

INTERACTIONS OF LIQUIDS WITH CELLULOSE

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by

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ABSTRACT

Three experimental approaches have been made to the investigation of cellulose-liquid interactions using native cotton fibres and a wide variety of non-aqueous liquids. The overall swelling of cellulose has been measured dilatometrically; the accessibility of immersed fibre has been measured by the thallation-methylation technique and the liquids have been compared in their ability to compete for sorption sites on cellulose.

The results of these experiments have been used to classify liquids as inert, interacting but non-swelling and swelling. The extent of interaction of the liquid appears to depend on molecular size and the magnitude and nature of intermolecular forces associated with it. The greatest interactions occur with small, polyfunctional molecules with H-bonding properties. Liquids with molar volumes greater than 100 c.c. or c.e.d. less than 100 cal/c.c. do not appear to swell or increase the accessibility of cellulose fibres.

The thallation accessibility method has been developed to measure the internal surfaces of fibres having various sources, treatments and degrees of swelling. The accessibility and swelling results as well as other data from the literature have been shown to be consistent with the concept of a microfibrillar structure of the fibre which swells by separation of the structural elements.

The extent of sorption of poly(vinyl acetate) by cellulose from solution in various solvents has been shown to be a function of solvent-solute competition for sorption sites.

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FOREWORD

This thesis describes a series of investigations on the interactions of liquids with cellulose. The work has been presented in different parts.

Part I gives a brief review of the morphology of cotton fibres and cellulose structure, intermolecular forces in cellulose and in pure liquids. Pertinent comments on the swelling of cellulose and its accessibility are also included.

Parts II, III, IV and V have been prepared in a form suitable for publication with little change. Each part is complete in itself, with its own introduction, experimental part, discussion and bibliography.

Part II deals with the accessibility of cellulose swollen in various organic liquids and examines the suitability of the method for measurement of internal surfaces in cellulose fibres.

Part III describes experiments on volumetric swelling of cellulose carried out by means of a new dilatometer.

Part IV deals with the study of solvent-solute competition for sorption sites on cellulose.

Part V correlates and examines the experimental results obtained under individual projects described in Parts II, III and IV, and those reported in the literature. The data are interpreted in terms of cellulose-liquid interactions and the structure of fibres.

Appendices on association in pure liquids and cohesive energy density are also given.

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PART I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

The physical properties of cellulose fibres are altered by immersion in liquids because of the interaction between cellulose and the immersion liquid. The interaction may range from wetting through penetration and swelling to partial or complete dissolution. The extent of the interaction depends upon the intermolecular forces in the liquid, the cellulose and between the two.

The results of cellulose-liquid interactions may be seen in dimensional changes, alteration in strength and deformation properties, accessibility and reactivity, thermal effects, etc. Such evidence of interactions is important from theoretical considerations and in technical processes involving cellulose fibres.

A large literature exists on the interactions of water and of some aqueous solutions with cellulose. Comparatively little is known about the interactions of cellulose and anhydrous organic liquids. A detailed and systematic study of this nature is of considerable importance to arrive at a comprehensive picture of the phenomenon.

In the present work a large number of anhydrous organic liquids were examined to investigate several aspects of cellulose-liquid interactions. The experimental results, and those from equivalent measurements reported in the literature, have been examined in the light of native fibre structure, the nature of the liquid and the interactions involved.

As a background to this study this introduction is a brief account of the current views regarding cotton fibre structure and of the intermolecular forces in the liquids and in cellulose.

A. FINE STRUCTURE OF CELLULOSE AND
MORPHOLOGY OF COTTON FIBRE

By chemical definition cellulose consists of long chain molecules of β 1:4 linked glucose units only. Cellulose is common to all plants and is an industrial raw material of great commercial importance. In its native form (wood, cotton, ramie, jute, seaweeds or bacterial cellulose), it is associated with non-cellulosic materials extractable by chemical means. When freed from all these substances, native celluloses from all sources (with only one known exception - seaweed *HALICYSTIS*) show certain common characteristics. They are transparent to ultra violet radiation, they are birefringent and usually give a more or less well defined X-ray diagram with characteristic arc spacings (1), i.e., they have the same crystal lattice.

That the native cellulose fibres possess a wall structure can be shown by suitable experimental techniques. The cell wall of a mature fibre consists of a primary wall and a secondary wall containing three layers: the outer secondary wall (S_1 layer); the middle layer (S_2 layer) and the inner secondary wall (S_3 layer). The S_3 layer which is also known as the tertiary wall constitutes the boundary of the central canal or the lumen. Besides differences in composition these layers differ in their physical organization.

By suitable swelling and staining techniques the S_2 layer can be shown to consist of several concentric layers or lamellae (Fig. I-1); their number depends upon the origin and the degree of maturity of the fibre. The bulk of the cellulose of the fibre is in the S_2 layer. The primary and the tertiary walls contain the bulk of the non-cellulosic material.

FIGURE I-1

ELECTRON MICROGRAPH OF NEVER-DRIED SPRUCE FIBRE CROSS-SECTION

(MOREHEAD; Ref. No. 2)



Cotton represents the purest form of naturally occurring commercial cellulose. The cotton fibre is a single celled hair that grows on the epidermis of the cotton seed within the boll for 15 to 18 days after flowering. During this time only the primary wall encloses the protoplasm. For the following 20 to 40 days bulk of the cellulose is deposited as the secondary wall on to the inside of the primary wall. The secondary wall does not start growing before the cell has reached 90 to 95% of its full growth(3).

The cotton fibre may average from 10 to 20 microns in diameter and 10 to 50 mm. in length (4). After these fibres (or the lint) have ceased to appear, a new crop of short and thick fibres called the "fuzz fibres" emerges from the adjacent cells. The fuzz fibres and the broken lint fibres left from the first ginning are removed by additional ginning and are known as linters.

The primary wall of cotton fibres is less than 1 micron thick (5) and besides cellulose contains pectic substances and waxes. It greatly influences the fibre behaviour towards dyeing, finishing, wettability, reactivity and other properties (6).

The S_1 layer (or the winding) is less than 1 micron thick (4) and differs in organization from all successive layers and from the primary wall. Both optical and electron microscopic techniques have shown it to be a continuous sheet of microfibril bundles spiralling around the fibre axis at an angle (3). On swelling the fibres, both the primary wall and the S_1 layer restrict uniform expansion of the S_2 layer.

It is doubtful if the tertiary wall contains much cellulose; it perhaps contains pectinous material. Cotton fibre rapidly dissolves in cupri-ethylenediamine leaving only the primary and the tertiary walls ('').

The S_2 layer (also called the cell wall thickening) is about 4 microns thick and shows some crystallinity directly after being deposited. Berkley and Kerr (8) are of the opinion that most of the crystallinity in the cotton fibre appears only after first drying. The concentric arrangement of lamellae in the S_2 layer of cotton fibre cross-sections has been well demonstrated (3,9-13). The primary wall and the S_1 layers are not usually seen in cross-sections. The number of these concentric layers or lamellae is related to the age of the fibres in days (3,9) and the lamellae are considered to be daily growth rings (9). A fully mature cotton fibre may contain 25-40 lamellae (3), which consist of closely packed microfibrils in a parallel system.

With the development of such powerful tools as X-ray and electron micrography there has been a rapid growth in the knowledge of microfibrils. The tendency now is to explain the characteristics of native cellulose in terms of its fibrillar structure.

The lamellae of the wall thickening are considered to be about 5 microfibrils thick (3) and separation into microfibrils can be achieved by beating in water (3,10). The length of the microfibril is indeterminate and is considered to be at least 5 microns (2). The dimensions of the cross-section vary with the origin of the fibre. According to Preston (13), the width may range from 80\AA (some seaweeds, woods) through 100\AA (some seaweeds, cotton) to $200 - 300\text{\AA}$ (VALONIA, etc.); thickness is considered

to be about half the width. However, using ultrasonic treatment on cotton, Frey-Wyssling (14) obtained microfibrils of $250 \times 250 \text{Å}^2$ and "elementary microfibrils" of 30×100 and $50 \times 60 \text{Å}^2$ cross-section. More recent estimates, however, consider the microfibril to be $\sim 35 \text{Å}$ in diameter (15-17).

The microfibril constitutes the smallest natural unit which can be made visible by available techniques.

The microfibrils in the wall thickening spiral around the fibre in a helix. The angle of spirals is characteristic of the species and can be determined with the help of X-rays. In ramie the microfibrils lie almost longitudinally while in the vessel elements of the angiosperm wood almost transversely. These may be considered extreme cases. In cotton the angle may be $28-42^\circ$ (18), and as distinguished from other fibres the spirals change direction from S to Z or vice versa. These reversals are randomly spaced along the length of the cotton fibres which tend to break preferentially at these points of reversal (19).

The microfibrils of seaweeds, e.g., VALONIA, SIPHONOCILADUS, etc. are exceptionally straight and well oriented. From the electron diffraction and other data it is concluded that these microfibrils are almost single crystals, or at least chains of almost entirely single crystals (1). When freed from amorphous incrusting substances and non-cellulosic crystalline materials (xylans, alginic acids, etc.) all celluloses so far examined give an X-ray diffraction diagram identical with or closely resembling that of VALONIA group (1).

It is now known that the cellulose crystal lattice can exist in at least four modifications. Cellulose I or the native cellulose found in wood, cotton, ramie, jute, etc., is the most common form. Regenerated cellulose or cellulose II has a special place in the textile industry. Table I-1 gives the crystal lattice dimensions of the four polymorphs of cellulose.

The arrangement of β 1:4 linked unbranched high polymeric cellulose chains in the microfibrils can give rise to some important results. According to "fringed-micellar" theory the chain molecules associate laterally in different degrees of parallelism passing through highly oriented regions (crystallites or micelles) and randomly arranged (amorphous) regions. These types of arrangements merge into each other through a whole spectrum of degrees of order. The amorphous portions are considered to be more reactive than the crystalline. Evidence collected in recent years, however, renders suspect the concept of fringed micellar theory.

Frey-Wyssling (20) and Preston (1) postulate a crystalline microfibril in which the chain molecules associate laterally through H-bonding in a high degree of orientation. The crystalline microfibrils are coated with a cortex of paracrystalline cellulose "in which the chains must be rather parallel though irregularly spaced" (1).

Manley (17) however, claims that the chain molecules are not laterally associated in the microfibrils but are folded regularly, concertina fashion, in the microfibrils and that cellulose is completely crystalline. Wadehra, Manley and Mason (21) suggest that the more reactive

TABLE I-1Lattice Dimensions of Polymorphic Forms of Cellulose (22)

Polymorph	Axis			
	a	b	c	β
Cellulose I	8.35 \AA	10.3 \AA	7.9 \AA	84°
Cellulose II	8.1 \AA	10.3 \AA	9.1 \AA	62°
Cellulose III	7.74 \AA	10.3 \AA	9.9 \AA	58°
Cellulose IV	8.11 \AA	10.3 \AA	7.9 \AA	90°

regions in cellulose arise not from amorphous cellulose of the fringed micellar theory or the paracrystalline cortex of Frey-Wyssling and Preston's model, but from the lattice imperfections of various kinds, e.g., chain folds and disorders in the mutual arrangement of the microfibrils.

However, the fact remains that the relative proportions of readily reactive (or accessible) regions and the less readily reactive (inaccessible) regions are of importance both from theoretical and technical considerations.

In the present work a model of cellulose swelling is proposed on the basis of the fibrillar structure of native fibres. It is suggested that swelling on immersion results from the mutual separations of the contiguous lamellar and fibrillar surfaces with the consequent increase of available reactive sites. Accessibility is thus visualized as predominantly a surface effect.

In order to assess the interactions of liquids with cellulose and to measure the increase in accessibility or the internal surface areas, it is imperative that the process of measurement does not alter the state of swelling or collapse of the samples.

A method of determining accessibility without altering the state of swelling or collapse of cellulose samples, wet or dry, has been developed during the present work.

B. COHESIVE FORCES IN CELLULOSE

Strong β 1:4 glycosidic linkages hold the anhydroglucose units (A.G.U.) along the b axis of the unit cell. These bonds have dissociation energies of the order of 80 kilocalories and are not attacked except by strong acids or alkalies with degradative results.

The three hydroxyl groups present on every A.G.U. are mainly responsible for the physico-chemical behaviour and cohesion of cellulose.

Intermolecular cohesion could arise from chemical bonds or van der Waals forces, especially H-bonds, depending upon the relative distances between the functional groups. Considering only the native cellulose and excluding all its derivatives, ether linkages can form under suitable conditions between hydroxyl groups of neighbouring chains. Occasional carboxylic groups - always present in native cellulose - can give rise to ester bonds (23). Such bonds, though not frequent, will most probably be very strong.

Perpendicular to the chains and to the plane of the anhydroglucose rings and parallel to the c axis of the lattice, the only existing attraction between the A.G.U.'s is due to van der Waals forces other than H-bonding. These forces are of the order of 2-3 kilocalories per mole (24).

By far the most important contributions to intermolecular cohesion arise from H-bonding. In the dry solid cellulose, both native and regenerated, all hydroxyl groups are H-bonded (25). The H-bonds may be inter- or intramolecular in nature (Fig. I-2).

(FIGURE I-2)

INTER- AND INTRAMOLECULAR H-BONDING IN $(10\bar{1})$ PLANES OF CELLULOSE II LATTICE

(I-2A): Mann and Marrinan; Ref. No. 27.

(I-2B): Liang and Marchessault; Ref. No. 28.

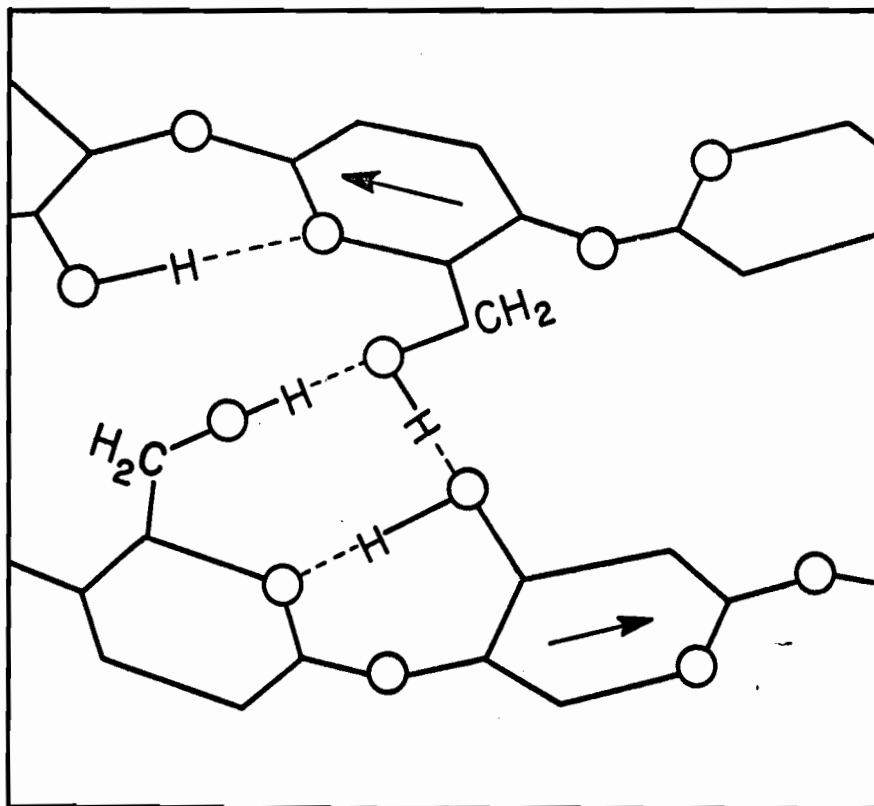


FIG. I - 2A

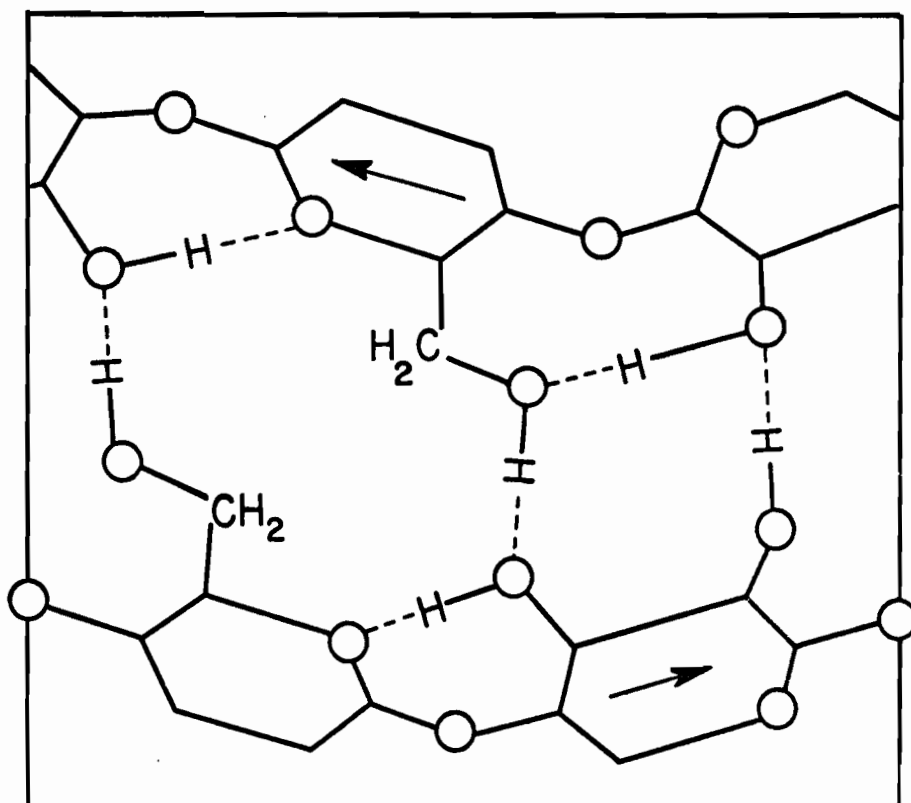


FIG. I - 2B

The average energy of the H-bond is approximately 5 kilocalories but their great number in cellulose makes up for strength. Cellulose thus, is an extreme example of a substance of great molecular cohesion (26) and is insoluble in water.

H-bonds in cellulose may have variable strength (25,29, 30) depending upon the relative distances between the bonding hydroxyls. It is suggested however, that in an unbranched linear high polymer like cellulose the variations in interfibre and intrafibre bonds arise not from the strength of the individual bonds but from their number and disposition. In a regularly spaced system of a large number of H-bonds, weakening or breaking of one bond involves a simultaneous weakening or breaking of a large number of neighbours. Such a "co-operative" strengthening makes each bond effectively much stronger than an isolated or an individual H-bond located in a group of irregularly spaced neighbours.

In dry cellulose the rigid H-bonding between the chains is responsible for the immobility of chains restricting elasticity to short range phenomenon only (31). The highly oriented regions (32), the occasional microfibrils wandering between the lamellae (1) or possible chemical bonds behave as crosslinks restricting swelling of cellulose fibres. The intramolecular H-bonds contribute to the low flexibility of the chain (31) and may also introduce steric factors in the interactions of cellulose with liquids.

The major cohesive forces (or major retardants to reactivity), therefore, arise from H-bonds which militate against swelling agents, penetrants and reactants. Small degree of substitution, e.g., acetylation will enhance reactivity since cohesion of cellulose is adversely affected by agents or conditions adversely affecting the H-bonds. Understanding of such conditions and the nature of liquid parameters influencing cellulose cohesion are thus of considerable importance.

C. INTERMOLECULAR ATTRACTIONS IN PURE LIQUIDS

When molecules, monoatomic or polyatomic are near enough to influence each other at least two forces - one of attractions and the other of repulsions - come into play. It is important to recognize different contributions possible to the total intermolecular forces. It is convenient, though not rigorous, to divide intermolecular forces into two types.

- (i) Short range forces (chemical or valence),
- (ii) Long range forces (van der Waals).

The van der Waals forces play an important role in the cohesion of solids and liquids having important bearing on such properties as volatility, solubility, miscibility, surface tension or plasticity - all of which depend upon intermolecular forces. The van der Waals forces may be classified (33, 34) as:

- (a) forces between permanent electrical dipoles - electrostatic or Keesom forces;
- (b) forces between a permanent electrical dipole and a dipole induced in another molecule - induction or Debye forces;
- (c) forces due to the interaction always occurring between electron systems - dispersion or London forces;
- (d) attractions due to H-bonding and
- (e) repulsion forces.

(a) Keesom forces:

The energy of interaction between two dipoles is purely electrostatic and depends upon the magnitude of the dipole μ , relative orientations and the distance of separation r . Since thermal effects tend to destroy orientations, the dipolar attractions diminish with the rising temperature. At intermediate temperatures attractive orientations are statistically preferred and Keesom (35), by averaging over all orientations, has shown that the average energy of electrostatic interaction

$$\bar{E}_{(es)} = - \frac{2\mu^4}{3r^6 kT} \quad (1)$$

when $\frac{\mu^2}{r^3} \ll kT$. However, when the two molecules are oriented in their most favourable positions, $\frac{\mu^2}{r^3} \gg kT$ and

$$\bar{E}_{(es)} = - \frac{2\mu^2}{r^3} \quad (2)$$

In the case of simple molecules as water and methanol, the dipole exercises its full action (36). However, strong steric hindrance or screening in large or bulky molecules (hexanol, benzyl chloride) will reduce the energy of interaction.

The average range of Keesom forces is 4.0 -- 5.0Å (30).

(b) Debye forces:

When subjected to an external field the electrons and the nuclei of even neutral molecules are displaced from their normal positions and the particle temporarily behaves polar. The induced dipole so acquired is directly proportional to the strength of the field F ;

$$\begin{matrix} \mu \\ \text{(ind)} \end{matrix} = \alpha F \quad (3)$$

where α is the polarizability of the molecules acquiring the induced dipole moment.

In addition to the possible contributions of permanent dipoles, the energy of an induced dipole in the field F is

$$\begin{matrix} E \\ \text{(ind)} \end{matrix} = -1/2 \alpha F^2 \quad (4)$$

It can be shown that the average energy

$$\begin{matrix} \bar{E} \\ \text{(ind)} \end{matrix} = - \frac{\alpha \mu^2}{r^6} \quad (5)$$

In the interaction of two dissimilar polar molecules the contributions to energy will be

$$\begin{matrix} \bar{E} \\ \text{(ind)} \end{matrix} = - \frac{\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2}{r^6} \quad (6)$$

and when the molecular species are the same

$$\begin{matrix} \bar{E} \\ \text{(ind)} \end{matrix} = - \frac{2\alpha \mu^2}{r^6} \quad (7)$$

The Debye or induction energy is temperature independent as orientation effects are not involved.

In the case of inert gases, which have no dipole moment, neither of the two effects has any significance. Since these gases do condense to liquids there must be a mode of interaction independent of electrical multipoles of any kind. These contributions to van der Waals forces are known as London or dispersion forces.

(c) Dispersion forces:

Any neutral atom or molecule can be visualized as a positive centre surrounded by an electronic cloud; quantum mechanically it behaves as an oscillator. Then, even in the lowest energy state an oscillator possesses an energy

$$E = 1/2 h \gamma_0 \quad (8)$$

and the atom or molecule shows a fluctuating dipole moment (35). The average value is zero but the instantaneous dipole is finite. This rapidly fluctuating dipole gives rise to an electric field and polarizes the other molecules or atoms. The instantaneous induced dipole is in phase and interaction with the instantaneous dipole producing it (35). The energy of such interaction, the dispersion energy, is given by

$$E_{(dis)} = -\frac{3}{4} \frac{h\gamma_0 \alpha^2}{r^6} \quad (9)$$

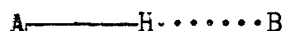
$$\text{or} = -\frac{3}{4} \frac{I\alpha^2}{r^6} \quad (10)$$

where I is the ionization potential of the molecules. Since the polarizabilities of organic groups differ more than their ionization energies, the polarizabilities largely determine the magnitude of the interactions (37). These forces are additive, non-specific and their strength depends upon the number and the 'looseness' of electrons (34). The average range of dispersion forces is between 3.5 and 4.5 Å (30).

(d) The H-bond:

The energies of the chemical bonds are of the order of tens of kilocalories. Dispersion forces or those arising from dipolar effects have energies ranging from a few tenths of kilocalories to 2 to 3 kilocalories. Between these two extremes lie the very important molecular interactions due to H-bonding with energies of about 5 kilocalories. A H-bond is produced by hydrogen atom between two electronegative atoms, e.g., F, O or N. The ability to form H-bond decreases with the decreasing ionogenic character of the bond as a consequence of decreasing electronegativity in the series FH, OH, NH and CH; with CH (as in CHCl_3) the H-bond produced is very weak. The H-bond is purely electrostatic in nature and is effective at $2.6\text{--}3.0\text{\AA}$ (30). Pimentel and McClellan (38) have given an excellent review of the subject.

We can write the general formula of a H-bond as



where A and B represent atoms of the same or different species and the broken line shows a H-bond. The more polar the A-H bond or the greater the effective negative charge on B the stronger is the H-bond produced. These conditions are realized when A is an acceptor for another H-bond or when B is attached to a H atom through a covalent bond (29). Thus



is stronger than



The hydroxyl containing compounds, therefore, associate through H-bonding to produce rings or chains of great length (Fig. I-3).

The H-bonds can be intermolecular or intramolecular. The former type involves association of two or more molecules of similar or dissimilar species and multiply bonded arrangements result. The intramolecular H-bonds are produced between functional groups within a single molecule.

The ability to form H-bonds and the strength of the bonds so produced depend upon the nature of functional groups and the steric factors relating to the molecular size and relative positions of the functional groups in the molecule. H-bonds are considered to possess varying strength depending upon the distances between the interacting groups (25,29, 30).

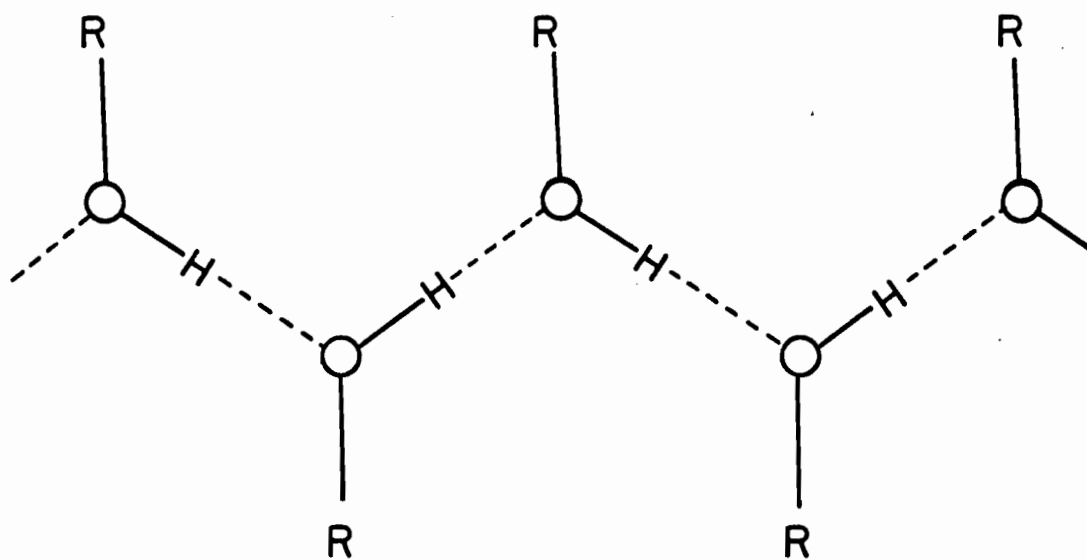
Simple molecules have greater probability of favourable orientation for H-bonding. Increased H-bonding facility in polyfunctional compounds (e.g., polyols) leads to increased cohesive energy density (c.e.d.) compared with monofunctional compounds of similar molecular size.

The intramolecular H-bonds are produced under rather stringent spatial conditions and their formation does not lead to association or increased c.e.d. The size of the ring produced by intramolecular H-bonding may affect the strength of the bond. Thus the H-bond in 1,4-butanediol is stronger due to the less strained 7 membered ring than in the 6 or 5 membered rings in 1,3-propanediol and ethylene glycol respectively (38-p.174).

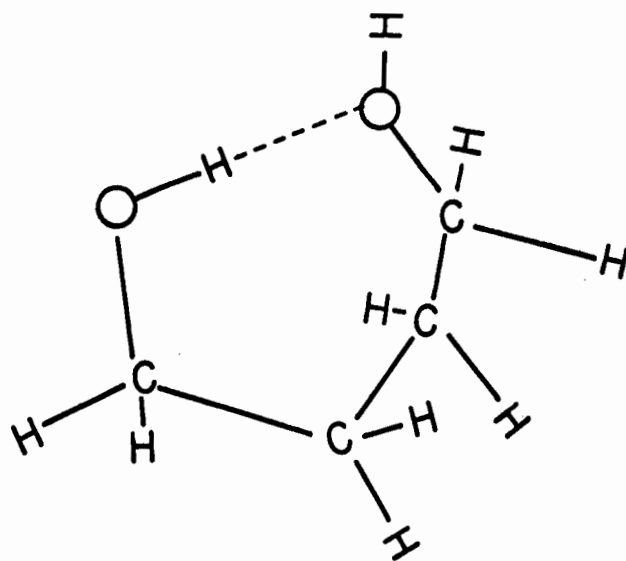
Generally speaking, liquids can be classified according to their ability to form H-bonds and the manner of forming such bonds.

FIGURE I-3

INTER- AND INTRAMOLECULAR H-BONDS IN LIQUIDS



Intermolecular H-bonds in monohydric alcohols



Intramolecular H-bonds in 1,4 - butanediol

- (i) Water, alcohols, carboxylic acids, primary and secondary amines are capable of forming H-bonds either by donating or by accepting a proton. Association results due to H-bonding between the molecules of the same liquid.
- (ii) Ketones, aldehydes, ethers, tertiary amines, etc. are not capable of donating a proton but they can accept one. They are not associated except when strong dipolar attractions exist. They H-bond with type (i).
- (iii) Halogenated compounds, e.g., CHCl_3 , C_2HCl_5 and possibly ethylene compounds which have their hydrogen activated, are capable of acting as proton donors. They H-bond with types (i) and (ii) but the bonds produced are weak.
- (iv) Saturated hydrocarbons, carbon disulphide, carbon tetrachloride are incapable of participating in H-bonds. They can be termed as "neutral".

Several methods exist for the detection of the H-bond and have been reviewed by Pimentel and McClellan (38).

(e) Repulsion forces:

Repulsion forces arise when the orbitals of two molecules are close enough to overlap. In conjunction with thermal effects and the attractive forces, the repulsive forces determine volume occupied by a liquid.

A reliable guide to the interplay of various forces in a liquid is its energy of vaporization. The energy of vaporization per

millilitre or c.e.d. is the summation of contributions due to dispersion forces, permanent and induced dipoles and the more specific interactions such as H-bonding (see Appendix B). It will be useful to examine the contributions by various intermolecular forces to the c.e.d. of a liquid.

Dispersion forces, exerted by all molecules whether polar or non-polar, are especially important in relation to non-polar liquids which have no other mode of interaction. In most cases, with the exception of very polar liquids or H-bonded compounds, the dispersion forces may account for 75-100% of the total molar cohesion (30).

Contributions by dipole effects are usually much less than by dispersion forces since the dispersion forces are orientation independent but dipole forces are not. A molecule favourably oriented with respect to the second may be unfavourably oriented with respect to the third. Since the dipole attractions are proportional to the 4th power of the moment, the attractions will increase rapidly with the increasing dipole moment if the dipoles of the molecules are exposed (39) as in acetone. Dipoles buried deep in the molecule (as in chloroform) make much smaller contributions to cohesion of the liquid (see Appendix B).

D. INTERMOLECULAR ATTRACTIONS BETWEEN CELLULOSE AND LIQUIDS

With the exception of thallation and methylation, the chemical reactions of liquids with cellulose are not of interest in relation to the present work. These two reactions, in which all the three hydroxyl groups of the A.G.U.'s are involved (40, 41), are basic to the method developed for the assessment of cellulose-liquid interactions (42).

Non-polar liquids, e.g., carbon tetrachloride, hexane or benzene have been described as incapable of penetrating (43) or swelling (44) cellulose. However, as will be seen later, they do substantially penetrate and show measurable interactions with cellulose. Apparently such interactions could arise only from dispersion forces. Dispersion forces also play important roles in the interactions of weakly polar liquids which have little or no H-bonding ability, since weak dipoles make only slight contributions to intermolecular attractions. Liquids with strong dipoles, however, may have appreciable interactions especially if the dipoles are not buried deep in the molecules.

Attempts have been made in the past to explain swelling of cellulose in terms of dipole moments (43,45,46) and dielectric constants (43,45,47-49) of the swelling liquids. The correlations, however, were unsuccessful except within the family of compounds. The failure of dielectric constants to correlate well with the observed swelling has been attributed to various factors (50). Liquids of higher polarity may not be able to penetrate fibres if steric factors involved are not favourable. Liquids with marked H-bonding ability, on the other hand, swell cellulose strongly; intracrystalline swelling agents cause abnormal expansion of the fibre.

As intermolecular cohesion in cellulose is primarily due to H-bonding, it is expected that liquids possessing strong H-bonding ability would be effective in reducing cohesion in cellulose. Water, alcohols, carboxylic acids, esters, etc. cannot penetrate the intramolecular regions or change the X-ray diffraction patterns of native cellulose. Amines (51) and certain other nitrogenous compounds are capable of penetrating and swelling even the intramolecular regions. The intramolecular swelling liquids produce definite complexes with cellulose having increased lattice spacings. Such complexes give characteristic diffraction patterns which are different from those of the original cellulose form. The removal of the swelling agent (e.g., by solvent exchange) results in the decomposition of the complex and collapse of the distended unit cell, usually yielding cellulose II from cellulose I or II forms originally present (51). Intramolecular swelling may also affect crystallinity (52-54). However, very little is known about the swelling potential of these liquids and the attendant changes in accessibility, mechanical properties, etc.

The concept of c.e.d. has also been invoked to explain cellulose-liquid interactions (49, 55-57). As will be shown in the sections to follow, c.e.d. by itself is an inadequate guide to cellulose-liquid interactions. Other important parameters, e.g., H-bonding, steric factors and morphology of native fibres have also to be considered.

The extent of interaction of a liquid with cellulose could be assessed by measuring fibre swelling, increased accessibility, polymer sorption, variations in pycnometric density, optical birefringence, heats of wetting or altered mechanical properties. The significance of these experimental methods and their results has been examined in Part V of this Thesis.

E. SWELLING OF CELLULOSE

Cellulose in the growing hair is deposited from an aqueous solution and the cell walls have a high water content. The lumen is distended and the fibre is tubular in shape (58). On drying the fibre collapses into a more or less flat and convoluted ribbon. The lumen too may collapse at several places along the fibre length.

The shape of the dried fibre depends upon the thickness of the undried cell walls. Very thin (immature) fibre dries into very flat ribbon of a rectangular contour which may be often twisted into a U or C (58). More mature fibre, having thicker s_2 layer and smaller lumen, undergoes little flattening on drying and has a nearly circular or elliptical cross-section. Shrinkage upon drying causes tension diagonal to the long fibre axis part of which is removed by convoluting (7).

Except in strong swelling liquids (mineral acids, caustic alkalies, amines), a native cotton fibre on rewetting is not likely to swell beyond the maximum volume occupied as a living undried hair. The increase in the length of the fibre on swelling is negligible as compared with increase in its diameter. Swelling therefore can be considered as proportional to the increase in the area of cross-section with little or no change in the perimeter due to the restricting outer walls.

Considering the influence of the shape of the dry fibre on its swelling behaviour Skau (59) introduced the concept of "circularity". When the primary wall is distended to its fullest capacity (maximum volume), the fibre would be circular. Thus a very flat fibre would have to swell

many times its dry volume before attaining maximum volume, i.e., a circular cross-section. This would involve a large increase in circularity. Nearly circular thick fibres will suffer only small increment in circularity.

Moore et al (loc. cit.) have shown that immature fibres do show greater change in shape on rewetting than the mature fibres but the differences are small and inconsistent. A part of the swelling may take place into the lumen -- a factor which was ignored by Skau (loc. cit.).

Optical and electron micrographs show that swelling of native fibres is not homogeneous but that the morphological structures separate from one another with large intervening spaces (Fig. I-1). Experimental results of the present work are consistent with this picture.

Several theories of cellulose swelling have been advanced (60) but all of them relate to water or aqueous solutions and fail to explain the interactions of non-aqueous liquids with cellulose or variations in its different physico-chemical properties with swelling.

In the present work a hypothesis is advanced regarding swelling of cellulose. It is suggested that volumetric swelling of cellulose on immersion is a response to the stresses which were fixed in the fibre during its initial drying.

The interactions of various anhydrous liquids with cellulose have been investigated by different methods. The experimental results are explained in terms of the nature of liquids, the fibrillar structure of native cellulose and the nature of the interactions.

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PART II

ACCESSIBILITY OF CELLULOSE BY THE THALLOUS ETHYLATE
METHOD - A MEASURE OF CELLULOSE-LIQUID INTERACTIONS

A. INTRODUCTION

In native cellulose fibres the basic structural elements are considered to be microfibrils which laterally associate to form the larger fibrils and lamellae of the fibre wall (1-5). This fibrillar structure may be highly porous (6-9) with large internal surface areas more or less accessible to reactants, impregnants or sorbates. The accessibility of these surfaces depends upon the extent of collapse or expansion of the fibre wall structure as a result of drying, reswelling or mechanical treatment.

Several methods of measuring cellulose accessibility exist and Tarkow (10) has given an excellent review of them. However, many of these methods (formylation, moisture regain, iodine sorption) themselves cause swelling of cellulose while others (x-ray diffraction, thallous ethylate) require dried samples. The observed accessibility thus refers not to the original samples, but to structures which have been altered before or during the process of measurement.

The accessibility of cellulose fibres immersed in various liquids is of interest in relation to cross-linking, impregnating, polymer grafting, esterification, dyeing and yarn and fibre modifications. The extent of these reactions or treatments and their effects on fibre properties depend on the degree of swelling and the internal surfaces which are accessible under the conditions of treatment.

This paper reports a method of determining accessibility and surfaces of cellulose samples which unlike previous methods, permits the measurement without changing the state of swelling of the fibres, wet or dry.

The method has been developed from a suggestion by Luce (11) and is based upon the reaction of cellulose with thallous ethylate in benzene. This reaction appears to be one of the few which can occur with cellulose in a non-swelling medium. The cellulose sample is swollen in the test liquid, solvent exchanged to benzene and reacted with thallous ethylate in benzene solution. The thallium so introduced in cellulose is displaced with methyl iodide and the methoxyl content of the sample determined.

It is assumed that the swollen structure of the immersed fibres is maintained during the solvent exchange process. The methoxyl content of a sample therefore, measures the accessible hydroxyl groups and surfaces which are exposed on immersion of the fibres in the test liquid.

The results obtained by the application of the method are interpreted in terms of cellulose-liquid interactions and the structure of native cellulose fibres.

B. EXPERIMENTAL

(a) MATERIALS:

(i) Filter pulp: Acid washed, dry dispersed cotton filter pulp having about 98.5% alpha cellulose was dried at 105°C for one hour and immersed in the test liquid for 24 hours. The swollen filter pulp was solvent exchanged to benzene directly or, if necessary, through acetone as described by Luce and Robertson (12). Polar liquids e.g., amines (13), acid amides and their derivatives (14) are strongly sorbed by cellulose and can be replaced completely by non-polar liquids only through intermediate polar solvents. Cellulose samples swollen in such liquids were solvent exchanged to benzene through acetone.

(ii) Thallous ethylate: Decinormal solution of thallous ethylate in benzene was prepared by the method of Assaf, Haas and Purves (15).

(iii) Solvents: Fisher reagent grade' solvents meeting A.C.S. specifications or the next highest quality solvents available were used. The solvents were further purified wherever possible, by methods suggested in the literature. Special care was taken to keep them dry. Carbon tetrachloride, benzene, toluene, pyridine, etc., were stored over sodium wire and filtered through a coarse fritted glass funnel before use.

(b) THALLATION AND METHYLATION:

Wet filter pulp suspended in benzene was treated by Purves' method, with the decinormal solution of thallous ethylate in benzene. Homogeneous penetration was ensured by displacing benzene with thallous ethylate solution under mild suction and allowing the latter to react with

cellulose for two hours at a time instead of one, as originally recommended by Purves. The thallium cellulosate was reacted with excess methyl iodide in benzene and the partially methylated cellulose was analyzed for methoxyl content by the Tappi method T209m45.

A correction to the sample weight for the occluded thallous iodide was based upon the determination of thallium (16). A known weight of partially methylated dry sample containing occluded thallous iodide was digested in concentrated nitric and sulphuric acids. Any possible thallic ion was reduced with excess sulphur dioxide. Thallium was precipitated as thallous chromate; the weight of thallous iodide in the sample was computed from that of the precipitate. From the analysis of 20 samples selected at random, a best fit curve between per cent occluded thallous iodide and the methoxyl content was constructed by the method of least squares. Weight of occluded thallous iodide for each sample was estimated from this curve.

Methoxyl content was expressed on the basis of the dry weight of the sample before thallation.

The average of duplicate determinations have been reported except where agreement was not good. In such cases further determinations were made to increase the significance of the mean.

C. RESULTS

A wide variety of anhydrous organic solvents were examined for their effect on the accessibility of cellulose fibres immersed in them. The results are reported in Table II-1 as per cent methoxyl on the basis of the dry weight of the original unsubstituted cellulose. Per cent of the hydroxyl groups reacted can be obtained by multiplying per cent methoxyl with the factor $100/57.4$.

In addition to the measurement of accessibilities produced in a standard filter pulp by different liquids, a few exploratory determinations were made of the accessibilities of other fibres. These are included in Table II-2.

TABLE II-1

Accessibilities of Cotton Filter Pulp Swollen in
Anhydrous Organic Liquids and Solvent Exchanged to Benzene

(1) Serial Number	(2) Classi- fication	(3) Solvent	(4) Per Cent Methoxyl	(5) Per Cent Hydroxyl Substituted
1.	●	1-Hexanol	0.48	0.84
2.	●	Cyclohexane	0.48	0.84
3.	▲	Benzene	0.49	0.85
4.	⊙	Diethyl oxalate	0.49	0.85
5.	▲	Carbon tetrachloride	0.51	0.89
6.	●	Xylene	0.53	0.92
7.	△	1-Butanol	0.54	0.94
8.	⊙	Methyl ethyl ketone	0.55	0.96
9.	⊙	n-Butyraldehyde	0.55	0.96
10.	⊙	Acetic anhydride	0.55	0.96
11.	⊙	Butyrolactone	0.57	0.99
12.	●	Dichlorobenzene	0.58	1.01
13.	⊙	Furfural	0.62	1.08
14.	△	2-Butanol	0.62	1.08
15.	●	Benzyl alcohol	0.65	1.13
16.	●	Toluene	0.67	1.17
17.	●	1-Pentanol	0.68	1.19
18.	●	Benzaldehyde	0.69	1.20
19.	●	Butyl acetate	0.70	1.22
20.	●	Tetrachloroethane	0.70	1.22

Cont'd.

TABLE II-1 (Cont'd.)

(1)	(2)	(3)	(4)	(5)
21.	▲	Chloroform	0.71	1.24
22.	●	Mono chlorobenzene	0.72	1.25
23.	●	Nitrobenzene	0.73	1.27
24.	●	1,1-Dimethoxyethane	0.76	1.32
25.	●	3-Pentanone	0.77	1.34
26.	●	1-Decene	0.79	1.38
27.	⊙	Acetonitrile	0.81	1.41
28.	●	Phenyl ether	0.82	1.43
29.	⊙	Methyl acetate	0.86	1.50
30.	⊙	Tetrahydrofuran	0.88	1.53
31.	▲	1,2-Dichloroethane	0.88	1.53
32.	●	Benzyl chloride	0.89	1.55
33.	▲	cis-Dichloroethylene	0.92	1.60
34.	▲	trans-Dichloroethylene	0.93	1.62
35.	△	Propionic acid	1.01	1.76
36.	●	Phlorol	1.04	1.81
37.	●	iso-Propyl ether	1.05	1.83
38.	⊙	Vinyl acetate (monomer)	1.18	2.06
39.	△	2-Propanol	1.18	2.06
40.	⊙	Nitromethane	1.20	2.09
41.	⊙	Ethyl acetate	1.26	2.20
42.	■	Morpholine	1.36	2.37

Cont'd.

TABLE II-1 (Cont'd.)

(1)	(2)	(3)	(4)	(5)
43.	△	Ethyl cellosolve	1.45	2.53
44.	△	1,4-Butanediol	1.46	2.54
45.	●	Methyl morpholine	1.54	2.68
46.	⊙	p-Dioxane	1.57	2.74
47.	■	Aniline	1.57	2.74
48.	⊙	Acetone	1.62	2.82
49.	■	Piperidine	2.70	4.70
50.	△	Ethanol	2.95	5.14
51.	■	Benzylamine	3.36	5.85
52.	■	Pyridine	4.33*	7.54
53.	△	Acetic acid	4.57	7.96
54.	△	1,3-Propanediol	5.33	9.29
55.	△	Diethylene glycol	6.76	11.77
56.	△	Methanol	7.11	12.39
57.	△	Glycerol	7.49	13.05
58.	△	Ethylene glycol	7.65	13.33
59.	■	Formamide	7.74	13.48
60.	△	Water	7.83	13.64
61.	■	Dimethylformamide	7.93	13.82
62.	■	Ethylenediamine	9.16	15.96

* Soaked for one week.

Classification: △, Associated, H-bonding, both proton acceptors and donors; ⊙, H-bonding, proton acceptors only; ▲, "inert"; ●, molar volume > 100 cc. and ■, intramolecular swelling agents.

TABLE II-2

Accessibilities of Various Cellulose Fibres

Sample	Per Cent Methoxyl	Internal Surface (m ² /gm.)	N-sorption ^(*) Areas (m ² /gm.)
1. Cotton filter pulp dried from water.	0.49	16.5	1.3
2. Cotton filter pulp swollen in water.	7.83	263.7	136-139
3. Viscose rayon dried from water.	0.79	26.6	-
4. Viscose rayon swollen in water.	8.50	286.3	-
5. Cotton filter pulp swollen in 0.1N aqueous sodium hydroxide.	7.40	249.2	-
6. Cotton filter pulp swollen in 1.0N aqueous sodium hydroxide.	6.45	217.2	-
7. Cotton filter pulp swollen in 5.0N aqueous sodium hydroxide.	7.14	240.5	-
8. Bleached sulphite wood pulp, unbeaten.	7.29	245.5	23.6
9. Whatman No. 1 filter paper, swollen in water.	9.02	303.8	122

(*) Reference No. 17.

D. DISCUSSION

(a) CRITIQUE OF THE METHOD:

If the methoxyl contents listed in Table II-1 are to be considered as valid measures of the accessibility of the various cellulose samples, several requirements must be fulfilled.

(i) The cellulose must be transferred to the reaction medium (benzene) without structural change or alteration in its accessibility. That is, the immersion of the sample (if dry), or the solvent exchange (if wet) must leave the fibre structure unaltered.

The volumetric swelling of dry cellulose in benzene is assumed to be negligible (11, 18). Benzene was chosen as a reaction medium on this basis. The lack of external evidence of swelling is assumed to indicate that the internal structure is similarly unchanged.

The assumption that solvent exchange from a more polar solvent to a less polar one, such as benzene, can be effected without change has been made by several workers (11, 12, 14, 19-21) but there has been little confirmatory evidence. The assumption rests primarily on the premise that shrinkage of a swollen structure is the result of surface tension forces and that these are absent during solvent exchange. However, evidence exists that in some special cases there is a definite shrinkage of immersed fibres. These cases involve such liquids as amines which produce excessive swelling as they are able to penetrate the crystal structure. In many cases they form complexes with cellulose. Their removal by solvent displacement results in the decomposition of the complex and shrinkage of the swollen lattice.

(ii) The methoxyl content is a direct measure of accessibility. That is, the thallation of exposed hydroxyls is complete and the subsequent replacement of thallium by the methyl group is quantitative; thallation does not increase accessibility and there are no side reactions with residual solvents.

Most of these aspects have been discussed by Purves and his co-workers (15, 22). It has been shown, primarily by using low molecular weight compounds, that the thallation and methylation reactions proceed to completion (23-26) under the conditions of the test and that crystalline or highly ordered regions are not penetrated (15, 22). Incomplete replacement of solvents in the steps preceding the reaction are known to occur up to about 2% by weight (27, 28). These amounts and their possible effect on the final methoxyl content are not known with any certainty. They are not, however, considered to be significant when the possible sources of interference are considered: dilution of reactants or reaction which could increase or decrease the final methoxyl content. The possibility however, remains that in water swollen samples the possible residual water could affect the fine structure of sample fibres by interfibre tension forces in the presence of immiscible benzene.

It is seen in Table II-1 that a cotton filter pulp sample dried from water can be substituted to give 0.49% methoxyl while the corresponding methoxyl for the water swollen sample carefully exchanged to benzene is 7.8%. These values correspond to 0.9% and 13.6% substitution of the hydroxyls.

It is of interest to relate these accessibilities to fibre structure. Previous workers (15,22) have calculated internal surfaces by assuming an appropriate value for the area of an anhydroglucose unit (AGU) and that three hydroxyls are accessible on each surface AGU. If one AGU is assumed to have an area of 52\AA^2 then the accessible areas of dry and water swollen fibres correspond to 16.5 and $264\text{ m}^2/\text{gm}$. cellulose respectively.

These values are compared with others from the literature in Table II-3.

The nature of this internal surface is of some interest. Conventionally accessibilities are discussed in terms of amorphous and crystalline cellulose, the former portion being more or less accessible. However there is growing evidence (3-5, 39, 40) that the native cellulose fibre should be regarded as a microfibrillar structure in which the microfibrils are wholly or predominantly crystalline; and accessibility is regarded as a measure of the availability of the microfibril surface. This availability is the inverse function of mutual bonding of the microfibrils to form larger microfibrils or lamellae.

The dimensions of the elementary microfibrils are the subject of some controversy (3-5, 40-42) the higher electron microscope resolutions leading to smaller estimates. All native cellulose microfibrils are now considered to have $\sim 35\text{\AA}$ diameter. Their surface area is thus $\sim 720\text{ m}^2/\text{gm}$ cellulose. If the elementary microfibrils are considered to be grouped into microfibrils of diameter $a\text{\AA}$, the exposed area will be

$\frac{252 \times 10^4}{a} \text{ m}^2/\text{gm}$; but if laterally bonded to form lamellae $b \text{ \AA}$ thick, the exposed area would be $\frac{1.26 \times 10^4}{b} \text{ m}^2/\text{gm}$. Thus our value of $264 \text{ m}^2/\text{gm}$ for a water swollen sample might speculatively be equated with alternative fibre models made up of fibrils of $a = 95 \text{ \AA}$ diameter or lamellae of thickness $b = 47 \text{ \AA}$.

The magnitude of these values is not unreasonable in the light of electron microscopic evidence although the 100 \AA fibrils may be considered more consistent with the reported observations (43).

Actual electron micrographs of thallated cellulose fibre cross-sections have been published by Asunmaa (44). In these the thallation does not appear to be regularly distributed in a uniform pattern but unpenetrated regions with dimensions ranging from 50 to 300 \AA may be detected.

Attention is drawn in Table II-2 to the similar accessibilities of swollen fibres from various sources and having varied swelling treatments. This observation has not been pursued further in this work but the structures of native, mercerized and regenerated cellulose might well be investigated or compared by application of the present method.

It is of interest that the areas indicated for the water swollen cotton filter pulp exceed the maximum values obtained for cotton (Table II-3) by nitrogen sorption (17) by a factor of two and are similar to areas inferred from water or ammonia vapour (32) sorption. The discrepancies are considerably larger when the samples dried from water are considered. Here, nitrogen sorption corresponds, more or less, with the superficial area of the fibre while the thallation method suggests an area 13 times larger.

TABLE II-3

Surface Areas and Accessibilities of Cellulose

(1)	(2)	(3)	(4)	(5)
Material & Treatment	Method	Per Cent Accessibility	Area m^2/gm	Reference
1. Cotton, filter pulp. Immersed in benzene directly.	$TlOC_2H_5$	0.9	16.5	Present work
Swollen in water and solvent exchanged to benzene.	"	13.6	263.7	"
2. Cotton, linters. Unswollen.	$TlOC_2H_5$	0.4	8	15
Swollen in 10% caustic soda, and dried from benzene.	"	10.1	195.3	15
3. Cotton, filter pulp. Immersed in benzene directly.	N adsorption	-	1.3	17
Swollen in water, solvent exchanged to benzene through methanol and dried.	"	-	67.3	17
Swollen in water, solvent exchanged to pentane through methanol and dried.	"	-	136-139	17
4. Cotton. Swollen in water, solvent exchanged to CO_2 through methanol and dried above critical temperature of CO_2 .	"	-	52-53	28
Swollen in water, solvent exchanged to pentane through methanol and dried.	"	-	47-52	28
Swollen in water, solvent exchanged to benzene through methanol and dried.	"	-	18.4	28

Cont'd.

TABLE II-3 (Cont'd.)

(1)	(2)	(3)	(4)	(5)
5. Cotton, unswollen.	N adsorption	-	0.6	29
6. Cotton, absorbent unswollen.	"	-	0.8	29
7. Cotton, boiled with 1% sodium hydroxide.	Water vapour sorption	-	128-140	28
8. Cotton. Before beating.	"	-	120	30
After beating.	"	-	142	30
9. Cotton	"	-	139	31
10. Cotton, purified.	"	-	220	32
11. Cotton, linters.	"	-	157	33
12. Cotton, purified.	NH ₃ gas adsorption	-	230	32
Cotton, purified.	Heat of wetting	-	140	32
13. Cotton, linters. Dewaxed with ethanol-benzene mixture and dried.	TlOC ₂ H ₅	1.46	-	34
14. Cotton.	D ₂ O exchange	40	-	35
15. Cotton.	HTO exchange	40		36
16. Cotton.	Formic acid	28	-	10
17. Cotton.	Density measurement	40	-	37
18. Cotton.	X-ray diffraction	30	-	37
19. Cotton.	Iodine sorption	9-17	-	38

The greater accessibility of the fibre to thallous ethylate in benzene could be due to one or more considerations. The cellulose fibre swells and becomes more accessible in benzene or the fibre shrinks sufficiently in cooling to -195°C to close off pores to nitrogen gas. An additional possibility is that the sorption of nitrogen on cellulose, like coal (45), is very temperature dependent and little is sorbed at low temperature.

There is some evidence of the porosity of dried cellulose fibres. Magne and Skau (7) immersed dry cotton in benzene and measured calorimetrically the amount of non-freezing benzene at 0°C . The results were interpreted to indicate that one gm. of cellulose contained enough accessible pores (assumed circular) of less than 282 \AA diameter to amount to 0.27cc. This represents a minimum void fraction of 30% and an internal area which is at least $19 \text{ m}^2/\text{gm}$ cellulose and is probably many times greater. Other evidence of substantial internal voids in dried native fibres is also available (6-9, 46).

If the cell wall does indeed contain substantial voids, the measurement of pycnometric densities suggests (Table II-4) that they are almost completely penetrated by all the displacement liquids. The results, however, suggest that the extent of penetration is an inverse function of the molecular volume of the penetrant.

The difference in volume inaccessible to benzene between dry and water swollen fibres is only about 2% of the cellulose volume while the thallation accessibility increases by a factor of 13. This, together with

TABLE II-4

Specific Volume of Cotton Cellulose in Various Liquids

Liquid	(a) Wet Specific Volume (cc/gm)	(a) Dry Specific Volume (cc/gm)	Molar Volume (cc/mol)	(b) Cohesive Energy Density (cal/cc)
Water	0.6226	0.6226	18.1	448.0
Glycol	0.6231	0.6416	55.9	215.3
Acetone	0.6269	0.6457	74.0	86.4
1,2-Dichloroethane	0.6260	0.6460	79.0	94.4
Benzene	0.6300	0.6470 0.6494(c)	89.4	81.9
Carbon tetrachloride	0.6306	0.6491	97.1	74.1
Diethyl phthalate	-	0.6596(c)	396	52.6

(a) Soley; Reference No. 27.

(b) Calculated from the boiling points and densities of liquids at 25°C. See Reference No. 47 and Appendix B.

(c) Meredith; Reference. No. 48.

Dry specific volume: Specific volume of cellulose directly immersed in the measurement liquid.

Wet specific volume: Specific volume of cellulose, swollen in water and solvent exchanged to the measurement liquid.

other evidence suggests that the accessibility is sensitively determined by the opening up of very small pores or inter-surface distances. This observation and data on non-freezing benzene (7) also suggest that while the bulk of cellulose structure can be penetrated by benzene, greater separation distances are required to permit the thallation reaction.

Caution must be exercised in comparing thallation accessibility with results of other methods. In many methods the state of swelling or collapse is changed by the measurement procedure; and it is the method which determines the result rather than the pre-test condition of the sample. Conrad (49) has tabulated accessibilities measured on cotton by various workers ranging from 1% by periodic oxidation to 75% by deuterium exchange.

The present method differs from these by substantially preserving the internal structure of the sample throughout the procedure and by measuring the accessibility of that structure to a reagent molecule of a moderate size.

(b) APPLICATION TO CELLULOSE-LIQUID INTERACTIONS:

Accessibilities have been measured for standard samples of cellulose fibres, pretreated by immersion in a variety of liquids and solvent exchanged to benzene. The objective was to evaluate the cellulose liquid interactions by measuring the extent of internal surfaces made accessible by the decreased internal cohesion on immersion in the test liquid. The results (Table II-1) show a range of methoxyl contents which, for the most part, lie between those obtained for dry collapsed fibres and those recorded for water swollen samples.

A discussion of liquid parameters which determine the extent of interaction will be found elsewhere (50). It may be sufficient to mention here that liquids which have low molecular volume and possess strong H-bonding functions generally interact most effectively.

An increase in accessibility, as we have interpreted it, implies a decrease in the internal cohesion of the fibres - a separation of fibrillar or lamellar elements. Thus accessibility should be related to the swelling of the fibre and to its mechanical properties.

An empirical measure of swelling is provided by the mercury displacement dilatometry (18) of pressed fibre pellets (density = 1). The comparison of swelling with thallation accessibility is shown in Fig. II-1. The lack of strong correlation is due to several factors. A major factor is that the swelling measurement is at equilibrium whereas the accessibility measurement is made after 24 hours' immersion only. In several of the liquids, the pellets require weeks to reach equilibrium (18). Although this slow swelling can be partially attributed to the compact nature of the pellet and to the consequent slow penetration of liquid or the frictional resistance to relative fibre movement, it is probably true that in many cases the equilibrium fibre swelling is not attained in 24 hours.

Other factors which preclude a direct relationship between dilatometric swelling and accessibility are related to the empirical nature of the swelling measurement. The change in pellet volume includes not only the increases in the thickness of the cell wall but also the increase in

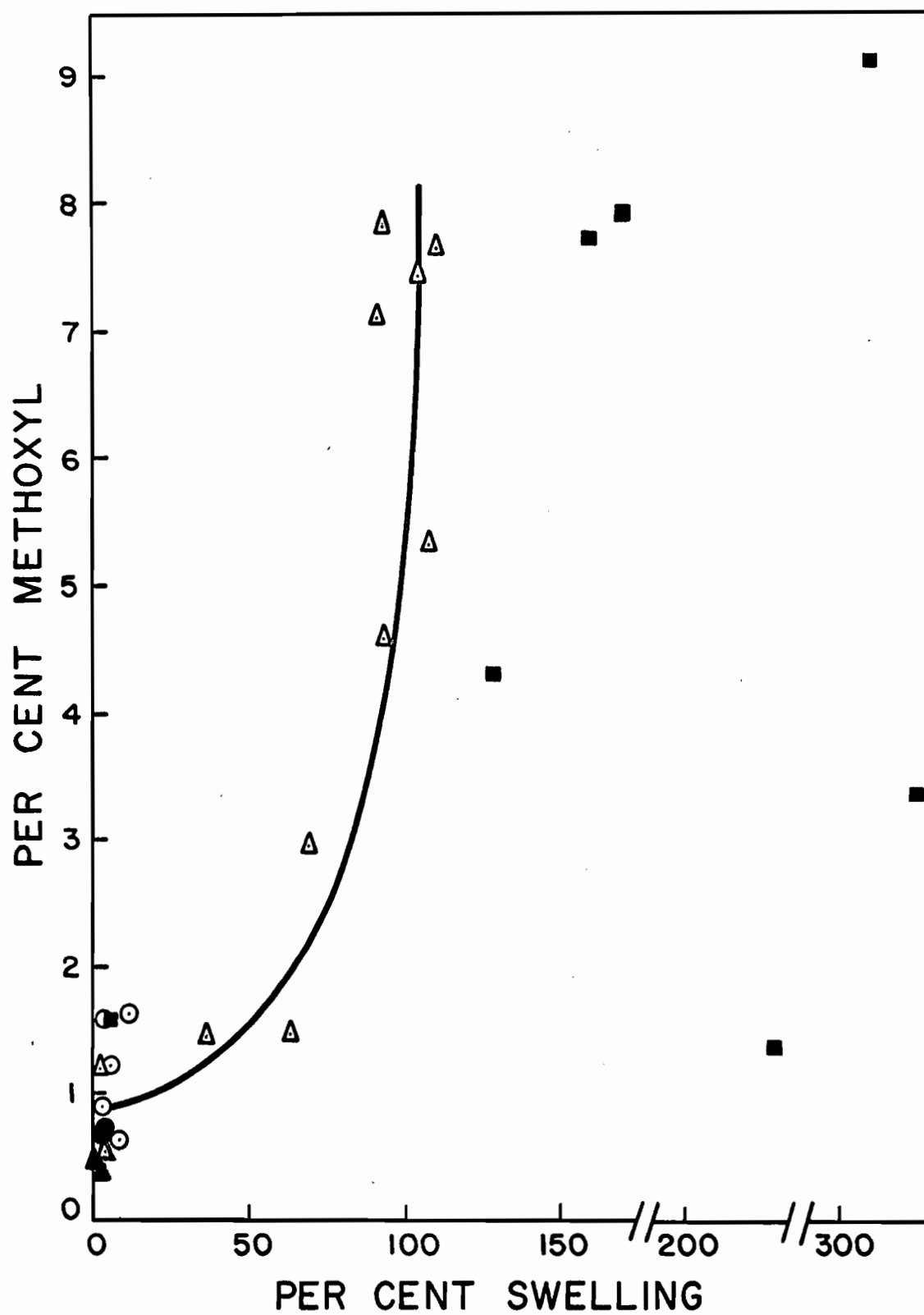
FIGURE II-1

ACCESSIBILITY AND SWELLING OF CELLULOSE

(Curve drawn through hydroxyl containing liquids)

LEGEND:

- △ H-bonding, proton donor and acceptor, associated;
- ⊙ H-bonding, proton acceptor only;
- ▲ "inert";
- molar volume > 100 c.c. and
- intramicellar swelling liquids.



circularity of the fibre (51, 52), changes in the lumen volume and the possible increase or decrease in the interfibre voids. In addition, it should be noted that separation of internal surfaces beyond a certain minimum distance increases the volume but not the accessibility of the fibre.

If the accessibility is related to internal cohesion, it should also be related to changes in the mechanical properties such as elastic modulus or tensile strength of fibres or structures made up of the fibres. The mechanical properties of cotton fibre were not measured but in a concurrent work (47) the modulus and strength of paper strips, immersed in various liquids, were measured. The paper was made from a high purity bleached wood pulp with no additives. These fibres are considered to be sufficiently similar to cotton fibres in their response to immersion to permit a qualitative comparison. The immersion times in the strength tests and accessibility experiments were similar.

The correlations are shown in Figs. II-2 and II-3. The loss in tensile strength is interpreted as a measure of the weakening of interfibre bonds which are presumed to occur between cellulose surfaces. The loss in modulus is ascribed to the increased flexibility of the fibre resulting from the reduction of internal cohesion. The correlation of modulus with strength (47) and of both with thallation accessibility is a strong evidence that the three measurements reveal the same phenomenon - the reduction in the strength of cellulose-cellulose bonds by the test liquids.

FIGURE II-2

ACCESSIBILITY OF CELLULOSE AND TENSILE STRENGTH
OF PAPER STRIPS IMMersed IN VARIOUS ORGANIC LIQUIDS

LEGEND:

- △ H-bonding, proton donor and acceptor, associated;
- ⊙ H-bonding, proton acceptor only;
- ▲ "inert";
- molar volume > 100 c.c. and
- intramicellar swelling liquids.

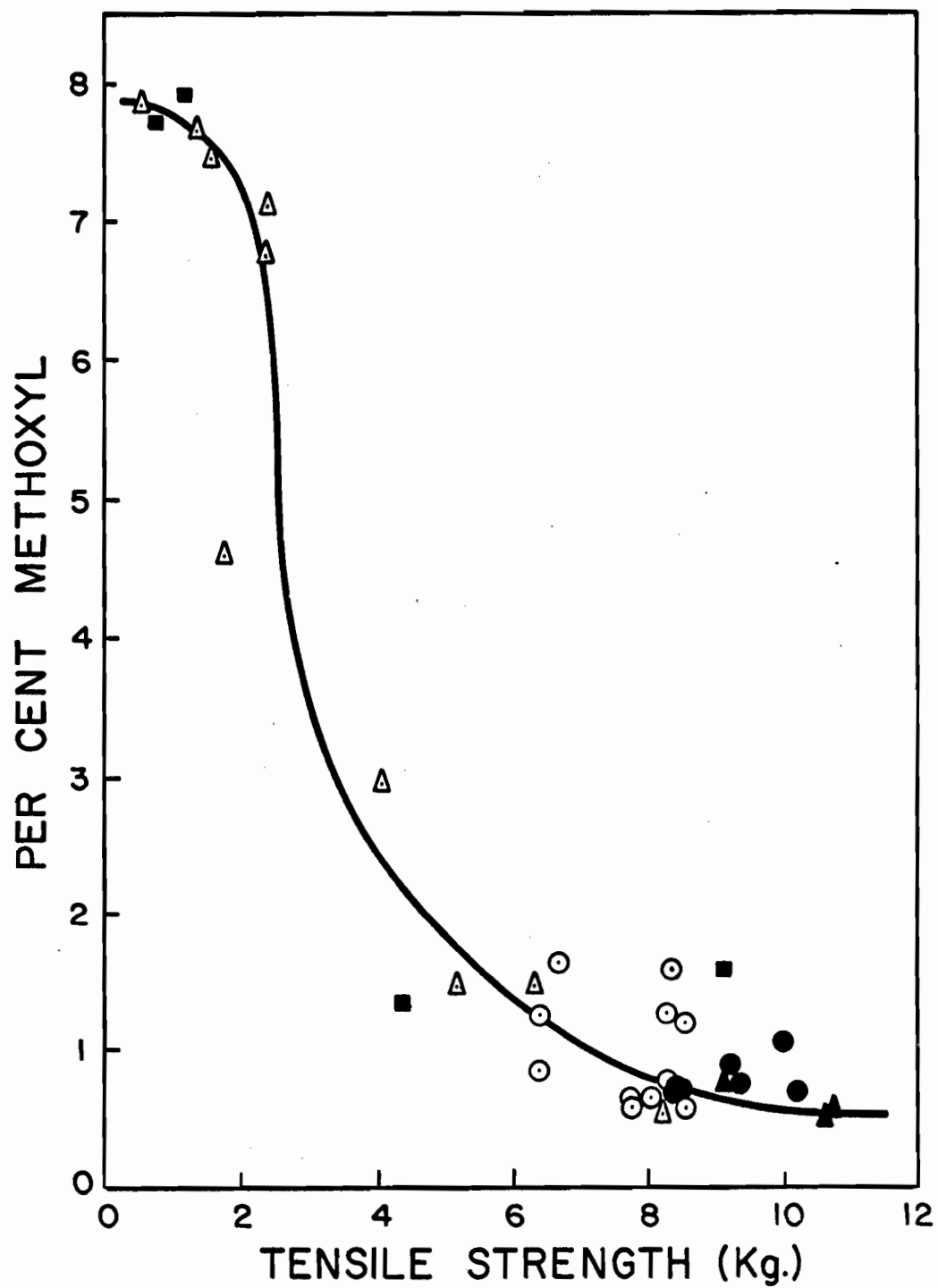
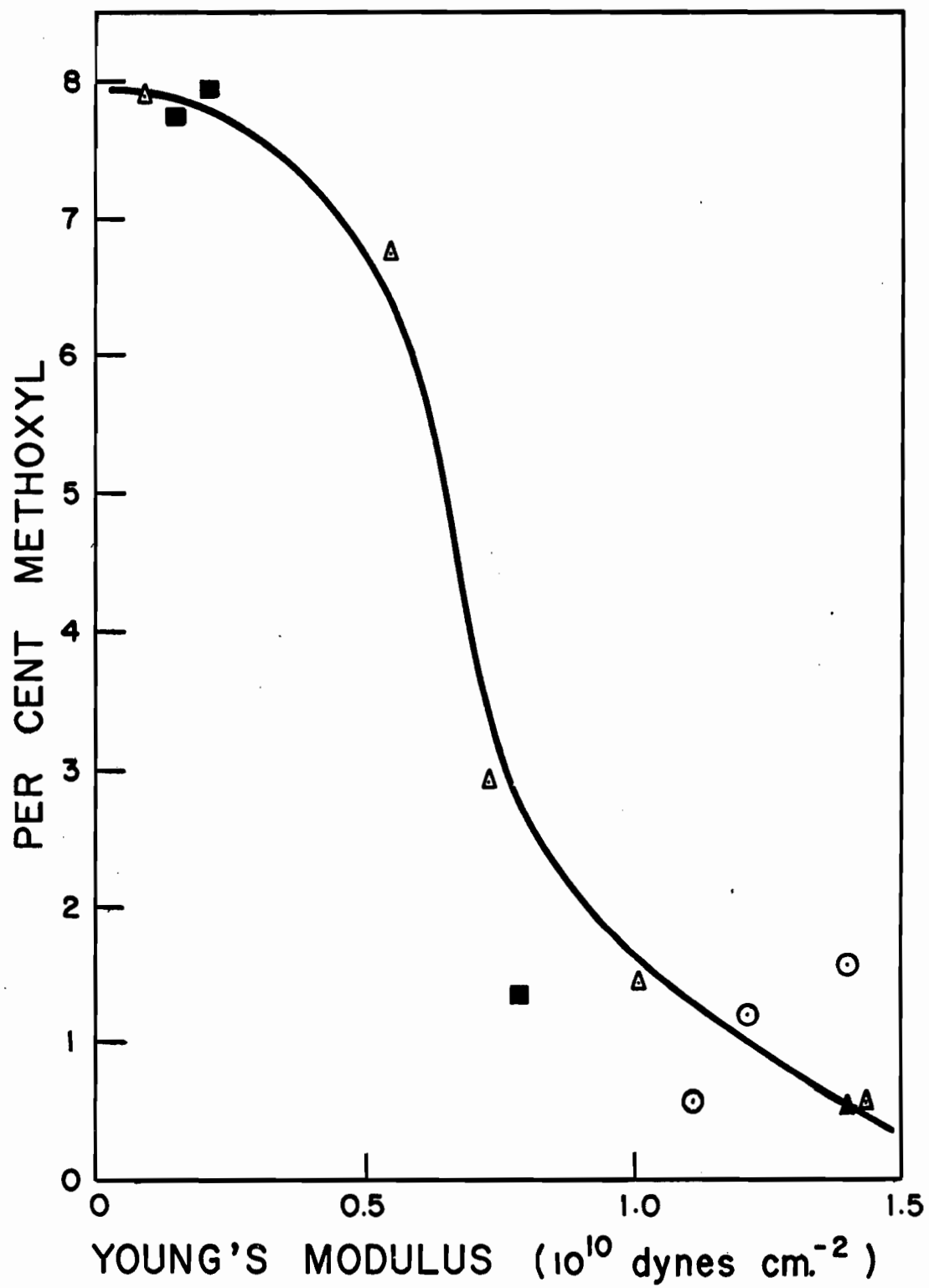


FIGURE II-3

ACCESSIBILITY OF CELLULOSE AND YOUNG'S MODULUS
OF PAPER STRIPS IMMERSSED IN VARIOUS ORGANIC LIQUIDS

LEGEND:

- △ H-bonding, proton donor and acceptor, associated;
- ⊙ H-bonding, proton acceptors only;
- ▲ "inert";
- molar volume > 100 c.c. and
- intramolecular swelling liquids.



E. CONCLUSIONS

1. Thallous ethylate method is a convenient measure of accessibility when it is desired to compare the extents of reaction which can be expected in various media.

2. The extent of reaction provides a measure of internal area which appears to be realistic and is related to the microfibrillar or lamellar structure.

3. The method has been successful in its application to the measurement of cellulose-liquid interactions as revealed by the degree to which the fibre structure is opened up by immersion in test liquids.

4. A drawback to the method, which is shared by other methods, is the uncertainty as to whether the internal fibre structure or accessibility is maintained during solvent exchange to the reaction medium.

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PART III

A DILATOMETRIC STUDY OF CELLULOSE-LIQUID INTERACTIONS

A. INTRODUCTION

The native cellulose fibre is formed in the presence of water, so that an expanded water swollen condition is its unstrained state. On drying, the lamellae and fibrils which form the fibre wall are drawn together by surface tension forces (1,2), the fibre shrinks and the porosity of the fibre wall decreases. The fibre shrinks primarily in cross-section, collapsing on its lumen to form a convoluted ribbon (3). The resultant distorted state is maintained by the formation of H-bonds between the structural elements of the collapsed fibre when water disappears.

On rewetting, the cellulose fibre swells, at least partly regaining its shape and volume. The structural elements of the fibre separate to a greater or lesser extent depending upon the history of the fibre and the conditions of rewetting. It is a thesis of this paper that bulk of the expansion is due to the "frozen in" stresses (4) tending to expand the fibre which become free to act when the interfibrillar H-bonding is reduced by interaction with water.

Immersion of dried cellulose fibres in non-aqueous liquids is expected to produce different degrees of swelling depending upon the ability of the liquid to reduce cohesion between different structural elements of the fibres. Several organic liquids and aqueous solutions (5,6) swell cellulose beyond the extent observed for swelling in water. In some of these cases part of the swelling can be attributed to intramolecular penetration or alteration of the crystal pattern. In others the mechanism

remains obscure. Thus the possibility of swelling mechanisms involving the expansion of the microfibrils themselves is not excluded; but it is suggested that for many liquids the bulk effects are due to the lamellar and fibrillar separations.

This paper reports the dilatometric swelling of pellets of cellulose fibres in a variety of anhydrous organic liquids and relates the results to other measurements of cellulose-liquid interactions. This work forms a part of a study (7-9) directed towards the elucidation of the nature and mechanisms of fibre swelling.

The use of dilatometry of pressed pellets, rather than the direct microscopic (10-14) or permeability (15-16) methods, to measure cellulose swelling offers advantages of convenience and reproducibility. There are, however, inherent uncertainties in the method which must be recognized. The measurements depend to some extent on the density of the pellets and the elastic and plastic properties of the fibres which may vary with the test liquid. When swelling in water of fibre pellets of different densities was compared, they showed a decrease of 16% in swelling over a density range from 1.0 to 1.36 gm/cc. Despite these shortcomings, the results of swelling of pellets obtained under identical conditions provide useful information regarding the nature and extent of liquid interaction and fibre swelling.

B. EXPERIMENTAL

(a) MATERIALS:

(i) Filter pulp: Acid washed, dry-dispersed and ash free cotton filter pulp was used throughout these experiments. The material contained about 98.5% alpha cellulose.

(ii) Solvents: Most of the solvents were Fisher 'reagent grade', meeting A.C.S. specifications. Others were of the next highest grade available. Special care was taken to dry the solvents. Benzene, carbon tetrachloride, etc., were kept over sodium wire, redistilled and stored again over sodium wire. They were filtered through a coarse fritted glass funnel before use. Ethanol, methanol and acetone were dried by methods recommended by Vogel (17). All solvents, except those stored over sodium wire, were kept over drierite.

(b) PREPARATION OF THE PELLETS:

A specially made hardened steel die was used to make pellets. About 0.415 gm. of air dry pulp was pressed in a laboratory press, under 10,000 psi for 10 minutes, to a predetermined volume of about 0.400 cc. The pellets (approximately 15 mm. in diameter and 2 mm. thickness) had a dull matte surface and a density of about 1.0. They were dried at 105°C. for one hour and stored in a desiccator over anhydrous calcium chloride for several days. During this interval they gained about 1.5% in volume. Exact volume of the pellets was determined with a micrometer measuring 0.01 mm. and on which ± 0.002 mm. could be estimated. Pellets so made had volumes and densities within a narrow range of ± 0.003 cc. and ± 0.02 gm/cc. respectively.

(c) DESCRIPTION AND OPERATION OF THE DILATOMETER:

The dilatometer was made entirely of Pyrex brand glass (Figures III-1, 2 and 3). All stop-cocks were lightly greased with high vacuum grease. The pellet was introduced in the lower bulb and the apparatus assembled. A specially made clamp (not shown) secured the middle and the bottom parts. The upper chamber of the middle component contained a few granules of drierite.

Air pockets in the mercury passages were removed by introducing and withdrawing mercury a few times. With stopcocks G and L closed, vacuum was applied and mercury admitted after a few minutes. With the pellet positioned against the middle of the disc H, the dilatometer was completely filled. G was then turned through 180° three or four times to fill the micro-pipette and to expel any air bubbles caught behind the stopcock. G and L were now closed and the apparatus placed in a water bath maintained at $25 \pm 0.02^\circ\text{C}$. Vacuum was gently broken through A carrying a drying tube. On opening G a small amount of mercury, held in the disc cavities, was expelled.

In case the room temperature was above 25°C , the mercury column receded into the micro-pipette. The correction to be applied could be directly read off the graduations.

The drying tube was now replaced with a funnel carrying the test liquid. With G and L closed vacuum was applied. About 5 cc. of the test liquid was introduced into I and the vacuum pump connected again. This removed air from the test liquid and the pellet. A receiver for

mercury was now placed under the nozzle of the micro-pipette, vacuum gently broken and G opened. The funnel in A was replaced with the drying tube. Since the tip of the micro-pipette was about 2 cm. higher than the disc H, the pellet swelled against a slight pressure.

The above procedure removed air from the pellet and ensured complete penetration of the voids in the pellet by the test liquid. This was confirmed from the weights of dry and wet pellets and the amount of swelling the pellet had undergone. Control experiments with water vapour only showed no detectable dilatometric swelling of the pellet in the first twenty minutes or so. It was safe to assume therefore, that with vapours of other liquids too, no swelling of the pellet took place during the setting up of the experiment.

Start of swelling was taken as the time of final opening of G. In order to study the kinetics of swelling receivers were changed and time noted. Swelling in a given time was calculated from the weight of mercury expelled. Swelling was considered complete when no more mercury was expelled for a day or two. At the end of the experiment, any drop of mercury hanging from the nozzle of the micro-pipette was brushed into the receiver with a camel hair brush.

Per cent swelling at 25°C. (Q_{25°) of filter pulp was obtained from the relation:

$$Q_{25^\circ} = \frac{V - V_0}{V_0} \times 100$$

$$= \frac{(\text{weight of mercury expelled}) \times 100}{V_0 \times 13.534}$$

where V_0 and V represented the initial and equilibrium volumes of the pellet respectively.

FIGURE III-1THE DILATOMETER

- A Quickfit SRB-10 female joint; takes a funnel or drying tube (not shown).
 - B To the vacuum pump.
 - C Three-way, V-bore, high vacuum stopcock.
 - D Quickfit B-24/29 male joint.
 - E Quickfit B-24/29 female joint.
 - F Micropipette, about 7 cm. (Kimax, 1/10 in 1/100 ml.)
 - G Sc - 1/3 high vacuum, two-way stopcock.
 - H Sintered glass disc, fine porosity.
 - I Pyrex sealing tube.
 - J Solid glass support.
 - K To mercury reservoir.
 - L Sc - 7/3 high vacuum three-way stopcock.
 - M Ground glass cap.
- (Clamp to secure bottom and middle components not shown.)

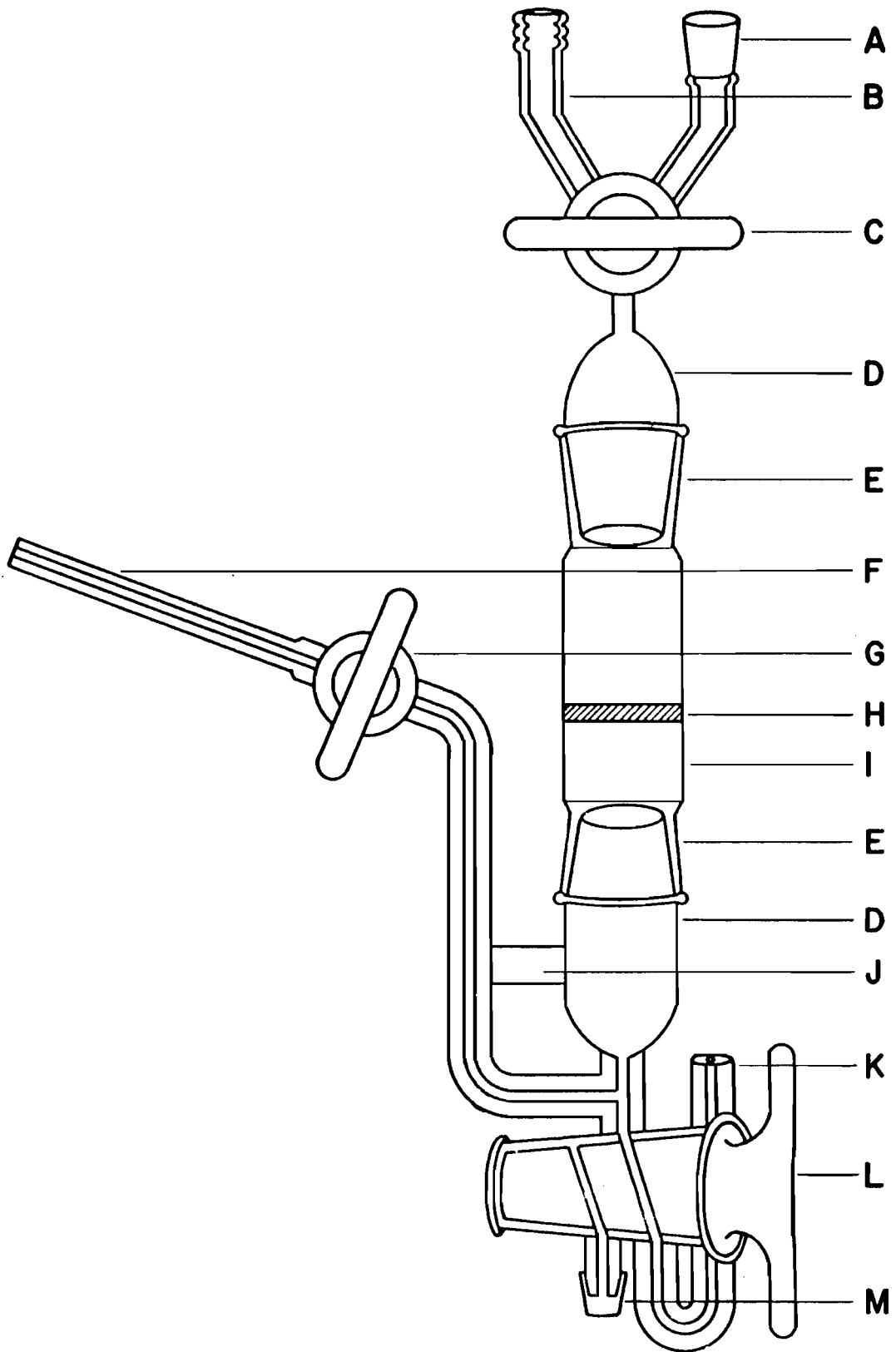


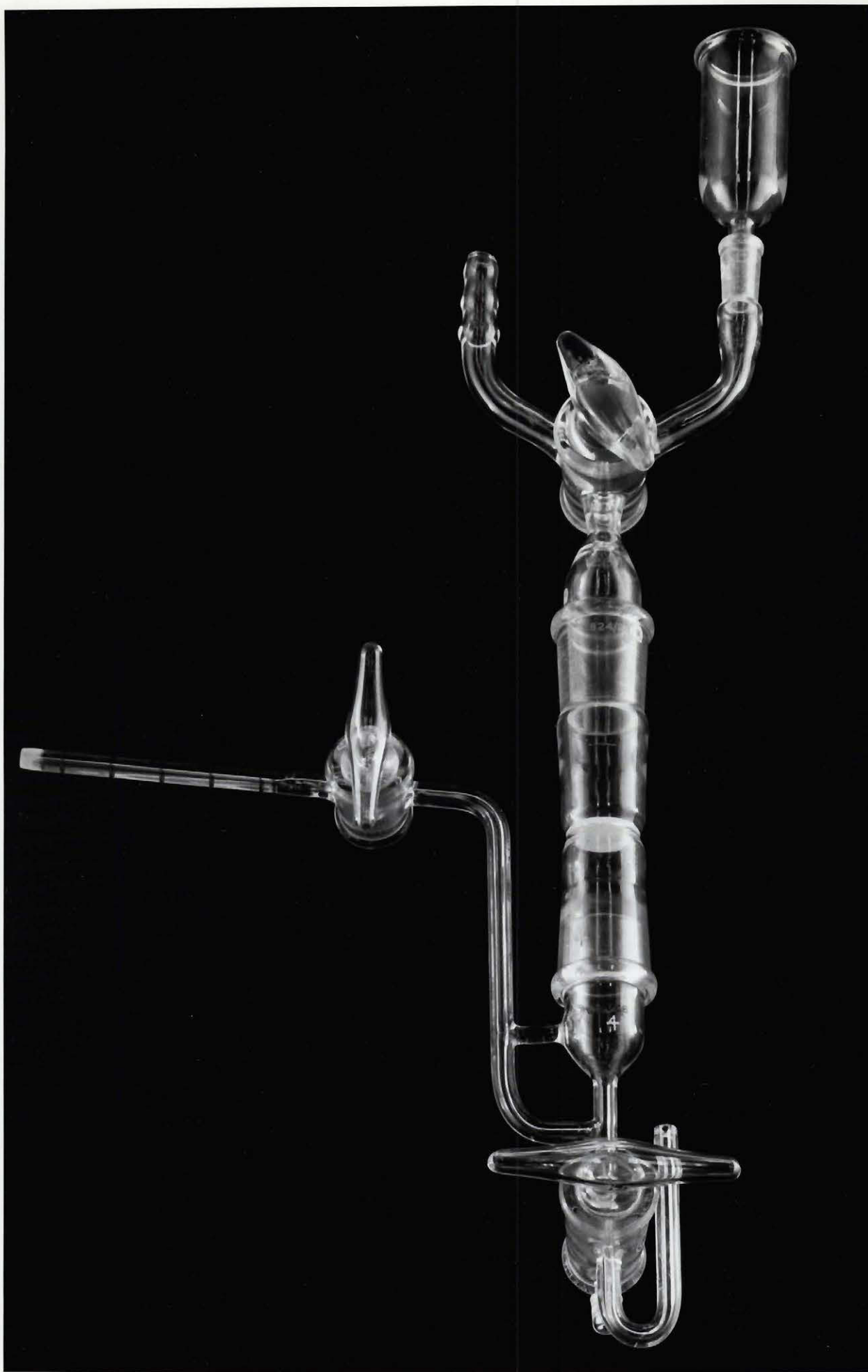
FIGURE III-2

THE DILATOMETER (DISASSEMBLED)



FIGURE III-3

THE DILATOMETER (ASSEMBLED)



C. RESULTS AND DISCUSSION

The swelling of cellulose is reasonably reproducible when measured by the present procedure. Results are given in Table III-1 together with those reported by other workers (18-20) using similar techniques. The liquids are arranged in a similar order by their swelling ability in the four investigations; there is a substantial quantitative agreement despite the different types of fibres and procedures used.

The swelling data are compared in Table III-2 with other measurements or evidence of cellulose-liquid interactions. Certain properties of swelling liquids which may be significant in relation to swelling are also included in this Table.

In most cases the initial rates of swelling are very fast. The time required by a liquid to swell the pellets to half the equilibrium volume (designated as $t_{0.5}$), varies widely. For water it is as low as 0.3 minute while nitrogenous compounds known or suspected of causing intramolecular swelling, generally take a long time to reach half the equilibrium swelling (Table III-2, column 10). The time $t_{0.5}$ showed no correlations with any single property of the swelling liquids investigated except a weak inverse relation with the molar volume. Presumably swelling rate is a complex function of several factors, e.g., surface tension, contact angle, viscosity, H-bonding ability, molar volume, etc.

TABLE III-1

Swelling of Cellulose by Anhydrous Organic Liquids

S/ No.	Swelling Liquid	Present Work, Cotton Filter Pulp (25°C.)	Kress and Bialkowsky (18) Spruce Sulphite Pulp (20°C.)	Schwabe and Philipp (19) Spruce Pulp (20°C.)	McKenzie (20) Eucalypt Alpha Pulp (20°C.)
1.	Carbon tetrachloride	1.1	-	-	-
2.	Toluene	-	-	3	-
3.	1-Pentanol	-	4.0	6	-
4.	1-Butanol	-	4.0	-	-
5.	Benzene	2.0	-	-	-
6.	2-Propanol	2.1	-	14	-
7.	Tetrahydrofuran	3.3	-	-	-
8.	p-Dioxane	3.9	-	-	-
9.	Furfural	-	8.0	-	-
10.	Nitrobenzene	4.4	17.0	4	-
11.	Aniline	5.0	15.0	-	-
12.	Nitromethane	6.0	-	-	-
13.	Acetone	11.7	-	6	27.6
14.	Ethyl cellosolve	36.7	-	-	-
15.	1,4-Butanediol	62.0	-	-	-
16.	Ethanol	69.1	40	28	42.0
17.	Methanol	90.6	62	52	-
18.	Methyl cellosolve	91.1	-	-	-
19.	Water	92.6	90	60	117.6
20.	Acetic Acid	93.6	-	-	-
21.	Glycerol	105.0	-	-	-
22.	1,3-Propanediol	108.3	-	-	-
23.	Ethylene glycol	109.8	89	-	-
24.	Pyridine	127.5	-	-	120.0
25.	Formamide	159.0	125	121	133.2
26.	Dimethylformamide	170.0	-	-	120.0
27.	Morpholine	229	-	-	-
28.	Ethylenediamine	310	-	-	222.0
29.	Benzylamine	325	-	-	-

TABLE III-2

Swelling of Native Cotton Cellulose by Anhydrous Organic Liquids

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
S/No.		Solvent	Per cent Swelling	Per cent Methoxyl	(d) c.e.d. (cal/cc)	Molar Volume (c.c.)	Dielectric Constant	Dipole Moment (Debye)	$t_{0.5}$ (Minutes)
1.	▲	Carbon tetrachloride	1.1	0.51	74.1	97.1	2.23	0.0	-
2.	▲	Benzene	2.0	0.49	81.9	89.4	2.27	0.0	-
3.	△	2-Propanol	2.1	1.18	96.3	77.0	18.3	1.68	-
4.	●	Toluene	3.0 ^(a)	0.67	79.8	106.8	2.38	0.39	-
5.	⊙	Tetrahydrofuran	3.3	0.88	83.6	81.2	-	1.17	-
6.	⊙	p-Dioxane	3.9	1.57	94.9	85.7	2.21	0.0	-
7.	△	1-Butanol	4.0 ^(b)	0.54	95.3	92.0	17.10	1.63	-
8.	●	1-Pentanol	4.0 ^(b)	0.68	87.8	109.1	13.9	1.80	-
9.	●	Nitrobenzene	4.4	0.73	122.7	102.6	34.8	4.27	-
10.	■	Aniline	5.0	1.57	125.5	91.5	6.9	1.59	-
11.	⊙	Nitromethane	6.0	1.20	150.0	53.9	35.8	3.57	-
12.	⊙	Furfural	8.0 ^(b)	0.62	126.8	83.2	41.9	3.61	-
13.	⊙	Acetone	11.7	1.62	86.4	74.0	21.3	2.86	6.700

Cont'd.

TABLE III-2 (CONT'D.)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
14.	△	Ethyl cellosolve	36.7	1.45	97.8	96.8	-	2.08	8,700
15.	△	1, 4 - Butanediol	62.0	1.46	150.3	88.8	30.2	2.55	18,000
16.	△	Ethanol	69.1	2.95	123.6	58.7	24.3	1.71	165
17.	△	Methanol	90.6	7.11	165.8	40.7	32.63	1.68	2.6
18.	△	Methyl cellosolve	91.1	-	114.0	79.3	16.0	2.04	125
19.	△	Water	92.6	7.83	448.0	18.1	78.5	1.87	0.3
20.	△	Acetic acid	93.6	4.57	153.4	57.6	6.15	1.75	320
21.	△	Glycerol	105.0	7.49	220.5	73.2	42.5	2.56	8,000
22.	△	1, 3 - Propanediol	108.3	5.33	177.5	71.8	35.0	2.50	1,500
23.	△	Ethylene glycol	109.8	7.65	215.3	55.9	41.2	2.28	700
24.	■	Pyridine	127.5	4.33 ^(c)	107.4	80.9	12.3	2.20	2,820
25.	■	Formamide	159.0	7.74	308.5	39.9	109.5	3.37	-
26.	■	Dimethylformamide	170.0	7.93	131.6	77.4	36.7	3.86	133
27.	■	Morpholine	229.0	4.03 ^(c)	105.7	87.1	7.3	1.75	3,700

Cont'd.

TABLE III-2 (CONT'D.)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
28.	■	Ethylenediamine	310.0	9.16	129.7	67.3	14.2	1.90	3.0
29.	■	Benzylamine	325.0	5.65 ^(c)	105.6	109.0	4.6	1.38	1,800

(a) Reference No. 19.

(b) Reference No. 18.

(c) Soaked for seven days.

(d) Calculated from the boiling points and densities of liquids at 25°C. See Reference No. 21 and Appendix B.

Classification: ▲ , associated, H-bonding, both proton acceptors and donors;

⊙ , H-bonding, proton acceptors only;

● , molar volume >100 cc;

▲ , "inert" and

■ , intramolecular swelling agents.

Attempts were made to correlate degree of swelling with several liquid parameters, e.g., cohesive energy density (c.e.d.), molar volume, dipole moment, H-bonding ability and degree of association. Apparently none of these properties produces a strong correlation although many of them show some relationship within the same homologous series or the same class of compounds. Swelling of cellulose in monohydric alcohols for example, shows good correlations with their c.e.d.'s and molar volumes (Table III-3). Similar correlations are seen in the case of other homologous series shown.

Of the liquids studied the hydroxylic compounds appear to show the best correlations between their properties and the extent of interaction with cellulose. The ability of such compounds to interact with cellulose is logically related to the size of the molecules and their configuration. Lack of steric hindrance to H-bonding leads to molecular association in the liquids and to a high probability of suitable orientation to interact with cellulose hydroxyls. Thus, in the homologous series which have been studied, decreasing molecular size or decreasing steric hindrance to association involving hydroxyl groups, lead to increased c.e.d. in the liquids and increased swelling of cellulose. Cellulose appears to reach a maximum swelling in the vicinity of 100-110% (Table III-3). This limit is probably structurally imposed and related to the volume of the fibre at its formation.

Table III-4 shows swelling of cellulose in certain hydroxylic liquids grouped according to the number of carbon atoms in the molecule. It is observed that polyfunctional liquids swell cellulose more than monofunctional liquids of comparable size. Thus among the four carbon compounds,

TABLE III-3

Swelling of Cellulose by Members of Various Homologous Series

Solvent	Formula	Swelling (Per cent)	Methoxyl Content (Per cent)	** c.e.d. (cal/cc)	t _{0.5} (Minutes)	Molar Volume 25°C. (cc/mole)
1. Ethyl cellosolve	HO.CH ₂ .CH ₂ .O.CH ₂ .CH ₃	36.7	1.45	97.8	8,700	96.8
Methyl cellosolve	HO.CH ₂ .CH ₂ .OCH ₃	91.1	-	114.0	125	79.3
Ethylene glycol	HO.CH ₂ .CH ₂ .OH	109.8	7.65	215.3	700	55.9
2. 1 - Pentanol	CH ₃ .CH ₂ .CH ₂ .CH ₂ .CH ₂ .OH	4.0*	0.68	87.8	-	109.1
1 - Butanol	CH ₃ .CH ₂ .CH ₂ .CH ₂ .OH	4.0*	0.54	95.3	-	92.0
2 - Propanol	CH ₃ .CH(OH).CH ₃	2.1	1.18	96.3	-	77.0
Ethanol	CH ₃ .CH ₂ .OH	69.1	2.95	123.6	165	58.7
Methanol	CH ₃ .OH	90.6	7.11	165.8	2.6	40.7
Water	HOH	92.6	7.83	448.0	0.3	18.1
3. 1, 4 - Butanediol	HO.CH ₂ .CH ₂ .CH ₂ .CH ₂ .OH	62.0	1.46	150.3	18,000	88.8
1, 3 - Propanediol	HO.CH ₂ .CH ₂ .CH ₂ .OH	108.3	5.33	177.5	1,500	71.8
Ethylene glycol	HO.CH ₂ .CH ₂ .OH	109.8	7.65	215.3	700	55.9
4. Glycerol	HO.CH ₂ .CH(OH).CH ₂ .OH	105.0	7.49	220.5	8,000	73.2
Ethylene glycol	HO.CH ₂ .CH ₂ .OH	109.8	7.65	215.3	700	55.9
Methanol	CH ₃ .OH	90.6	7.11	165.8	2.6	40.7

(*) Kress and Bialkowsky; Ref. No. 18.

(**) Calculated from the boiling points and densities of liquids at 25°C.

See Ref. No. 21 and Appendix B.

butanol swells cellulose only 4% while butanediol containing two hydroxyl groups swells it 62%. In ethylene glycol monoethyl ether swelling is intermediate - 36.7%. The greater swelling potential of the polyfunctional compounds is related to their greater H-bonding facility and greater probability of suitable orientations for interactions with cellulose.

Evidence from this section and experiments on thallation accessibility (7) and strength loss in paper strips (21), shows that liquids containing hydroxylic groups in conjunction with the carbonylic (acetic acid) or the etheric (cellosolves) groups, have stronger interaction with cellulose than the liquids containing only carbonylic or etheric groups (aldehydes, ketones, esters or ethers). No explanation is offered for this apparent "activation" of carbonylic or etheric H-bonding sites by hydroxylic functions present in the same molecule.

The lack of correlation of swelling with di-electric constants or dipole moments is to be noted in Tables III-2 and III-4 because of the attempts of previous workers (16, 18, 22-25) to establish such relationships.

The nitrogenous compounds among the swelling liquids are of various classes and provide little basis for comparison. On the basis of consensus of criteria discussed elsewhere (26), none of them are highly associated except for formamide. The amines (benzylamine, ethylenediamine and presumably aniline) are known to be intramolecular swelling agents (27,28). From the above observed behaviour it appears that some or all of the remainder (morpholine, formamide, dimethylformamide and pyridine) may also swell the intramolecular regions. That swelling in most cases is greater

TABLE III-4

Swelling of Cellulose by Polyfunctional Compounds
(Groups according to the number of carbon atoms.)

No. of C Atoms	Solvent	Formula	Swelling (Per cent)	Methoxyl Content (Per cent)	Molar Vol- ume 25°C. (cc/mole)	** c.e.d. (cal/cc)	Dielectric Constant	Dipole Moment (Debye)
0	Water	HOH	92.6	7.83	18.1	448.0	78.50	1.87
2	Ethanol	CH ₃ .CH ₂ OH	69.1	2.95	58.7	123.6	24.30	1.71
	Acetic acid	CH ₃ .COOH	93.6	4.57	57.6	153.4	6.15	1.75
	Ethylene glycol	HOCH ₂ .CH ₂ .OH	109.8	7.65	55.9	215.3	41.20	2.28
3	2 - Propanol	CH ₃ .CH(OH).CH ₃	2.1	1.18	77.0	96.3	18.30	1.68
	Methyl cellosolve	CH ₃ O.CH ₂ .CH ₂ OH	91.1	-	79.3	114.0	16.00	2.04
	Glycerol	CH ₂ OH.CH(OH).CH ₂ OH	105.0	7.49	73.2	220.5	42.50	2.56
	1,3 - Propanediol	HOCH ₂ .CH ₂ .CH ₂ OH	108.3	5.33	71.8	177.5	35.00	2.50
4	1 - Butanol	CH ₃ .CH ₂ .CH ₂ CH ₂ .OH	4.0*	0.54	92.0	95.3	17.10	1.63
	Ethyl cellosolve	CH ₃ .CH ₂ O.CH ₂ .CH ₂ OH	36.7	1.45	96.8	97.8	-	2.08
	1,4 - Butanediol	HO.CH ₂ .CH ₂ .CH ₂ .CH ₂ OH	62.0	1.46	88.8	150.3	30.20	2.55

(*) Kress and Bialkowsky; See Ref. No. 18.

(**) Calculated from boiling points and densities of liquids at 25°C.
See Ref. No. 21 and Appendix B.

than in alcohols may be due both to intramicellar swelling directly and to weakening or reduction in the restraints to swelling exerted by the primary wall or winding layer of the secondary wall.

It is interesting to note that all the test liquids swell cellulose pellets to some extent just as all immersion liquids reduce the strength of paper. It cannot be stated whether the interaction with inert liquids like carbon tetrachloride or toluene actually involves swelling of cellulose fibres or whether the increase in volume is a function of interfibre friction or other effect.

Another significant observation is that very few liquids can be found which produce intermediate swelling, that is, swelling between 10 and 90-100%. The impression is left that interfibrillar bonds do not span a wide range of strengths so that a given liquid is either capable or incapable of destroying the bulk of them, and that intermediate interactions are rare.

If the hypothesis is correct that swelling observed on immersion of dry fibres is primarily due to their tendency to recover their original shape as interfibrillar or interlamellar cohesion is reduced by the liquid interaction, then swelling should be accompanied by increases in accessibility, surface areas, sorptive capacity, etc. These properties can be at least qualitatively demonstrated by experimental data (Parts II and IV of this Thesis).

D. ABSTRACT

Swelling of native cotton cellulose has been determined with a new dilatometer. Despite some uncertainties connected with the measurement of pellets of fibres, the results are reproducible and provide useful information regarding cellulose-liquid interactions and the fibre structure.

Strong H-bonding ability and lack of steric hindrances (small molecular size, polyfunctional character) contribute strongly to the effectiveness of liquids as swelling agents. Polyfunctional compounds swell cellulose more than monofunctional compounds of comparable size. An apparent maximum swelling of about 100-110% in hydroxylic liquids is probably imposed by structural restraints. Certain nitrogenous compounds swell cellulose more than hydroxylic compounds but the relative effectiveness within the former group has not been investigated.

None of the liquid parameters shows a strong correlation with volumetric swelling though some relationships are seen within the same homologous series or class of compounds.

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PART IV

A NOTE ON SOLVENT-SOLUTE COMPETITION FOR SORPTION SITES ON CELLULOSE

A. INTRODUCTION

The extent of sorption of a polymer from solution on a sorbent is strongly affected by the solvent used - not only because of the interaction of the solvent with the solute but because its interaction with the substrate can also be important.

Solvent-solute interactions in polymer systems have been extensively investigated and a large literature exists. The Flory-Huggins parameter is a measure of this interaction in polymer solutions and is theoretically related to the configuration of the polymer molecule in solution (1-4). A more empirical criterion of probable solvent-solute interaction is based on the cohesive energy densities (c.e.d.'s) of the two components. A 'good' solvent is one in which the Huggins parameter is less than 0.5 or in which the c.e.d.'s of the solvent and polymer are closely similar (4-6). A 'good' solvent differs from a 'poor' solvent in that the intrinsic viscosity is high in the former and the tendency of the polymer to sorb on exposed substrates is minimum. This relationship of c.e.d. differences, intrinsic viscosity and extent of sorption has been demonstrated experimentally by Kangle and Pacsu (7) and Ellerstein and Ullman (8).

A previous investigation (9) of the role of the solvent in the sorption of poly(vinyl acetate) on cellulose from solution had emphasized the role of solvent-sorbent interactions. The results suggested that in this system competition between solvent and polymer for sorption sites was more important than solvent-solute interactions.

This investigation was intended to test the earlier hypothesis by extending the range of solvents used and to obtain further information concerning cellulose-liquid interactions to be related to other collateral investigations (10-12). Both pure solvents and binary mixtures are included in this study. The substrate, as in the earlier investigations, was water-swollen cellulose solvent exchanged to the appropriate solvent. It was assumed that the extent of accessible cellulose surface was the same in all systems.

B. EXPERIMENTAL

The procedure followed was essentially the same as described by Luce (13) and Luce and Robertson (9).

(a) MATERIALS:

(i) Filter pulp: Acid washed, dry dispersed cotton pulp manufactured by Carl Schleicher and Schuell Company having a 98.5% alpha cellulose content was dried at 105°C for one hour, swollen in water for 24 hours and then solvent exchanged to an appropriate solvent directly or through acetone if necessary. The procedure is described in detail by Luce and Robertson.

(ii) Poly(vinyl acetate): Grade Gelva V-25 of commercial poly(vinyl acetate) supplied by Canadian Resins and Chemicals Ltd., with average (osmotic pressure) molecular weight of 100,000 was dissolved in dry benzene, filtered through coarse fritted glass funnel and freeze-dried.

(iii) Reagents: All reagents were Fisher 'reagent grade' meeting A.C.S. specifications. Benzene dried over sodium wire and redistilled was stored over sodium wire. Fresh quantities were filtered as needed. All other reagents were distilled through a 45 cm. long column packed with 1/8 inch glass helices.

(b) MEASUREMENT OF EXTENT OF SORPTION:

The number of milligrams of poly(vinyl acetate) sorbed by 1 gram (dry weight basis) of cellulose, water-swollen and solvent exchanged to the test liquid at an equilibrium concentration of 4 gm./litre of poly(vinyl acetate) in solution in the test liquid for 48 hours, is termed

'extent of sorption'. These values were obtained by interpolating the experimental isotherms. Although sorption continued at a slow rate after 48 hours, for convenience, concentration after this interval is termed equilibrium concentration.

The amount of the polymer sorbed was determined from difference in weights of the polymer in solution before and after the sorption period.

To about 0.5 gm. of the sorbent suspended in the test liquid in tared centrifuge tubes was added 5 ml. of concentrated polymer solution. The amount of the polymer so added was determined by pipetting exactly the same volume of the concentrated polymer solution into a tared aluminum dish, evaporating and drying in vacuo at 55° and reweighing.

To the centrifuge tubes, in the case of sorption from binary mixtures, were added varying amounts of the second liquid and the volume of the solution made up to 25 ml. with the first liquid. In the case of sorption from pure solvents, volume was made up with the test liquid only. The tubes were thermostated at $25 \pm 0.02^\circ\text{C}$ for 48 hours and weighed. The final concentration of the supernatant liquid was determined by finding its density by means of a pycnometer, the contents of which were washed into a tared aluminum dish, evaporated, dried and weighed. The remainder of the solvent in the centrifuge tube was evaporated and the tube and its contents reweighed. The data are sufficient to calculate polymer sorption and equilibrium concentration.

C. RESULTS AND DISCUSSION

Table IV-1 summarizes the sorption data for pure solvents. Several of these values are taken from previous work (9).

The data are plotted in Fig. IV-1 where the abscissae are the c.e.d.'s of the solvents as calculated from their molar volumes, boiling points and application of the Hildebrand rule (14). The selected solvents include several having no H-bonding properties, some having proton acceptor properties only and one -- methanol -- having both acceptor and donor functions.

The H-bonding properties of the solvents employed may be assessed in a variety of ways (15). In the present case the proton acceptor properties are of chief interest and these may be gauged by infrared methods in which compounds containing hydroxyl groups are introduced in the test liquids in dilute solutions and the shift or broadening of the hydroxyl stretching frequency is observed. It has been claimed that the degree of the shift measures the H-bonding potential (16-17) although others (18) have sounded a note of caution. A survey of the available data (15-17, 19) suggests that, in consensus, the H-bonding capability is in the order:

water > methanol > dioxane > acetone > methyl ethyl ketone >
ethyl acetate > acetonitrile > nitromethane > nitrobenzene >
1,2- dichloroethane > benzene > carbon tetrachloride.

TABLE IV-1

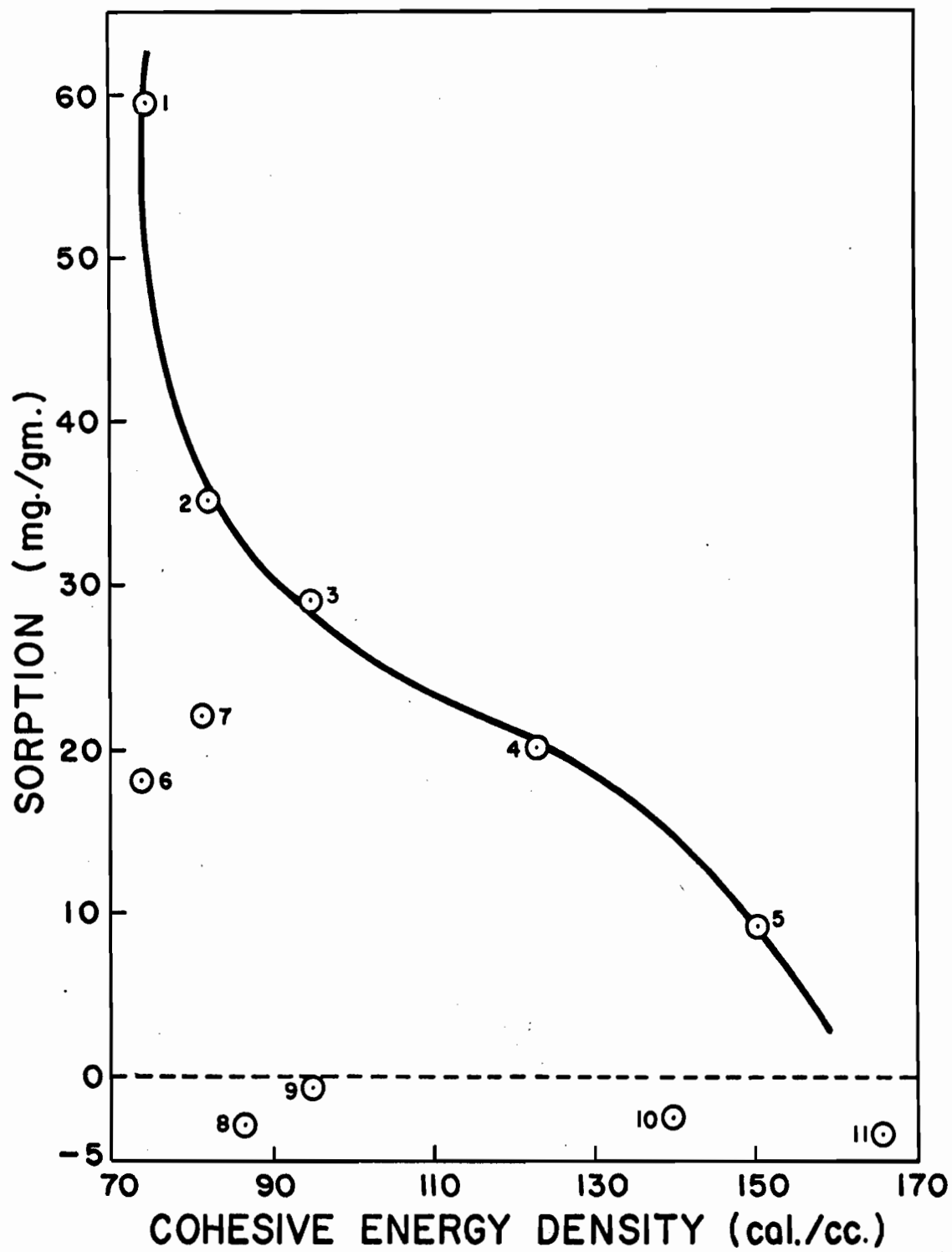
Sorption of Poly(vinyl acetate) by Cellulose Swollen in Water
and Solvent Exchanged to Different Solvents

Solvent	Cohesive Energy Density* (cal/cc.)	Sorption (mg/gm.)
1. Carbon tetrachloride	74.1	59.4
2. Benzene	81.9	35.0
3. 1,2-Dichloroethane	94.4	29.0
4. Nitrobenzene	122.7	20.0
5. Nitromethane	150.0	9.0
6. Ethyl acetate	73.2	18.0
7. Methyl ethyl ketone	81.0	22.0
8. Acetone	86.4	- 3.0
9. p-Dioxane	94.9	- 0.8
10. Acetonitrile	139.8	- 2.5
11. Methanol	165.8	- 3.6

* Calculated from the boiling points and densities of liquids at 25°C. See Ref. No. 21 and Appendix B.

FIGURE IV-1

SORPTION OF POLY(VINYL ACETATE) FROM PURE SOLVENTS



It is to be seen that the points representing solvents with little or no H-bonding ability may be joined in a smooth curve showing a decrease in sorption as the c.e.d. of the solvent increases. The H-bonding solvents permit less polymer to be sorbed and in some instances indicate a negative sorption. The negative value is interpreted in terms of preferential sorption of the solvent on the available sites to the more or less complete exclusion of the polymer.

The competition for the sorption sites on the cellulose is further demonstrated by experiments in which binary mixtures were used. Table IV-2 and Fig. IV-2 summarize some of the experiments. In each instance benzene was one component to which the second component was admixed as described above. The added component reduced the polymer sorbed, the effect being generally greater, the greater the H-bonding capacity of the additive.

The experimental results appear to be consistent with the following picture of the solvent - poly(vinyl acetate) - cellulose system. The hydroxyl groups on cellulose are the sorption sites (9) and are capable of participating in H-bonding either as donors or acceptors (15). Thus poly(vinyl acetate) may be sorbed on accessible hydroxyls because of the acceptor properties of the ester groups (15). Another ester -- ethyl acetate -- can compete for the available sites when it is the solvent while other solvents which are stronger proton acceptors compete more successfully.

TABLE IV-2

Sorption of Poly(vinyl acetate) from Binary Mixtures by Cellulose
Swollen in Water and Solvent Exchanged to Various Solvents.

	(1)	(2)	(3)		(4)
	Water Swollen Cellulose Solvent Exchanged to	Second Solvent Added	Composition of Binary Mixture (Mole Per cent)		Sorption ($\frac{\text{mg. PVAC}}{\text{gm. cellulose}}$)
	(a)	(b)	(a)	(b)	
1.	Benzene	Acetonitrile	100.0	0.0	35.0
			92.9	7.1	36.4
			79.3	20.7	35.0
			68.7	31.3	34.7
			53.7	46.3	21.9
			47.6	52.4	14.0
2.	Benzene	Nitromethane	100.0	0.0	35.0
			95.0	5.0	32.0
			85.6	14.4	31.4
			74.8	25.2	29.1
			50.4	49.6	14.1
3.	Benzene	Acetone	100.0	0.0	35.0
			82.8	17.2	32.5
			71.8	28.2	30.0
			64.4	35.6	20.0
			51.4	48.6	3.0

Cont'd.

TABLE IV-2 (Cont'd.)

	(1)	(2)	(3)		(4)
4.	Benzene	p-Dioxane	100.0	0.0	35.0
			87.5	12.5	21.9
			76.6	23.4	21.9
			54.6	45.4	2.6
5.	Benzene	Methanol	100.0	0.0	35.0
			91.3	8.7	6.7
			74.8	25.2	4.1
			53.7	46.3	1.4
			32.2	67.8	-1.2
6.	Benzene	Water	100.0	0.0	35.0
			99.8	0.2	33.1
			99.6	0.4	26.2
			99.1	0.9	17.0
			98.2	1.8	16.0
			97.3	2.7	8.1
7.	Methanol	Benzene	100.0	0.0	- 4.7
			98.0	2.0	- 6.1
			94.0	6.0	- 5.8
			84.0	16.0	- 6.9
			69.0	31.0	- 4.1

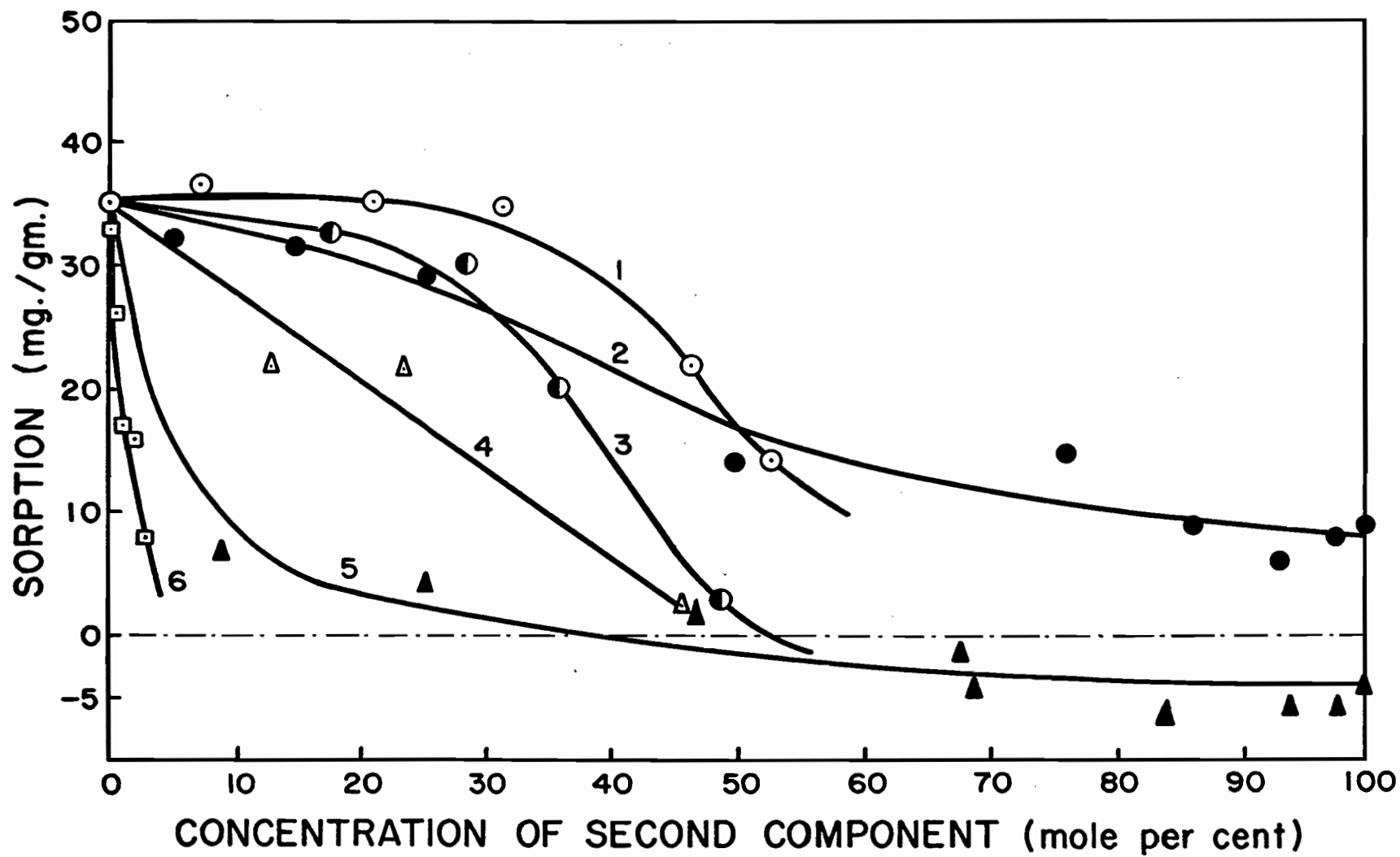
Cont'd.

TABLE IV-2 (Cont'd.)

(1)		(2)	(3)		(4)
8.	Nitromethane	Benzene	100.0	0.0	9.0
			97.4	2.6	8.0
			92.7	7.3	5.8
			85.9	14.1	8.9
			76.0	24.0	14.9

FIGURE IV-2SORPTION OF POLY(VINYL ACETATE) FROM BINARY MIXTURES

In each case benzene is one of the components. Sorption is plotted as a function of the mole per cent of the second component: (1), acetonitrile; (2), nitromethane; (3), acetone; (4), dioxane; (5), methanol and (6), water.



When the solvent has little or no H-bonding ability the competition it offers for sorption sites is greater the higher the c.e.d. If the c.e.d. of cellulose is assumed to be high (20), the observed behaviour may be interpreted in the manner suggested by Gee (4) for swelling of polymers with liquids - the interaction of polymer and solvent is greater the closer are their c.e.d.'s.

The c.e.d. of poly(vinyl acetate) is reported to be 88.4 (5). The prediction that sorption is least when the c.e.d. of the solvent approaches that of the solute and is greater as the difference increases, is not fulfilled in the present results.

D. ABSTRACT

Sorption of poly(vinyl acetate) on preswollen and solvent exchanged cellulose from solutions in pure solvents and their binary mixtures has been studied. It was found that sorption of the polymer is explainable in terms of the cohesive energy density of the non H-bonding liquids and in terms of H-bonding ability for others. With the increase in cohesive energy density or in the H-bonding ability of the solvent, sorption decreases by varying degrees.

A solvent-solute competition is set up for sorption sites on cellulose. No minimum in sorption versus cohesive energy density isotherms was detected in the region where cohesive energy densities of the solvent and the solute were similar.

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PART V

CELLULOSE-LIQUID INTERACTIONS

A. INTRODUCTION

When a dried native cellulose fibre is immersed in water, water penetrates the fibre and the physical and mechanical properties of the fibre are altered. The fibre swells, particularly in diameter, its tensile strength increases (1-3) and it becomes more deformable (4-7). The internal surface areas increase (7-10) resulting in greater accessibility to sorbents or reagents (10-12).

The immersion of fibres in non-aqueous liquids may produce similar changes, but in varying degrees. In a non-polar liquid the interaction is small but measurable. With increasingly polar liquids the interaction is greater and the changes in properties of the fibres may approach those observed with water. Some liquids swell fibres considerably more than water does; in a few the fibres are dissolved.

This thesis examines the behaviour of cellulose fibre in non-aqueous liquids which swell cellulose fibres but do not alter their crystalline structure. Three experimental techniques have been used in this investigation to provide new information on cellulose-liquid interactions. These are described briefly below and in detail elsewhere (10,13,14). While these new data will be emphasized, other experimental results from the literature have been drawn upon to obtain a more complete picture.

The current experimental techniques referred to are:

- (i) the dilatometric measurement of swelling of cellulose pellets in various liquids by mercury displacement (13);

- (ii) the measurement of the accessibility of fibres swollen in various liquids by the Purves' (12) thallation-methylation method (10,15) and
- (iii) the comparison of the attractive forces between various liquids and cellulose by measuring the extent of sorption of a polymer from the liquid onto expanded cellulose in competition with the solvent (11,14).

These data provide some empirical information about cellulose-liquid interactions. To interpret the observations it is necessary to consider the probable structure of the cellulose fibre, the mechanism of fibre swelling on immersion and the possible interactions between cellulose and various liquids. These topics are treated in the next two subsections. The experimental results are then introduced and discussed and an attempt is made to arrive at a comprehensive description of cellulose-liquid interactions.

(a) STRUCTURE AND SWELLING OF CELLULOSE FIBRES:

The microfibrillar structure of cellulose fibres has been demonstrated and described by several workers (16-19). The arrangement and orientation of the fibrils in the cell wall are reasonably well understood. The submicroscopic structure is however, still a matter of conjecture. The size of the elementary microfibril, its degree of crystallinity and the manner of its association into fibrils or lamellae are not agreed upon. Despite continuing disagreement and conflicting observations, there appears to be a growing weight of evidence that the elementary

microfibril has a characteristic dimension of $\sim 35 \text{ \AA}$ (20-22), and that the microfibrils are associated into lamellae or layers in the cell wall (16-19).

It is suggested that the microfibrillar structure confers on the dry native cellulose fibre an appreciable porosity. This view is supported by some experimental evidence. Direct weighing and microscopic measurements have led to estimates of $\sim 35\%$ porosity in cotton (23), $\sim 10.5\%$ in ramie (24,25) and $\sim 55\%$ in wood fibres (26). The measurement of non-freezing benzene in immersed cotton indicates a porosity of $\sim 30\%$ in the dry fibre (27). The flexibility and folding endurance of cotton fibre is indirect mechanical evidence of porosity or lack of adhesion between the highly crystalline structural elements of which the fibre is made. Contrary evidence is provided by nitrogen sorption experiments at -195°C . which indicate that the surface accessible to gaseous nitrogen is little more than the superficial external area (7,9,28).

While incontrovertible evidence on this disputed point is not presented in this thesis, the results of experiments are more easily interpreted if a substantial porosity in the unswollen fibre is assumed.

The fibrillar structure which has been discussed and the experimental results which follow pertain primarily to cotton fibres. It is, however, assumed that there is sufficient similarity of structure in all native cellulose fibres that experimental data based on ramie or high alpha wood pulp or other cellulose fibres may be introduced as pertinent information.

A significant aspect of the fibre structure is the existence of hydrogen bonding which is assumed to contribute to the forces involved in the cellulose crystal (29-31), to the cohesion of the microfibrils to form larger structural unit (17,31,32) and to the interfibre bonding which occurs in paper (33-36). Some of the cellulose-cellulose bonding in fibres and in paper can probably be ascribed to less specific van der Waals forces (36).

The suggested microfibrillar structure of cellulose and the crystalline nature of the microfibrils raise the question of mechanism of swelling of cellulose fibre on immersion. The assumed lack of mixing at the molecular level precludes swelling which is primarily caused by an increase in entropy as in the case of swelling of rubber in benzene (37). The same lack of molecular mixing also differentiates the cellulose water system from other swelling systems involving polar polymers and polar liquids. The swelling of polar polymers in polar liquids (nitrocellulose in acetone) is presumed to occur in two stages (38,39). In the first stage the liquid molecules are sorbed on the polar surface with the evolution of heat and decrease in entropy due to molecular orientation. Multilayer formation follows but with reduced heat and entropy effects. The second stage is similar to the hydrocarbon-benzene system in that the driving force is the entropy of mixing and ultimately the polymer dissolves unless there is effective or actual cross-linking.

The crystallinity of cellulose readily explains the lack of its solubility in water but at the same time it is an obstacle to explaining the swelling which does occur. Large dimensional changes occur without

change in crystallinity and are presumably due to increased spacing between fibrils or fibril aggregates rather than between chain molecules.

Presumably the first stage of swelling involves the sorptive orientation of liquid molecules on the surfaces of cellulose through H-bond formation. Also involved in the first stage, and becoming predominant in the second, is the decrease in mechanical free energy. The mechanical free energy represents structural stresses which were built up during the shrinkage and drying of the fibre from its original wet and swollen state.

Lloyd and Alfrey (40) have considered a somewhat analogous system - a system in which a cross-linked polymer swells from a volume which is less than the volume at which cross-linking occurred. The free energy of the shrunken system assists in the swelling of the cross-linked structure towards its nascent volume. The role of mechanical forces on internal stresses in promoting swelling may also be demonstrated by assigning appropriately large values to q_0 , the reference degree of swelling in the Hermans' equation (41,42).

The picture that emerges is that the native cellulose fibre is laid down in the wet and expanded state. On drying it collapses and contorts due to large surface tension forces. The collapsed and strained configuration is fixed by hydrogen bonds or van der Waals forces between the adjacent structural elements. On re-immersion, swelling occurs until

$$\frac{\delta \Delta F_m}{\delta V} = - \frac{\delta \Delta F_i}{\delta V} \quad (1)$$

where ΔF_m represents the (mechanical) free energy in the system due to dried-in stresses, and ΔF_i , the free energy associated with the cellulose-liquid interaction.

The ΔF_i involves the energetics of
 liquid-liquid + cellulose-cellulose \rightleftharpoons 2 liquid-cellulose (2)
 and thus involves the association energies and entropy effects of the three molecular combinations.

The process represented by equation 2 will proceed to the right as long as ΔF_i decreases even in the absence of internal stresses. The mechanical stresses when superposed, can be visualized as making the process irreversible inasmuch as whenever an appropriately situated cellulose-cellulose bond is broken, the structural elements move apart and the reverse action is suppressed.

The hypothesis that mechanical forces of uncertain magnitude play a role in fibre swelling removes the possibility of making any quantitative thermodynamic treatment of swelling.

The cellulose-liquid interactions which just have been discussed are designed to explain the gross swelling of the fibres. Significant interactions can, however, occur without structural swelling. Sorption and competition for sorption sites on existing surfaces can have important consequences. The principles governing this behaviour are those of surface chemistry and the concept of internal stresses needs not be invoked when the interactions are weak or the molecules are too large to penetrate effectively the substrate.

(b) THE PROPERTIES OF THE INTERACTING LIQUIDS:

The interaction of the test liquids with cellulose ranges from sorption through penetration to swelling. The properties of the liquids which determine the extent of interaction are assumed to include molecular shape and size as well as interaction forces. While sorption on the superficial surface of the fibres or spreading (wetting) are primarily a matter of energetics, the more substantial interaction leading to penetration and swelling involves steric effects. Liquids which are to swell cellulose must be able to approach the bonding sites, effect a reduction in the cellulose-cellulose bond and also to suppress rebonding by association with the freed bonding sites.

Equation 2 suggests that the process must be regarded in two ways. Firstly, the cohesive or molecular attractive forces between the liquid molecules will oppose cellulose-liquid interaction and secondly molecular attractive forces between the liquid and cellulose will force the equilibrium to the right.

Both aspects of the liquids-their cohesion and interaction potential-are related to several factors which are not independent. All these factors in turn depend upon the molecular constitution, shape and H-bonding ability.

Apparently it is possible to speak only qualitatively of the various factors because of the strong influence of steric effects which cannot be expressed numerically and which may influence liquid cohesion and cellulose-liquid interaction differently.

Strong interaction with cellulose appears to be related primarily to H-bonding properties of the liquid (particularly when a proton acceptor and donor), and to the size and steric effects which determine the ease of H-bond formation.

A measure of H-bonding properties is provided by infrared methods developed by Gordy (43). In this method the proton acceptor properties of a liquid may be compared by measuring the shift of the -OD stretching band when deuterated methanol is mixed with the test liquid. A similar technique for measuring proton donor properties in a test liquid can be based upon the change of a carbonyl stretching band in admixed diethyl ketone. Despite reservations about the quantitative significance of these measurements (44) they can at least provide an indication of low, medium or high hydrogen bonding activity.

Weak interactions with cellulose are still possible and can be measured or assessed though no H-bonding functions exist. Such interactions are ascribed to dispersion and dipole interaction forces.

The dispersion and dipole interaction forces due to the liquid can be estimated by the cohesive energy density (c.e.d.) of the liquid itself (45). The total c.e.d. may be conveniently approximated by Hildebrand (46) rule:

$$\frac{E^V}{V} = \delta^2 + w^2 \quad (3)$$

where E^V is the internal energy of vaporization; V , the molar volume; δ^2 , the energy (cal/cc.) due to dispersion forces and w^2 , the contributions (cal/cc.) by the dipole interactions.

The dipole interaction energy w^2 can be calculated by two alternative equations due to Bottcher (47). However, the equations are valid and give identical results for non-associated liquids only. Since the equivalence of the two equations rests upon the validity of Onsager equation, disagreement reflects failure of the Onsager equation (48) and indicates association in the liquids. Criteria of association which are basically equivalent have been suggested by Kumler (49) and Pauling (50).

Thus, on the basis of the Bottcher and Onsager equations it is possible to classify liquids as (i) non-polar, (ii) polar unassociated and (iii) polar associated; and on the basis infrared experiments by Gordy (43) and others, liquids can be classified as strong, medium or weak proton acceptors, donors or both.

The forces due to dispersion effects, dipoles or H-bonding are significant in two ways. Interactions between the liquid molecules increase its c.e.d. and thus oppose cellulose-liquid interactions (equation 2); but at the same time they represent the forces which are available to promote cellulose-liquid interaction.

Whether the interaction is strong or weak will depend upon how the internal stresses affect the energy of interfibre bonds, on

the balance of forces discussed above and on the steric factors which govern whether the liquid molecules can make an effective approach to the reactive sites on cellulose. The steric factors depend on the fine structure of the fibre and on the size, shape of the molecule and the orientation of its functional group or groups. It might be predicted that small simple molecules would be most effective and that the effectiveness of larger molecules would be increased if they contained more than one functional group.

Molar volume has been taken as a measure of molecular size as a matter of convenience.

B. EXPERIMENTAL RESULTS AND THEIR SIGNIFICANCE

Several aspects of cellulose-liquid interactions may be described: adsorption, wetting or spreading, displacement of one liquid by another, penetration or swelling, etc.

These may be frequently observed or measured directly (contact angle (51,52), extent of sorption), or may be investigated indirectly by heat effects (heats of wetting), optical (birefringence (24)), electrical (dielectrical dispersion (53)) or mechanical (fibre strength (33-35)) properties.

It is proposed to consider several different kinds of evidence of cellulose-liquid interactions and to attempt a synthesis of these observations into a general framework.

(a) HEATS OF SORPTION AND WETTING:

Evidence of the interaction of water with cellulose is provided by the integral heat of wetting which amounts to 10-12 cal/gm. cellulose for native fibres and 20-22 for regenerated cellulose (54,55). Since differential heat of sorption on dry cellulose (about 294 cal/gm water) is independent of the nature of cellulose, the difference in integral heats is considered to indicate the relative areas available for water sorption in the two forms of cellulose. This 2:1 ratio has received considerable confirmation (54-57).

The interactions of a few other liquids have been measured and data exist on the extent of sorption and the integral heats of wetting (Table V-1), but data on the differential heats of sorption are not available.

A quantitative heat balance has not been determined for these cellulose-liquid interactions. In the simplest assumption, if the interactions are wholly due to the making and breaking of H-bonds, it is not possible to specify the number broken or formed in removing a molecule of water from bulk liquid to a sorption site on cellulose. It has been suggested (58) for example, that one water molecule can be sorbed by the formation of two hydrogen bonds with two cellulose hydroxyl groups. Presumably this would be possible only for a limited number of water molecules because of the exacting spatial requirements. H-bonds can vary greatly in strength with the distance between active centres and the stresses applied to the bond. Thus the evaluation of the strength of the intra-cellulose bonds on the surfaces of dry fibres, is uncertain.

Despite the uncertainties concerning the mechanisms involved, the heats of wetting should provide a numerical indication and comparison of liquid interaction with cellulose. There are, however, large discrepancies among the experimental values reported in the literature which largely preclude their correlation with present studies. It has also been noted that inert hydrocarbon liquids show exothermic heats of wetting with cellulose (59-61) which cannot be attributed to bond interactions. The source of this heat evolution is not clear but may be analogous to ethyl cellulose-hydrocarbon systems described by Barrer et al (62).

TABLE V-1

Integral Heats of Wetting of Cotton Cellulose in Various Liquids

Liquid	Heat of Wetting (cal/gm)	(*) Extent of Sorption (mg/gm)	References to Heats of Wetting
1. Water	11.6 11.0	210	59 60,64
2. Formic acid	9.4	-	59
3. Formamide	9.0	-	59
4. Acetic acid	7.4	190	59
5. Methanol	7.3 7.1	112	59 63
6. Ethanol	6.6 0.7	86-90	59 63
7. 2-Propanol	5.2 0.6 0.0	50	59 63 60
8. 1-Butanol	3.5 0.0	15	65 60
9. Pentane	3.0	-	59
10. Acetone	2.8	25	59
11. Hexane	1.6	-	60
12. 1-Pentanol	1.3	-	65
13. Ethylene glycol	0.0	-	59,60
14. Glycerol	0.0	-	59

(*) Reference No. 66.

(b) COMPETITIVE SORPTION:

Evidence of the interaction of cellulose with liquids of low H-bonding capacity is provided by solvent-solute competition for sorption sites (11,14). In these experiments water-swollen fibres were solvent exchanged to a variety of solvents from which the sorption of poly(vinyl acetate) was measured under standard conditions of sorption time, equilibrium polymer concentration and sample size. The extent of sorption is assumed to reflect inversely the successful competition of the solvent with the polymer for the sorption sites. Solvents which can participate in H-bonding may prevent the sorption of poly(vinyl acetate) completely (Figs. IV-1).

The same technique can be extended to investigate stronger interactions by using binary solvents composed of a relatively non-interacting liquid (benzene) and varying amounts of a more active test liquid. The competition of this latter component with polymer for sorption sites may then be assessed (Fig. IV-2).

(c) PYCNOMETRY AND LIQUID PENETRATION:

Cellulose is wetted (contact angle less than 90°) by most liquids when immersed and the liquids penetrate the porous cell wall. The degree of penetration is revealed by the pycnometric densities of cellulose fibres. Comparison of several immersion liquids shows results which are significant in relation to fibre structure and to cellulose-liquid interactions.

The pycnometric specific volume of cotton cellulose in various liquids is given in Table II-4. The specific volume calculated from X-ray data is 0.6321 (67). The greater penetration of the liquid is indicated by the lower cellulose specific volume and may be related either to molecular volume of the penetrant or its interaction with cellulose or both.

When water swollen fibres are solvent exchanged to the pycnometric liquid, the fibre, in an expanded state admits more liquid but the differences in specific volumes in the various inactive liquids still persist.

(d) DILATOMETRY:

The gross swelling of cellulose may be followed by microscopic or dilatometric techniques. Several investigators have measured the swelling of pellets (68,69) or pads (70) of cellulose of unit density. Mercury displacement dilatometry was used in this work with some experimental improvements such as evacuation of the sample before admitting the swelling liquid (13). Despite some reservations about the principle of the method which are described elsewhere several trends were observed which have significance in this study. The data are assembled in Table III-2.

The effects of molecular size, H-bonding ability and poly-functionality are readily seen. The swelling ability of homologues of increasing molecular size is demonstrated by the several series of alcohols in Table III-3, while the influence of introducing functional groups in a molecule are shown by Table III-4.

(e) BONDING STRENGTH IN PAPER:

If the hypothesis is correct that the fibre swelling is primarily due to reduction in bonding within the cell wall, then swelling is presumably accompanied by a decrease in the cellulose-cellulose bonds between the fibres. This decrease in interfibre bonding should be detectable by the measurement of mechanical properties of the fibres or structures formed from them. Since the mechanical properties of single fibres are difficult to measure because of sampling and manipulative problems, evidence of the decrease in bonding is obtained by measuring the strength properties of paper. Two measurements have been considered.

(i) The tensile strength of paper strips immersed in the test liquids is assumed to indicate the loss in interfibre cellulose-cellulose bonds (33-35). (ii) The elastic Young's modulus of immersed paper strips is assumed to measure the flexibility or decrease in intrafibre bonding of the fibres in the strip (34). These data are included in Table V-2.

(f) ACCESSIBILITY:

The separation of intrafibre surfaces with swelling also implies an increase in internal surface of the fibres. A method of measuring changes in accessibility is provided by the thallation-methylation technique in which fibres swollen in the test liquid are solvent exchanged to benzene and their accessibility measured by a technique already described (10). The results are presented in Tables II-1 and V-2 expressed as per cent methoxyl and also as per cent substitution.

The present investigation has extended earlier work by Luce and Robertson (11) in which the accessibility of cellulose fibres was measured by the sorption of poly(vinyl acetate) from benzene onto fibres swollen in the test liquid and solvent exchanged to benzene. The extent of sorption from the inert benzene was assumed to reflect the surface made accessible to the polymer molecules by the initial immersion liquid. Results from this and the previous investigation are included in Table V-2.

(g) BIREFRINGENCE:

Frey-Wyssling and Speich (24) have measured the birefringence of (ramie) cellulose fibres immersed in various liquids. On the basis of these results liquids appear to behave in one of the three different ways:

- (i) The birefringence is not affected by immersion in "lipophilic" liquids without H-bonding functions.
- (ii) The birefringence is increased with the increasing difference between the refractive indices of cellulose and the immersion liquid. The liquids are aldehydes, nitrogen bases and alcohols which do not swell cellulose. These liquids can adsorb on cellulose through H-bonding functions.
- (iii) The birefringence is reduced sharply in liquids that swell cellulose strongly such as glycerol and glycol.

TABLE V-2

Mechanical Properties of Paper Soaked in Various Liquids

(1) S/ No.	(2) Class	(3) Immersion Liquid	(4) Tensile Strength (Kg)	(5) Young's Modulus (10^{10} dyne/cm ²)	(6) Per Cent Methoxyl	(7) Sorptive Capacity (mg/gm)
1.	▲	Carbon tetrachloride	10.70	-	0.51	3.0
2.	▲	Benzene	10.60	1.390	0.49	3.9
3.	●	Toluene	10.20	-	0.67	-
4.	●	Isopropyl ether	10.00	-	1.05	-
5.	●	Nitrobenzene	9.44	-	0.73	7.0 ^(d)
6.	▲	1,2-Dichloroethane	9.20	-	0.88	0.8
7.	■	Aniline	9.19	-	1.57	4.6
8.	▲	Chloroform	9.14	-	0.71	-
9.	⊙	Vinyl acetate (monomer)	8.56	-	1.18	-
10.	⊙	Butyraldehyde	8.54	-	0.55	-
11.	●	3-Pentanone	8.48	-	0.77	-
12.	●	Benzaldehyde	8.48	-	0.69	0.8
13.	●	Benzyl alcohol	8.40	-	0.65	-
14.	⊙	Ethyl acetate	8.31	-	1.26	2.7
15.	⊙	p-Dioxane	8.31	1.400	1.57	-
16.	▲	1-Butanol	8.25	1.430	0.54	3.3
17.	⊙	Furfural	8.07	-	0.62	4.9
18.	⊙	Methyl ethyl ketone	7.75	-	0.55	-
19.	⊙	Butyrolactone	7.69	1.110	0.57	-
20.	⊙	Acetone	6.70	-	1.62	2.4

Cont'd.

TABLE V-2 (Cont'd.)

(1)	(2)	(3)	(4)	(5)	(6)	(7)
21.	⊙	Nitromethane	6.42	1.210	1.20	-
22.	⊙	Acetonitrile	6.41 ^(d)	-	0.81	-
23.	▲	1,4-Butanediol	6.36 ^(d)	-	1.46	-
24.	▲	Ethyl cellosolve	5.17	1.01	1.45	-
25.	■	Morpholine	4.35	0.780	1.36	28.5
26.	▲	Ethanol	4.05	0.740	2.95	5.7
27.	■	Pyridine	2.74	0.610	4.33 ^(c)	16.5 ^(d)
28.	▲	Diethylene glycol	2.39	0.550	6.76	-
29.	▲	Methanol	2.35	-	7.11	14.3
30.	▲	Acetic acid	1.72 ^(d)	-	4.57	-
31.	▲	Glycerol	1.56 ^(d)	-	7.49	18.7
32.	▲	Ethylene glycol	1.35	-	7.65	-
33.	■	Dimethyl formamide	1.13	0.208	7.93	48.7
34.	■	Formamide	0.78	0.127	7.74	36.1
35.	▲	Water	0.52	0.098	7.83	45.2
36.	⊗	None	12.0	-	-	-

(a) Ref. No. 34.

(c) Soaked for one week.

(b) Ref. No. 11.

(d) Ref. No. 71.

CLASSIFICATION: ▲ , Associated, H-bonding, both proton donor and acceptor;
 ⊙ , H-bonding, proton acceptors only;
 ▲ , "inert";
 ● , Molar volume > 100 c.c. and
 ■ , Intracellular swelling agents.

C. SIGNIFICANCE OF RESULTS IN RELATION TO FIBRE STRUCTURE

When dried fibres are immersed in various liquids their volume, accessibility and mechanical properties change in a way which may be explained by a consideration of the fibre structure that has been assumed. What has been proposed in fact is that changes in volume, accessibility and mechanical properties reflect different aspects of the same phenomenon - the reduction in the bonding of the microfibrils and fibril aggregates which constitute the cell wall. The concept of dried-in stresses causing the separation of the debonded elements and increasing the fibre volume has been introduced.

The accessibility of water-swollen fibres as measured by thallation has led to the calculation of an internal surface of $264 \text{ m}^2/\text{gm}$. This area is similar in magnitude to the maximum areas obtained by nitrogen, water, ammonia (10-Table III-3) or phenol (72) sorption. If it is assumed that the area measured is the surface of aggregates of microfibrils, it can be shown (10) that it suggests structural elements of the size observed in the electron micrographs - fibres $\sim 100 \text{ \AA}$ in diameter or lamellae $\sim 50 \text{ \AA}$ in thickness.

The surface area obtained by thallation accessibility measurements on unswollen fibres does not agree so well with other methods. The value of $16.5 \text{ m}^2/\text{gm}$. is higher by a factor of 13 than the corresponding nitrogen sorption values. On the other hand, if it is accepted that the porosity of collapsed fibres included 0.27 cc/gm . of pores below 282 \AA radius (27), then the internal surfaces must be much greater than $16.5 \text{ m}^2/\text{gm}$.

An explanation for discrepancies between nitrogen sorption and thallation results is that the fibre may swell in benzene to the extent that internal surfaces become accessible. Although throughout this work benzene has been assumed to be non-swelling, this assumption has not been rigorously proven. That the strength loss of immersed paper is appreciable and that the dilatometric swelling of compressed cellulose fibres in benzene, though slight is measurable, may be significant.

The situation is by no means clear. It is probable that there are large internal surfaces in the porous fibre wall which are associated with very fine capillaries of molecular dimensions. The accessibility of these surfaces is dependent on the size of the penetrating molecule as indicated by the pycnometric densities. In the case of thallation procedure the accessibility is probably limited by the space required for penetration by thallous ethylate molecule and to its appropriate orientation for reaction.

Many of the liquids which change the optical birefringence of fibres on immersion (24) are relatively non-swelling. However, it would appear that they must penetrate and occupy capillaries within the fibre to produce the observed effects (73).

The pycnometric specific volumes provide evidence of the existence and significance of very fine capillary spaces in the fibre wall. The difference in the volume inaccessible to benzene between dry and water swollen fibre is only about 2% of the volume of cellulose but the

accessibilities differ by a factor of 13. This suggests that the capillary dimensions are of the order of 10-20 Å°. It is noteworthy that penetration by various test liquids shows the same differences in swollen and unswollen fibres suggesting that in both conditions the factors influencing penetration are the same. This influence is assumed to be primarily of the relative size of the capillaries and liquid molecules.

However, evidence exists which shows that this assumption may not be completely valid. Studies of the analogous system of densities of cellulose nitrate measured in various liquids (74) appear to show increasing densities with polymer-liquid interaction forces rather than with molecular size.

D. SIGNIFICANCE OF THE RESULTS IN RELATION TO THE MECHANISM OF SWELLING

The measurement of strength of paper immersed in various liquids (33-35) demonstrates that all liquids reduce interfibre bonding (Table V-2) and that through suitable choice of immersion liquid the paper strength can be reduced to any value between the dry and water immersion strength.

Dilatometric swelling and thallation accessibility experiments bring out a significant aspect. The swelling tends to be either negligible or close to 100%; and accessibilities tend to group around 0.5-1.5% or around 7-8% methoxyl. Liquids producing intermediate effects have been sought but their number is limited.

This behaviour is reasonable when it is considered that the bond strength is measured in the immersed paper experiments by stressing the bond to failure. In the measurement of fibre swelling the cellulose cohesive bonds are probably weakened by all liquids but they do not fail unless the bond strength becomes less than the existing internal stresses. Thus, if fibres are placed in a series of liquids which increasingly reduce paper strength, swelling will only occur with those liquids which reduce the bond strength below a certain level. Swelling in the vicinity of 100% results when more active liquids are used.

The distinction between the swelling and non-swelling liquids is rather clearcut when based upon dilatometric swelling or accessibility measurements. However, as will be seen in the next section, there is a sufficient variation in behaviour within the two groups to permit the detection of significant differences in cellulose-liquid interactions.

Correlations among the various measurements of cellulose-liquid interactions have appeared throughout the thesis and serve to illustrate some of the points which have been discussed.

The correlation of thallation accessibility with swelling is depicted in Fig. II-1 and has been discussed elsewhere (10). It is noted that some substantial swelling is required before the accessibility is increased from the minimal levels. The accessibility of the unswollen fibres indicates the ready penetration by thallous ethylate of existing pores in the structure. It is therefore rather surprising that this accessibility does not increase directly with swelling as further pores are opened up or increased in size.

The accessibility as measured by polymer sorption shows a similar trend (11,14). The ratio of thallation accessibility to polymer accessibility is shown in Fig. V-1. As the accessibility increases the ratio falls indicating that as the capillaries are opened up beyond a certain amount further expansion does not affect the accessibility to thallous ethylate as much as it admits greater amounts of the polymer.

The correlations between accessibility and tensile strength of immersed paper (Fig. II-2) and between swelling and tensile strength (Fig. V-2) demonstrate the rather sharp distinction between strongly and weakly interacting liquids and the anomalous behaviour of the nitrogen bases as compared to the hydroxyl compounds.

FIGURE V-1

THE RATIO thallation accessibility AS A FUNCTION OF
polymer sorption
POLYMER SORPTION BY THE CELLULOSE SAMPLES

(The numbers refer to Table V-2.)

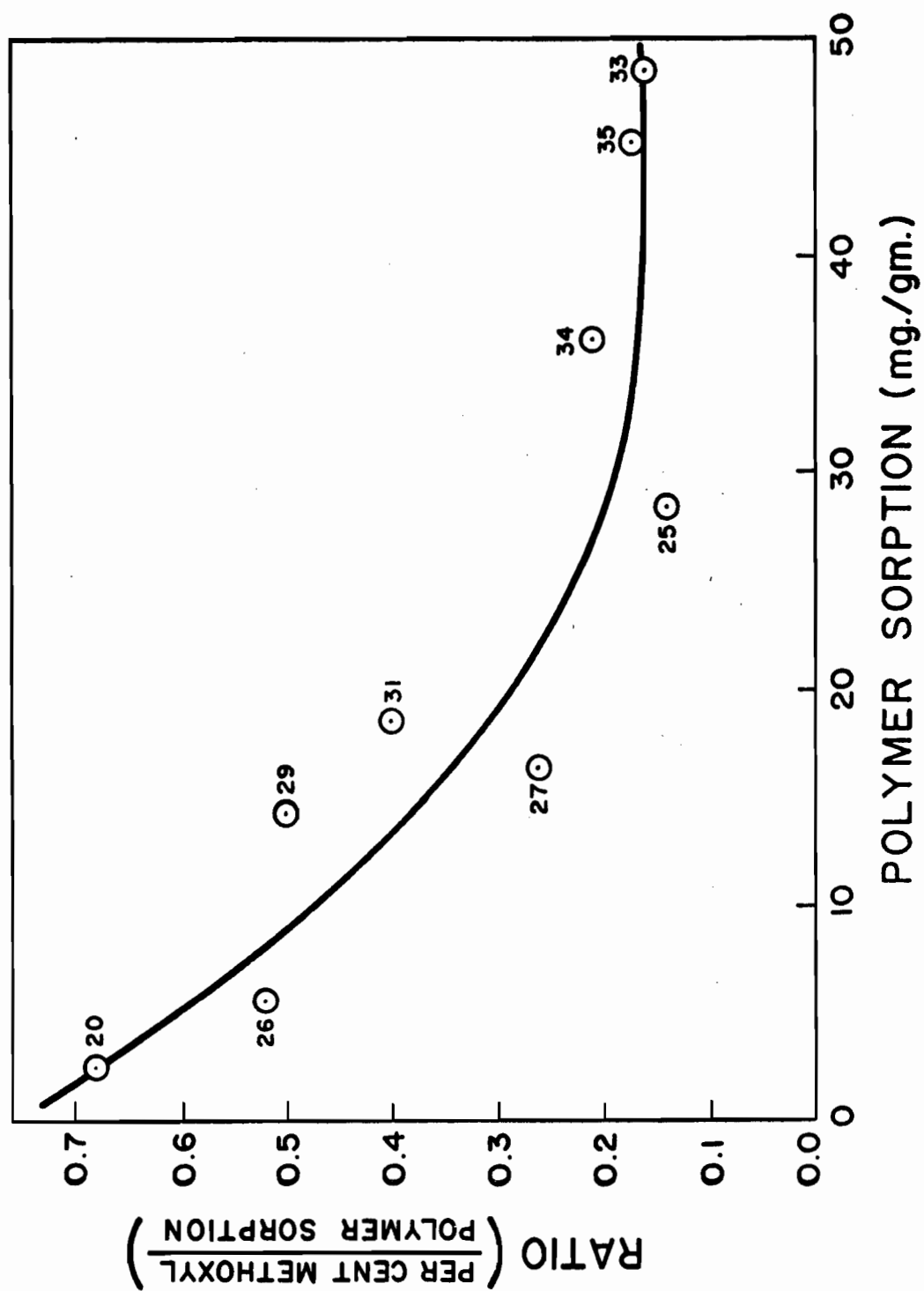
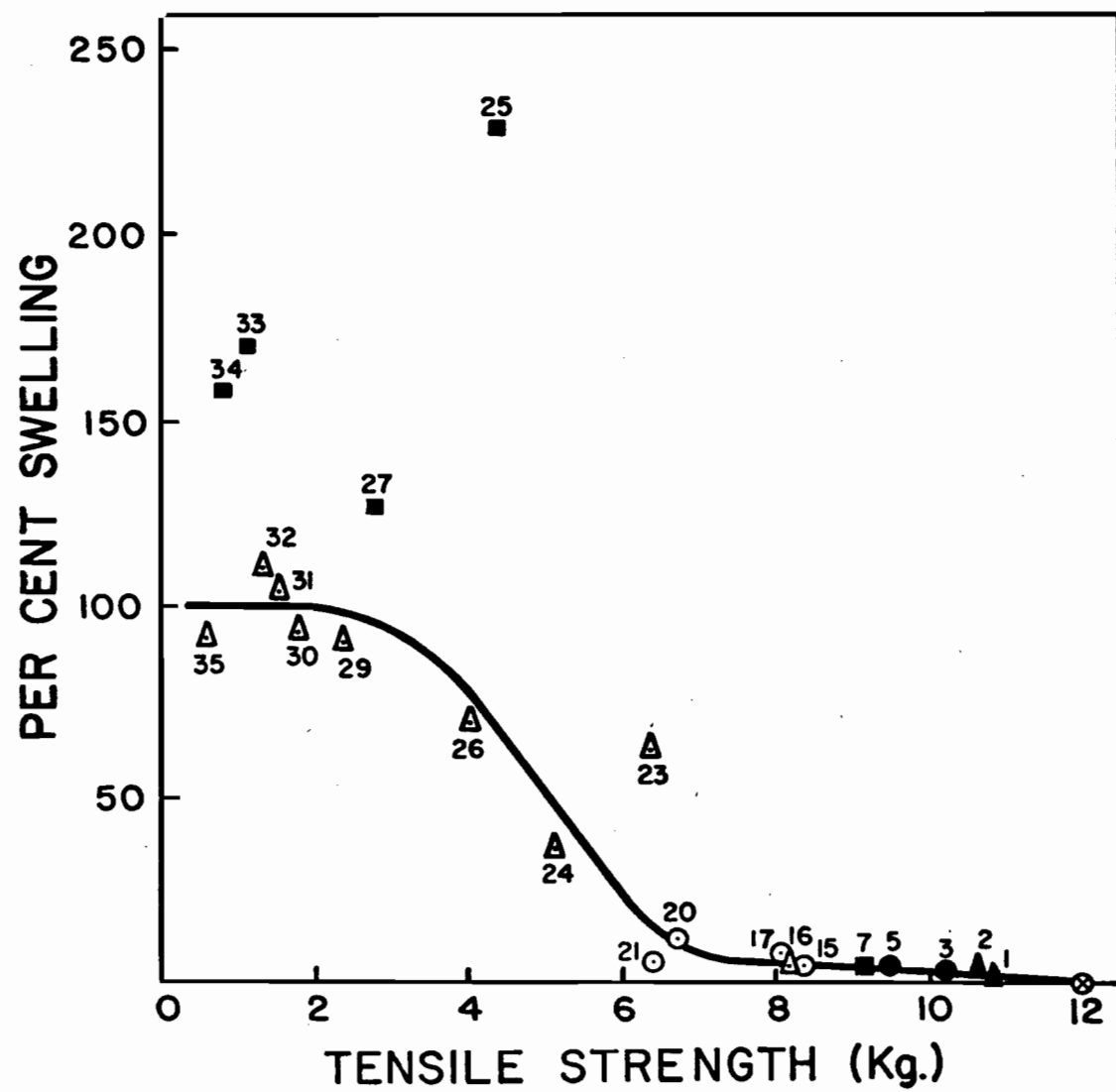


FIGURE V-2VOLUMETRIC SWELLING OF CELLULOSE AND TENSILE STRENGTH
OF PAPER STRIPS SOAKED IN VARIOUS LIQUIDSLEGEND:

- △ H-bonding, proton donor and acceptor, associated;
- ⊙ H-bonding, proton acceptor only;
- ▲ "inert";
- molar volume > 100 c.c. and
- intramicellar swelling liquids.

(The numbers refer to Table V-2.)



E. SIGNIFICANCE OF THE RESULTS IN RELATION TO THE ROLE OF THE

LIQUID IN CELLULOSE-LIQUID INTERACTIONS

In the experimental results which have been surveyed in this paper, the cellulose has been assumed to be uniform in properties while the interacting liquid was varied. Some of the liquid properties which might be expected to affect the extent of interaction have been discussed. It is now proposed to examine to what extent the liquid properties can be related to the extent of their interaction with cellulose.

It has been pointed out that measurement of swelling and of accessibility provides a reasonably clearcut distinction between swelling and non-swelling liquids. This classification is also provided by the measurement of mechanical properties of immersed paper (34). A sub-grouping of the non-swelling liquids appears to be well-defined in birefringence experiments (24). A group of "lipophilic" liquids does not affect the double refraction of cellulose (Fig. V-3). Another group, composed of higher alcohols, aldehydes and nitrogen bases shows sufficient interaction to increase the birefringence although they appear to have no swelling properties. Both these groups are sharply differentiated from swelling liquids which decrease the birefringence.

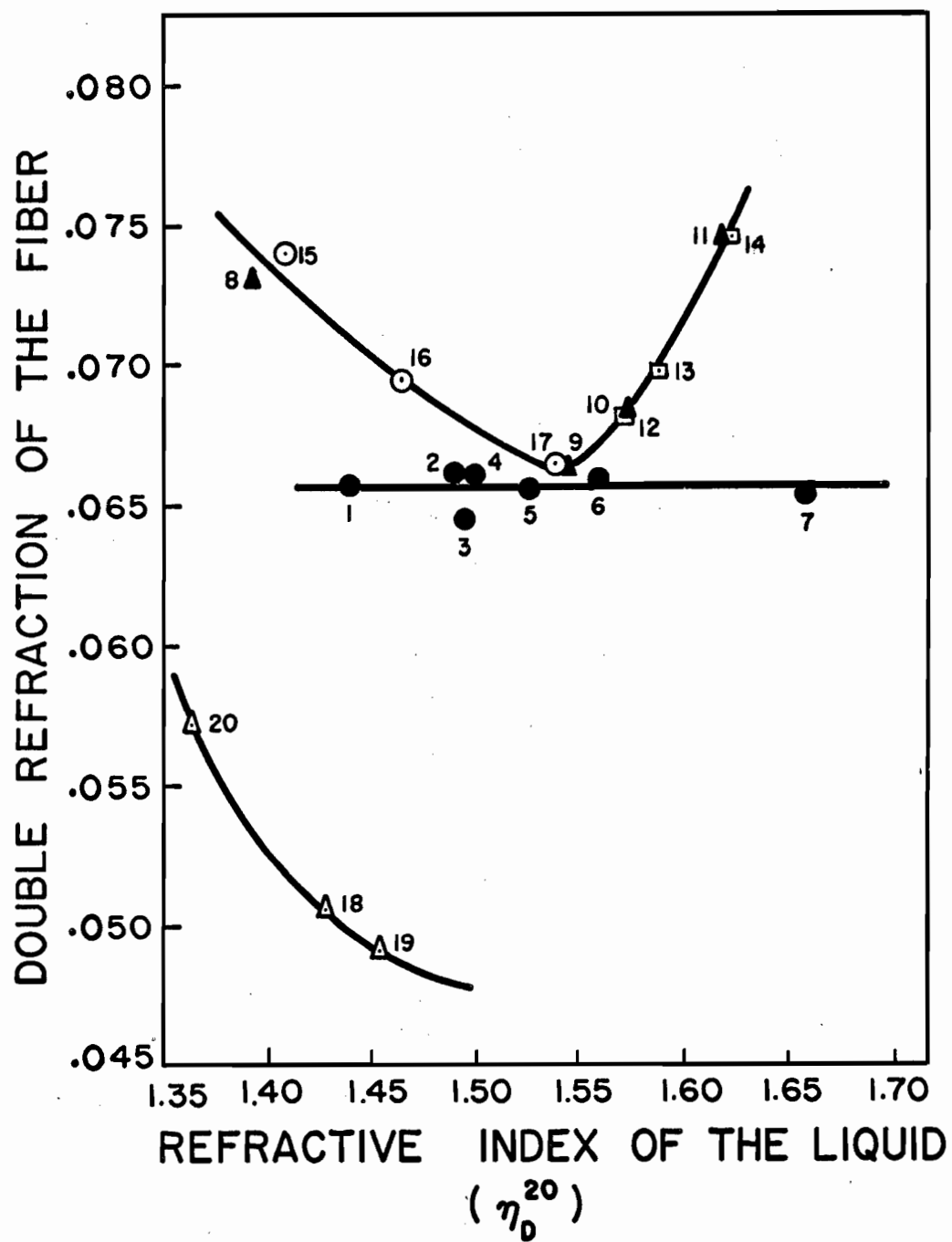
This classification into (i) inert liquids, (ii) interacting but non-swelling liquids and (iii) swelling liquids can be traced in the other reported experiments although the differentiation may not be so clearcut as in the birefringence experiments cited above.

FIGURE V-3

DOUBLE REFRACTION OF CELLULOSE FIBRES IN VARIOUS LIQUIDS

LEGEND:

- Lipophilic Compounds: (1), amyl bromide; (2), xylene;
(3), toluene; (4), benzene; (5), chlorobenzene;
(6) bromobenzene and (7), α bromonaphthalene.
- ▲ Aldehydes: (8), acetaldehyde; (9), benzaldehyde;
(10), salicylaldehyde and (11), cinnamaldehyde.
- ☐ Nitrogen bases: (12), methyl aniline; (13), aniline
and (14), quinoline.
- ⊙ Alcohols (non-swelling): (15), amyl alcohol;
(16), cyclohexanol and (17), benzyl alcohol.
- △ Alcohols (swelling): (18), glycol; (19), glycerol
and (20), ethanol.



In Table V-3 an attempt is made to assign the experimental liquids to their appropriate class and to draw some conclusions about cellulose-liquid interactions from considerations of the liquid parameters which are included in the Table.

The liquids appearing in Table V-3A show minimal interaction with cellulose by the experiments described and are labelled "inert" liquids. In addition their low level of molecular interaction is indicated by their low cohesion energy (c.e.d. ≤ 82) and by the lack of any configuration likely to confer appreciable H-bonding properties.

Table V-3B contains by far the largest group. The liquids do not swell cellulose appreciably by the selected criteria but interaction with cellulose is either experimentally demonstrated or there is a potential interaction because of H-bonding functions (hydroxyl groups, ether linkages, nitrogen atoms) or large dipole interactions (as indicated by Bottcher equations). Many of the liquids are associated as discussed in Appendix A.

Table V-3C includes liquids which have been found to swell cellulose significantly. They are subdivided into hydroxyl compounds and nitrogen bases.

The liquids which swell cellulose have (with the exception of benzyl amine) molar volumes less than 100 and (with the exception of piperidine or ethyl cellosolve) c.e.d. greater than 100.

These two criteria, molar volume and c.e.d., appear to supply a rough basis for classification. Most of the liquids in Table V-3B fail to meet at least one of the criteria. If all liquids with a molar volume greater than 100 or a c.e.d. less than 100 are excluded, we are left with

acetic anhydride	aniline
acetonitrile	diethyl oxalate
butyrolactone	propionic acid
furfural	
nitromethane	

These liquids appear to have sufficient intermolecular energy (based on c.e.d.) to interact with cellulose and a sufficiently small molecular size to attain the bonding sites. However, they do not swell fibres or show other evidence of strong interaction. In the first five liquids the c.e.d. exceeds 100 due to strong dipole contributions. Although this dipole interaction is large enough to cause molecular association in the liquid, it probably involves energy which cannot be recovered by interaction with cellulose as energy is recovered in the case of H-bonding (equation 2).

Aniline, diethyl oxalate and propionic acid remain anomalies in that they have all the recognized requirements to swell cellulose but they fail to do so.

Table V-3 thus provides evidence that the significant factor in promoting the gross swelling of cellulose is small molar volume and large intermolecular forces when these are derived from H-bonding and not from non-specific interactions.

However, the broad general classification should not obscure the fact that significant and more detailed relationships may be shown within these groups.

Several points can be illustrated by considering first the behaviour of hydroxylic compounds.

Water and alcohols are markedly associated through H-bonding. Despite this strong association they show generally strong cellulose-liquid interactions although they might exhibit a finite contact angle on a cellulose surface as a result of high cohesion energy (51).

The decrease in interaction in the ascending homologous series of alcohols is demonstrated by decreasing extent of sorption, heats of wetting (Table V-1), extent of polymer sorption (Table V-2), increasing immersed paper strength and Young's modulus (Table V-2). The same trend is demonstrated in the present work by dilatometric swelling (Tables III-2 and III-3) and immersed accessibility (Tables II-1 and III-3).

TABLE V-3A

"Inert" Liquids

(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Liquid	Experi- mental Method (*)	Cohesive Energy Density (cal/cc)	w^2 (cal/cc)	Molar Volume (c.c.)	A = Asso- ciated N = Non- Associated
1.	Benzene	A,B,P,S.	82	0.0	89	N
2.	Carbon tetrachloride	A,P,S.	74	0.0	97	N
3.	Chlorobenzene	A,B.	82	4.13	102	N
4.	Chloroform	A,P.	82	3.60	81	N
5.	Cyclohexane	A.	68	0.0	109	N
6.	1-Decene	A.	57	-	190	?
7.	Heptane	P.	54	-	147	N
8.	Isooctane	P.	50	-	166	N
9.	Silicone oil	P.	-	-		?
10.	Tetrabutyl tin	P.	46	-	329	?
11.	Toluene	A,B,P,S.	80	0.14	107	N
12.	Xylene	A,B.	81	0.0	124	N

(*) Experimental methods: A represents accessibility; B, optical birefringence; P, paper strength and S, dilatometric swelling method.

TABLE V-3B

Interacting Non-swelling Liquids

(1)	(2)	(3)	(4)	(5)	(6)	
	Liquid	Experi- mental Method (*)	Cohesive Energy Density (cal/cc)	w^2 (cal/cc)	Molar Volume (c.c.)	A = Asso- ciated N = Non- Associated
1.	Acetic anhydride	A.	102	17.9	95	A
2.	Acetone	A,P,S.	86	32.4	74	A
3.	Acetonitrile	A.	140	117	53	A
4.	Aniline	A,B,P,S.	126	5.5	92	N
5.	Benzaldehyde	A,B,P.	111	17.7	101	SA
6.	Benzyl alcohol	A,B,P.	148	5.7	104	A
7.	Benzyl chloride	A.	98	-	115	?
8.	1-Butanol	A,P,S.	95	7.2	92	A
9.	2-Butanol	A.	87	6.7	92	A
10.	Butyl acetate	A.	69	3.1	132	N
11.	Butyl cellosolve	P.	84	-	131	A
12.	Butyraldehyde	A,P.	81	19.5	88	N
13.	Butyrolactone	A,P.	162	-	77	?
14.	Diacetone alcohol	P.	87	-	125	A
15.	Dichlorobenzene	A.	100	-	113	?
16.	1,2-Dichloroethane	A,P.	94	13.7	79	N
17.	Diethyl oxalate	A.	126	-	84	?
18.	Dimethoxy ethane	A.	72	-	104	?
19.	Dimethyl aniline	P.	93	3.0	127	N
20.	p-Dioxane	A,P,S.	95	0.0	86	N

Cont'd.)

TABLE V-3B

(1)	(2)	(3)	(4)	(5)	(6)	(7)
21.	Ethyl acetate	A,P.	73	5.6	99	N
22.	Furfural	A,P,S.	127	47.0	83	A
23.	1-Hexanol	A.	82	3.4	125	A
24.	Isopropyl ether	A,P.	49	1.1	141	N
25.	Methyl acetate	A	81	8.3	80	N
26.	Methyl aniline	B,P.	110	4.5	109	N
27.	Methyl ethyl ketone	A,P.	81	20.6	90	A
28.	Methyl morpholine	A.	79	-	110	N
29.	Nitrobenzene	A,P,S.	123	43.0	103	N
30.	Nitromethane	A,P,S.	150	97.5	54	A
31.	1-Pentanol	A,B,S.	88	5.7	109	A
32.	3-Pentanone	A,P.	77	14.2	106	A
33.	Phenyl ether	A.	93	-	159	?
34.	Phlorol	A.	106	-	118	?
35.	2-Propanol	A,S.	96	10.3	77	A
36.	Propionic acid	A	129	0.9	75	A
37.	Tetrachloroethane	A	94	6.1	105	N
38.	Tetrahydrofuran	A,S.	84	-	81	?
39.	Vinyl acetate (monomer)	A,P.	76	-	92	?

(*) Experimental methods: A represents accessibility; B, optical birefringence; P, paper strength and S, dilatometric swelling method.

TABLE V-3C
Swelling Liquids.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Liquid	Experi- mental Method (*)	Cohesive Energy Density (cal/cc)	w^2 (cal/cc)	Molar Volume (c.c.)	A = Asso- ciated N = Non- Associated
(i)						
1.	Acetic acid	A,P,S.	153	15.7	58	A
2.	1,4-Butanediol	A,P,S.	150	19.2	89	A
3.	Diethylene glycol	A,P.	138	-	95	A
4.	Ethanol	A,B,P,S.	124	18.0	59	A
5.	Ethyl cellosolve	A,P,S.	98	-	97	A
6.	Ethylene glycol	A,B,P,S.	215	39.1	56	A
7.	Glycerol	A,B,P,S.	221	29.4	73	A
8.	Methanol	A,P,S.	166	37.6	41	A
9.	Methyl cellosolve	P,S.	114	13.9	79	A
10.	1,3-Propanediol	A,S.	178	25.2	72	A
11.	Water	A,P,S.	448	230	18	A
(ii)						
1.	Benzylamine	A,S.	106	3.2	109	N
2.	Dimethylformamide	A,P,S.	132	57.0	77	SA
3.	Ethylenediamine	A,S.	130	17.1	67	A
4.	Formamide	A,P,S.	308	161	40	A
5.	Morpholine	A,P,S.	106	7.6	87	N
6.	Piperidine	A.	84	2.8	99	N
7.	Pyridine	A,P,S.	107	16.2	81	N

(*) Experimental methods: A represents accessibility; B, optical birefringence; P, paper strength and S, dilatometric swelling method.

The decrease in interaction observed with increasing chain length of the monohydric alcohols may be attributed partially to steric effects. Such steric hindrance is expected to be reduced in polyhydric alcohols because of the greater possibility of orientation favourable to interaction. This prediction is strongly supported by data in Table III-4. Greater swelling of cellulose is observed with polyhydric alcohols as compared with the corresponding monohydric alcohols. This is further supported by the accessibility results and by data from the literature based upon paper strength experiments (33,34).

Due to lack of significant changes, trends in the interacting but non-swelling and the "inert" groups cannot be demonstrated by dilatometric swelling or accessibility measurements. In this work their interactions with cellulose have been observed by experiments on solvent-solute competition for sorption sites and in concurrent research (34) the differences were assessed by immersed paper strength.

Non-polar liquids, or liquids with little or no H-bonding properties, competed for sorption sites more successfully as their c.e.d.'s were higher (Fig. IV-1). This correlation of interaction and c.e.d. is substantiated by data on immersed paper strength (Table V-4) and the different loss of accessible surface when expanded cellulose is dried from several non-polar solvents (4,75).

Polar liquids or liquids possessing H-bonding functions compete with the polymer for sorption sites, and in many cases prevent the polymer sorption completely. Their relative interaction could best be investigated

TABLE V-4

Strength Loss in Paper Soaked in Various Non-polar Liquids

S/No.	Solvent	(*) Strength Loss (per cent)	(**) Cohesive Energy Density (cal/cc)	Molar Volume (cc)
1.	Chloroform	23.8	82	81
2.	1,2-Dichloroethane	23.3	94	79
3.	Toluene	15.0	80	107
4.	Benzene	11.7	82	89
5.	Carbon tetrachloride	10.8	74	97
6.	Heptane	8.3	54	148
7.	Isooctane	5.8	50	166

(*) Robertson; Reference No. 34.

(**) Calculated from the boiling points and densities of the liquids at 25°C. See Reference No. 34 and Appendix B.

by the sorption of the polymer from a binary mixture of the test liquid with an inert liquid. Under these conditions it could be shown that the interaction increased as the H-bonding ability of the liquid increased (Fig. IV-2).

Exploratory experiments using dilatometry and thallation or polymer accessibility have been carried out with some nitrogenous compounds which are known or suspected of penetrating and swelling the cellulose crystal lattice. The results have been included in the data and graphs. No systematic investigation was carried out and no conclusions can be drawn other than observing that some of them swell cellulose more than water does but without commensurate increase in accessibility.

The interaction of liquids with cellulose may be summarized as follows:

Non-polar liquids increase in affinity for cellulose as their cohesive energy density increases, reflecting an increase in intermolecular dispersion forces.

Polar, non-associated compounds, in general, increase in interaction with increase in c.e.d. However, the ability to participate in H-bonding has an overriding significance.

Polar associated compounds, chiefly the hydroxylic compounds, show greater interaction as they are smaller and/or contain more than one functional group.

F. ABSTRACT

Three experimental approaches have been made to the investigation of cellulose-liquid interactions using native cotton fibres and a wide variety of non-aqueous liquids. The overall swelling of cellulose has been measured dilatometrically; the accessibility of immersed fibres has been measured by the thallation-methylation technique and the liquids have been compared in their ability to compete for sorption sites on cellulose.

The results of these experiments have been used to classify liquids as inert, interacting but non-swelling, and swelling. The extent of interaction of the liquid appears to depend on molecular size and the magnitude and nature of intermolecular forces associated with it. The greatest interactions occur with small, polyfunctional molecules with H-bonding properties. Liquids with molar volume greater than 100 c.c. or, c.e.d. less than 100 cal/c.c. do not appear to swell or increase the accessibility of cellulose fibres.

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APPENDIX A

SOME CRITERIA OF ASSOCIATION IN PURE LIQUIDS

An attempt has been made in this thesis to relate the extent of cellulose-liquid interactions with properties of the liquid (Part V). Since the interaction presumably requires that a liquid molecule must be separated from the bulk liquid to be sorbed or bonded or otherwise associated with cellulose, it is of interest to enquire into the forces between molecules of the liquid. If the molecular configuration is appropriate, dipole interaction or H-bonding can lead to association between liquid molecules and therefore affect their ability to interact with cellulose.

Criteria which have been used by various workers (1-5) have been based on the relationship of various parameters of the liquid, primarily the dipole moment and the dielectric constant. These are theoretically related through Onsager equation (4,6).

$$\mu^2 = \frac{9kTM}{4\pi N_A d} \times \frac{(\epsilon - \eta_D^2)(2\epsilon + \eta_D^2)}{\epsilon(\eta_D^2 + 2)^2} \quad (1)$$

Where k is the Boltzmann's constant; M , the molecular weight; N_A , the Avogadro number; ϵ , the dielectric constant; d , the density; η_D , the refractive index for sodium lines at $T^\circ K$ and μ , the dipole moment of the vapour if the liquid is not associated.

If the value of μ , experimentally determined, differs significantly from that given by equation 1, it is assumed that the deviation is due to association. This procedure has been used implicitly by Gjaldbaek and Andersen (5).

The decision as to whether a liquid is associated or not may be more quickly made by plotting ϵ versus μ or by plotting $\sqrt{\epsilon - \eta_D^2}$ versus μ . Deviations from a smooth curve in the first, and deviations from a straight line through the origin in the second are considered to be evidence of association. The first method, suggested by Pauling (3) and the second, which is due to Kumler (2), are almost equivalent to the method invoking equation 1 because of the lack of variation in η_D and the insensitivity of the equation to this value.

Differences in decisions based upon the three methods arise only in borderline cases and can frequently be settled by other evidence.

Plots based on Pauling criterion and on Kumler relation are given in Figures A-1 and A-2. The ordinate in A-2 includes a correction factor, $\frac{M_d}{M_o d}$, where M_o and d_o are the molecular weight and density of a reference liquid (cyclohexane at 25°C in this Appendix) and, M and d , the molecular weight and density respectively of the liquid under examination. This factor eliminates, from the above relation, the influence of variations in the number of molecules in unit volume of the liquids at a given temperature (2). The two plots give equivalent results and the classification of liquids as associated or non-associated is included in Part V (Table V-3).

FIGURE A-1

RELATION BETWEEN DIELECTRIC CONSTANTS AND DIPOLE MOMENTS
OF VARIOUS LIQUIDS - THE PAULING CRITERION OF ASSOCIATION

LEGEND:

- Non-associated liquids,
- ⊙ Associated liquids.

(The numbers refer to Table A-1.)

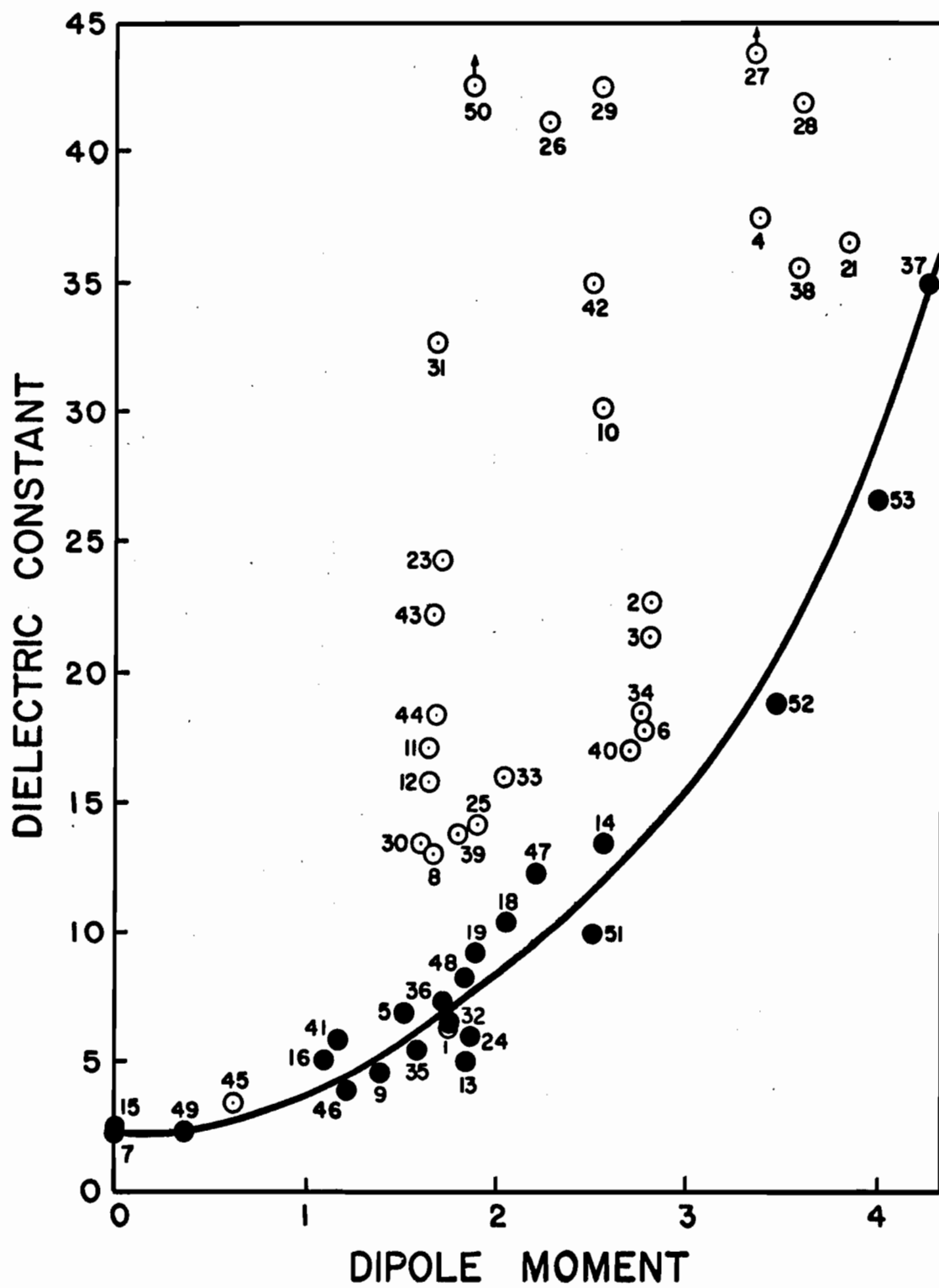


FIGURE A-2

RELATION BETWEEN $\sqrt{(\epsilon - n^2)}$ CORRECTED AND DIPOLE MOMENTS
OF VARIOUS LIQUIDS - THE KUMLER CRITERION OF ASSOCIATION

LEGEND:

- Non-associated liquids,
- ⊙ Associated liquids.

(The numbers refer to Table A-1.)

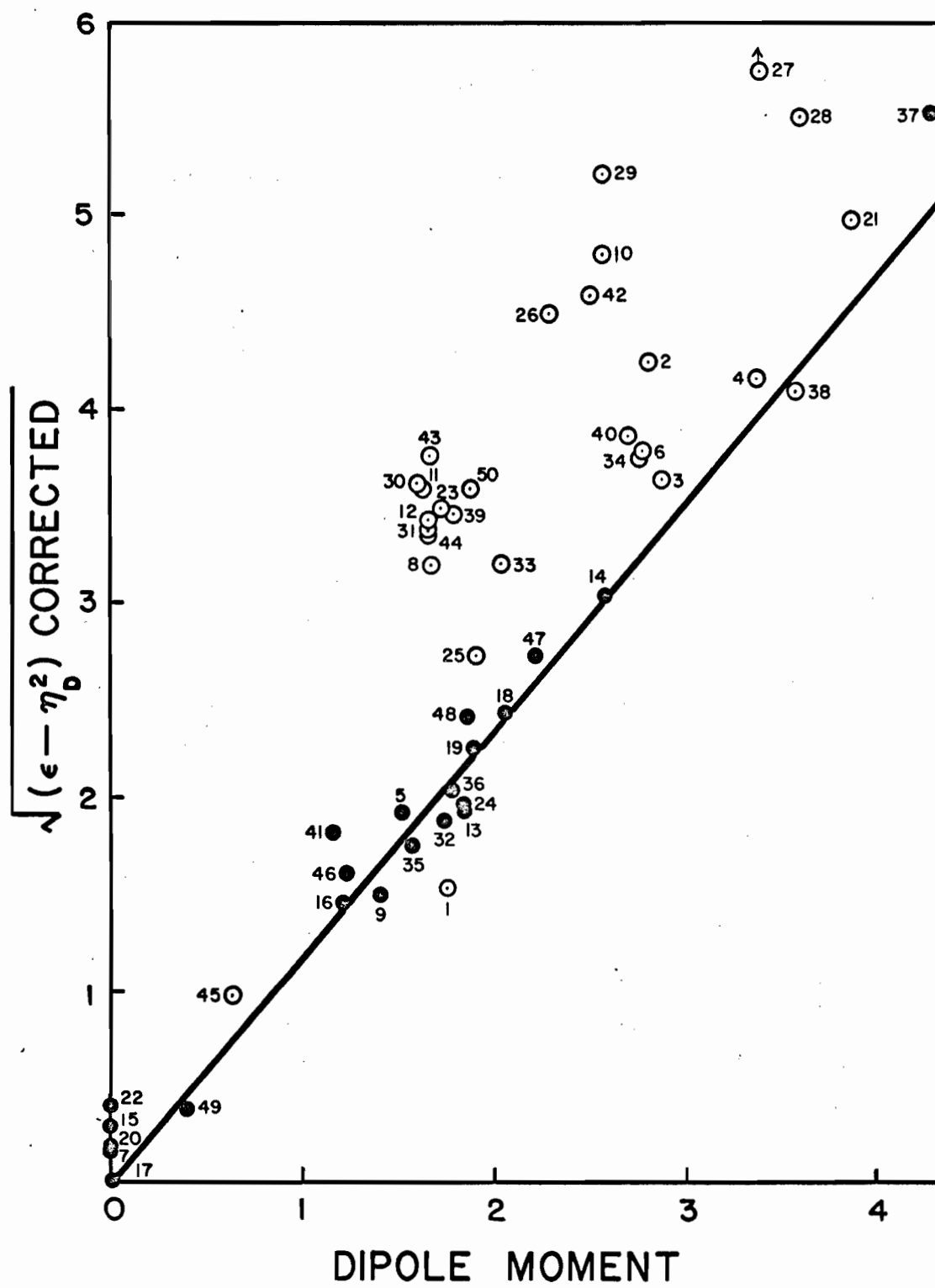


TABLE A-IClassification of Liquids - Key to Figures A-1 and A-2

Number	Solvent	Number	Solvent
1.	Acetic acid	28.	Furfural
2.	Acetic anhydride	29.	Glycerol
3.	Acetone	30.	1-Hexanol
4.	Acetonitrile	31.	Methanol
5.	Aniline	32.	Methyl acetate
6.	Benzaldehyde	33.	Methyl cellosolve
7.	Benzene	34.	Methyl ethyl ketone
8.	Benzyl alcohol	35.	Monochlorobenzene
9.	Benzylamine	36.	Morpholine
10.	1,4-Butanediol	37.	Nitrobenzene
11.	1-Butanol	38.	Nitromethane
12.	2-Butanol	39.	1-Pentanol
13.	Butyl acetate	40.	3-Pentanone
14.	Butyraldehyde	41.	Piperidine
15.	Carbon tetrachloride	42.	1,3-Propanediol
16.	Chloroform	43.	1-Propanol
17.	Cyclohexane	44.	2-Propanol
18.	1,2-Dichloroethane	45.	Propionic acid
19.	cis-Dichloroethylene	46.	isoPropyl ether
20.	trans-Dichloroethylene	47.	Pyridine
21.	Dimethylformamide	48.	Tetrachloroethane
22.	p-Dioxane	49.	Toluene
23.	Ethanol	50.	Water
24.	Ethyl acetate	51.	Dichlorobenzene
25.	Ethylenediamine	52.	Benzyl cyanide
26.	Ethylene glycol	53.	Propionitrile
27.	Formamide		

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APPENDIX B

COHESIVE ENERGY DENSITIES OF LIQUIDS

The concept of cohesive energy density (c.e.d.), developed by Hildebrand and Scott (1) to predict the miscibility of non-polar liquids, has been extended, though rather empirically, to polar liquids, associated liquids and to high polymers. Gee (2), Bristow and Watson (3) and several others have used the concept to explain the solubility behaviour of polymeric substances. Broughton and Wang (4), Thode and Guide (5) and more recently Robertson (6) have used c.e.d. to explain interactions of liquids with cellulose.

Ideally, two liquids involving no specific interactions, will intermix freely if the heat of mixing ΔH_m is zero. The heat of mixing is calculated by Hildebrand's (1) relation:

$$\Delta H_m = V_m \left[\left(\frac{\Delta E_1}{V_1} \right)^{1/2} - \left(\frac{\Delta E_2}{V_2} \right)^{1/2} \right]^2 v_1 v_2 \quad (1)$$

where ΔH_m = overall heat of mixing, calories;

V_m = total volume of the mixture, c.c.;

ΔE = energy of vaporization of component 1 or 2, calories;

V = molar volume of the component 1 or 2, c.c. and

v = volume fraction of component 1 or 2, a dimensionless quantity.

The heat of mixing will be zero if

$$\frac{\Delta E_1}{V_1} = \frac{\Delta E_2}{V_2} \quad (2)$$

The term $\frac{\Delta E}{V}$ is known as the cohesive energy density. According to equation (2) the maximum interaction takes place when c.e.d.'s of the two components are equal or close.

The square root of c.e.d. (usually designated by the symbol δ) is known as solubility parameter since it is an important quantity in determining solubility behaviour. Burrell (7) has reviewed different methods of determining the solubility parameters of monomeric and polymeric materials.

The c.e.d. is a summation of all intermolecular forces e.g. dipole interactions - permanent or induced, dispersion forces, repulsion forces and the more specific interactions as H-bonding. The total cohesion in a liquid is determined by the number, species and arrangement of atoms in the molecules. In many cases, primarily in compounds of low polarity, the c.e.d. may be calculated simply by summing the contributions of the component atoms or groups of atoms (8). Intermolecular H-bonding leads to association and large contributions to c.e.d.

Gjaldbaek and Andersen (9) have shown that, for non-associated liquids, the energy of vaporization or c.e.d. can be expressed as

$$\frac{E^V}{V} = \frac{\Delta H^V - RT}{V} = \delta'^2 + w^2 \quad (3)$$

where E^V = internal energy of vaporization per mole, calories;

V = the molar volume, c.c.;

ΔH^V = is the heat of vaporization at temp. $T^\circ K$ and

R = the gas constant.

In the above equation the symbol δ' represents contribution (cal/cc) to cohesion energy arising from dispersion forces; w^2 signifies the contributions (cal/cc) due to dipole interactions (see Appendix A).

The value of ΔH^V at 25°C is calculated from Hildebrand's (1) relation

$$\Delta H^V = 23.7T_b + 0.02T_b^2 - 2950 \quad (4)$$

in which T_b represents the boiling point °K of the liquid.

Experimentally determined values of c.e.d. for several of the solvents used in the present work are available in literature, but not for all. There is lack of agreement in several cases. In order to follow a uniform pattern, values of c.e.d. at 25°C for all solvents used were calculated from equations (3) and (4) and are given in Table B-I.

Application of the above equations to associated liquids is not strictly valid but the factors which cause departures from ideal behaviour are presumably the ones which influence correlations sought in this work. The values of c.e.d. so calculated are always lower than the experimentally determined values for liquids which are H-bonded or are associated through strong dipolar effects. However, the calculated values provide a convenient basis for comparison of liquids for their interactions with cellulose.

TABLE B-I

Cohesive Energy Densities of Various Organic Liquids at 25 °C.

(1)	(2)	(1)	(2)
Solvent	c.e.d. (cal/cc)	Solvent	c.e.d. (cal/cc)
Acetic acid	153.4	Ethylenediamine	129.7
Acetic anhydride	101.7	Ethylene glycol	215.3
Acetone	86.4	Formamide	308.5
Acetonitrile	139.8	Furfural	126.8
Aniline	125.5	Glycerol	220.5
Benzaldehyde	111.1	1 - Hexanol	82.3
Benzene	81.9	Methanol	165.8
Benzyl alcohol	147.6	Methyl acetate	81.2
Benzylamine	105.6	Methyl cellosolve	114.0
Benzyl chloride	98.0	Methyl ethyl ketone	81.0
1, 4 - Butanediol	150.3	Methylmorpholine	79.1
1 - Butanol	95.3	Mono chlorobenzene	81.5
2 - Butanol	87.4	Morpholine	105.7
Butyl acetate	68.7	Nitrobenzene	122.7
Butyraldehyde	81.1	Nitromethane	150.0
Butyrolactone	162.2	1 - Pentanol	87.8
Carbon tetrachloride	74.1	3 - Pentanone	76.6
Chloroform	81.8	Phenyl ether	92.8
Cyclohexane	67.6	Phlorol	105.8
1 - Decene	57.3	Piperidine	84.3
Dichlorobenzene	100.3	1, 3 - Propanediol	177.5
1, 2 - Dichloroethane	94.4	1 - Propanol	106.2
cis-Dichloroethylene	84.0	2 - Propanol	96.3
trans-Dichloroethylene	78.8	Propionic acid	129.3
Diethylene glycol	138.2	iso-Propyl ether	48.7
Diethyl oxalate	125.6	Pyridine	107.4
1, 1 - Dimethoxyethane	71.9	Tetrachloroethane	94.1
Dimethylformamide	131.6	Tetrahydrofuran	83.6
p-Dioxane	94.9	Toluene	79.8
Ethanol	123.6	Vinyl acetate (monomer)	76.2
Ethyl acetate	73.2	Water	448.0
Ethyl cellosolve	97.8	Xylene	81.2

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CONCLUDING REMARKS AND SUGGESTIONS FOR FURTHER WORK

CONCLUDING REMARKS AND SUGGESTIONS FOR FURTHER WORK

During the present work different approaches were made to the study of cellulose-liquid interactions. The results obtained have shown the desirability of continuing various aspects of the study through different parallel approaches. To provide logical basis for correlations and to arrive at a comprehensive picture of the phenomenon it may be necessary, in some cases, to modify the existing methods or to devise new techniques.

In view of the foregoing, the following suggestions are made for further work. It is hoped that from the information so collected it will be possible to arrive at a better understanding of the interactions of liquids with cellulose. It will also be possible to establish the validity, or otherwise, of the suggested mechanism of swelling, the "frozen in" stresses and the influence of fibre structure on accessibility and mechanical properties of the fibres.

A. ACCESSIBILITY:

(i) Thallation accessibility of non-crystalline cellulose and examination of the results in relation to the accessibilities of similar samples reported in the literature (e.g., Wadehra, Manley and Mason (1)), and in relation to the present accessibility hypothesis based on the fibrillar structure of native cellulose.

(ii) Use of other thallos alkoxides to determine the effect, if any, of the reactant size.

(iii) Use of low cohesive energy density hydrocarbons (heptane) as medium for thallation accessibility to determine the effect, if any, of the reaction medium.

(iv) Accessibility of preswollen and solvent exchanged samples of cellulose by deuteration or tritiation with a non-swelling deuterated or tritiated compound by modifications of procedures described by Mason and his coworkers (1-3).

(v) Accessibilities of various fibres (cotton, wood pulp, tyre rayon, ramie valonia, etc.) from different pretreatments (dried, never dried, swollen, etc.) as a method of investigating fibre structure.

(vi) Analytical investigation of the completeness (or otherwise) of removal of swelling solvents, e.g., nitrogen compounds.

B. DILATOMETRY:

(i) Swelling of cellulose pellets of different densities in water and intramolecular swelling liquids by a procedure similar to Ovcharenko experiments for clays (4) to determine the relative roles of increase in voids and increase in cellulose volume during the gross swelling of cellulose.

(ii) A systematic study of swelling of cellulose, native and regenerated, in anhydrous organic intramolecular swelling agents and examination of the results in relation to the nature of the test liquids and morphology of the fibres.

C. CELLULOSE-LIQUID INTERACTIONS:

Test of the validity of the hypothesis that polyfunctional compounds have stronger interactions with cellulose than monofunctional compounds of comparable size.

D. PYCNOMETRIC DENSITY:

(i) Experiments to investigate whether molecular size or cellulose-liquid interactions (or both) influence penetration of cellulose structures by various liquids. This could be achieved by (a) determining pycnometric density of cellulose swollen in water and solvent exchanged to different liquids and (b) by determining pycnometric density of cellulose swollen in different liquids and solvent exchanged to the same neutral liquid.

(ii) Quantitative determination of any residual solvents, immersion or intermediate.

E. NON-FREEZING LIQUIDS:

Study of the amounts of non-freezing liquids in native fibres at different temperatures. It is suggested that liquids selected should be of different types, e.g., "neutral" (benzene, cyclohexane), interacting but non-swelling (cyclohexanol) and swelling liquids (water). This may provide useful information regarding the pore size distributions and internal surface areas corresponding to the various pore size ranges.

F. SURFACE PROPERTIES:

Determination of the contact angles of various liquids with native and regenerated cellulose and calculation of the energies of interactions involved.

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CLAIMS TO ORIGINAL RESEARCH

1. A method of measuring accessibilities of cellulose samples (immersed or dry) without substantially altering their state of swelling or collapse has been developed.

Accessibilities of cellulose samples preswollen in a large variety of liquids have been determined.

2. A new dilatometer incorporating improved features has been constructed and the gross swelling of native cotton fibres has been measured in several anhydrous organic liquids.

3. Polymer sorption, by preswollen samples, from solutions in pure liquids and in binary mixtures has been measured.

4. Test liquids have been classified as "inert", interacting but non-swelling and swelling. The extent of interaction has been shown to depend upon the molecular size and the magnitude and nature of the molecular forces involved.

It has been demonstrated that stronger interactions occur with small polyfunctional molecules with strong H-bonding properties and that polyfunctional compounds show greater interactions with cellulose than monofunctional compounds of similar size.

5. It has been shown that thallation accessibility is a measure of the internal surface areas of the cellulose samples and that the method provides a means of measuring cellulose-liquid interactions.

6. The concept has been introduced that swelling of cellulose on immersion is a response to the stresses fixed by H-bonds during the initial drying of the fibres.

7. Increments in accessibility or internal surface areas, gross swelling of the fibres and alteration in mechanical properties have been explained on the basis of the above suggested model and have been shown to be different aspects of the same phenomenon - the reduction in cellulose-cellulose bonds on immersion.

8. The existence of a solvent-solute competition for sorption sites on cellulose has been established. It has been shown that the greater the cohesive energy density of non-polar liquids or the greater the H-bonding capacity of polar liquids the greater is the competition offered to the polymer for sorption sites on cellulose.