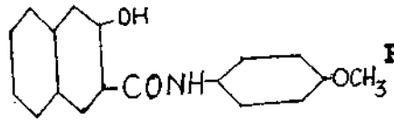
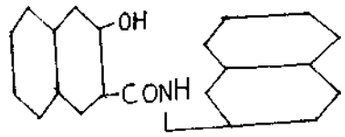
The reduced product was washed several times with distilled water, steeped in 0.01 M acetic acid for 30 minutes and further washed with distilled water till free from acid. It was air-dried and conditioned at 65% r.h. and 30°C.

f. Oxidation of periodate oxycellulose with sodium chlorite[64]

30 gm of periodate oxycellulose were treated with solution containing 0.10 M sodium chlorite in 1.5 M acetic acid for 72 hours. The flask and container were constantly shaken. The oxidised sample was air-dried and conditioned at 65% r.h. at 30°C.

3.1.2 CHEMICALS

A. Arylamides of 2 - hydroxy - 3 - naphthoic acid and their derivatives

Chemical Name	Chemical Structure	Brenthol	Naphthol	Molwt	M.p(°C)
1. β-Naphthol		-	-	144.2	122
2. Phenylamide of 2-hydroxy-3-naphthoic acid		AS	AS	263	249
3. 4' -Methoxy-phenylamide of 2-hydroxy-3-naphthoic acid		PA	AS-RL	293	230
4. 2' -Naphthylamide of 2-hydroxy-3-naphthoic acid		BN	AS-SW	313	244

3.2 Purification of Naphthols[65]

The commcerical samples of Naphthols β , AS, AS-RL, and AS-SW obtained from Nortex Ltd., Kaduna were purified as follows:

Each Naphthol was dispersed in boiling distilled water for a few minutes and filtered hot. This was repeated several times until the filtrate was free from any coloration. The purpose of this treatment was to remove all water-soluble

impurities from the compound. The Naphthol was then treated with a 2% aqueous sodium bicarbonate solution to remove unconverted β - oxynaphthoic acid. The suspension was filtered hot, washed with hot 2% bicarbonate and then hot distilled water to remove all sodium bicarbonate (effervescence test with dilute HCl on filtrate). To remove water insoluble impurities from the sample the residue remaining after the sodium bicarbonate treatment was pasted with ethyl alcohol and dissolved in a small amount of concentrated sodium hydroxide solution (about 40%), the solution diluted with distilled water and filtered. The 'naphthol' was precipitated from the alkaline solution by gradual addition of 10% HCl solution accompanied by vigorous stirring. The resulting dispersion was filtered and the residue washed free of acid (till no precipitate with silver nitrate and no blue spot with Congo Red paper). The 'naphthol' was then crystallized from solvents like ethanol, glacial acetic acid, etc. and the purity checked from its melting-point and the analysis of the elements present.

B. OTHER CHEMICALS

1. Sodium chloride - (B.D.H.) Analar Quality
2. Sodium Borate (Borax Analar quality
3. Sodium hydroxide Analar quality
4. Sodium silicate
5. Hydrochloric acid Analar Quality

6. Lissapol
7. Dispersing agent
8. Sodium metaperiodate — Analar quality
9. Sodium chlorite — Analar quality
10. Sodium borohydride — Laboratory Reagent quality.

3.3 ESTIMATION OF THE ABSORPTION OF NAPHTHOLS BY CELLULOSIC FIBRES

Several methods have been used by different workers in the estimation of 'naphthols' in aqueous alkaline solutions. These include:

1. The estimation of nitrogen[66]
2. Gravimetric method[66]
3. The coupling of the 'naphthol' with a suitable diazotized amine[67, 68]
4. Iodimetric method[69]
5. Colorimetric measurement[66, 70]
6. Alkalimetric or potentiometric titration method[71]
7. Volumetric method involving the use of suitable indicators e.g. Alkali Blue 6B[72]
8. Ultraviolet absorption method[73]

Of these the last two methods appear to give the most reliable results. In the present work the ultraviolet absorption method developed by C.H. Giles[73] was employed. Aqueous alkaline solutions of 'naphthol' have been found to give a high absorption in the ultraviolet region of the

spectrum at 365 and 404.7 mμ wavelengths. The 365 mμ wavelength which gives a stronger absorption and the more linear calibration curves was used. An SP500 Unicam spectrophotometer with silica cells of 1 cm thickness was used in the present study for the estimation of naphthols.

3.3.1 Dissolution of Naphthols

The naphthol solution was prepared by pasting exactly 5 g. of the purified naphthol with 0.2g. dispersing agent (sodium salt of oleyl sulphate), 5 ml hot water and 10 ml 2.5N sodium hydroxide solution. More hot distilled water (50 ml) was added and the mixture boiled to give a clear solution. It was then made up to a litre with cold distilled water.

3.3.2 Calibration Curve

To establish a calibration curve and to check the accuracy of the ultraviolet absorption method the following procedure was adopted. A stock solution containing exactly 5g/l of Naphthol was prepared as described above. Dilutions were made from the stock solution to give a series of solutions having optical densities within the range of the instrument scale. The optical densities were plotted against the concentrations. A linear relationship was found for the whole range of concentrations employed. Further concentrations (1,2,3, etc. g/l.) of naphthol solutions were prepared, suitable dilutions made and the optical densities determined. The concentrations of

the solutions were computed from the calibration curve. The accuracy of the determinations was within ± 0.2% .

Table III Determinations of Naphthols in Stock solutions

Weight (W) of Naphthol taken (g)	Dilution	Optical Density	Wt. calc. from calibration curve (g)
Naphthol			
5.0010	40	0.789	
	33⅓	0.963	
	30	1.044	
3.0120	20	0.962	3.0070
1.0070	50/7	0.882	0.9978
Naphthol AS			
5.0000	100	0.345	
	50	0.690	
	33⅓	1.035	
3.000	50	0.410	2.9984
1.000	20	0.345	1.0000
Naphthol AS-RL			
5.0000	100	0.420	
	50	0.838	
	33⅓	1.250	
3.0010	50	0.505	3.0015
1.2500	25	0.420	1.2505
Naphthol AS.SW			
5.0000	100	0.415	
	50	0.834	
	33⅓	1.252	
3.0100	50	0.505	3.0110
1.0000	20	0.420	1.0050

3.3.3 Determination of Naphthol in solution

Naphthol solution containing 5g./1. of naphthol was prepared as before. 1 g. samples of cellulose (making allowance for moisture content) were treated with 50 ml. of the naphthol solution in a 100 ml Quickfit pyrex conical flask. Nitrogen gas was bubbled through the solution and the flask, with its contents, was suspended in a waterbath at $30 \pm 1^{\circ}C$. A blank (or control) was also set up. At the end of about 1.5 times the equilibrium time the reacted solution and the blank were analysed spectrophotometrically for the naphthol content. This consisted in measuring the optical densities of the solution at suitable dilutions and reading off their concentrations from the calibration curve. The original concentration was then calculated from the knowledge of the dilution factor.

The amount absorbed by the cellulosic fibre was calculated from the difference in the concentrations of the blank and the experimental.

3.4.1 Equilibrium absorption of alkali by standard cellulose, alkali-treated cellulose and the chemically modified celluloses.

The equilibrium time of absorption of sodium hydroxide of two different initial concentrations was first determined. This consisted in measuring the variation of pH with time till no further change in pH was observed.(see Fig. 6).

In all future studies of equilibrium absorption of sodium hydroxide at different pH values in the absence or presence of sodium chloride at least 1.5 times the equilibrium time was allowed.

About 1g. of the cellulose sample (allowance being made for moisture content) was treated with sodium hydroxide of various concentrations for 1.5 times the 'equilibrium time'. At high initial alkali concentrations polythene bottles instead of Quickfit flasks were used as alkali has been known to attack the glass. The flasks or bottles with their contents were suspended in a water bath maintained at 30 $\pm$ 0.5°C. Nitrogen gas was bubbled through the alkali solution so as to displace any carbon dioxide present in the vessels. At the end of the absorption, the pH of the final equilibrium solution was measured and its concentration was determined as follows: To a known volume of the solution an excess of hydrochloric acid was added and it was then titrated potentiometrically with a standard borax solution. The initial

concentrations of the alkali solutions were determined from the control in a similar way. The amount of alkali absorbed was calculated from the difference between the control and the experimental solutions.

The plots of amount of alkali absorbed versus pH of equilibrium solution are shown in figs 7 to 11 for the different samples studied.

3.4.2 Equilibrium Absorption of Naphthols by standard cellulose at different sodium hydroxide concentrations.

The 'naphthols' used in this investigation were:

1. Naphthol AS
2. Naphthol AS-SW
3. Naphthol AS-RL
4. β - Naphthol.

Two solutions A and B having the following compositions were prepared:

Solution A:

5g. Naphthol + 0.20g. dispersing agent + 5.845 g. sodium chloride dissolved in 25 ml. of 1N sodium hydroxide solution and made up to 1 litre with distilled water.

Solution B:

5g. Naphthol +020g. dispersing agent + 5.845 g. sodium chloride dissolved in 25 ml of 4N NaoH and made up to 1 litre with distilled water. Solutions of different pH values but having the same concentrations of naphthol, dispersing agent and sodium chloride were made by mixing different proportions of solutions A and B.

Naphthol absorption as a function of pH was followed from the difference in concentrations of naphthol, determined spectrophotometrically, of the control and the experimental solutions. The experiments were carried out at 30 $\pm$0.5°C; the material to liquor ratio was kept at 1:50. At the start

of the experiments nitrogen gas was bubbled through the solutions to expel carbon dioxide and the reacting mixture was left long enough to attain equilibrium.

The absorptions in the presence of 0.05M and 0.01M NaCl and in the absence of NaCl were also followed for each of the naphthols studied.

Figs 12 to 15 show the dependence of absorption on alkali concentration at different salt concentrations. The absorptions of Naphthols AS and AS-RL by the modified celluloses in the absence and presence of added salt were also studied. The results obtained are plotted in figs 16 and 17.

3.4.3 The effect of varying temperature on the absorption of arylamides of 2 - hydroxy -3-naphthoic acid by standard cellulose

The following arylamides were used in this investigation:

(i) Naphthol AS (Phenylamide of 2-hydroxy-3-naphthoic acid)

(ii) Naphthol AS-RL (4-methoxyphenylamide of 2-hydroxy-3-naphthoic acid)

Arylamide solution containing 5g./1 was used. The material to liquor ratio of 1:50 was employed. The absorption was measured for five different temperatures between 25 - 90°C. Fig. 18 shows the plot of absorption against temperature for the two arylamides studied.

3.444 **Effect of varying concentration on the absorption of arylamides of 2 - hydroxy - 3 - naphthoic acid by standard Cellulose**

The arylamides used were:

a) Naphthol AS (Phenylamide of 2-Hydroxy-3-naphthoic acid)

b) Naphthol AS-RL (4-methoxy phenylamide of 2-hydroxy-3-naphthoic acid).

A stock solution containing 20 g./100 ml of the arylamide was prepared and dilutions made therefrom to give a series of concentrations in the range 1 - 50 g/l. The pH of each solution was adjusted to pH 12.50. The material to liquor ratio was kept at 1:50 and the experiment was carried out at 30 ± 1°C.

The experiment was repeated in the presence of three different concentrations of sodium chloride at 30 ± 1°C and in the presence of 0.10m NaCl at 20 ± 0.5°C. The plots of amount of arylamide absorbed versus concentration of arylamide in solution at equilibrium are shown in figs 19 and 20.

Table IV Equilibrium - Time curve for the absorption of sodium hydroxide by standard cellulose at 30°C

Sample No.	Time (Mins.)	pH
1	0	11.69
2	1	9.60
3	3	8.58
4	5	8.57
5	16	8.56
6	30	8.55
7	45	8.55
8	60	8.55
9	180	8.55

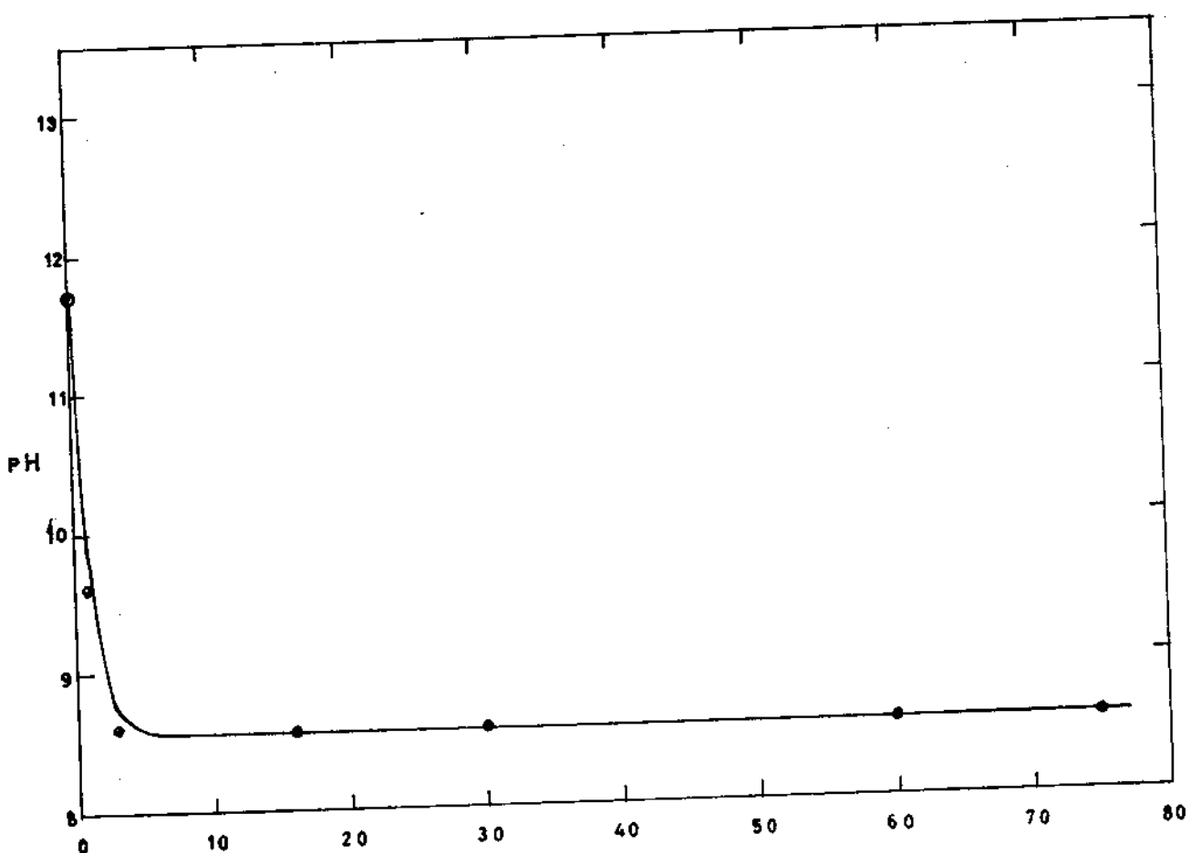


FIG. 6 EQUILIBRIUM-TIME CURVE FOR CELLULOSE-SODIUM HYDROXIDE ABSORPTION AT 30°C

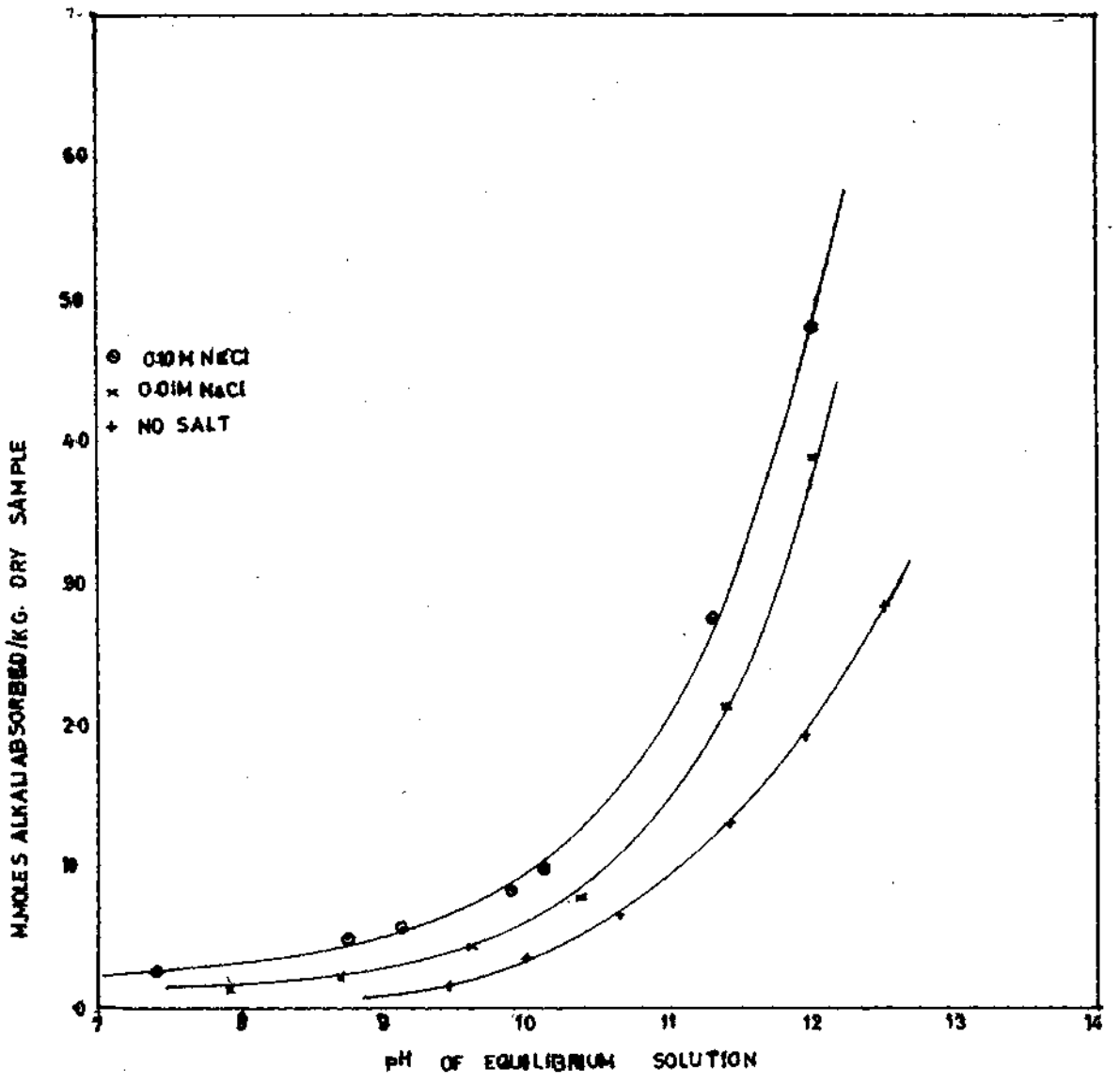


FIG. 7. ALKALI ABSORPTION BY STANDARD CELLULOSE AT 30°C

Table V Alkali absorption by standard cellulose at 30° C

Sample No.	pH of equilibrium solution	mmoles alkali absorbed /kg. dry sample
No salt		
	8.10	0.25
1	9.42	1.79
2	10.00	4.43
3	11.42	6.50
4	11.42	13.28
5	12.51	28.46
6		
0.01 MNaCl		
	7.90	1.05
1	8.68	2.11
2	9.57	4.22
3	9.96	4.85
4	10.36	7.59
5	11.40	21.08
6	11.98	38.58
7		
0.10 M NaCl		
	7.41	2.77
1	8.75	4.90
2	9.12	5.33
3	9.92	8.10
4	10.16	9.80
5	11.30	27.70
6	12.00	47.95
7		

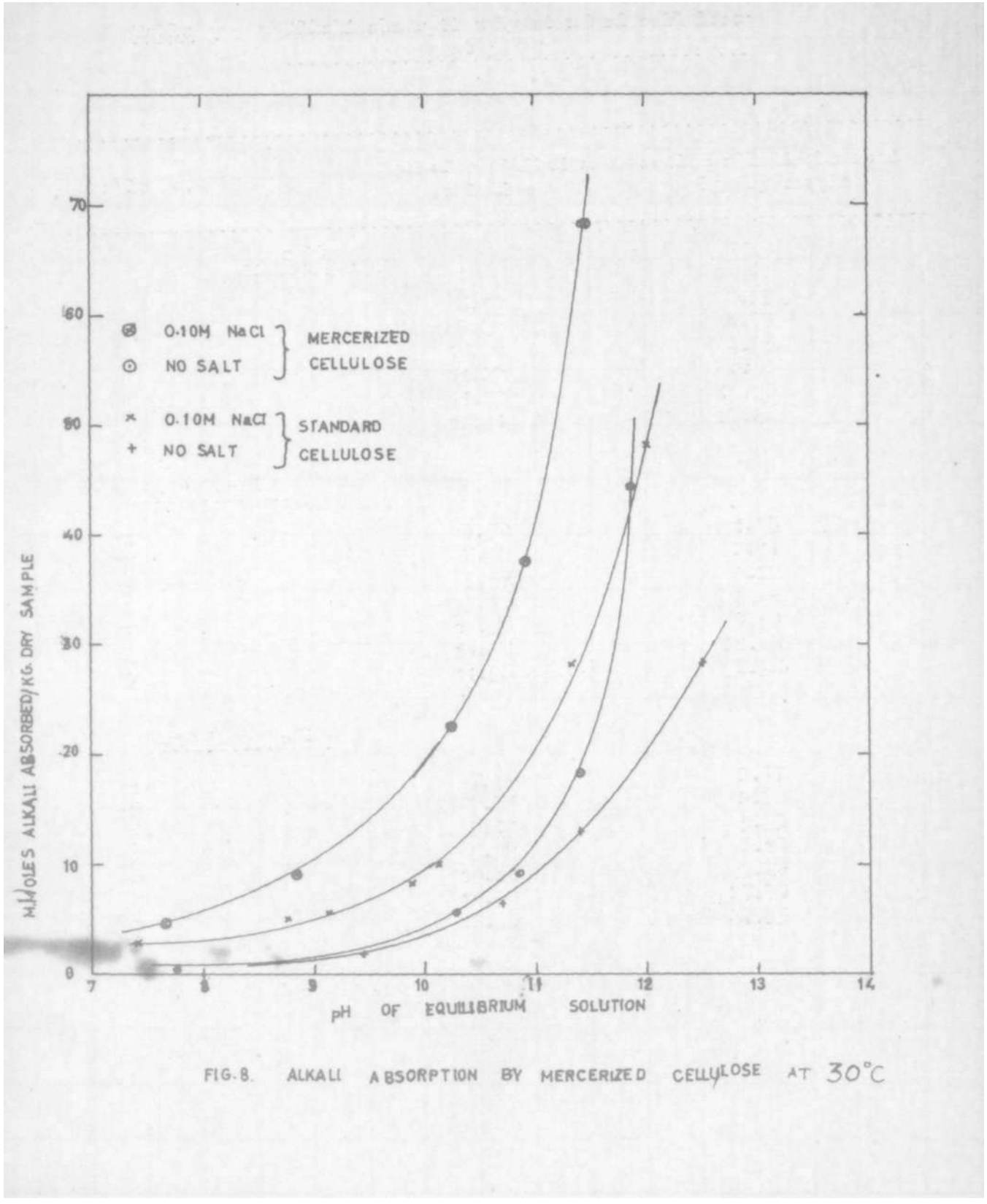


FIG. 8. ALKALI ABSORPTION BY MERCERIZED CELLULOSE AT 30°C

Table VI Alkali absorption by mercerized Cellulose at 30°C

Sample No.	pH of equilibrium solution	mmoles alkali absorbed /kg. dry sample
No salt		
1	7.74	0.42
2	10.28	5.48
3	10.83	9.28
4	11.32	10.54
5	11.44	18.13
6	11.85	44.27
0.10M NaCl		
1	7.65	4.50
2	8.83	9.00
3	10.23	22.30
4	10.88	37.50
5	11.52	68.00

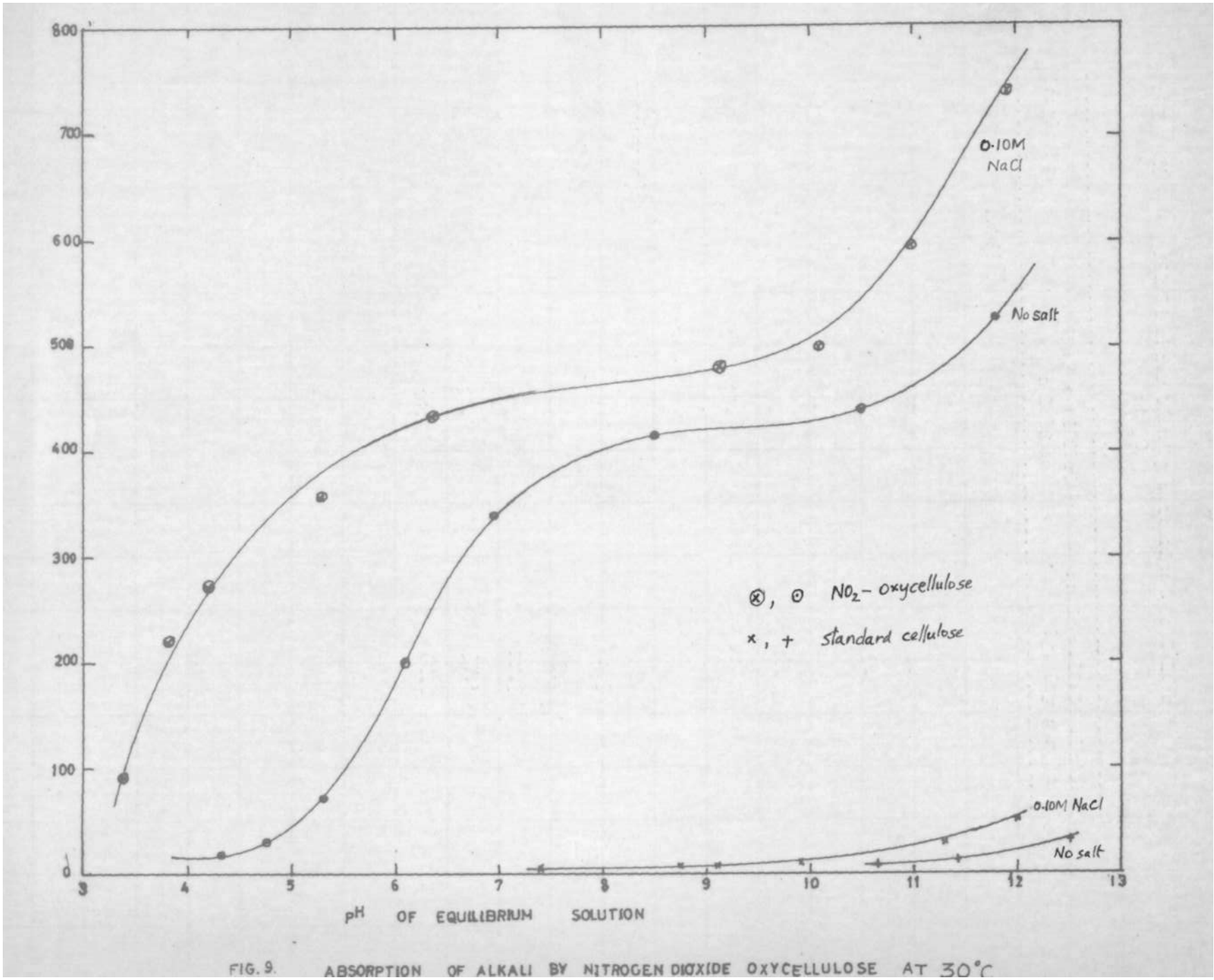


FIG. 9. ABSORPTION OF ALKALI BY NITROGEN DIOXIDE OXYCELLULOSE AT 30°C

Table VII Alkali absorption by nitrogen dioxide oxycellulose at 30°C

Sample No.	pH of equilibrium solution	mmoles alkali absorbed /kg dry sample
No salt		
1	4.37	20.66
2	4.75	24.87
3	5.32	75.25
4	6.95	355.8
5	8.50	422. 0
6	10.51	449. 0
7	11.10	467. 7
8	11.81	557. 1
9	13.00	982. 9
0.10 M NaCl		
1	3.37	96.96
2	3.82	179. 6
3	4.20	235. 0
4	5.28	377. 5
5	6.36	457. 2
6	9.11	504. 8
7	10.06	521. 5
8	10.97	572. 3
9	11.93	777. 6

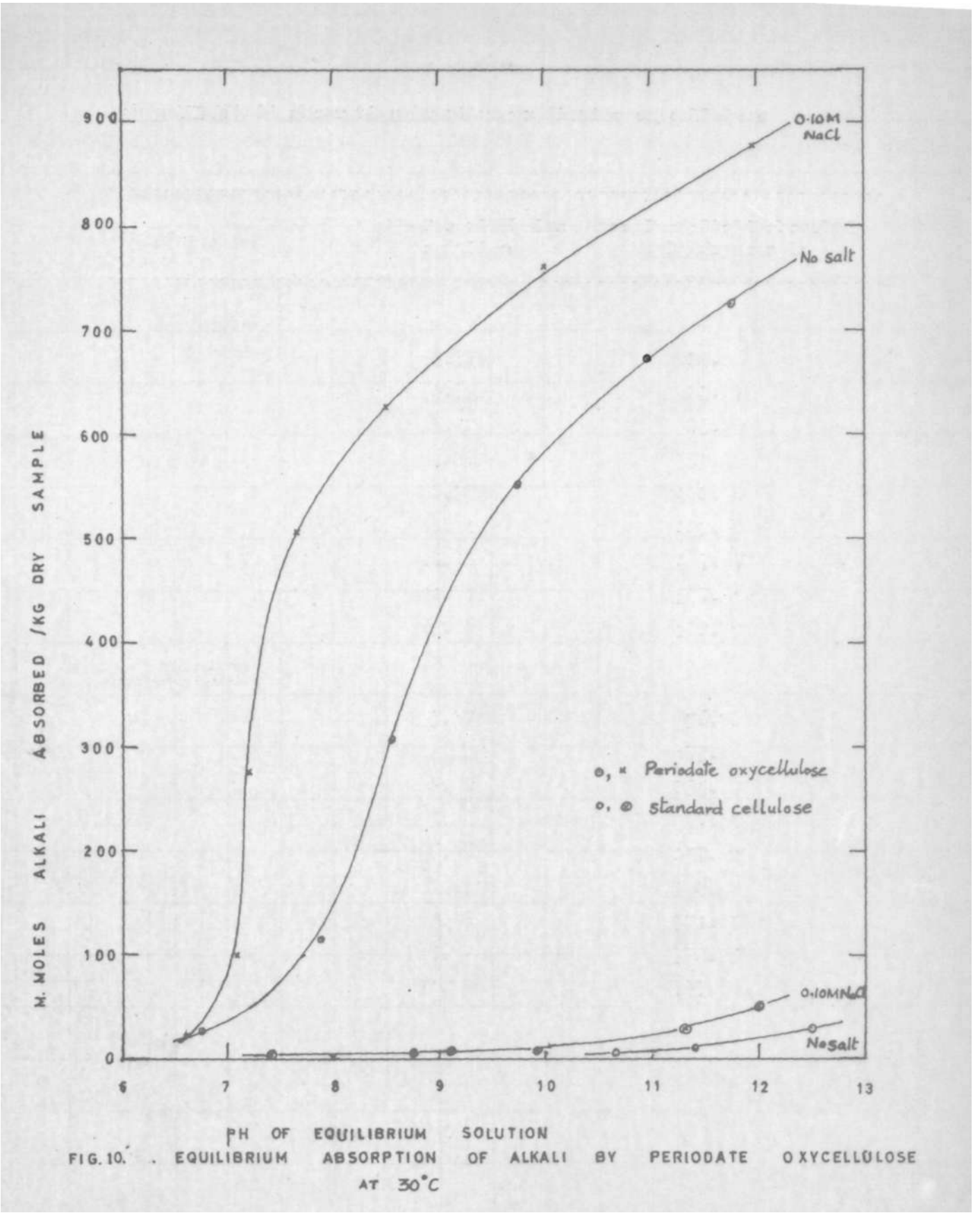


FIG. 10. . EQUILIBRIUM ABSORPTION OF ALKALI BY PERIODATE OXYCELLULOSE AT 30°C

Table VIII Alkali absorption by periodate oxycellulose at 30°C

Sample No	pH of equilibrium solution	mmoles alkali absorbed /kg dry sample
No salt		
1	6.74	27.9
2	7.87	115.6
3	8.61	306.1
4	9.75	550.0
5	10.70	649.5
6	11.72	725.1
0.10M NaCl		
1	6.58	23.7
2	7.07	100.0
3	7.21	276.3
4	7.66	507.4
5	8.48	625.0
6	10.00	759.6
7	11.95	875.0

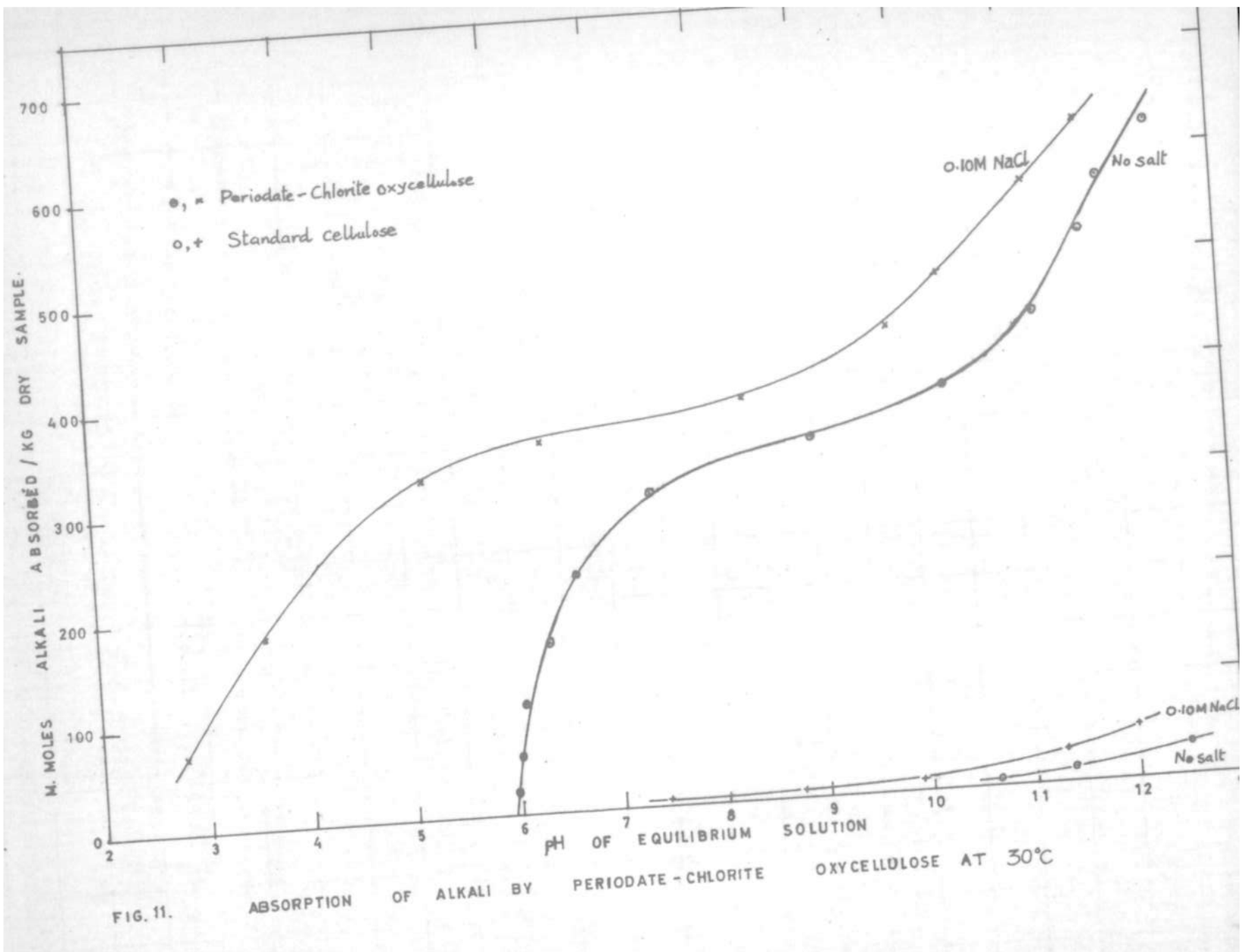


FIG. 11. ABSORPTION OF ALKALI BY PERIODATE - CHLORITE OXYCELLULOSE AT 30°C

Table XI Alkali absorption by periodate - chlorite oxycellulose

Sample No.	pH of equilibrium solution	mmoles alkali absorbed/kg. dry sample
No salt		
1	5.97	17.46
2	6.03	53.90
3	6.08	103. 1
4	6.36	159. 8
5	6.65	223. 4
6	7.41	295. 0
7	8.98	340. 4
8	10.35	383. 1
9	11.20	446. 5
10	11.70	521. 3
11	11.90	570. 3
0.10M NaCl		
1	2.80	72.66
2	3.60	178. 1
3	5.20	320. 2
4	6.37	352. 1
5	8.35	380. 0
6	9.80	440. 0
7	10.37	486. 8
8	11.16	571. 8
9	11.73	626. 3

Table X Absorption of β - naphthol by standard cellulose

Ionic Strength (M)	pH of equilibrium solution	mmoles naphthol absorbed/ kg. dry sample
0	11.23	8.46
	11.85	9.22
	12.12	9.22
	12.23	9.14
	12.47	9.20
	12.53	9.15
0.05	11.25	9.61
	11.82	10.47
	12.02	10.52
	12.23	10.61
	12.52	10.58
0.10	11.34	13.05
	11.85	12.98
	12.00	13.17
	12.32	13.21
	12.45	13.20
	12.51	13.23

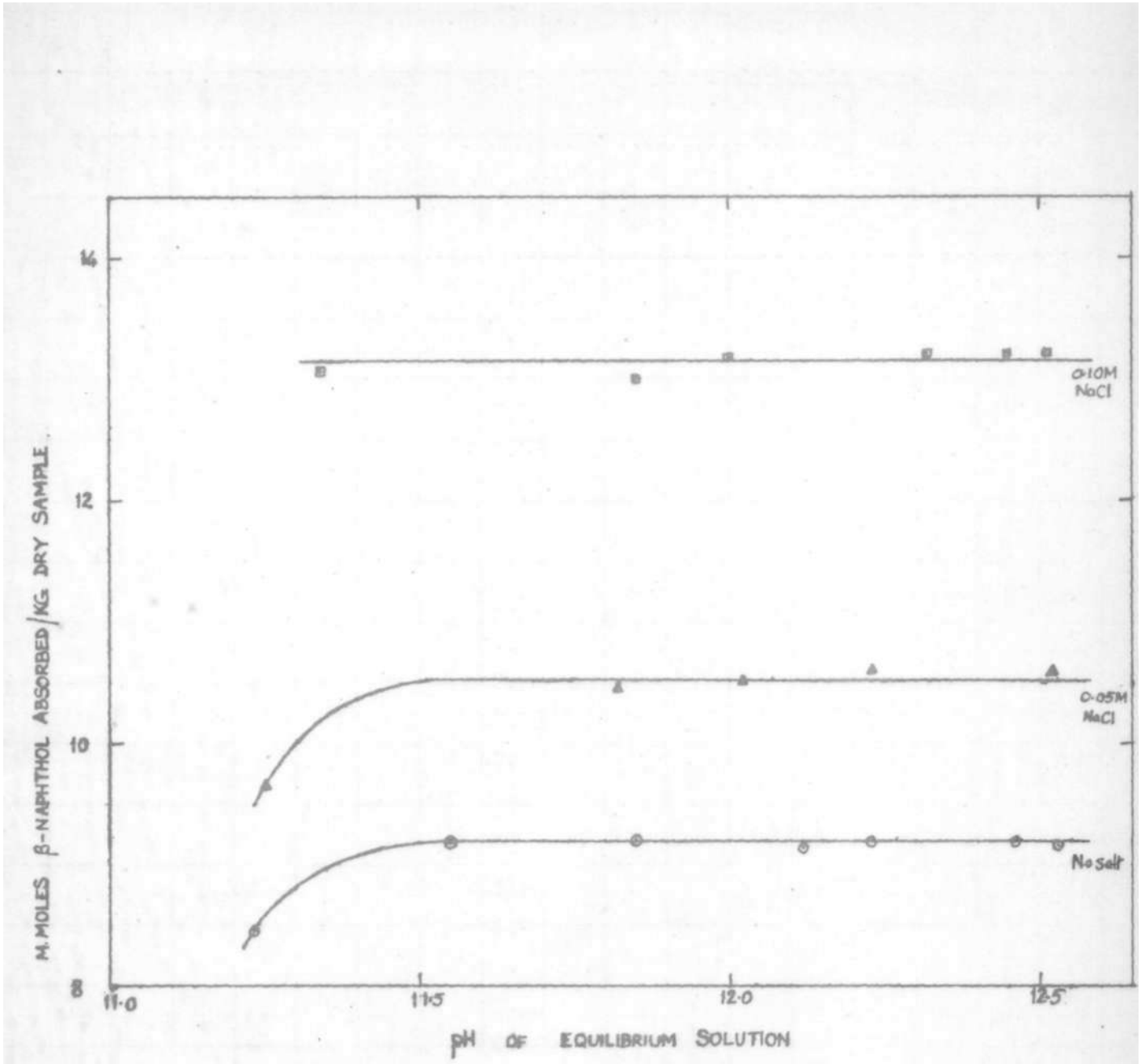


FIG 12. EQUILIBRIUM ABSORPTION OF β-NAPHTHOL BY STANDARD CELLULOSE AT 30°C

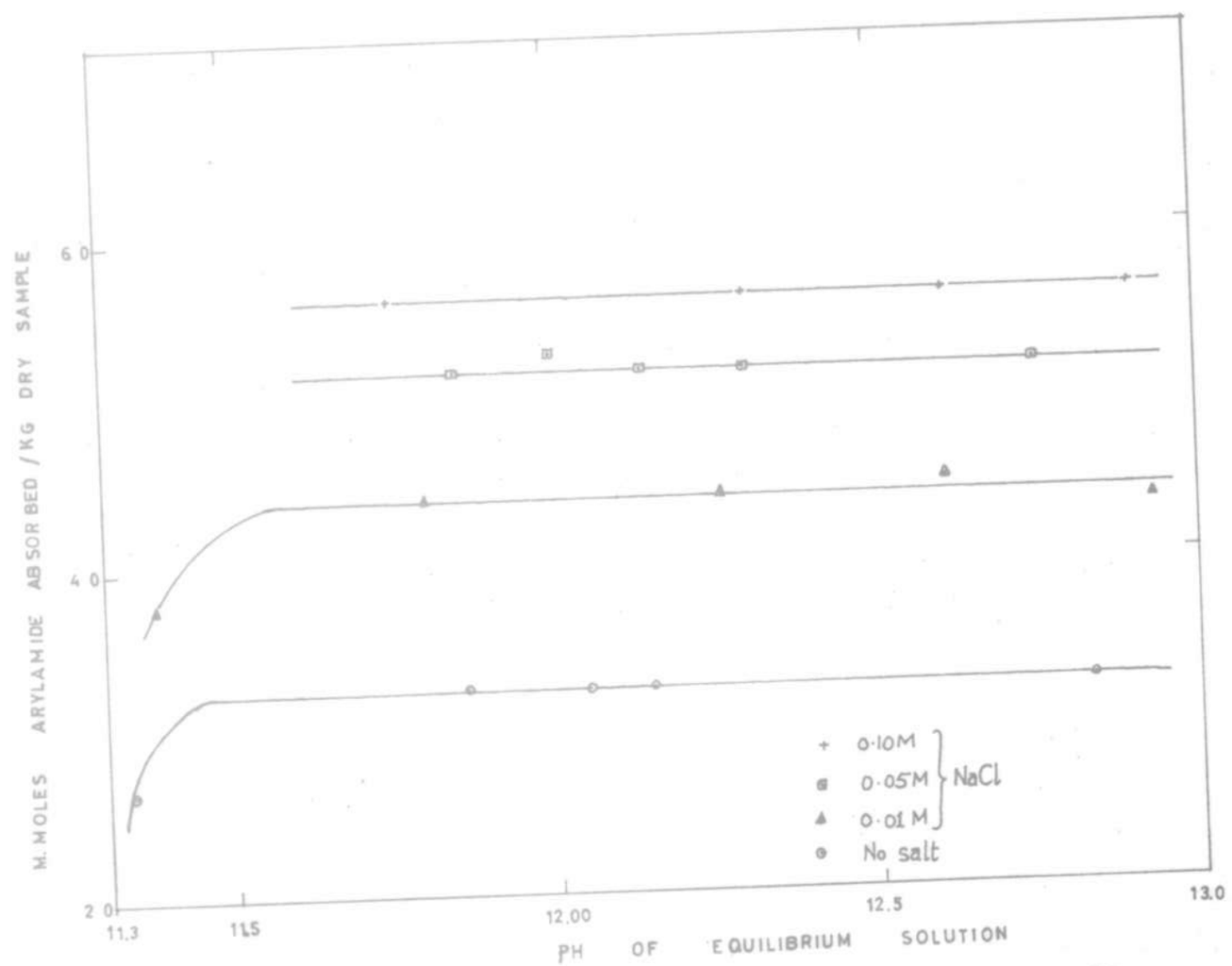


FIG. 13. EQUILIBRIUM ABSORPTION OF NAPHTHOL AS- BY STANDARD CELLULOSE AT DIFFERENT PH'S (at 30°C)

Table XI Absorption of Naphthol AS by standard cellulose at 30°C

Sample No.	pH of equilibrium solution	Mmoles Naphthol absorbed/ kg. dry sample
No Salt		
1	11.34	28.64
2	11.86	32.49
3	12.05	32.13
4	12.15	32.13
5	12.83	32.13
0.01M NaCl		
1	11.38	37.85
2	11.80	43.92
3	12.10	43.92
4	12.26	43.92
5	12.61	44.62
6	12.93	43.39
0.05M NaCl		
1	11.50	51.82
2	11.85	51.82
3	12.02	52.70
4	12.14	51.82
5	12.30	51.82
6	12.76	51.82
0.1CM NaCl		
1	11.42	54.45
2	11.76	56.21
3	12.12	57.97
4	12.30	56.21
5	12.61	56.21
6	12.87	56.21

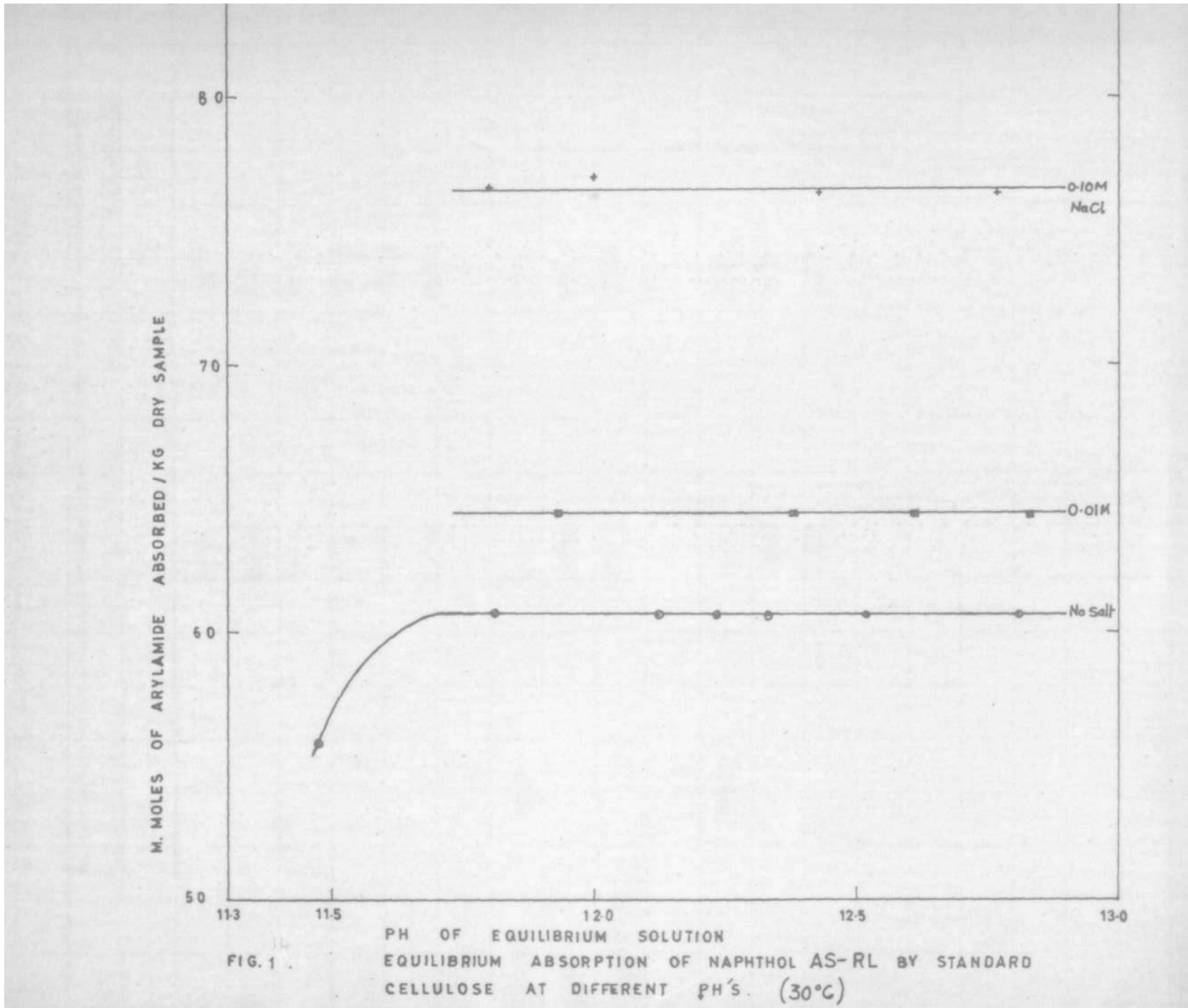


FIG. 1. EQUILIBRIUM ABSORPTION OF NAPHTHOL AS-RL BY STANDARD CELLULOSE AT DIFFERENT PH'S. (30°C)

Table XII Absorption of Naphthol AS-RL by Standard cellulose

Ionic Strength (M)	pH of equilibrium solution	mmoles Naphthol absorbed /kg. dry sample
0	11.81	54.87
	12.11	57.95
	12.23	57.95
	12.33	57.95
	12.39	58.29
	12.52	58.05
0.05	12.13	73.46
	12.34	73.46
	12.56	73.46
0.10	12.00	79.08
	12.37	79.08
	12.62	79.08

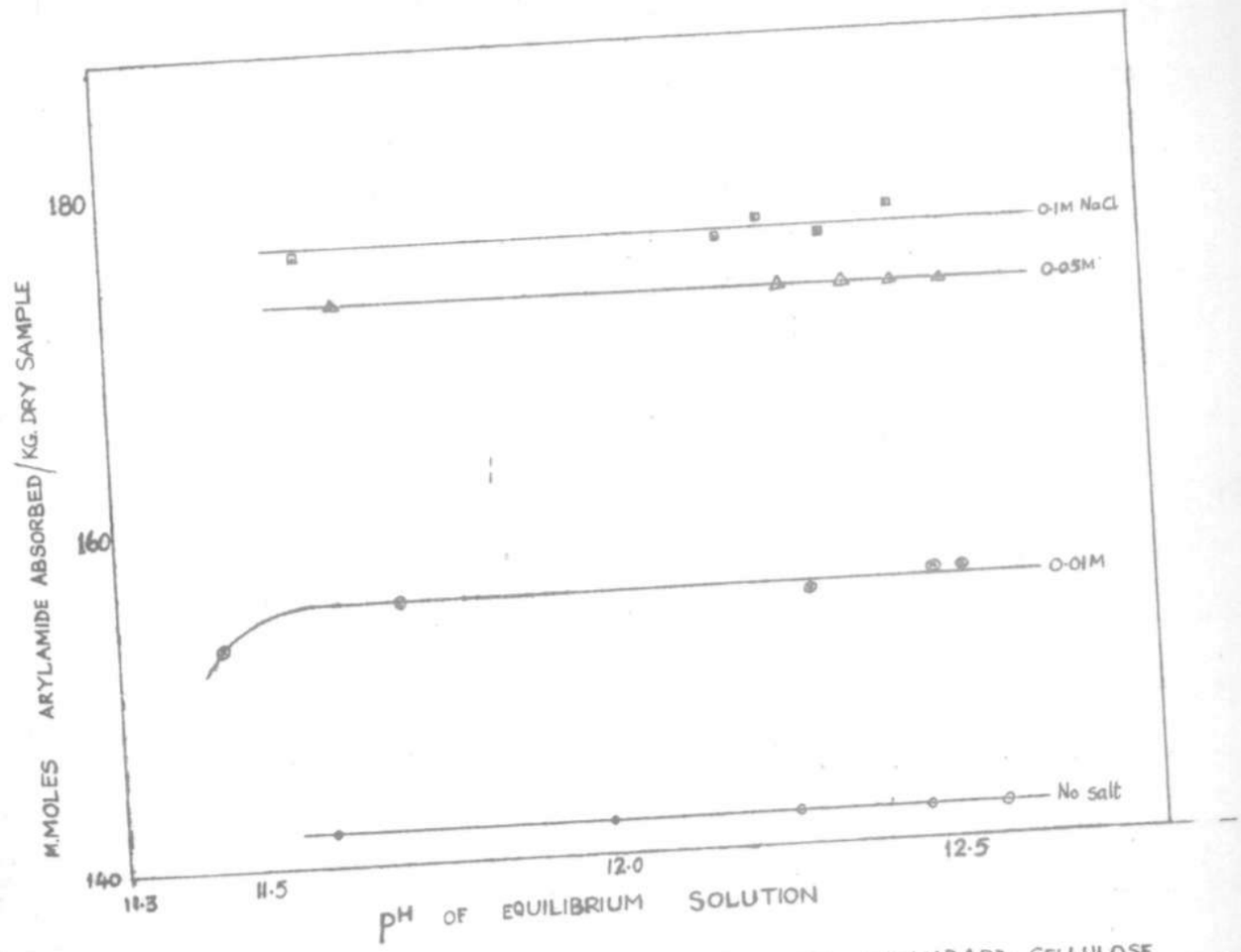


FIG 15. ABSORPTION OF NAPHTHOL AS-SW BY STANDARD CELLULOSE AT 30°C

Table XIII Naphthol AS-SW absorption by standard cellulose at 30°C

Ionic Strength (M)	pH of equilibrium naphthol solution	mmoles Naphthol absorbed /kg. dry sample
0	11.60	142.2
	12.00	142.2
	12.27	142.2
	12.46	142.2
	12.57	142.2
0.01	11.45	153.3
	12.30	155.5
	12.48	156.7
	12.52	156.3
0.05	11.63	173.4
	12.28	173.4
	12.37	173.1
	12.44	173.4
	12.51	173.4
0.10	11.58	175.7
	12.19	176.0
	12.25	177.3
	12.34	176.0
	12.44	177.6

Table XIV Absorption of Naphthol AS by sodium borohydride-reduced periodate oxycellulose at 30°C

Sample No.	pH of equilibrium solution	mmoles Naphthol absorbed/ kg. dry sample
1	11.43	44.57
2	12.06	45.83
3	12.17	45.83
4	12.38	45.83

Table XV Absorption of Naphthol AS by nitrogen dioxide oxycellulose at 30°C

Sample No.	pH of equilibrium solution	mmoles Naphthol absorbed/ kg dry sample
No Salt		
1	11.50	21.08
2	12.06	21.08
3	12.23	21.08
4	12.35	21.08
5	12.61	21.08
0.1CM NaCl		
1	11.62	26.36
2	12.00	26.36
3	12.31	26.36
4	12.48	26.36

Table XVI Absorption of Naphthol AS by mercerized cellulose

Sample No.	pH of equilibrium solution	mmoles Naphthol absorbed/kg. dry sample
No Salt		
1	12.14	65.88
2	12.34	65.88
3	12.41	65.88
4	12.76	65.88
0.1OM NaCl		
1	11.57	100.1
2	12.22	105.4
3	12.30	105.4
4	12.50	105.4
5	12.80	104.8

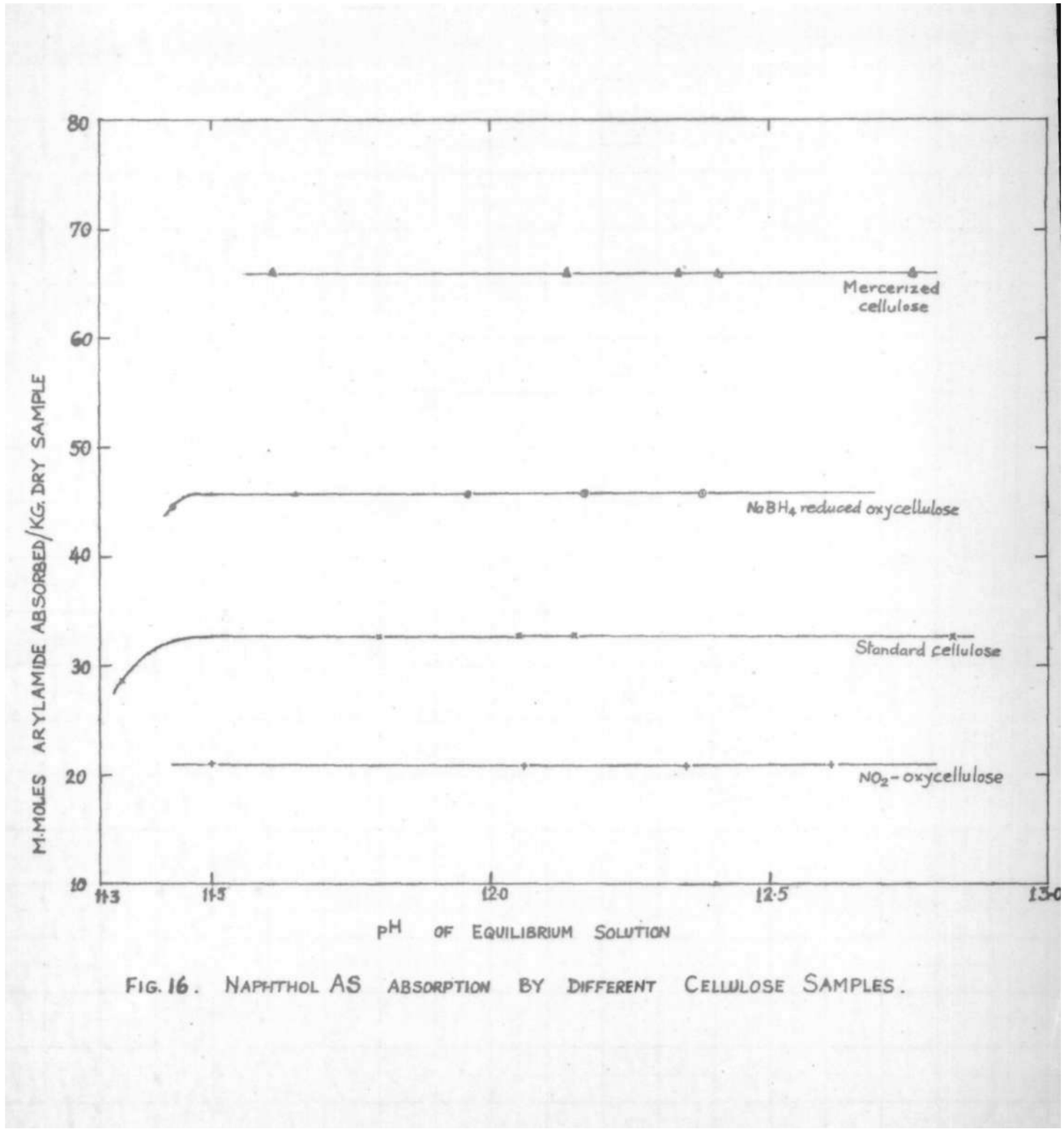


FIG. 16. NAPHTHOL AS ABSORPTION BY DIFFERENT CELLULOSE SAMPLES.

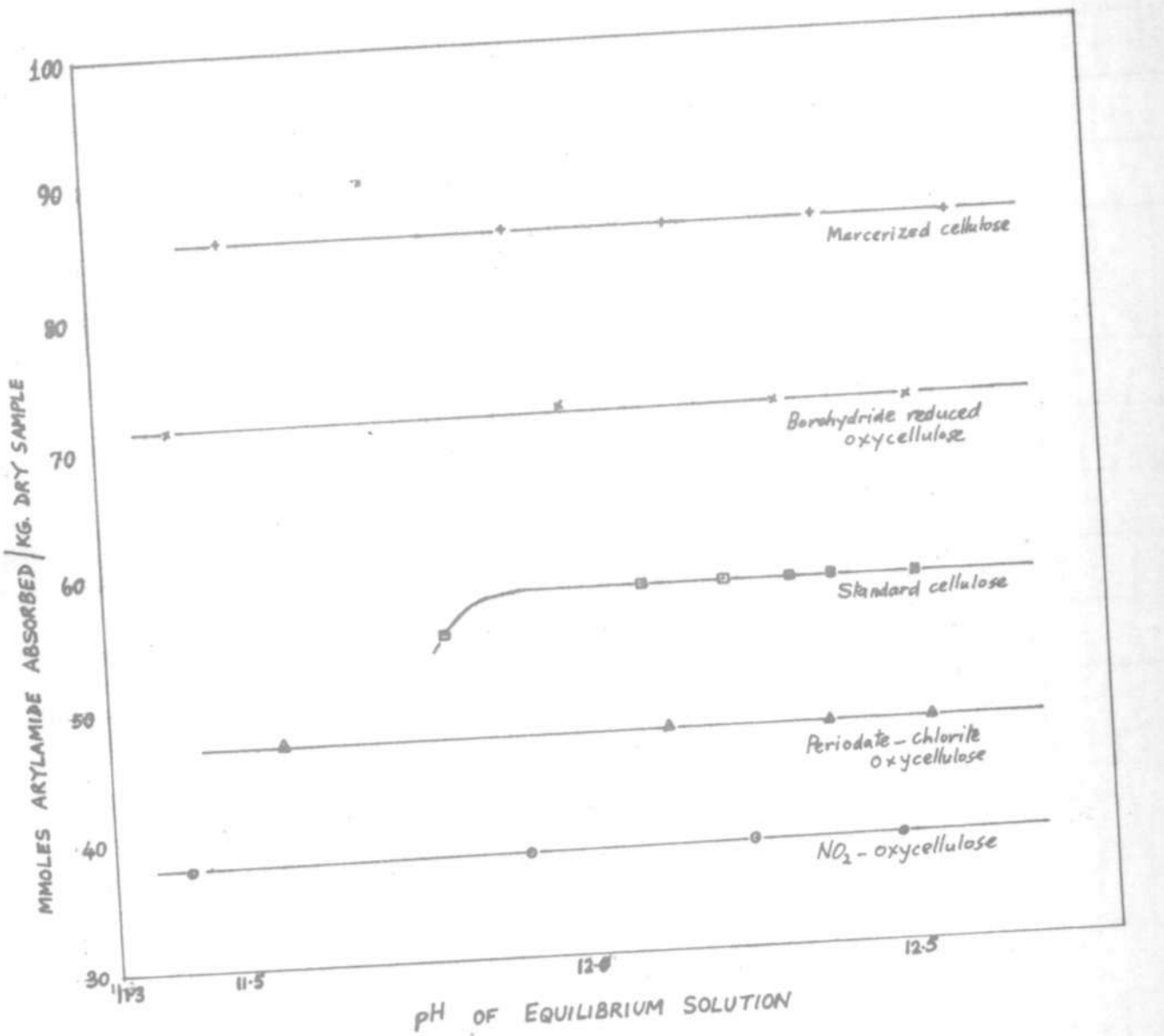


FIG. 17. ABSORPTION OF NAPHTHOL AS-RL BY DIFFERENT CELLULOSE SAMPLES AT 30°C (No added salt)

Table XVII Absorption of Naphthol AS-RL by NO_2 - oxycellulose

Sample No.	pH of equilibrium solution	mmoles arylamide absorbed/ kg. dry sample
No salt		
1	11.41	37.66
2	11.93	37.66
3	12.26	37.66
4	12.48	37.66
0.10M NaCl		
1	11.37	55.23
2	12.10	56.47
3	12.35	56.47
4	12.67	56.47

Table XVIII Absorption of Naphthol AS-BL by periodate- chlorite oxycellulose

Sample No.	pH of equilibrium solution	mmoles arylamide absorbed/kg. dry sample
No salt		
1	11.56	46.97
2	12.14	46.97
3	12.38	46.97
4	12.53	46.97
0.10M NaCl		
1	11.42	59.06
2	12.23	60.44
3	12.51	60.44
4	12.63	61.23

Table XIX Absorption of Naphthol AS-RL by mercerized cellulose at 30°C

Sample No.	pH of equilibrium solution	m.moles arylamide absorbed/ kg. dry sample
No salt		
1	11.50	85.63
2	11.93	85.63
3	12.17	85.63
4	12.39	85.63
5	12.59	85.63
0.10M NaCl		
1	11.49	116. 0
2	12.01	117. 4
3	12.28	116. 0
4	12.44	116. 0
5	12.61	116. 0

Table XX Absorption of Naphthol AS-RL by borohydride reduced oxycellulose

Sample No.	pH of equilibrium solution	m.moles arylamide absorbed/ kg. dry sample
No salt		
1	11.41	70.14
2	12.00	72.08
3	12.32	71.66
4	12.52	71.66
0.10M NaCl		
1	11.38	73.51
2	11.81	73.77
3	12.06	75.08
4	12.33	73.77
5	12.48	73.77

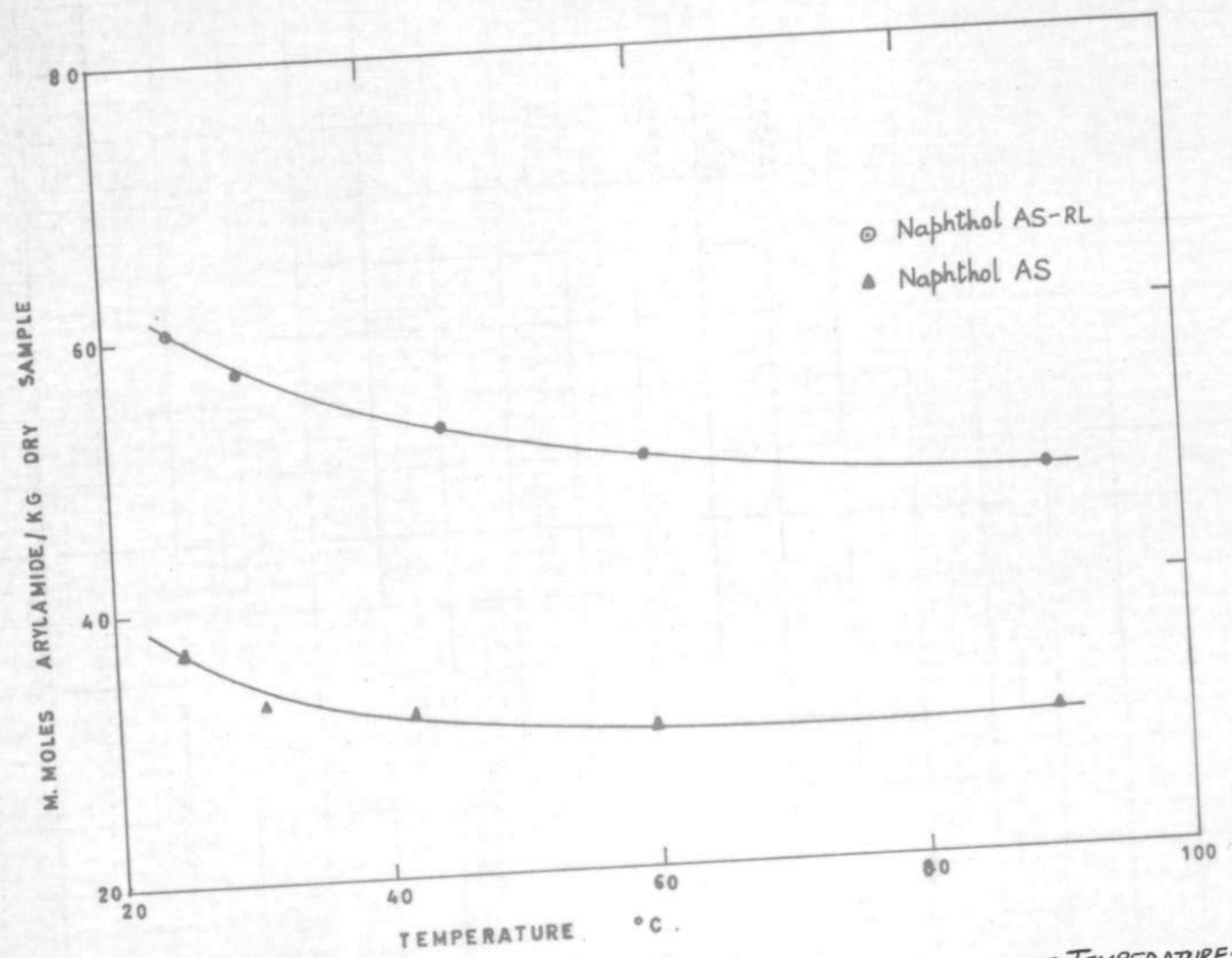


FIG. 18. ABSORPTION OF NAPHTHOLS AS, AS-RL AT DIFFERENT TEMPERATURES.

Table XXI Absorption of Naphthols AS, AS-RL by standard cellulose at different temperatures

Naphthol	Temperature(°C)	mmoles naphthol absorbed /kg. dry sample
AS-RL	25	60.57
	30	57.95
	45	52.69
	60	50.06
	90	48.21
AS	25	37.10
	31	32.93
	42	31.70
	60	30.20
	90	30.00

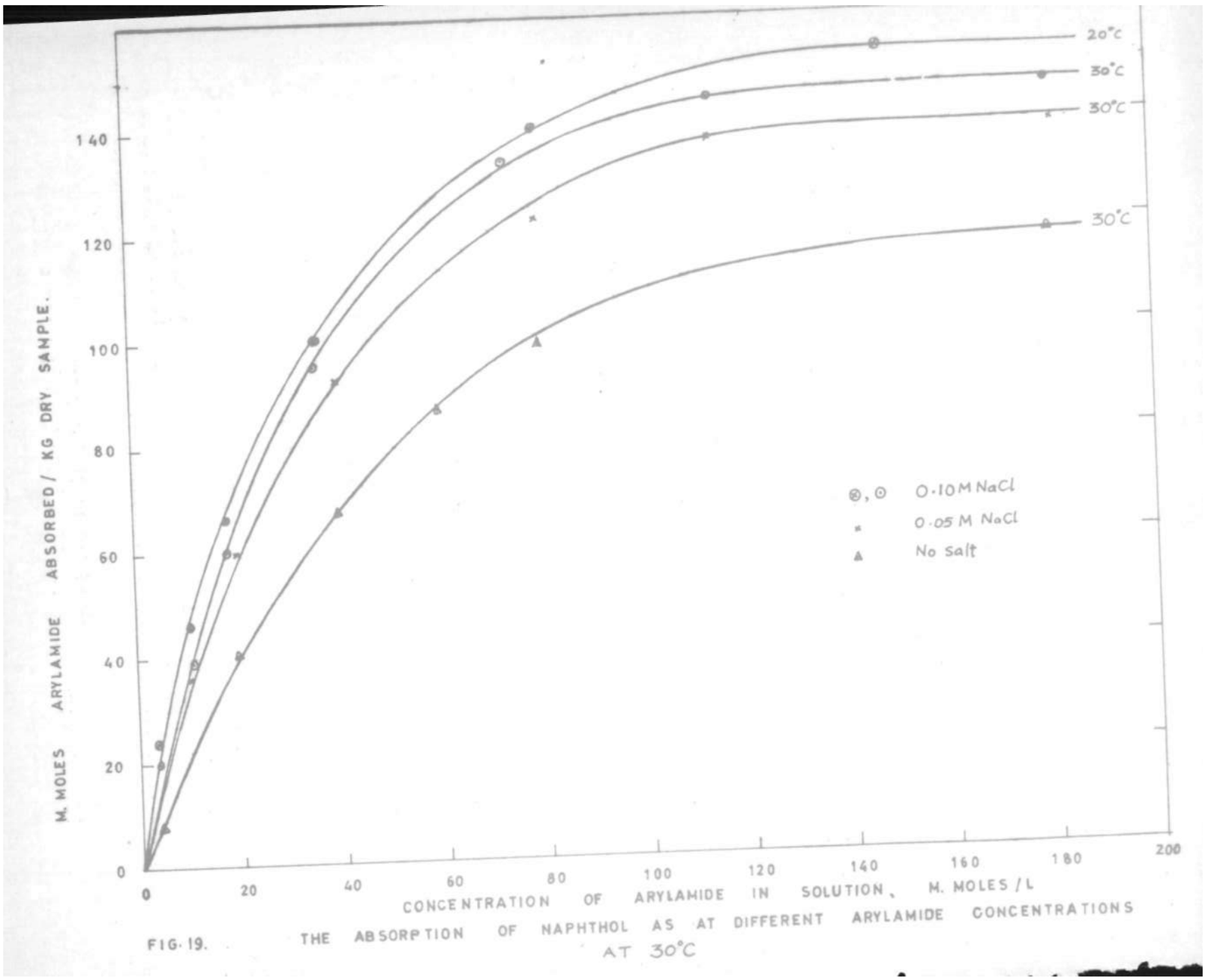


FIG. 19. THE ABSORPTION OF NAPHTHOL AS AT DIFFERENT ARYLAMIDE CONCENTRATIONS AT 30°C

Table XXII Absorption of Naphthol AS at different arylamide concentrations

Concentration of arylamide in solution, m.moles/l.	Concentration of arylamide on fibre, m. moles/l	Concentration of arylamide in solution, m.moles/l	Concentration of arylamide on fibre, m.moles/l.
No salt, 30°C		0.10M NaCl, 30°C	
3.75	7.39	3.56	20.02
19.88	40.21	10.90	38.64
40.00	67.10	18.06	60.08
59.94	86.12	36.80	95.00
80.00	98.34	73.25	133.0
180.1	117.4	114.2	144.4
		180.0	145.4
0.05M NaCl, 30°C		0.10M NaCl, 20°C	
3.60	18.97	3.48	23.50
11.18	39.14	10.65	46.01
20.00	60.08	17.75	66.20
40.43	92.10	36.62	100.5
80.00	122.0	80.00	139.0
114.5	131.4	147.5	153.7
181.3	138.2		

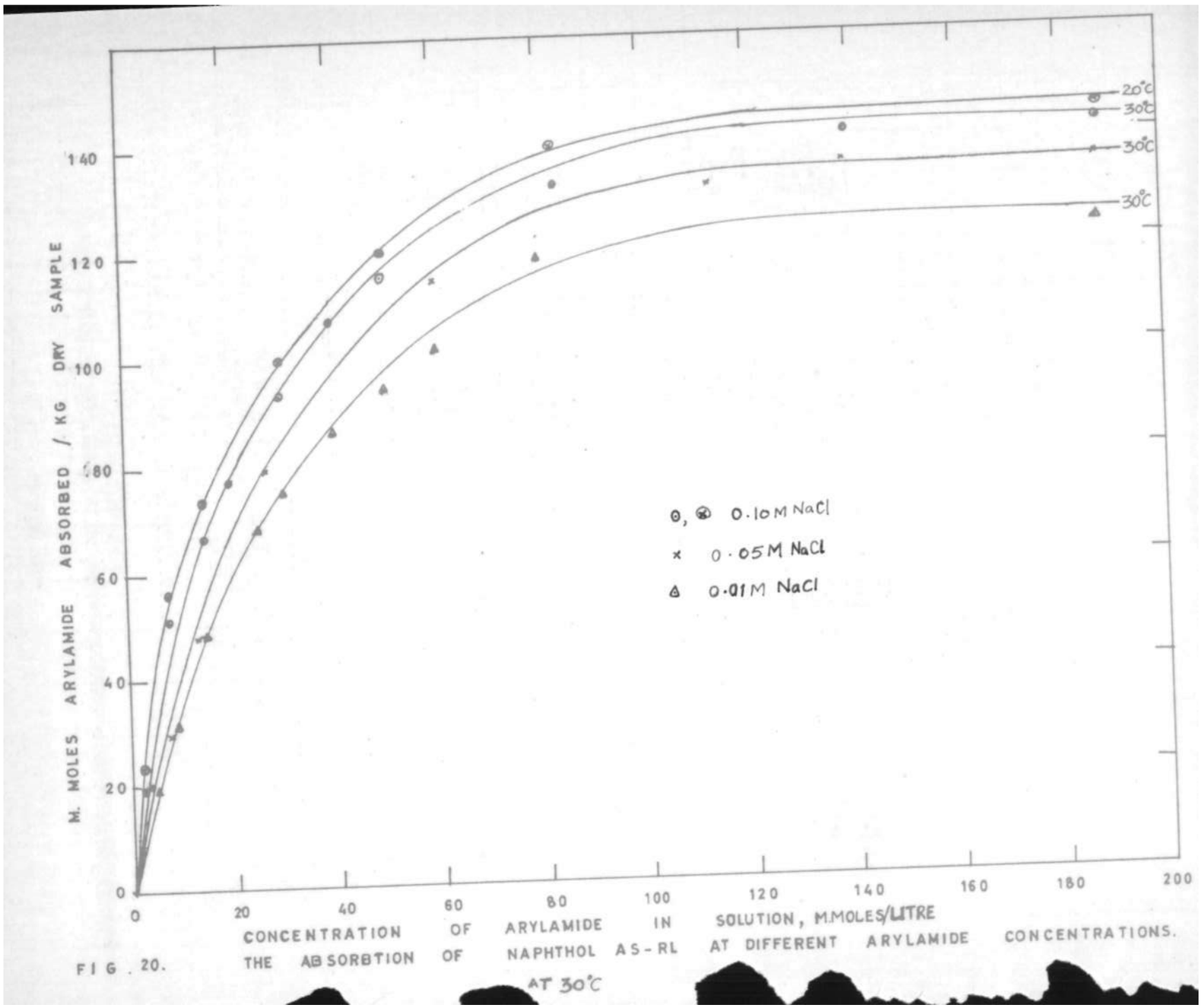


FIG. 20. THE ABSORBTION OF NAPHTHOL AS-RL AT DIFFERENT ARYLAMIDE CONCENTRATIONS. AT 30°C

Table XXIII Absorption of Naphthol AS - RL at different arylamide Concentrations

Concentration of arylamide in solution m.moles /l.	Concentration of arylamide on fibre, m.moles/l.	Concentration of arylamide in solution m.moles/l.	Concentration of arylamide on fibre, m.moles/l.
0.01M NaCl, 30°C		0.10M NaCl, 30°C	
2.00	8.00	2.28	19.50
5.10	19.50	7.75	46.11
9.12	31.20	27.00	89.56
15.17	48.31	30.00	94.00
25.10	67.92	35.11	100.5
30.05	74.83	40.20	107.4
40.00	85.97	80.13	131.7
50.03	94.12	139.5	141.0
60.00	101.0	187.5	141.9
80.00	118.0		
187.5	122.9		
0.05M NaCl, 30°C		0.10M NaCl, 20°C	
2.59	13.17	2.50	23.42
5.00	20.04	7.00	56.03
13.50	47.64	15.10	73.50
37.21	79.00	30.00	100.0
60.00	114.2	50.06	119.5
113.5	131.2	83.20	139.0
139.5	135.3	187.5	144.8
187.5	141.7		

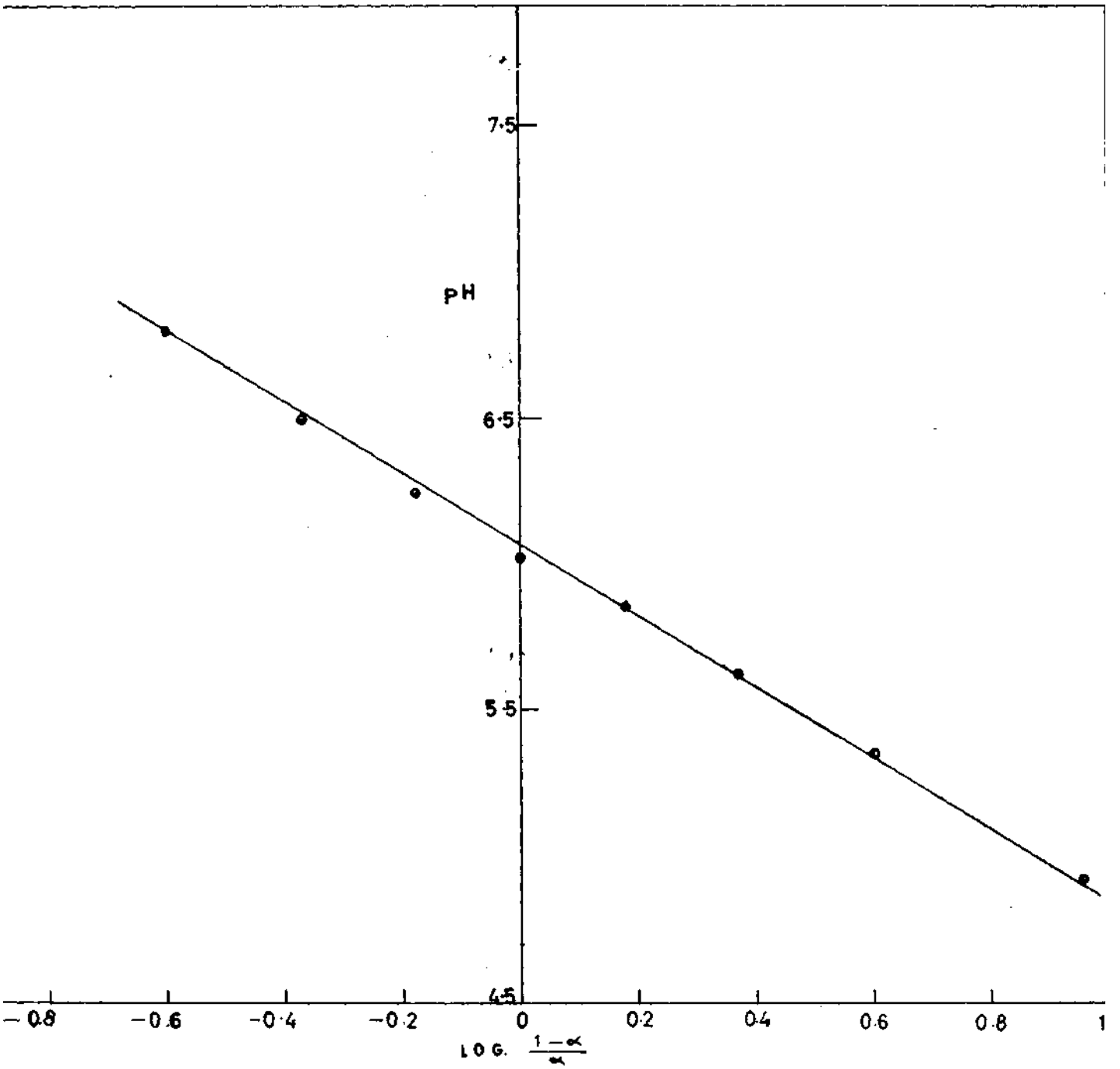


FIG. 21. PLOT OF PH VS LOG $\frac{1-\alpha}{\alpha}$ FOR NITROGEN DIOXIDE OXYCELLULOSE

(No added salt)

Table XXIV Calculated values of Dissociation constants for Nitrogen dioxide oxycellulose using $pH = pK_o' - \log \frac{1-\alpha}{\alpha}$

α	pH	$\log \frac{1-\alpha}{\alpha}$	pK_o'
No Salt			
0.1	4.97	0.95	5.92
0.2	5.35	0.60	5.95
0.3	5.63	0.3680	6.00
0.4	5.85	0.18	6.03
0.5	6.07	0	6.07
0.6	6.27	-0.18	6.09
0.7	6.50	-0.37	6.13
0.8	6.80	-0.60	6.20

α	pH	$\log \frac{1-\alpha}{\alpha}$	pK_o'
0.10M NaCl			
0.1	3.12	0.95	4.07
0.2	3.40	0.60	4.00
0.3	3.65	0.37	4.02
0.4	3.92	0.18	4.10
0.5	4.23	0	4.23
0.6	4.60	-0.18	4.42
0.7	4.98	-0.37	4.61
0.8	5.42	-0.60	4.82

Using $pH = pK_o' - \log \frac{1-\alpha}{\alpha} + 0.4343 \frac{\psi F}{RT}$

α	$pH + \log \frac{1-\alpha}{\alpha}$	$0.4343 \sinh^{-1} C_r/2C_s$	pK_o'
0.10M NaCl			
0.1	4.07	0.16	3.91
0.2	4.00	0.30	3.70
0.3	4.02	0.44	3.58
0.4	4.10	0.51	3.59
0.5	4.23	0.60	3.63
0.6	4.42	0.67	3.65
0.7	4.61	0.73	3.88
0.8	4.82	0.77	4.05

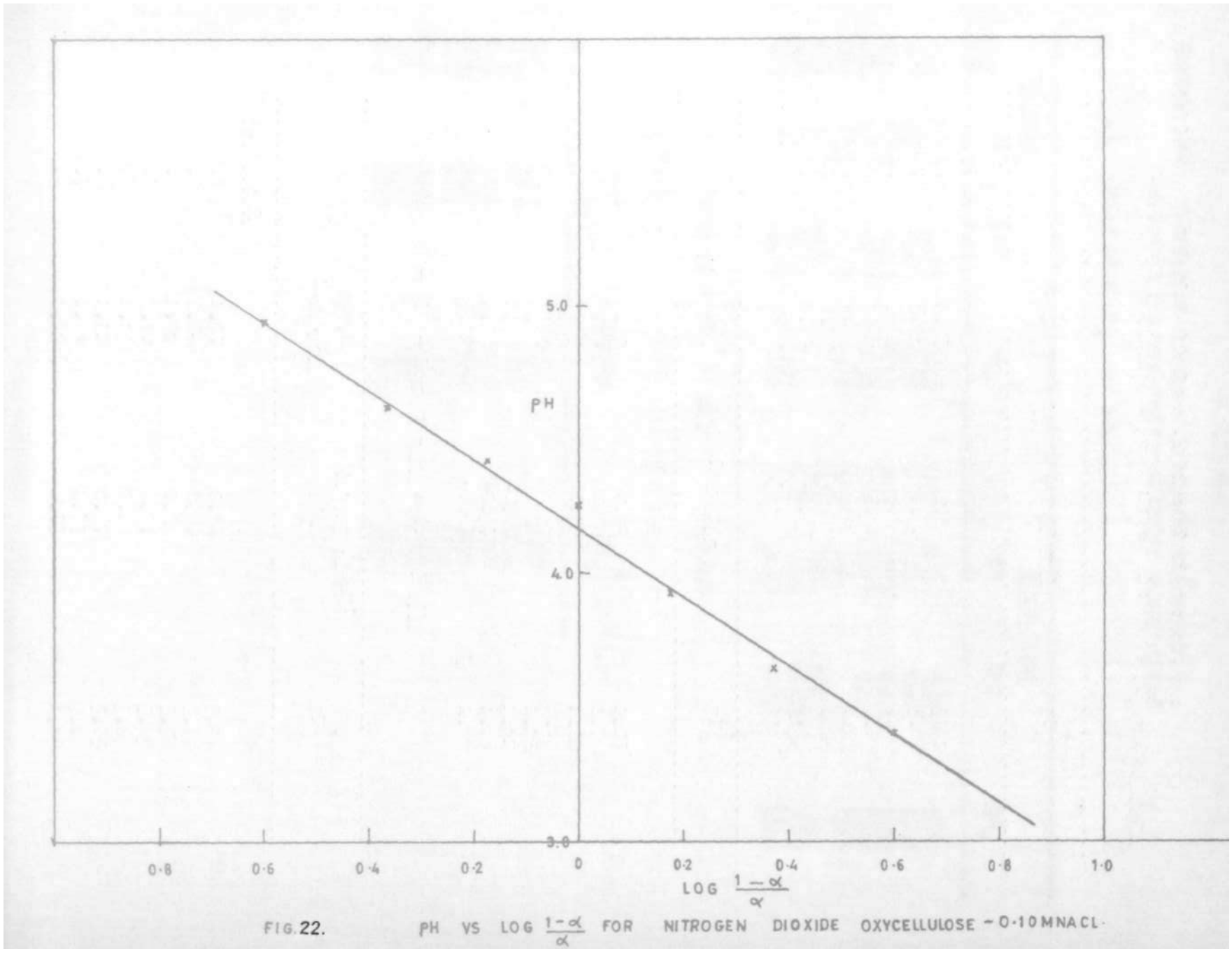


FIG. 22. PH VS LOG $\frac{1-\alpha}{\alpha}$ FOR NITROGEN DIOXIDE OXYCELLULOSE - 0·10 MNACL·

Table. XXV Calculated values of Intrinsic dissociation constants for periodate - chlorite oxycellulose

a) Using $pH = pK_o^{\dagger} - \log \frac{1-\alpha}{\alpha}$

	No salt				0.1M NaCl		
α	pH	$\log \frac{1-\alpha}{\alpha}$	$pK_o^{\dagger}$	pH	$\log \frac{1-\alpha}{\alpha}$	$pK_o^{\dagger}$
0.1	6.00	0.95	6.95	2.4	0.95	3.51
0.2	6.05	0.60	6.65	2.80	0.60	3.40
0.3	6.12	0.37	6.49	3.05	0.37	3.42
0.4	6.21	0.18	6.39	3.33	0.18	3.51
0.5	6.32	0	6.32	3.61	0	3.61
0.6	6.47	-0.18	6.29	3.94	-0.17	3.77
0.7	6.68	-0.37	6.31	4.34	-0.37	3.97
0.8	7.00	-0.60	6.40	4.73	-0.60	4.13

b) Using $pH = pK_o^{\dagger} - \log \frac{1-\alpha}{\alpha} + 0.4343 \sinh^{-1} C_f/2C_s$

0.10M NaCl

α	pH+ $\log \frac{1-\alpha}{\alpha}$	0.4343 $\sinh^{-1} C_f/2C_s$	$pK_o^{\dagger}$
0.1	3.51	0.11	3.40
0.2	3.40	0.22	3.18
0.3	3.42	0.32	3.10
0.4	3.51	0.40	3.11
0.5	3.61	0.47	3.14
0.6	3.77	0.54	3.23
0.7	3.97	0.60	3.37
0.8	4.13	0.65	3.48

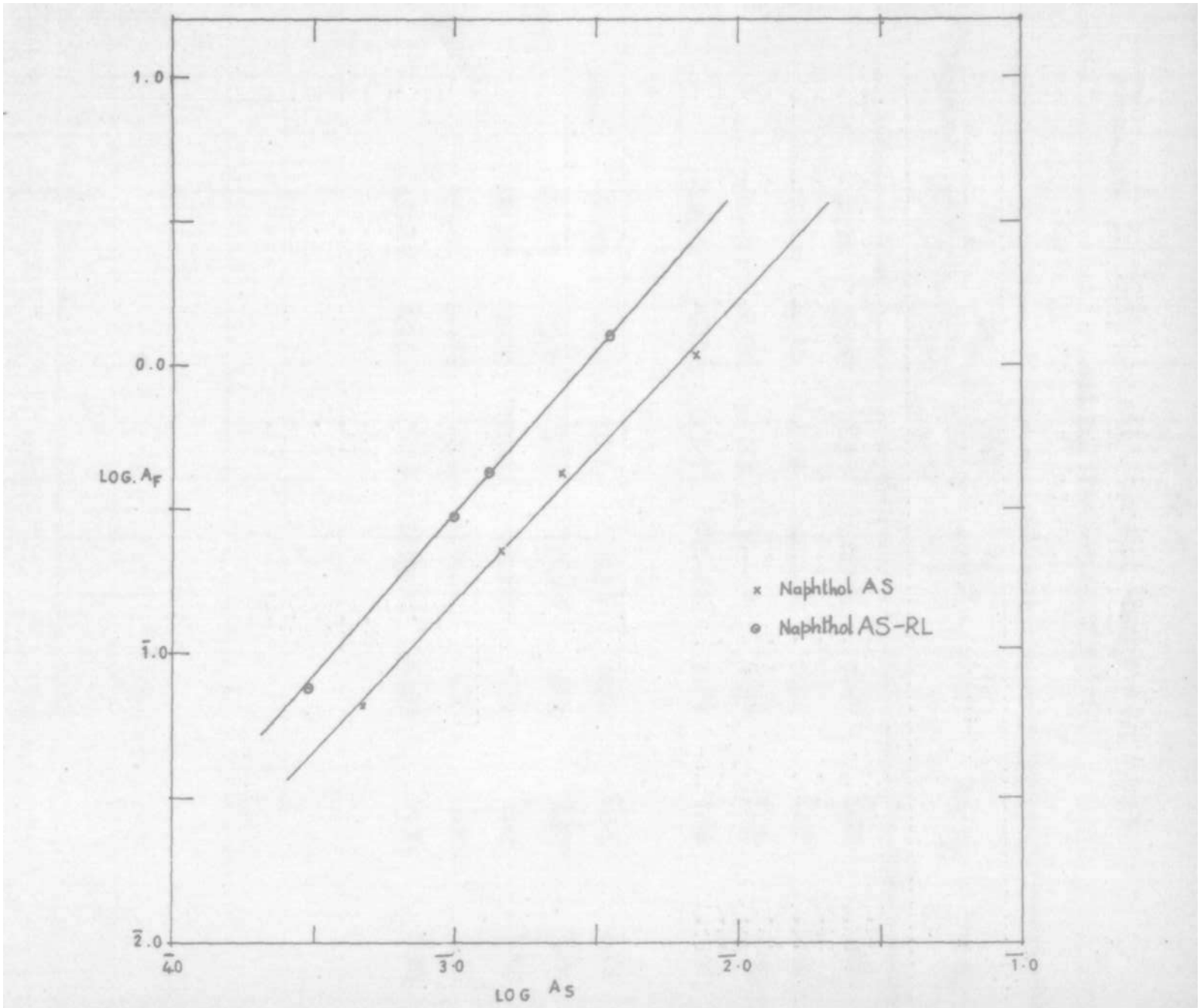


FIG. 23. PLOTS OF LOG. IONIC PRODUCTS FOR NAPHTHOLS AS & AS-RL

Table.XXVI Log ionic products calculated using V = 0.3 mole/l. and Na_f^+ from Donnan relations

Naphthol	Ar_f moles/l x 10^{-3}	Ar_s moles/l x 10^{-3}	Na_f^+ moles/l x 10^{-3}	A_f x 10^{-3}	A_s x 10^{-3}	log A_f	log A_s
AS	66.73	3.56	8.96	66.44	0.47	$\bar{2}.92$	$\bar{4}.67$
	128.80	10.90	15.15	225.40	1.44	$\bar{1}.35$	$\bar{3}.16$
	200.30	18.06	22.23	494.60	2.38	$\bar{1}.69$	$\bar{3}.38$
	302.10	36.80	32.40	1088.00	4.84	0.04	$\bar{3}.68$
AS-RL	64.99	2.28	8.54	61.66	0.30	$\bar{2}.79$	$\bar{4}.48$
	153.30	7.75	17.43	296.90	1.02	$\bar{1}.47$	$\bar{3}.01$
	183.30	10.00	20.74	422.50	1.32	$\bar{1}.63$	$\bar{3}.12$
	325.00	26.85	34.64	1251.00	3.53	0.10	$\bar{3}.55$
	439.20	83.50	46.28	2258.00	10.99	0.35	$\bar{2}.04$

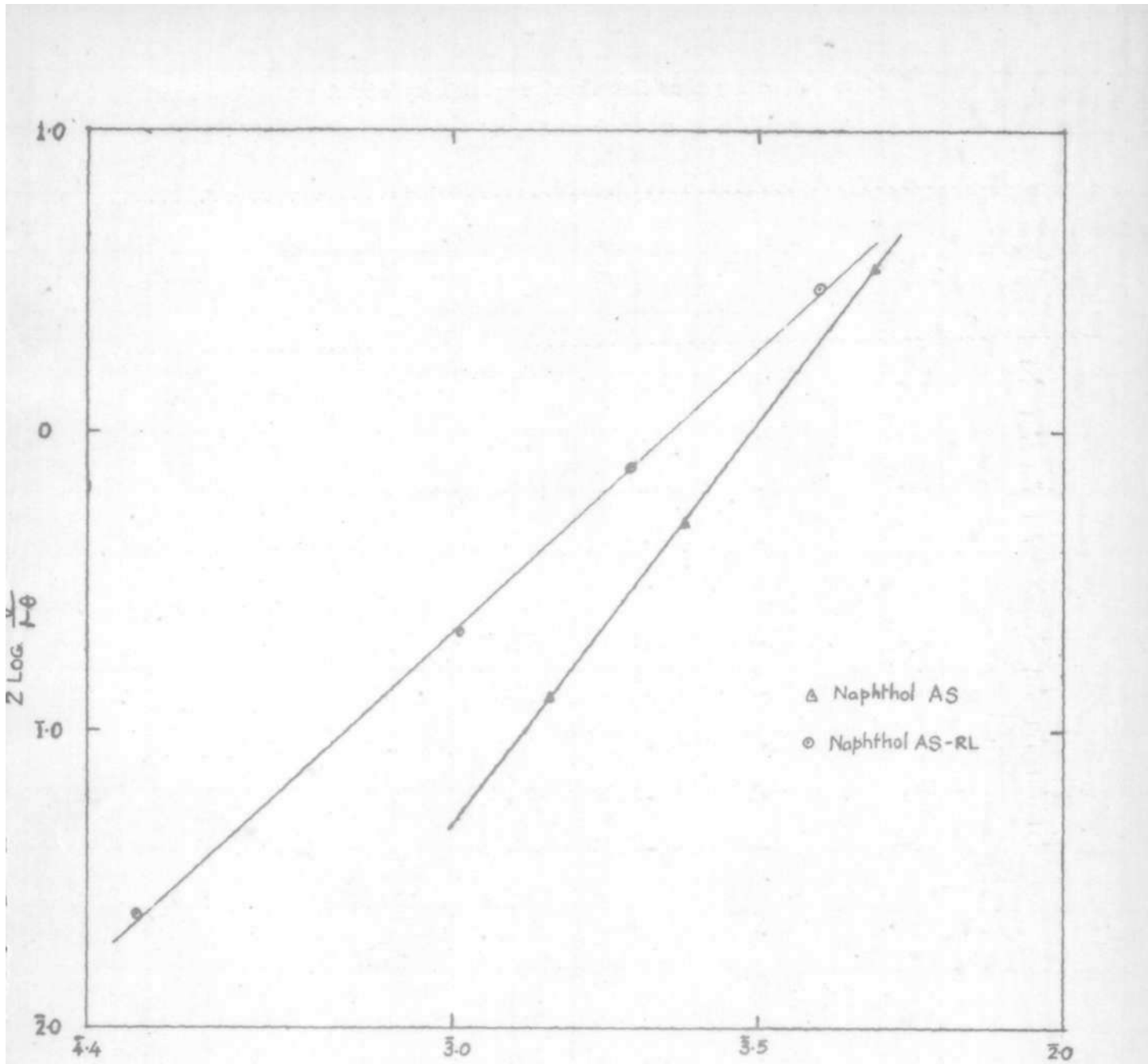


FIG. 24. PLOTS OF $2 \log \frac{p}{1-p}$ VS. LOG A_S FOR NAPHTHOLS AS AND AS-RL

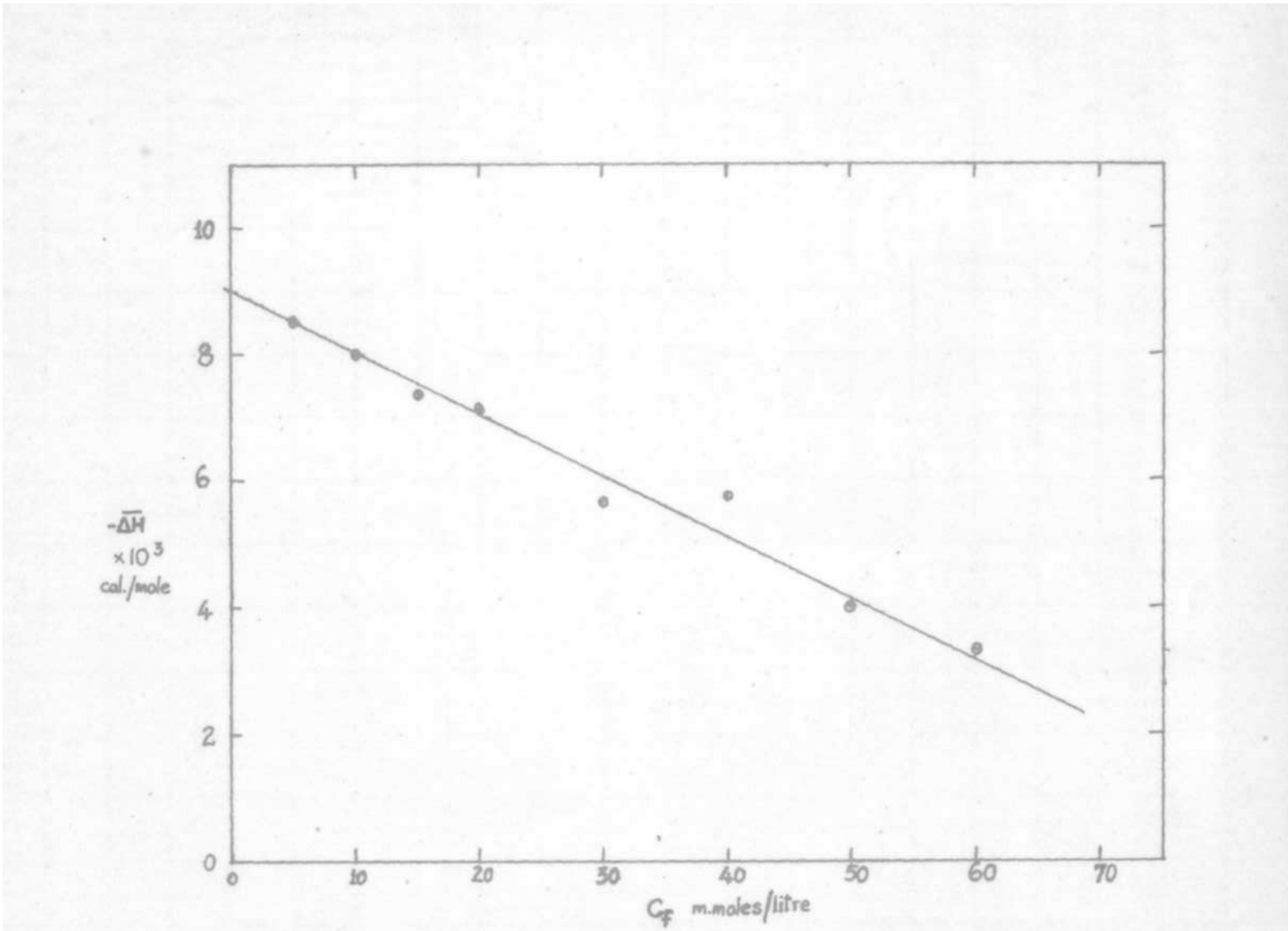


FIG.25 THE DIFFERENTIAL HEAT OF ABSORPTION AT DIFFERENT NAPHTHOL UPTAKE FOR NAPHTHOL AS

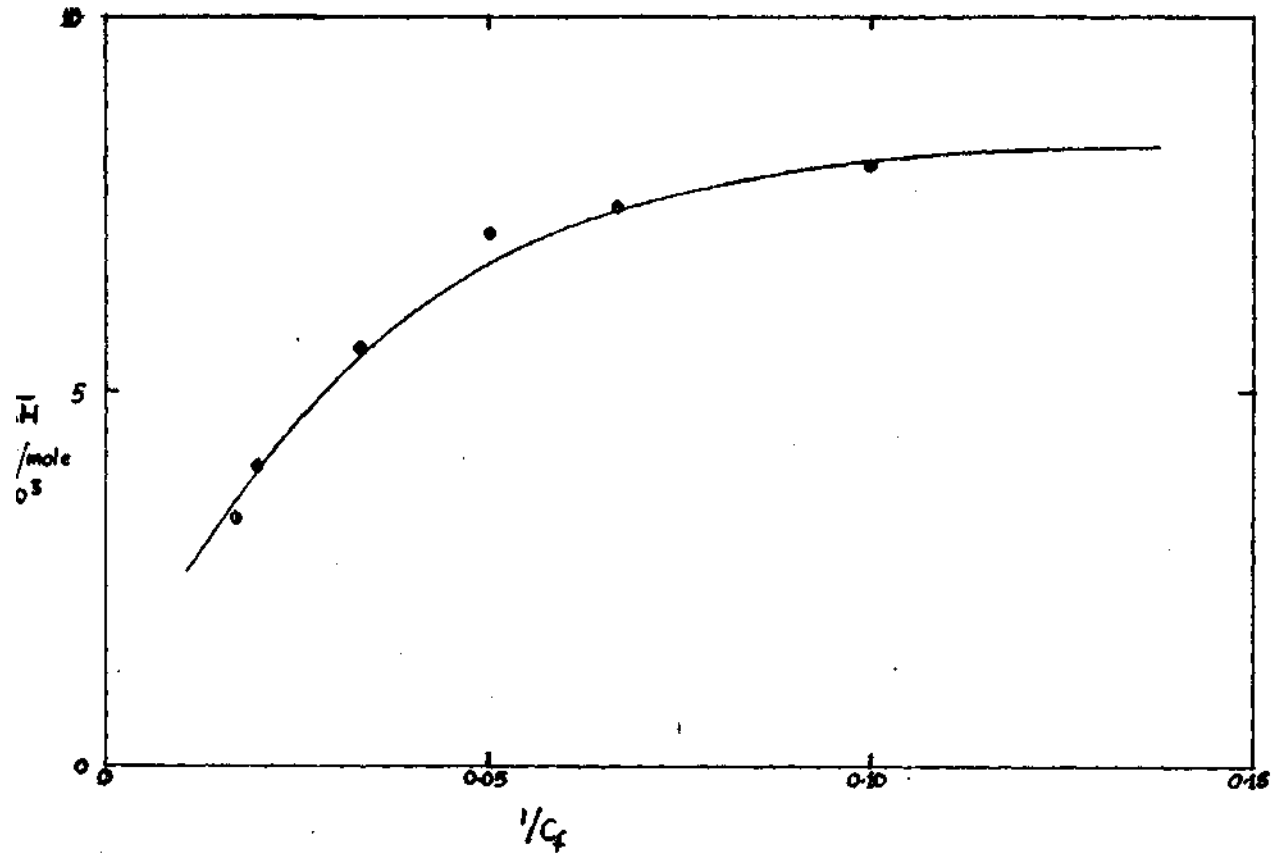


FIG. 26 PLOT OF $-\bar{\Delta}H$ VS $1/C_f$ FOR NAPHTHOL AS.

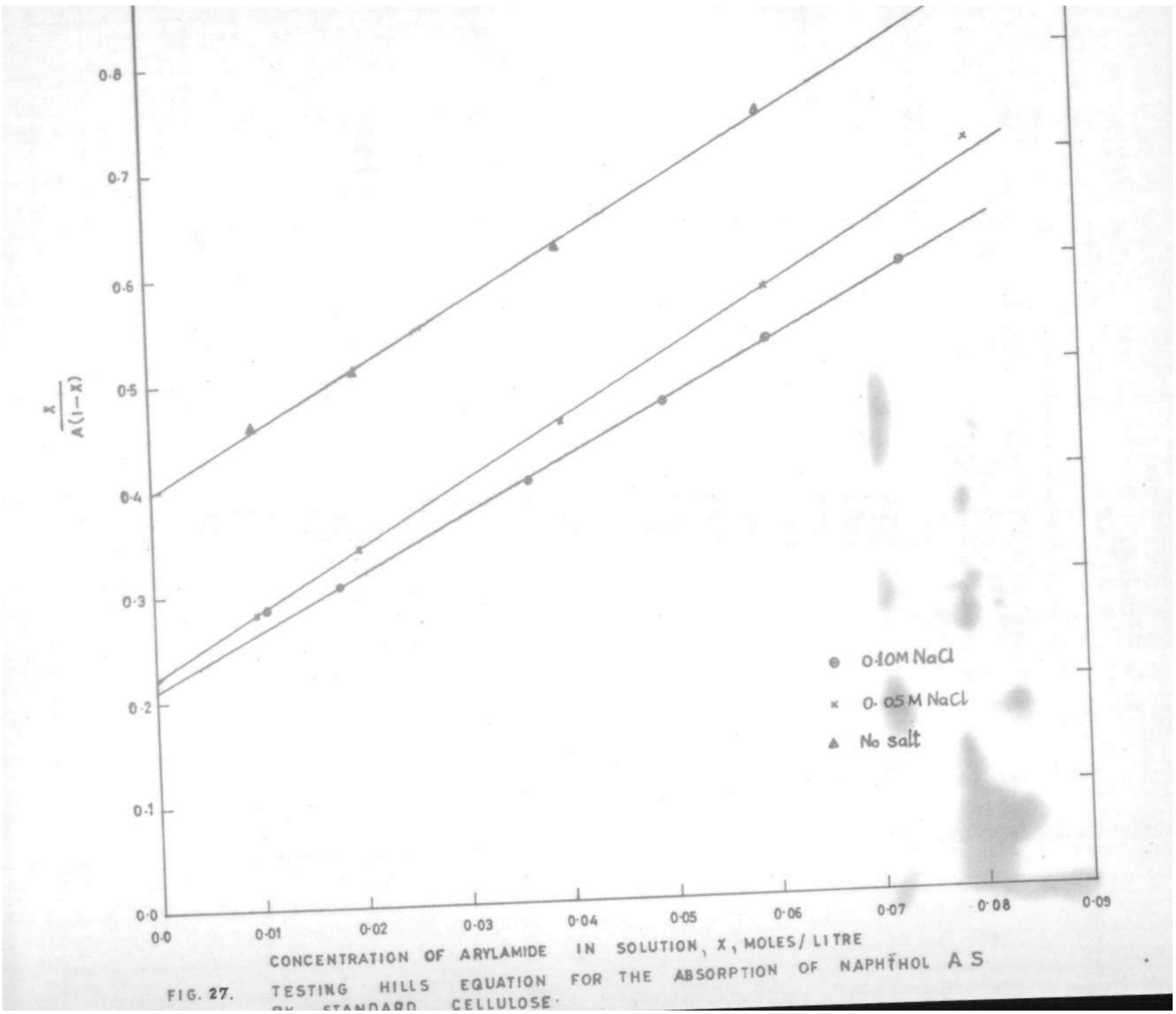


FIG. 27. TESTING HILLS EQUATION FOR THE ABSORPTION OF NAPHTHOL AS BY STANDARD CELLULOSE.

Table XXVII Testing Hill's equation for the absorption of Naphthol AS by standard cellulose at 30°C

Mole fraction of Naphthol in solution, $X.10^{-3}$	Mole fraction of Naphthol on fibre, $Ax10^{-3}$	$\frac{X}{A(1-x)}$
0.1OM NaCl		
3.56	20.02	0.19
5.00	23.00	0.22
10. 9	38.64	0.29
18.06	60.08	0.31
36.65	94.84	0.40
50.00	111. 0	0.47
60.00	124. 0	0.53
73.25	133. 0	0.59
0.05M Na Cl		
10. 0	36. 0	0.28
20. 0	60	0.34
40.	92	0.45
60	111	0.58
80	122	0.71
No Salt		
10	22	0.46
20	40	0.51
40	67	0.62
60	86	0.74
80	98	0.89

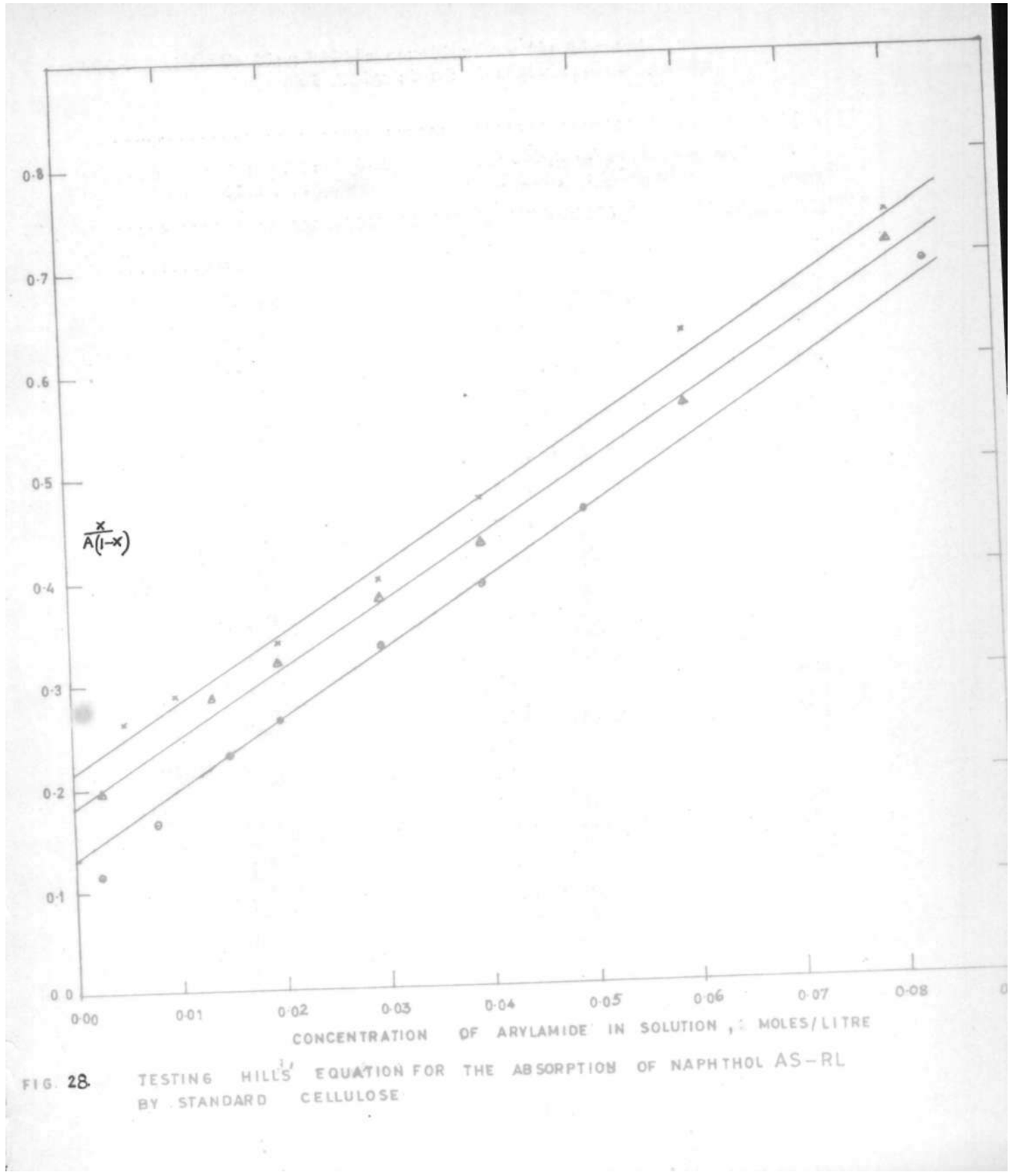


FIG. 28. TESTING HILL'S[17] EQUATION FOR THE ABSORPTION OF NAPHTHOL AS-RL BY STANDARD CELLULOSE

Table XXVIII Testing Hill's equation for the absorption of Naphthol AS-RL by standard cellulose

Mole fraction of Naphthol in solution, $X \cdot 10^{-3}$	Mole fraction of Naphthol on fibre, $Ax10^{-3}$	$\frac{X}{A(1-x)}$
0.10M NaCl		
2.28	19.5	0.12
7.75	46.11	0.17
15.0	66.5	0.23
20.0	77.0	0.26
30.0	92.5	0.33
40.0	107.0	0.39
50.0	115.0	0.46
83.5	131.7	0.69
0.01M NaCl		
2.59	13.17	0.20
10.00	38.00	0.27
13.40	47.43	0.29
20.00	64.00	0.32
27.15	79.05	0.35
30.00	83.00	0.37
40.00	96.50	0.43
60.00	114.0	0.56
80.00	122.0	0.71
0.005M NaCl		
5.0	19.0	0.26
10.0	35.0	0.29
20.0	60.5	0.34
30.0	78.0	0.40
40.0	88.5	0.47
60.0	101.0	0.63
80.0	118.0	0.74

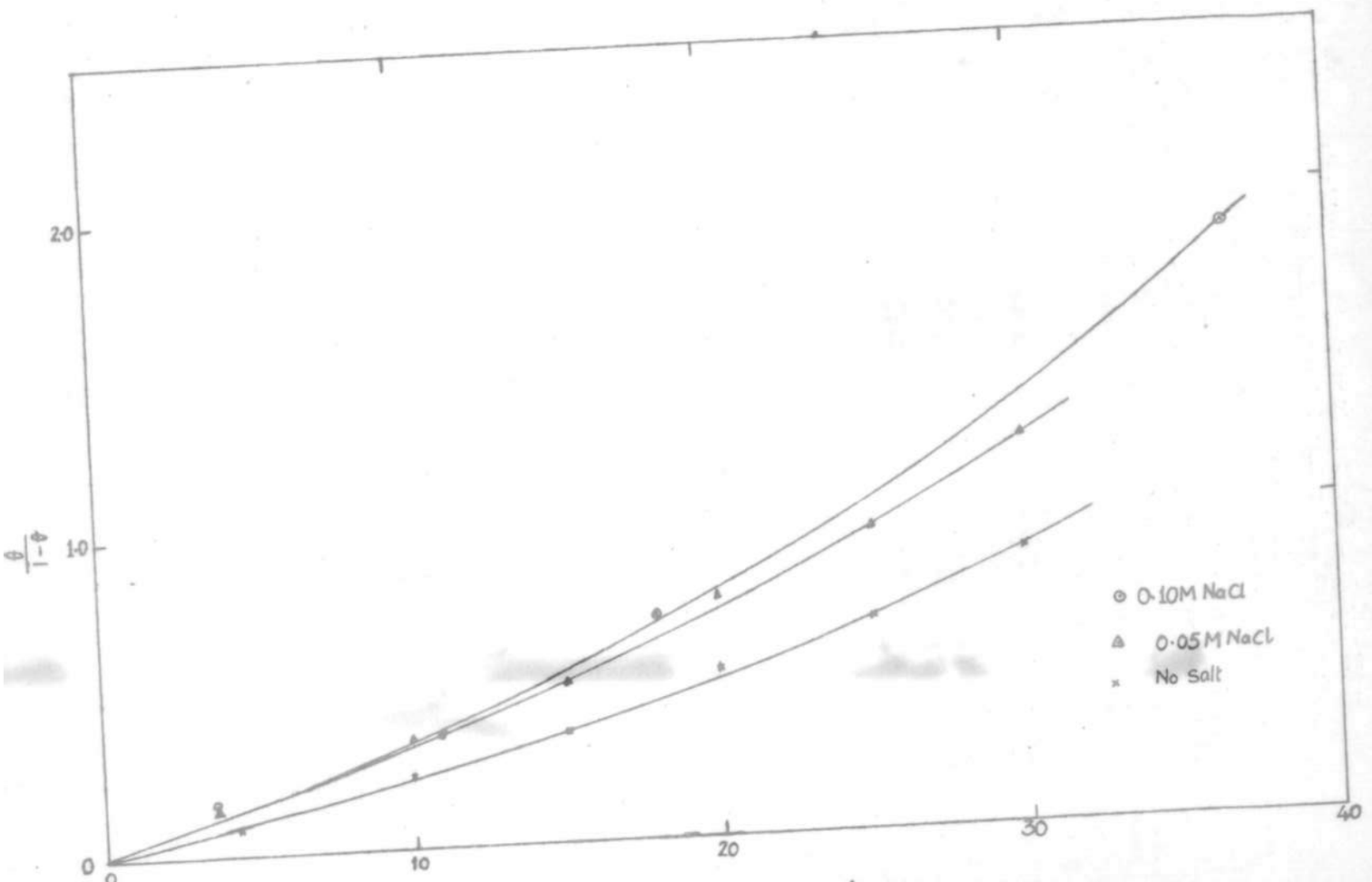


FIG. 29. LANGMUIR ISOTHERMS FOR NAPHTHOL AS ABSORPTION BY STANDARD CELLULOSE AT 30°C

Table XXIX Langmuir isotherm for Naphthol AS absorption by standard cellulose at 30°C

$[Ar_s^-]$ x 10^{-3} mole/l	$[Ar_f^-]$ x 10^{-3} mole	θ	$\frac{\theta}{1-\theta}$
0.10M NaCl			
3.56	20.02	0.14	0.16
10.90	38.64	0.26	0.36
18.06	60.08	0.41	0.70
36.80	95.01	0.65	1.86
0.05M NaCl			
3.58	17.91	0.13	0.15
10.00	36.00	0.26	0.35
20.00	60.00	0.43	0.76
30.00	76.50	0.55	1.23
15.00	46.00	0.33	0.50
25.00	67.50	0.49	0.94
No Salt			
4.30	9.00	0.08	0.08
10.00	22.00	0.19	0.23
15.00	30.50	0.26	0.35
20.00	40.00	0.34	0.52
25.00	47.00	0.40	0.67
30.00	54.40	0.46	0.87

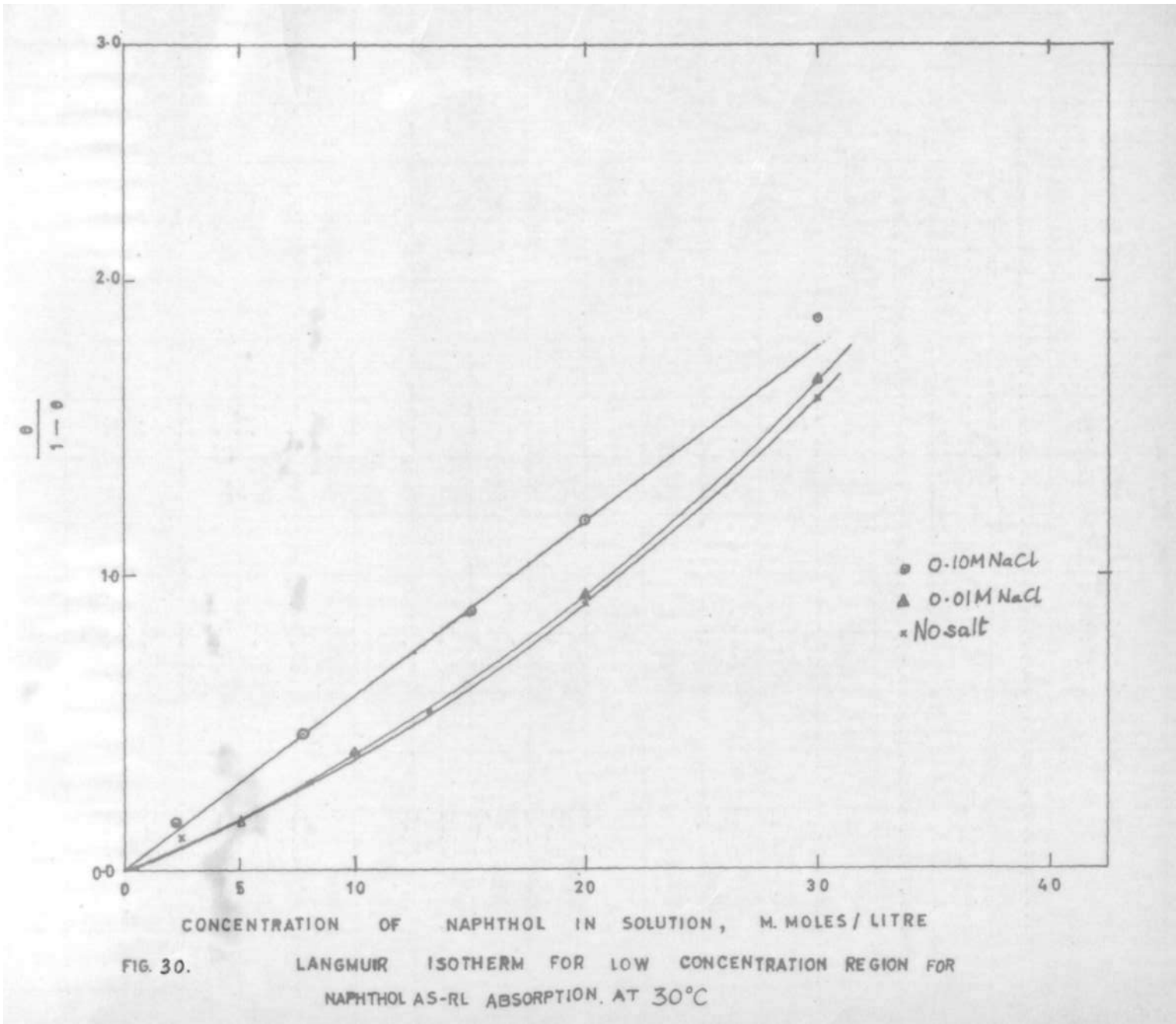


FIG. 30. LANGMUIR ISOTHERM FOR LOW CONCENTRATION REGION FOR NAPHTHOL AS-RL ABSORPTION AT 30°C

Table XXX Langmuir isotherm for Naphthol AS-PL absorption by standard cellulose

$[Ar_g^-]$ x 10^{-3} mole	$[Ar_f^-]$ x 10^{-3} mole	θ	$\frac{\theta}{1-\theta}$
0.10M NaCl			
2.28	19.50	0.14	0.16
7.75	46.11	0.32	0.48
15.00	66.50	0.46	0.88
20.00	77.00	0.54	1.18
30.00	92.50	0.65	1.87
0.05M NaCl			
5.00	19.00	0.15	0.18
10.00	30.00	0.28	0.39
20.00	60.50	0.48	0.94
30.00	78.00	0.62	1.66
0.01M NaCl			
2.59	13.17	0.10	0.11
8.02	29.86	0.22	0.28
13.40	47.43	0.35	0.54
20.00	64.00	0.47	0.90
30.00	83.00	0.61	1.60

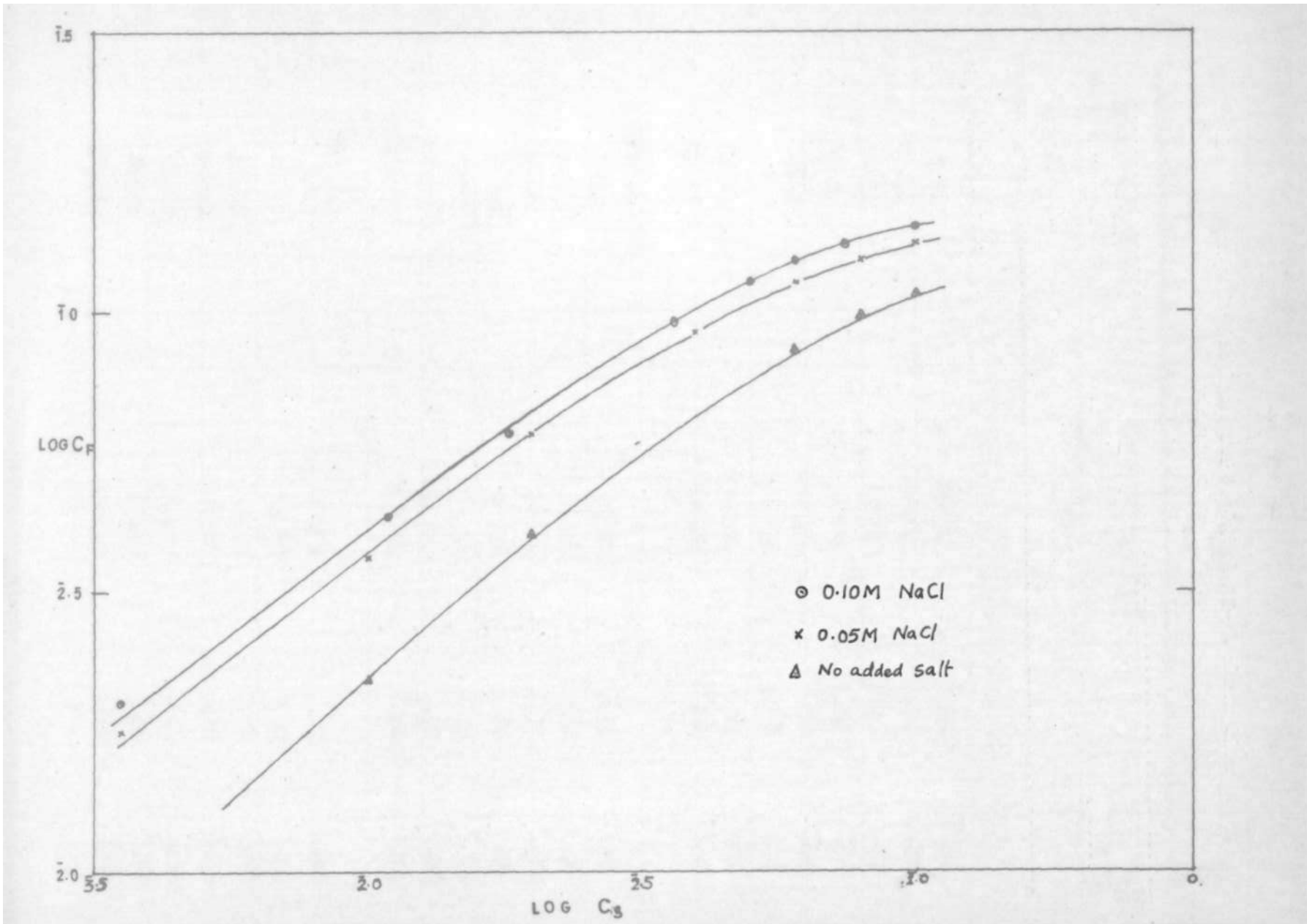


FIG. 31. FREUNDLICH ISOTHERM PLOTS FOR NAPHTHOL AS ABSORPTION BY STANDARD CELLULOSE AT 30°C

Table XXXI Freundlich isotherm plots for AS

Conc. of Naphthol on soln. C_s, moles/l $\times 10^{-3}$	Conc. of Naphthol on fibre C_f, moles/l $\times 10^{-3}$	log C_s	log C_f
0.10M NaCl			
3.56	20.02	$\bar{3}.55$	$\bar{2}.30$
10.90	38.64	$\bar{2}.04$	$\bar{2}.59$
18.06	60.08	$\bar{2}.26$	$\bar{2}.78$
36.65	94.84	$\bar{2}.56$	$\bar{2}.98$
50.00	111.00	$\bar{2}.70$	$\bar{1}.05$
60.00	124.00	$\bar{2}.78$	$\bar{1}.09$
73.25	133.10	$\bar{2}.87$	$\bar{1}.12$
100.00	142.00	$\bar{1}.00$	$\bar{1}.15$
0.05M NaCl			
3.58	17.91	$\bar{3}.55$	$\bar{2}.25$
10.00	36.01	$\bar{2}.00$	$\bar{2}.56$
20.00	60.00	$\bar{2}.30$	$\bar{2}.78$
40.00	92.00	$\bar{2}.60$	$\bar{2}.96$
60.00	111.00	$\bar{2}.78$	$\bar{1}.05$
80.00	122.00	$\bar{2}.90$	$\bar{1}.86$
100.00	133.00	$\bar{1}.00$	$\bar{1}.12$
No Salt			
5.00	10.00	$\bar{3}.70$	$\bar{2}.00$
10.00	22.00	$\bar{2}.00$	$\bar{2}.34$
20.00	40.00	$\bar{2}.30$	$\bar{2}.60$
40.00	67.00	$\bar{2}.60$	$\bar{2}.83$
60.00	86.00	$\bar{2}.78$	$\bar{2}.93$
80.00	98.00	$\bar{2}.90$	$\bar{2}.99$
100.00	108.00	$\bar{1}.00$	$\bar{1}.03$

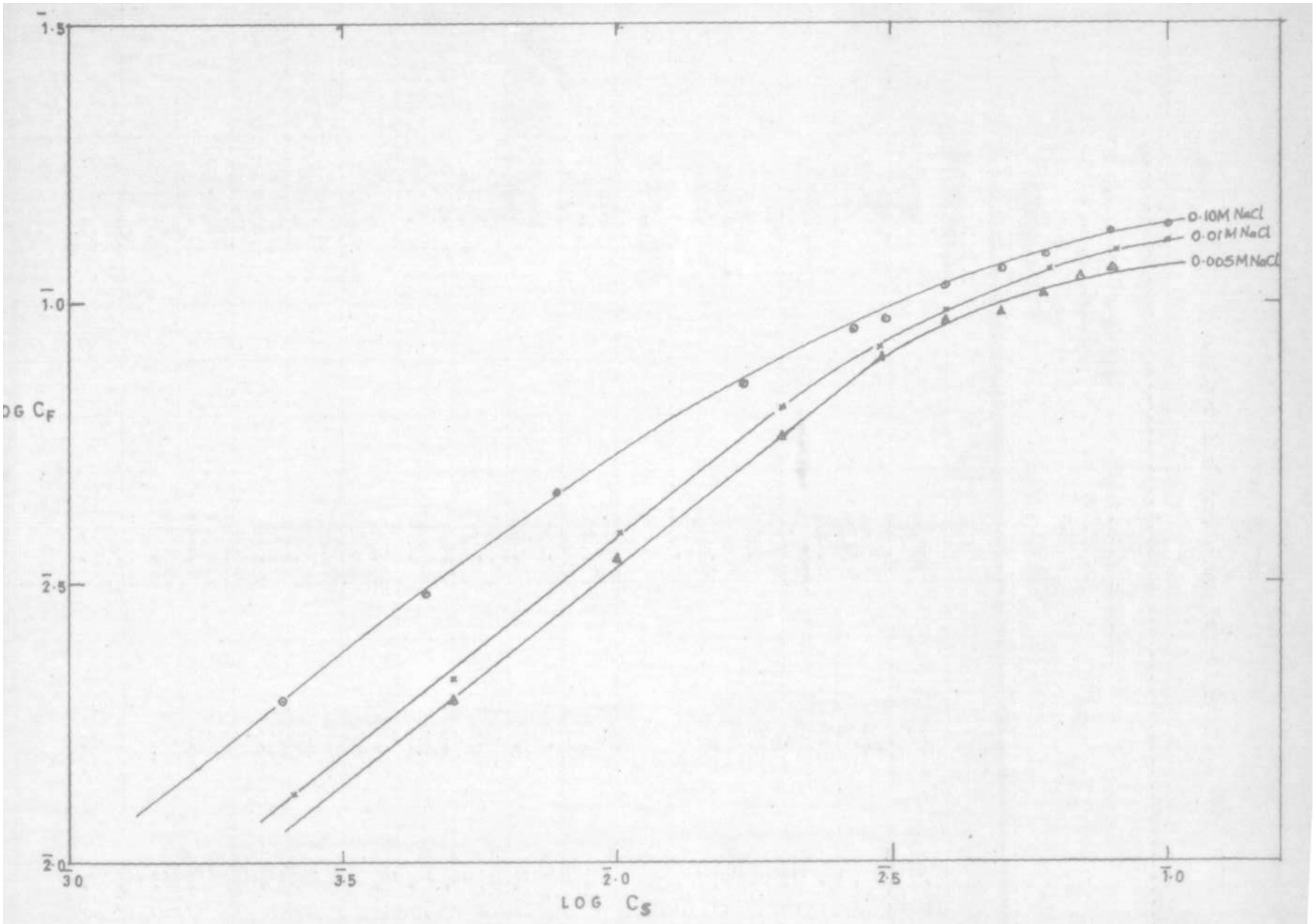


FIG. · FREUNDLICH ISOTHERM PLOTS FOR NAPHTHOL AS-RL ABSORPTION BY STANDARD CELLULOSE AT 30°C

Table XXXII Freundlich isotherm plots for Naphthol AS-RL

Conc. of naphthol in soln. moles/l C_s moles x 10^{-3}	Conc. of naphthol on fibre C_f moles x 10^{-3}	log C_s	log C_f
0.10M NaCl			
	19.50	$\bar{3}.36$	$\bar{2}.29$
2.28	46.11	$\bar{2}.89$	$\bar{2}.66$
7.75	89.56	$\bar{2}.43$	$\bar{2}.95$
27.00	94.00	$\bar{2}.48$	$\bar{2}.97$
30.00	100.50	$\bar{2}.54$	$\bar{1}.00$
35.00	107.00	$\bar{2}.60$	$\bar{1}.03$
40.00	115.00	$\bar{2}.70$	$\bar{1}.06$
50.00	122.00	$\bar{2}.78$	$\bar{1}.09$
60.00	133.00	$\bar{2}.90$	$\bar{1}.12$
80.00	136.00	$\bar{1}.00$	$\bar{1}.13$
100.00			
0.05M NaCl			
	13.17	$\bar{3}.41$	$\bar{2}.12$
2.59	21.00	$\bar{3}.70$	$\bar{2}.32$
5.00	38.50	$\bar{2}.00$	$\bar{2}.58$
10.00	65.00	$\bar{2}.30$	$\bar{2}.81$
20.00	82.50	$\bar{2}.48$	$\bar{2}.92$
30.00	95.50	$\bar{2}.60$	$\bar{2}.98$
40.00	114.00	$\bar{2}.78$	$\bar{1}.05$
60.00	124.30	$\bar{2}.90$	$\bar{1}.09$
80.00	129.20	$\bar{1}.00$	$\bar{1}.11$
100.00			
	8.00	$\bar{3}.30$	$\bar{2}.90$
2.00	19.50	$\bar{3}.70$	$\bar{2}.29$
5.00	35.00	$\bar{2}.00$	$\bar{2}.54$
10.00	57.50	$\bar{2}.30$	$\bar{2}.76$
20.00	79.50	$\bar{2}.48$	$\bar{2}.90$
30.00	93.00	$\bar{2}.60$	$\bar{2}.97$
40.00	96.00	$\bar{2}.70$	$\bar{2}.98$
50.00	104.00	$\bar{2}.78$	$\bar{1}.02$
60.00	111.00	$\bar{2}.84$	$\bar{1}.04$
70.00	115.00	$\bar{2}.90$	$\bar{1}.06$
80.00			

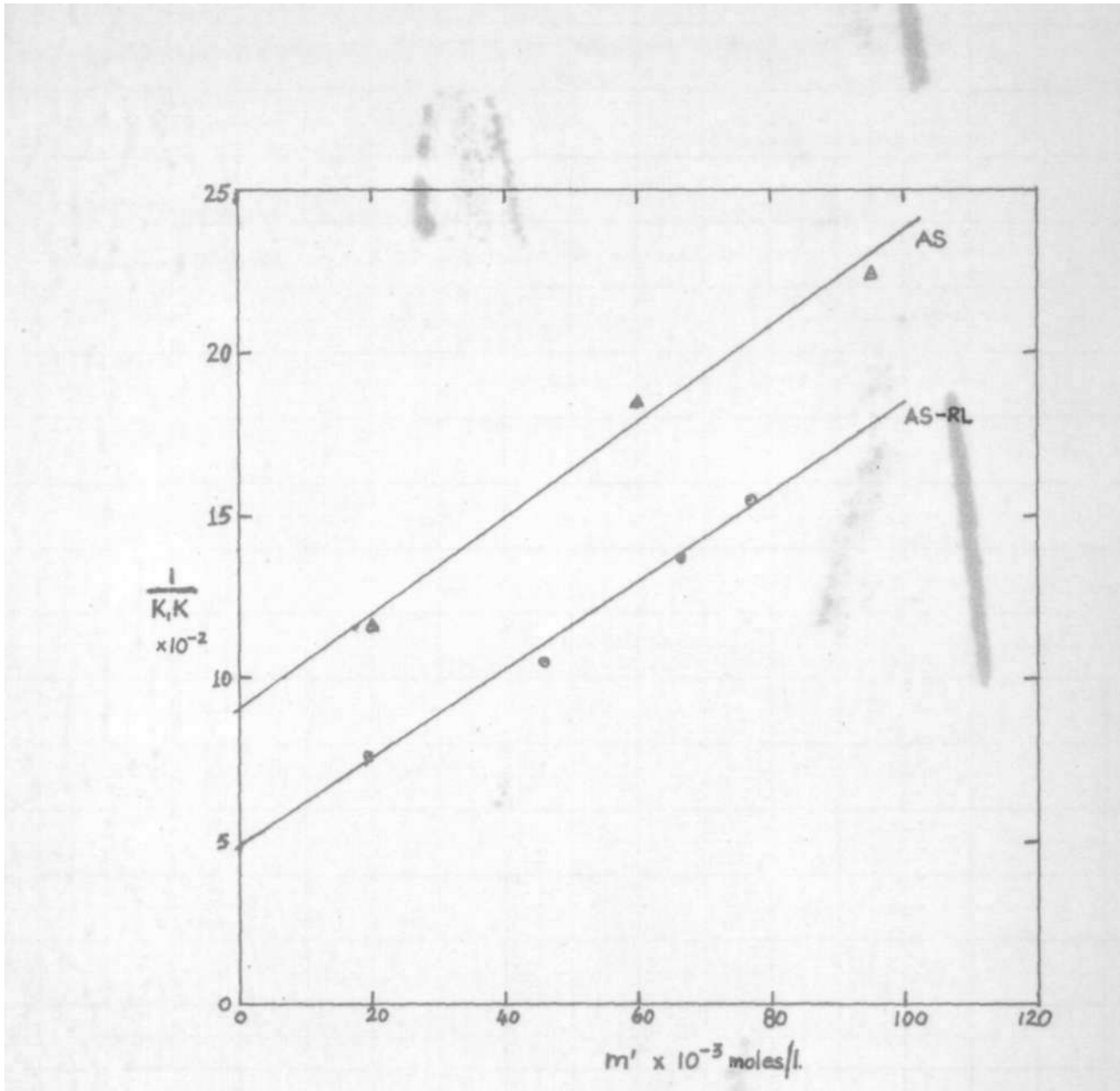


FIG. 33. PLOTS OF $\frac{1}{K_1K}$ VS. m' FOR NAPHTHOLS AS AND AS-RL.

Table XXXIII Absorption of different Naphthols by alkali-pretreated cellulose

Naphthol	pH of equilibrium alkali solution	mmoles Naphthol absorbed/ kg. sample
AS		
(0.10M NaCl)	8.89	67.73
	9.65	69.11
	10.14	69.08
	11.84	69.22
	12.23	69.15
AS-SW		
(No added salt)	7.41	150. 2
	9.61	148. 4
	10.91	150. 2
	11.84	150. 2
	12.02	150. 2
AS-RL		
(No added salt)	7.03	72.44
	9.94	72.44
	11.38	72.44
	11.88	72.44
	12.00	72.44

4.0 CHAPTER FOUR

4.1 D I S C U S S I O N

4.1.1 Alkali Absorption by Standard Cellulose

Fig. 7 shows the curves for alkali absorption by standard cellulose as a function of pH in the presence and absence of added sodium chloride. The absorption is virtually complete in the first five minutes of the reaction as shown by the equilibrium - time curve (Fig. 6). At low alkaline pH's the reaction is merely the absorption of the sodium hydroxide by the hydroxyl groups of cellulose. At higher pH's however it appears as if compound formation may be occuring. This is indicated by the much greater uptake of alkali in the presence of added salt, similar to the effect of salt on the absorption of arylamides by cellulosic fibres (see later).

CHEMICALLY MODIFIED CELLULOSES

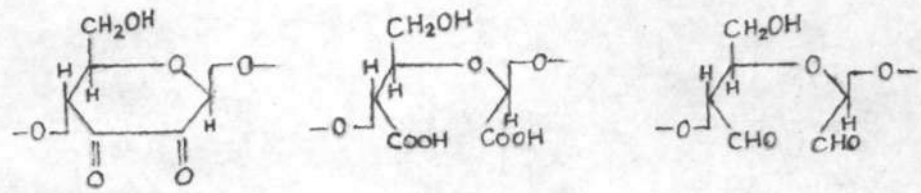
Purpose of the experiments

The experiments were carried out to observe the effects of the introduction of groups like carboxyl (-COOH), aldehyde (-CHO) and three primary alcoholic ($-CH_2OH$) groups on the cellulose molecule on its absorptive capacity in terms of alkali and naphthol uptake.

The oxycelluloses

The preparations of these have already been described (see pages 38 - 40). The choice of the reagents used depends on the specificity of their action. Attack on the anhydroglucose unit in cellulose can take place in four positions. Reaction at the 2 and 3 carbon atoms gives rise to keto groups or the breaking of the ring to two aldehyde groups which may be further oxidised to carboxyl groups. Attack on the primary hydroxyl group in the 6 - position may form aldehyde, keto or carboxyl groups. The possible products arising from such reactions may be represented as follows:





Nitrogen dioxide oxycellulose. Gaseous nitrogen dioxide is specific for the primary alcoholic group, producing mainly a carboxyl group. Such acids are known as uronic acids. The effect of alkali on the celluronic acids of nitrogen dioxide

oxycellulose has been investigated by Fowler et al[74] from which the following conclusions may be drawn:

a) the resulting celluronic acids are alkali-soluble when the carboxyl content is sufficiently high.

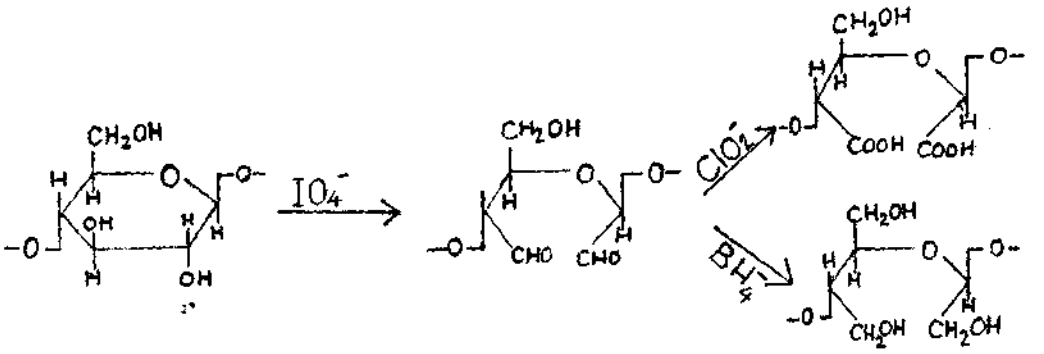
b) apart from carboxyl groups which should not produce alkali instability in celluronic acids, oxidation of the carboxyl groups could form aldehyde or ketone groups or enediol structure by isomerization of the latter. Aldehyde groups in simple organic compounds are attacked rapidly - sometimes explosively - by NO_2; hence their presence in substantial amounts in celluronic acid is doubtful. Ketone groups in certain compounds are less readily attacked by this oxidant and such groups may be present in this oxidised cellulose.

Periodate oxycellulose and its oxidation and reduction products

Periodic acid is used for the oxidation of secondary alcoholic groups of the α-glycol type. For the oxidation of cellulose, periodic acid or its sodium salt is specific for the hydroxyls on the 2 and 3 carbon atoms of the anhydroglucose unit, oxidising them to aldehyde groups by breaking the ring. This product is known as periodate oxycellulose.

Treatment of this product with chlorous acid causes

further oxidation of the aldehyde groups to carboxyls. On the other hand, treatment with a reducing agent like sodium borohydride reduces the aldehyde groups to primary hydroxyls.



Alkali absorption by Chemically Modified Celluloses.

Mercerized Cellulose

Though the aim of the mercerization treatment is not principally to introduce any chemical modification of the cellulose structure it is appropriate to treat mercerized cellulose under this section so as to compare its absorptivity with that of standard cellulose and of the other forms of modified celluloses. The purpose of mercerization is to induce increased absorptive power and reactivity by opening up the cellulose structure, making available a larger number of hydroxyl groups for combination.

Fig. 8 shows the plots of alkali uptake against the pH of the equilibrium solution for mercerized cellulose alongside those for standard cellulose for comparison. The much increased absorption shown by the former is in agreement with the view that the expanded

structure increases the absorptive power of the fibre.

The oxycelluloses.

The titration curves for nitrogen dioxide oxycellulose, periodate - chlorite oxycellulose, and periodate oxycellulose are shown in figs. 9, 11, and 10, respectively. The first portions of figs. 9 and 11 represent essentially the titration of the carboxyl groups by alkali. After all the carboxyl groups have been titrated the curves assume a flat shape. It was however observed that the amount of carboxyl groups present could not be estimated quantitatively from the curves as shown by the non-coincidence of the flat regions of the curves for the presence and absence of added salt. The exact effect of added salt here is not easy to see but it is possible that the increased absorption by the unoxidised hydroxyl groups in the 2 and 3 positions of the anhydroglucose unit in the presence of added salt may account for the displacement of the two curves in this region.

The absorption by periodate oxycelluloses shows a continuous increase with increasing pH of alkali solution (i.e. it does not show a maximum in the pH range studied (Fig. 10)). At high pH's the oxycellulose dissolves in the alkali. This alkali sensitivity is conferred on it by the presence of aldehydic groups[75] .

Also in the present study it was observed that the increase in alkali absorption for the same increment in amount of added salt is greater for the oxycelluloses than for standard cellulose. Since

there are more negatively charged groups i.e. the carboxyl groups present on the oxycelluloses, the screening effect of added salt is more pronounced. This is in good agreement with the electrostatic theory of the salt effect.

Calculation of Dissociation constants

Apparent Dissociation constant pK_a'

By making use of the equation[76]

$$pH = pK_a' - n \log \left(\frac{1-\alpha}{\alpha}\right) \qquad (1)$$

where α is the degree of dissociation of the acid, the apparent dissociation constant pK_a' may be found for the carboxyl groups of the oxycelluloses. In figs. 21 and 22 the plots of the pH of the external solution against $\log \left(\frac{1-\alpha}{\alpha}\right)$ for nitrogen dioxide oxycellulose are shown. The pK_a' value is the pH of the solution at $\log \left(\frac{1-\alpha}{\alpha}\right) = 0$ i.e. at $\alpha = 0.5$. The slope of the plot gives the value of n. The values of n obtained in the present study are 1.22 in absence of salt and 1.28 in the presence of 0.10M sodium chloride.

Application of the Gibbs - Donnan Theory[77] to the calculation of Dissociation constants.

The Gibbs - Donnan theory has been applied with success to the dissociation of solid polyelectrolytes by Chatterjee and Marinsky[78], Gustafson[79], Mathieson and Whewell[80] and Mathieson and Shet[81]. In applying the theory these workers made two alternative assumptions:

1) an equipotential between the sorbed solution inside the resin and the external solution.

2) equipotential between the sorbed solution and the polymer chains.

The two assumptions thus represent limiting cases, the former suitable for highly swollen resins and the latter suitable for resins and fibres which show little swelling.

The intrinsic dissociation constant is given by

$$K_0' = \left[\alpha/(1-\alpha)\right] a_{H1} \exp\left\{(\psi_P - \psi_F)F/RT\right\} \qquad (2)$$

where α is the degree of dissociation, a_{H1} is the hydrogen ion activity in the sorbed solution, F the Faraday, ψ_P and ψ_F represent the assumed uniform potential on the chains and the sorbed solution respectively and $(\psi_P - \psi_F)$ is the change in potential due to the release of a hydrogen ion from within the fibre. For equilibrium between the fibre and external solution whose pH is measured the Gibbs - Donnan equations give that

$$RT \ln \frac{a_{H1} a_{M2}}{a_{H2} a_{M1}} = -\pi\left(\bar{V}_H - \bar{V}_M\right) - \left(\Delta\mu_H^\circ - \Delta\mu_M^\circ\right) \qquad (3)$$

where M refers to a univalent metallic cation, subscripts 1 and 2 to the fibre and external solution respectively, and π, $\bar{V}$ and $\Delta\mu^\circ$ represent the osmotic pressure, partial molar volume, and change of standard chemical potential between fibre and external solution. Only a single simple anion is present, and the

$\bar{V}_s'$ are assumed independent of pressure. Combining these equations gives, for the pH of the external solution

$$pH_2 = pK_o - \log \frac{1-\alpha}{\alpha} + \log \frac{aM1}{aM2} + \frac{0.4343}{RT}\left[(\psi_P - \psi_F)F - \pi(\bar{V}_H - \bar{V}_M) + \Delta\mu_M^\circ - \Delta\mu_H^\circ\right] \quad (4)$$

For a fibre which shows little swelling $\psi_F \simeq \psi_P$ and equation (4) reduces to that used by Mathieson and Whewell[80] i.e.

$$pH_2 = pK_o' - \log \left[(1-\alpha)/\alpha\right] + 0.4343\ \psi_P \cdot F/RT \quad (5)$$

$$\text{Since } \log \frac{aM1}{aM2} = -\psi_P F - \pi \bar{V}m - \Delta\mu_M^\circ \quad (6)$$

To apply these equations we need information on ψ_P, $\Delta\mu^\circ$ and aM1. π is calculable from water absorption data, and the term in π has been shown to be negligible[81]. In these systems it is reasonable to regard $\Delta\mu^\circ$ as zero.

The basis of equation (5) may be stated as follows:

$$\text{For a normal acid, } pH = pK_o' - \log \frac{1-\alpha}{\alpha} \quad (7)$$

For a polyacid we must add to it another term, giving

$$pH = pK_o' - \log \frac{1-\alpha}{\alpha} + \frac{0.4343}{kT}\left(\frac{\partial G}{\partial \nu}\right)_K \quad (8)$$

where ν is the charge on the polymer and the last term gives the change in free energy with charge at constant ionic strength.

For a solid polyacid in equilibrium with solution we then have either

$$pH = pK_o' - \log \frac{1-\alpha}{\alpha} + \frac{0.4343}{RT}\left[\psi_P - \pi\bar{V}_H - \Delta\mu_H^\circ\right] \quad (9)$$

$$\text{or } pH = pK_o' - \log \frac{1-\alpha}{\alpha} + \log \frac{a_M'}{a_M} + \frac{0.4343}{kT} \left(\frac{\partial G}{\partial \nu}\right)_K \qquad (10)$$

where a_M' and a_M are activities of concentrations in fibre and solution, ψ is the electrostatic potential on the fibre, $\bar{V}_H$ is the partial molar volume of H^+ ion, π the osmotic pressure difference and $\Delta\mu_H^\circ$ the change in standard chemical potential (if any).

The simplest treatment (which works for wool and nylon [83]) is to calculate ψ from an assumed Boltzmann distribution $C_i' = C_i \exp(-e\psi/kT)$. It gives, for a 1 : 1 electrolyte $e\psi/kT = \sinh^{-1} C_f/2C_s$ where C_f is the concentration of fixed charges on the fibre and C_s is the salt concentration. Equation (5) is obtained by negeloting π and $\Delta\mu_H^\circ$ in equation (9). If the acid anion has some affinity for the fibre the Boltzmann assumption brings this in as a non-zero value of $\Delta\mu_H^\circ$ but for C_i' this is negligble.

For ion exchange resins this does not work and equation (10) was used , with $(\partial G/\partial \nu)_K = \psi F$ and the term in π and $\Delta\mu_H^\circ$ neglected, but with ψ calculated from the equation of Katchalsky and Lifson [84] for randomly kinked chains. This worked quite well.

The results of the present work, for nitrogen dioxide oxycellulose and periodate - chlorite oxycellulose are shown in Table XXIV. In the absence of salt the pK_o' values obtained using equation (7) are much higher than expected for normal

carboxylic groups. However, the pK'_o values calculated for the presence of salt using equation (5) yielded values below that for normal carboxylic groups. It would therefore imply that the calculation of the dissociation constant based on the assumption that there is a uniform potential distribution throughout the fibre and utilising equation (5) does not apply to the oxycelluloses studied. The oxycelluloses are therefore behaving as polyacidic resins which show reduced pK'_o values. **in absence of salt**[85].

Effect of increasing alkali concentration on the equilibrium absorption of arylamides by standard cellulose and the modified celluloses at constant ionic strengths

Standard cellulose.

All the arylamides studied showed a small initial increase in uptake with increasing pH of the equilibrium solution, until a maximum value of amount taken up is reached, after which there is no further increase (See figs. 12 to 15). It was observed that, generally, solutions of the arylamides were cloudy at pH values below pH 11 making it unreliable to determine the absorption at such pH's. It was therefore not possible to study the initial rise in absorption to lower pHs.

Within the pH range in which the investigation was carried out, it has been shown that very little swelling of the cellulosic fibre occurs (longitudinal swelling only of the order of 1% at alkali concentration of 10g./l)[86]. It is therefore unlikely that the uptake of arylamide would change substantially.

Modified Celluloses.

The results for the modified celluloses showed a similar trend as for standard cellulose i.e. no change in uptake after an initial small rise to a maximum value (Figs. 16 and 17).

The relative amounts of arylamide absorbed by the different samples were in the order mercerized cellulose > periodate oxycellulose reduced with borohydride > standard cellulose > the oxycelluloses. The results are compared in Figs. 16 and 17. The following conclusions may be drawn from this observation.

a) the physical structure of a cellulosic fibre has a marked effect on its absorption capacity.

b) the main chemical groups on the cellulose which are responsible for absorption of coupling components are the hydroxyl groups.

c) primary hydroxyl groups show greater absorption than secondary ones. This is shown by the fact that the borohydride reduced periodate oxycellulose which has three primary hydroxyl groups shows much greater absorption than standard cellulose with one primary and two secondary hydroxyls. However, the effect of steric factors may also be in operation here since the borohydride-reduced oxycellulose has an open structure with regard to the bond linking the 2 and 3 carbon atoms which was broken during the periodate oxidation. The removal of the steric hinderance, as a result of this open structure, may also account for the higher

absorption shown by the borohydride reduced oxycellulose as it would permit the easier access of arylamide ions to the hydroxyl groups in the 2 and 3 positions.

The loss of some crystallinity resulting from the chemical treatment may be another factor responsible for the increased absorption of this reduced oxycellulose.

d) the presence of carboxyl groups on cellulose decreases the absorptive power.

e) aldehyde groups are soluble in alkali at high alkaline pH's, hence do not account for much absorption.

The effect of added salt on the equilibrium absorption of all the arylamides by the cellulose samples studied was to increase the uptake. This might be due to two factors:

i) salt brings about a reduction in the solubility of the arylamide thereby promoting the possibility for aggregation which itself aids absorption [87].

ii) as stated earlier(page 30), in aqueous solution the surface of cellulose has a negative potential and a repulsive force is therefore set up on the approach of the negatively charged arylamide ion, thus inhibiting absorption. This repulsion is greater the more negative charges are present on the cellulose surface. This effect is shown in the present investigation by the reduction in absorption shown by oxidised celluloses as compared with standard cellulose. The effect of the addition of sodium chloride is for the sodium ions

to screen the cellulose surface by forming a cloud of positively charged ions above it and thereby facilitating the close approach of the arylamide ion to the cellulose surface for absorption to take place.

Effect of alkali pretreatment on naphthol absorption

1g. samples of standard cellulose were treated with 50 ml. of sodium hydroxide solutions of different low concentrations in 250 ml. pyrex conical flasks with glass stoppers. Nitrogen gas was bubbled through the flasks which were then suspended in a waterbath at 30°C.

At the end of this time the sample was quickly transfered to a small circular piece of terylene cloth and into a centrifuge tube. The liquid was sucked out of the sample by centrifuging for 5 minutes at about 500 r.p.m.

Meanwhile the pH of the equilibrium alkali solution was measured and the amount of alkali absorbed by the sample determined potentiometrically from the difference in concentrations of experimental and control solutions.

The sample, from which excess alkali had been sucked out (by centrifuging), was steeped in 50 ml. of the naphthol solution (5g./l.). After equilibrium was reached the amount of naphthol taken up was measured spectrophotometrically.

The results (see TableXXXIII) show an increased absorption of naphthol by standard cellulose which had been treated with alkali preceding treatment with naphthol solution. However there appeared

to be no difference in absorption with different initial amounts of alkali absorbed. Two conclusions may therefore be drawn.

1. The effect of the alkali initially taken up is to neutralize the carboxyl groups on the cellulose and to facilitate the entry of naphthol molecules.

2. The fibre is little swollen by the alkali in this range of concentrations as shown by the constancy of the naphthol absorption at different initial amounts of alkali absorbed.

Effect of temperature on equilibrium absorption of arylamides by standard cellulose

The effect of temperature on the equilibrium absorption of arylamides (phenylamide and 4 - methoxyphenylamide of 2- hydroxy - 3 - naphthoic acid) at constant concentration of arylamide (5g./l) and pH (12.50) was studied at five temperatures between 25° and 90°C. The results obtained are plotted in Fig. 18 and indicate that the equilibrium absorption decreases with increasing temperature of the bath. A similar effect of temperature on the absorption of direct cotton dyes by cellulosic fibres has been observed by Neale et al[88], and of arylamides of 2-hydroxy-3-naphthoic acid by cellulosic fibres by Daruwala and Mehra[89]. The effect of increased temperature would be to increase the solubility of the arylamide and decrease aggregation. Since the formation of aggregates of the coupling component is a necessary factor for its absorption the observed effect of temperature is accounted for. Also, it has been shown that the absorption of arylamides by

cellulosic fibres is an exothermic reaction [90]. An increase in temperature must therefore cause a reduction in the equilibrium absorption.

Effect of varying concentration on the equilibrium absorption of arylamides by standard cellulose at constant ionic strength

In this set of experiments the concentration of arylamide in the bath was varied between 2 to 200 millimoles/litre. The ionic strength of the solution and the temperature of the bath were kept constant. Figs. 19 and 20 show the variation of amount of arylamide absorbed with concentration of the bath for the 2 arylamides studied. The uptake of coupling component was found to increase with increasing concentration of arylamide in solution as has been shown by previous workers[91-92]. The variation is rapid at first but decreases gradually until a constant (saturation) value is reached at high concentrations of arylamide.

Peters and Vickerstaff [93] have suggested that the driving force during dyeing can best be represented by the Gibbs free energy changes involved and have termed the tendency for dye to pass from the solution phase to the fibre phase the affinity, given by

$$-\Delta G = RT \ln \frac{A_f}{A_s}$$

where A_f and A_s are the activities of the dye in the fibre and solution phase respectively. Because of the difficulty in expressing

the activity of the dye in the fibre phase they introduced a term for the volume V of cellulosic fibre which they obtained arbitrarily from the absorption of Chrysophenine G by cellulosic fibres which gave linear plots of unit slope when the logarithm of ionic products in the fibre and in the solution at equilibrium were plotted. The activities A_f and A_s are given by

$$A_f = \frac{[Na_f^+]^z [Ar_f^-]}{V^{(z+1)}}$$

where $[Na_f^+]$ and $[Ar_f^-]$ are the concentrations in g. ions/l. of sodium ions and arylamide anions in the fibre phase respectively and z represents the number of charges on the arylamide ion.

Similarly,

$$A_s = [Na_s^+][Ar_s^-]$$

where $[Na_s^+]$, $[Ar_s^-]$ are the concentrations of sodium and arylamide respectively in the solution.

In the present study the concentrations of sodium ions in the fibre phase (Na_f^+) at different arylamide concentrations were calculated applying Donnan equilibrium conditions to the fibre - solution system and Dunn's[94] volume term V = 0.30 mole/l. for cotton. These values were then used to calculate the ionic product (A_f) in the fibre phase. A_s was also calculated from a knowledge of the concentration of sodium ions in solution and the amount of arylamide in solution (See Table XXVI). The plots of log A_f against log A_s were

found to be linear (Fig.23) and to have a slope close to unity for each of the arylamides studied (1.04 and 1.12 for Naphthol AS and Naphthol AS-RL respectively), which justifies the use of Dunn's volume term. The values of the affinity obtained for the two arylamides studied in the present work were found to be in good agreement with those obtained by Dunn using the same volume term (See Table XXXIV). Also the affinity values obtained were constant for a fairly wide range of concentrations of arylamide in the fibre and in solution.

Table XXXIV. Values of affinities of Naphthol AS and AS-RL for standard cellulose at different arylamide concentrations at 0.1M ionic strength

Naphthol	Concentration of arylamide in solution, m.moles/l.	Concentration of arylamide on fibre m.moles/l.		Affinity values obtained in present work cal/mole	Mean Affinities obtained by Dunn[94] cal/mole
AS	3.56	66.73		2984	
	10.9	128,8		3045	
	18.1	200.3		3216	
	36.8	302.1		3109	
			Mean	3088	3100
AS-RL	2.28	64.99		3208	
	7.75	53.3		3407	
	10.00	183.3		3476	
	26.85	325.0		3534	
	83.5	439.2		3210	
			Mean	3367	3490

The treatment above assumes complete dissociation of the arylamide in the fibre phase; thus the activity of the arylamide would vary depending on which of three mechanisms is in operation during the process. Vickerstaff[95] has considered these three mechanisms, namely:

1. Both dye anions and sodium ions are adsorbed on specific sites in the fibre in a monomolecular layer and are not subjected to interference, either electrical or steric from adjacent adsorbed anions.

2. Only the dye anions are adsorbed on specific sites, while the sodium ions are diffusely adsorbed.

3. Both the dye anions and sodium ions are attracted to the fibre-solvent interface and there is a possibility of formation of a multi-molecular layer.

By mechanism 2 account must be taken not only of the sodium ions required for electrical neutrality but also of those surrounding the arylamide ions in the fibre phase. This would require the use of Dannan's equation to calculate the concentration of the sodium ions. The results of the present work indicate that mechanism 2 holds as seen from the near unit slope obtained for the log ionic products plot in which the Na_f^+ was calculated from a Donnan membrane formulation for the system. Daruwala and Kulkarni[96] have also considered the above mechanisms in connection with the absorption of the direct dyes Benzopurpurine 4B and Chloramine Purple 10BC

by cotton at 80°C and 90°C respectively, in the presence of 5g./l. sodium chloride. By comparing the slope for the plot of $(z + 1) \log \frac{\theta}{1 - \theta}$ versus $\log [D_s] . [Na_s^+]$ with that for the plot of $\log \left(\frac{\theta}{1 - \theta} \right) \left(\frac{Na_f^+}{V} \right)^z$ against $\log [D_s] . [Na_s^+]^z$ where θ is the fraction of sites occupied and the subscripts represent the appropriate substances in solution and in fibre respectively. They obtained a slope nearer unity for the latter than for the former. They have therefore concluded that mechanism 2 rather than mechanism 1 must be operating. The method of Daruwala and Kulkarni was applied to the present study and the results obtained for the two arylamides studied are in good agreement with their contention (cf Figs. 23 and 24).

4. A fourth possible mechanism is that some of the anions are strongly adsorbed on specific localized sites while others are only loosely held. This last mechanism may be tested using Hill's statistical approach (see later).

The differential heats of absorption at different concentrations of arylamide on fibre have been calculated for Naphthol AS in the presence of 0.10M sodium chloride. The differential heat of sorption, $\overline{\Delta H}$, is the amount of heat developed when a very great amount of partially swollen substance absorbs 1g. of absorbate. $\overline{\Delta H}$ may be obtained from the relation:

$$\ln \frac{m_1}{m_2} = \frac{\overline{\Delta H}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where m_1, m_2 are the concentrations of naphthol in solution at constant C_f at temperatures T_1 and T_2

where C_f = concentration of naphthol on fibre.

R is the gas constant.

The values of $\overline{\Delta H}$ calculated from this equation for different values of C_f are given in Table XXXV, and the variations of $\overline{\Delta H}$ with C_f and $1/C_f$ are represented graphically in Figs. 25 and 26.

Table XXXV. Differential heats of absorption $\overline{\Delta H}$ calculated for Naphthol AS at different arylamide concentrations on fibre (5g./l. NaCl)

C_f m.moles/kg. fibre	m_1 mmoles/l.	m_2 mmoles/l	$-\overline{\Delta H}$ cal./mole	$1/C_f$ x 10^{-3}
5	0.8	1.3	8,531	0.200
10	1.5	2.7	7,995	0.100
15	2.5	3.8	7,362	0.067
20	3.4	5.1	7,124	0.050
30	5.8	8.0	5,656	0.033
40	8.3	11.5	5,731	0.025
50	11.4	14.3	3,983	0.020
60	15.0	18.1	3,303	0.017

It can be seen that $-\Delta H$ is higher at lower values of C_f and decreases as C_f increases. This indicates that at low values of C_f the arylamide is firmly bound to the cellulose surface and that as the amount of naphthol on the fibre increases the strength of the

naphthol-cellulose bond decreases. This would also suggest that initially a monolayer of naphthol is formed on the fibre, followed by multilayers which are less firmly held. The value of ΔH for $C_f = 0$ (9,000 cal./mole) represents the binding energy of the monolayer while that for $1/C_f = 0$ (less than 1,500 cal./mole) is a measure of the binding energy of the diffuse layers.

The statistical treatment of Hill[97] adapted to sorption of a solute from solution

The general theory considers a monolayer to be held strongly on specific sites, which provides secondary sites for sorption of more molecules in the form of multilayers. The treatment by Hill leads to a final equation similar to the general equation of the B.E.T. theory[98].

If A is the total number of molecules sorbed per unit mass of fibre, X the number of such molecules sorbed strongly on specific localized sites of equal energy, and B the total number of such localised sites per unit mass, then the X molecules may be distributed in the B sites in

$$B\,!/(B - X)\,!\,X\,!\ \text{ways.}$$

The remaining (A - X) molecules are distributed on top of the X molecules of the first layer in

$$(A - 1)\,!\,/(A - X)\,!\,(X - 1)\,!\ \text{ways in the second layer.}$$

If E_1 and E_2 are the energies of a molecule in the first monolayer and in the second layer respectively, the partition

functions for the first monolayer and the second layer are

$$Q_1 = \frac{B!}{(B-X)!\,X!} \left[j_1 \exp (E_1/kT) \right]^X \qquad (1)$$

$$Q_2 = \frac{(A-1)!}{(A-X)!\,(X-1)!} \left[j_2 \exp (E_2/kT) \right]^{(A-X)} \qquad (2)$$

where j_1 and j_2 are the statistical weights, k the Boltzmann constant and T the absolute temperature.

At equilibrium the free energy is a minimum and since $\Delta F = -RT \ln Q$

then $$\frac{\ln Q_1\ Q_2}{X} = 0 \qquad (3)$$

Hence from (1), (2) and (3)

$$(A-X)(B-X) = X^2 . \frac{j_2}{j_1} \exp \left[(E_2 - E_1)/kT \right] \qquad (4)$$

It is assumed that $\frac{A-X}{A} = x$

where x is the mole fraction of the adsorbate in the solution.

Then (4) becomes

$$\frac{A}{B} = xd / (1-x)(1-x+xd) \qquad (5)$$

where $\frac{1}{d} = (j_2 / j_1) \exp \left[(E_2 - E_1)/kT \right]$ (6)

Hence (5) gives

$$\frac{x}{A(1-x)} = \frac{1}{Bd} + \frac{(d-1)\,x}{Bd} \qquad (7)$$

If the theory is obeyed, a plot of $\frac{x}{A(1-x)}$ versus x should give a linear plot, with slope $(d-1)/Bd$ and intercept $\frac{1}{Bd}$, from which B and d can be calculated.

The results of the present investigation were used to test the application of Hill's treatment to the sorption of coupling components by cellulosic fibres. The plots of $\frac{x}{A(1-x)}$ versus x for the two arylamides studied (Figs. 27 and 28) were linear for a considerable range of x for different salt concentrations. The values of B, the total number of specific localized sites of equal energy per unit mass calculated from the plots are given in Table XXXVI.

From the values of B obtained the number of moles of sorption sites appear fairly constant except in the presence of 0.10M salt concentrations when the number of such sites on the fibre appear to have increased. This might be due to the sorption of chloride ions by the hydroxyl groups of the cellulose. This would indicate that chloride ions show some affinity for cellulosic fibres. However, the results of this investigation are not sufficient to draw a firm conclusion on this.

The difference between the values of B for Naphthol AS and Naphthol AS-RL arises from the fact that the molecules of the former can penetrate more of the cellulose structure on account of their smaller size.

Table XXXVI Values of B, d and $(E_1 - E_2)$ calculated from the curves of $\frac{x}{A(1-x)}$ vs x

Ionic Strength (M)	B moles of sorption sites per kg. sample		d		$(E_1 - E_2)$ cal./mole	
	AS	AS - RL	AS	AS-RL	AS	AS-RL
0	0.162	-	15.60	-	1653	-
0.01	-	0.149	-	31.28	-	2072
0.05	0.151	0.151	27.59	36.89	1993	2167
0.10	0.182	0.165	26.14	46.75	1963	2313

From a knowledge of the dry weight of the cellulose fibre previously determined (0.9488 g./g. wet sample) the total number of moles of hydroxyl groups per kg. cellulose sample was calculated to be 17.58. In comparison with this value the number of moles of localized sorption sites B obtained from Hill's treatment is extremely small and would indicate that only a very small fraction of total available sites actually takes part in the attachment to the arylamide ion. Alternatively, it can be viewed that the arylamide ion is held by a large number of hydroxyl groups. Thus since B is measured in terms of the arylamide ion on fibre rather than of actual hydroxyl groups constituting the sorption sites, B represents only a unit (sub-multiple) of the number of hydroxyl groups providing attachment for the arylamide. However the

argument that a large number of hydroxyl groups provide attachment for the arylamide ion cannot be very strong since because of the relatively small size of the ion (unless considerable aggregation is assumed, a case which cannot be stretched too far) only a small number of hydroxyl groups will be available to it (the primary hydroxyl groups of cellulose are separated by a distance of about 5.15 A°).

d represents the evaporation - condensation term. From equation (6) the difference in the energies of a molecule in the first monolayer and in the second layer can be evaluated. The values of $(E_1 - E_2)$ calculated, assuming a value of unity for (j_2 / j_1) are also given in Table XXXVI above. The positive values obtained for $(E_1 - E_2)$ indicate that the first monolayer of arylamide ions is more firmly held to the cellulose surface than the second and other layers. This is expected as it is the first monolayer that is directly held to the sorption sites whereas the other layers are only indirectly attached.

The values of $(E_1 - E_2)$ calculated assuming the value of unity for the ratio of the statistical weights (j_2 / j_1) bear no relationship to the values of the differential heat of absorption $-\overline{\Delta H}$, determined experimentally from the relation

$$\ln \frac{m_1}{m_2} = \frac{\overline{\Delta H}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

The assumption of the simple value of unity for the ratio j_2 / j_1 can therefore not be valid.

Langmuir isotherm

The equations and assumptions of the Langmuir isotherm have already been discussed (see pages 24 and 25). The plots of $\frac{\theta}{1-\theta}$ against C_s for the two arylamides studied are shown in figs. 29 and 30. It can be seen that the plot for the absorption in the presence of 0.10M sodium chloride is fairly linear up to a concentration of about 25 mmoles/l of naphthol in solution. Thereafter there is marked deviation from linearity. At lower salt concentrations curves rather straight lines are obtained even at low concentrations.

Freundlich isotherm

Figs. 31 and 32 show the plots of logarithm of the concentration of naphthol on the fibre versus the logarithm of the concentration of Naphthol in solution for Naphthol AS and Naphthol AS-RL. The graphs are linear for a fairly wide range of concentration (0 to 60 mmoles/l) of Naphthol in solution. However at higher concentrations there is a marked departure from linearity.

Hailwood and Horrabiu's Solution approach[99]

Several workers have criticized the application of absorption isotherms to polymer - water systems on the grounds that such theories are only applicable to systems with a definite rigid surface and that such an internal surface does not exist for a polymer. These workers have therefore adopted the approach based on the solution of the polymer in the solvent. Hermans[100] and Katz[101] consider that a hydrate is formed initially, followed at higher regains by the absorption of water to form a solid solution.

The solution theory has several advantages over multimolecular theories. It overcomes the difficulty of deriving an isotherm based on two-dimensional absorption, and treats the sorbate as liquid water. Applied to wool Barrer[102] combines a molecular sorption process with a subsequent solution process. He suggests that an initial energetic absorption occurs on localized sites (CO and NH) according to the Langmuir isotherm, followed by an independent process of sorption by mixing with polypeptide chains in the same way as the sorption of liquids by rubber[103] and plastics[104].

The treatment by Hailwood and Horrabin which is applicable to wool-water and cellulose-water systems assumes two adsorptions: one by compound formation with a definite unit in the fibre and the other by simple solution. The compound formation gives rise to a series of hydrates. For only one of such hydrates considered they obtained an isotherm given by

$$\frac{M \cdot r}{1800} = \frac{K \cdot h}{1-K \cdot h} + \frac{K \cdot K_1 \, h}{1+K \cdot K_1 h}$$

where $K = a/x$

M = residue molecular weight

h = relative humidity

$K_1 = w_1/w_o \cdot a$

w_1 = mole fraction of hydrate

w_o = mole fraction of unhydrated polymer

a = mole fraction of dissolved water

r = regain

By adjusting the parameters K, K_1 and M (though M cannot be adjusted very much) the experimental isotherm can be obtained.

Suppose for the present case we treat the cellulose + water as a single system; then the naphthol forms a definite compound with cellulose while also forming a simple solution with cellulose + water. Assuming this solution to be ideal (not true, of course!) then $K_1 = \frac{w_1}{w_o \cdot a}$

where w_1 = mole fraction of naphthol compound

w_o = mole fraction of cellulose free of naphthol

a = mole fraction of uncombined naphthol in cellulose,

from an equilibrium in the fibre:

free cellulose residue + free naphthol cellulose residue:naphthol compound.

w_o a w_1

Hence $K_1 = \frac{w_1}{w_o a}$ (1)

We also have the equilibrium

naphthol in solution free naphthol in fibre

m a

and $K = \frac{a}{m}$ (2)

where m = mole fraction of naphthol in solution.(assuming ideality in all cases and that absorption of naphthol does not affect most of water).

Both K and K_1 are unknown; however m is known and $(a + w_1)$ is also known provided we assume that one naphthol molecule combines with one cellulose residue.

From (1) and (2),

$$K_1 = \frac{w_1}{w_o \cdot K} \qquad (3)$$

Now $(w_o + w_1) = w$, the mole fraction of cellulose residues in the fibre m' the mole fraction of naphthol in the fibre is given by

$$m' = a + w_1 = a + w - w_o$$
$$= w + a - w_o = w + Km - w_o$$
$$\text{and} \quad w_o = w + Km - m' \qquad (4)$$

Putting (4) in (3)

$$K_1 = \frac{w_1}{mK\,(w + Km - m')}$$

$$\text{and } K_1K = w_1 / (w + Km - m')m$$

$$\frac{1}{K_1K} = \frac{wm}{w_1} + \frac{Km^2}{w_1} - \frac{m'm}{w_1}$$

$$= \frac{m}{w_1}(w - m') + \frac{Km^2}{w_1} \qquad (5)$$

Since m is small, m^2 will be smaller still, hence we can neglect the last term in equation (5).

Suppose as $m' \to 0$, $w_1 \to m'$

$$\text{then } \lim_{m' \to 0} \frac{1}{K_1K} = \frac{m}{m'}(w - m') = \frac{mw}{m'} - m = \frac{w}{m'} - 1$$

with this assumption, $\frac{1}{K_1K}$ can be calculated, since m, m' and w are known, and a plot made of $\frac{1}{K_1K}$ versus m'. Substituting for $\frac{1}{K_1K}$ in equation (5) for finite concentrations, w_1 can be evaluated, from which the individual values of K_1 and K may be found using also the relation $w_1 = m' - a$.

Table XXXVII . Values of K, K_1 calculated for different values of m and m'

m $\times 10^{-3}$ mole	m' $\times 10^{-3}$ mole	w $10^{-2} \times$ mole	$\frac{1}{K_1 K}$ $\times 10^{-2}$	K $\times 10^{-3}$	K_1 $\times 10^{3}$
Naphthol AS					
3.56	20.02	67.33	11.61	-2.81	-3.07
10.90	38.64	67.33	17.89	-3.67	-1.53
18.06	60.08	67.33	18.42	-2.22	-2.45
36.80	95.01	67.33	22.40	-1.09	-4.11
Naphthol AS-RL					
2.28	19.50	67.33	7.64	-4.39	-2.99
7.75	46.11	67.33	10.54	-2.58	-3.68
15.00	66.50	67.33	13.70	-1.67	-4.37
20.00	77.00	67.33	15.49	-1.00	-6.46

The values of $\frac{1}{K_1 K}$ calculated for different values of m' and m are shown in Table XXXVII above. The variation of $\frac{1}{K_1 K}$ with m' is also shown in Fig. 33. K represents the equilibrium constant for the equilibrium between the naphthol in solution and on fibre while K_1 is the stability constant for the cellulose: naphthol complex.

The values of K and K_1 are supposed to be constant for each of the arylamides studied. That they show a variation at different values of m' is an indication that the Hailwood and Horrabin treatment does not apply to the cellulose - naphthol system without further modifications. The deviation arises from the nature of the assumptions made, e.g. the

assumption of an ideal solution applied to the range of concentrations employed in the present investigation is an oversimplication. Also the assumption that $w_1 \rightarrow m'$ as $m' \rightarrow 0$ where w_1 is the mole fraction of naphthol-cellulose compound and m' is the mole fraction of naphthol in the fibre may not apply strictly since at low values of m' aggregation of naphthol is negligible and compound formation may therefore not be significant. The naphthol within the fibre would be held by physical rather than chemical forces.

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