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THE EFFECT OF CELLULOSE ON THE STRUCTURE OF WATER: VIEW 1

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Synopsis The apparent thermal expansion of cellulose immersed in liquid water, $d\phi_2/dT$ is several times that of dry cellullose. A similar but greater disparity is observed when the temperature dependence of the apparent specific volume of glucose in aqueous solution is compared with the thermal expansion of crystalline glucose. This effect appears to be a general one for polyols such as glucose and glycerol and can be interpreted in terms of a 'mixture' theory of water structure. Water is pictured as being made up of small short-lived clusters which may be classified as either solidlike or fluidlike. The solidlike component consists of rigid, hydrogen bonded ring structures (tetramer, pentamer, hexamer). The fluidlike component consists of non-rigid, less hydrogen bonded, chain structures (dimer, trimer, star pentamer). Surfaces rich in hydroxyl groups appear to act as structure breakers by causing an increase in the proportion of the fluidlike component in the water adjacent to the interface. With cellulose, this perturbed layer consists of the non-rigid chain structures, hydrogen bonded to the -OH groups on the surface. The high values for $d\phi_2/dT$ for glucose and cellulose are caused by the high thermal expansion of the perturbed layer.

Introduction

LIQUID water may be regarded as the amniotic fluid of paper. We pulp, wash, screen, bleach and papermake all in a very aqueous milieu. Although our products are usually sold containing only a minor proportion of sorbed water, liquid water plays a major role in their manufacture. As papermakers, therefore, it is entirely appropriate that we concern ourselves with the properties of liquid water and particularly with its behaviour at the fibre/water interface. The present report deals with the molecular arrangement of water molecules adjacent to a cellulose surface immersed in liquid water.

Under the chairmanship of Dr H. Corte

In the first section of the report a brief account is given of the concepts currently held on the structure of water. Particular attention will be paid to the so-called 'mixture' theory in which water is visualised as a mixture of a solidlike component and a fluidlike component, the two being in equilibrium with each other. The second section of the report will contain some results on volume/temperature relationships in aqueous systems with particular emphasis on systems in which carbohydrate molecules are in contact with liquid water. Finally, in the light of these results, an attempt is made to elucidate the effect of a cellulose surface on the structure of water.

It should be noted that the concepts put forward in the present paper are similar to those described in several previous publications from the author's laboratory.⁽¹⁻⁷⁾ Since the original work, however, theories on water structure have evolved and a more realistic picture is now possible. Nevertheless, the basic ideas are essentially the same as those first proposed by Ramiah and Goring⁽¹⁾ twelve years ago.

The structure of water

ALTHOUGH water is the most common liquid on the earth's surface, it possesses rather unusual properties. It should not be a liquid at all at ambient temperatures. Nitrogen and sulphur are next to oxygen in the periodic table yet both ammonia and hydrogen sulphide are gases at room temperature. This indicates that there must be substantial forces of attraction between molecules of liquid water to produce a condensed phase at such relatively high thermal energies.

To obtain a clearer picture of the nature of these intermolecular forces, let us consider the properties of a single water molecule. The angle between the two O—H bonds is 106 degrees. This is rather near the angle of 109 degrees between the lines joining the centre of a tetrahedron to its four corners. Then, the hydrogen atom of an O—H group can be hydrogen-bonded to the oxygen atom of another water molecule. Thus it is not surprising that water molecules tend to be found arranged into structures in which each oxygen atom is tetrahedrally bonded to four hydrogen atoms. Each hydrogen atom is then held by a covalent and a hydrogen bond, the two bonds being almost colinear. One structure of this type is found in the most common form of ice, Ice I. As shown in Fig. 1, the crystal structure of Ice I is rather open and, in fact, is similar to that of the tridymite form of silica.⁽⁸⁾

Some time ago, Bernal and Fowler⁽⁹⁾ proposed that when ice melts to water many of the hydrogen bonds are retained. The structure is perturbed to the extent that the long-range order in the solid is destroyed. However, the liquid still possesses a high degree of order over short distances and therefore



Fig. 1—The crystal structure of ice (after Némethy and Scheraga)⁽⁸⁾

can be regarded as a quasi-crystalline system with a short-range structure similar to that of a solid.

No one will quarrel seriously with the extremely simple qualitative picture given above. However, there has been considerable controversy over the next step, i.e., the development of a quantitative theory for liquid water which will permit the prediction of the behaviour of the liquid from the basic properties of the molecule. There seem to be as many theories as there are leaders in the field. The theories can be divided into two classes each grouped about a different conceptual view of water. In one, water is pictured as continuum at the molecular level with the hydrogen bonds 'bent' or distorted in some way to correspond to the properties of the liquid. In the other type of theory, water is regarded as a mixture of species in dynamic equilibrium with one another but with each species capable of an independent existence over distances of several molecular diameters and for times of 10^{-12} seconds or greater. It is not yet possible to say whether the continuum models correspond more closely to reality than the mixture models. However, Franks⁽¹⁰⁾ has pointed out that at the present time the mixture models are the more favoured

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Fig. 2—Polarity produced in hydrogen bonding between water molecules leading to further hydrogen bonding (after Frank,⁽¹²⁾ Némethy and Scheraga)⁽⁸⁾

ones particularly for the interpretation of the effects of solutes on the physical properties of water.

In the present paper no attempt will be made to review, even superficially, the current theories of water structure. Rather I have chosen one theory and have tried to apply this to the question of the cellulose/water interface. The theory is that being developed by Scheraga and co-workers and is based on the concept of water as a mixture of a highly hydrogen bonded, rigid, solidlike component with a less hydrogen bonded, non-rigid, fluidlike component.

The approach of Scheraga and his colleagues was initially based on the concepts proposed by Frank and Wen⁽¹¹⁾ twenty years ago. Frank and Wen were particularly interested in co-operative behaviour in the hydrogen bonding of water molecules. They pointed out that when a hydrogen bond forms between two water molecules, a considerable polarity is developed. The dipole produced makes it more likely that a second hydrogen bond will form, then a third, and so on. This effect is shown in Fig. 2. In this way, several hydrogen bonds can form rather suddenly in a small volume of liquid. A short time afterwards, this particular hydrogen bonded volume will 'melt' due to thermal energy in the liquid. In the meantime another small volume will become hydrogen bonded elsewhere. Thus small elements of volume are rapidly transformed into ice-like clusters and rapidly melted. Frank and Wen⁽¹¹⁾ used the term 'flickering clusters' when describing their theory.

About fifteen years ago, Némethy and Scheraga⁽⁸⁾ used the flickering cluster concept proposed by Frank and Wen⁽¹¹⁾ to develop an empirical quantitative theory for the physical behaviour of liquid water. Their model for the structure of water is shown in Fig. 3. At any instant of time, some of the water molecules are tetra-co-ordinated into clusters which are ice-like. The remaining water molecules exist as an unbonded liquid, forming a mixture in which the clusters are embedded. Clusters continuously form and disappear, their average lifetime being about 10^{-11} sec. Némethy and Scheraga applied



Fig. 3—Model for the structure of water used by Némethy and Scheraga in their original theory⁽⁸⁾

a statistical thermodynamic treatment to derive the partition function for H_2O molecules over five energy levels corresponding to four, three, two, one and no hydrogen bonds per molecule. They predicted an average cluster size which was rather large; it was 91 H_2O molecules at 0° C falling to 25 H_2O molecules at 70° C. Over the same temperature range the fraction of hydrogen bonds unbroken fell from 0.53 to 0.36.

The original theory of Némethy and Scheraga⁽⁸⁾ gave calculated values of the free energy, enthalpy and entropy of liquid water between 0° C and 70° C which agreed with the experimental data to better than 3 per cent. The predicted temperature dependence of the heat capacity was too high but errors in the specific heat are characteristic of theories of the physical behaviour of water.⁽⁸⁾ By making reasonable assumptions concerning the specific volumes of the ice-like and unbonded components, it was possible to predict fairly accurately the change of volume with temperature for liquid water. The characteristic maximum in density arose because the decrease in volume between 0° C and 4° C due to melting of the ice-like component to form the denser unbonded liquid was greater than the increase in volume between 0° C and 4° C due

to the thermal expansion of both components. However, a major flaw in the theory was the requirement that about one half of the water molecules existed in the form of fairly substantial molecular icebergs of low density. Using low angle X-ray scattering, Narten and Levy⁽¹³⁾ showed that there are no appreciable fluctuations of density in regions larger than a few molecular diameters. A second questionable feature of the theory was the prediction that about one half of the molecules in liquid water were completely free from hydrogen bonds. This is contrary to the opinion of several authors who, mainly on the basis of spectroscopic evidence, have questioned the existence of a substantial proportion of unbonded molecules in liquid water.⁽¹⁴⁻¹⁶⁾

In a later paper, Hagler, Scheraga and Némethy⁽¹⁷⁾ pointed out that several basic errors were made in the original theory of Némethy and Scheraga⁽⁸⁾ and that these errors led to incorrect predictions of the average value of cluster size and the mole fraction of unbonded molecules.

Scheraga and his co-workers have continued to develop their theories on the structure of liquid water.^(18, 19) In a recent paper, Lentz, Hagler and Scheraga (LHS)⁽²⁰⁾ present an improved statistical thermodynamic treatment of the cluster model. A quantum mechanical analysis by means of the *ab initio* LCAO-MO method is used to make an estimate of the co-operative effects in hydrogen bonding within individual clusters. As before, a partition function is derived and the thermodynamic properties of liquid water are calculated over the range 0–100° C using only two adjustable parameters. The theory shows the usual imprecision with respect to the heat capacity but gives quite good agreement with experiment for the free energy, the internal energy and the entropy. Moreover, the intermolecular vibration spectrum is calculated and is found to represent the experimental behaviour reasonably well.

The distribution of cluster species resulting from the LHS treatment⁽²⁰⁾ is rather different to that given by the original theory of Némethy and Scheraga.⁽⁸⁾ Virtually all of the clusters are small and contain six water molecules or less. This is in agreement with the low angle X-ray scattering data⁽¹³⁾ since there are no extensive regions of a low density ice-like phase. Also there are few unbonded molecules (less than 1 per cent at 0° C) in agreement with the conclusions of Stevenson⁽¹⁶⁾ and others.^(14, 15) A further result of the theory is that ring species predominate in the clusters because of the stability produced by the extra hydrogen bond in a ring.

The distributions of cluster sizes produced by the LHS theory for temperatures of 0° C, 50° C and 100° C are shown in Fig. 4. The clusters containing 4, 5 or 6 water molecules are ring structures and are therefore rather rigid. The dimer and the trimer are linear and are therefore less rigid structures than the



Fig 4—Calculated distributions of the mole fraction of water molecules in various cluster species at three temperatures from Lentz, Hagler and Scheraga⁽²⁰⁾

rings. The star pentamer, 5^* , is grouped with the dimer and the trimer because it, too, is expected to behave as a non-rigid structure. A conceptual drawing of the structure of water at 50° C is given in Fig. 5.

From the above we see that the picture of liquid water which emerges from the LHS theory is that of a mixture of various types of small clusters of H_2O molecules. The clusters may be divided into two broad groups as follows:

- 1. The 'solidlike' component consisting of rigid, hydrogen bonded, ring structures (tetramer, pentamer, hexamer).
- 2. The 'fluidlike' component consisting of non-rigid, less hydrogen bonded, chain structures (dimer, trimer, star pentamer).

As the temperature is increased hydrogen bonds are broken and the proportion of the solidlike component will diminish while the fluidlike component will increase. The number of hydrogen bonds per water molecule and the weight fractions of the solidlike and fluidlike components at 4° C were calculated from the distributions given by Lentz, Hagler and Scheraga⁽²⁰⁾ and are shown in Table 1.

Although the LHS treatment does not allow the quantitative prediction



Fig. 5—Conceptual drawing of the various cluster species found in equilibrium in liquid water

of the P–V–T properties of liquid water, it is possible to derive some very approximate values of the volume and thermal expansion of the solidlike and fluidlike components. Using molecular models, Lentz, Hagler and Scheraga⁽²⁰⁾ were able to estimate the effective diameter of a water molecule in each of the clusters. From their data, the average diameter of H₂O in the solidlike clusters is 3·14 Å and in the fluidlike clusters, 2·98 Å (taking the diameter of an H₂O molecule to be the same in the trimer and the star pentameter). If we assume that,

- *1.* the volume of liquid water is the sum of the volumes of the solidlike and fluid-like components,
- 2. the specific volumes of the solidlike and the fluidlike components are proportional to the cubes of the diameters of the water molecule in the rigid and non-rigid clusters,
- 3. the thermal expansion of the solidlike component is equal to $\frac{2}{3}$ of what the thermal expansion of ice would be at 4° C (0.00020 ml/g° C (1) plus $\frac{1}{3}$ the thermal expansion of the fluidlike component, and
- 4. at 4° C, the increase in volume with temperatures due to the normal thermal expansion of the solidlike and fluidlike components is exactly balanced by the decrease in volume due to the conversion of some of the solidlike components to the liquidlike component,

it is not difficult to compute values for the specific volumes and thermal expansions of the solidlike and fluidlike components at 4° C. These results, given in Table 1, are in no way meant to be exact but should be regarded as a rough guide to the volume/temperature behaviour of the solidlike and

UNPERTURBED LIQUID

PERTURBED LAYER



Fig. 6—Diagram showing the perturbed layer produced when a surface is submerged in water

fluidlike components of liquid water. The figures indicate that the fluidlike component is denser and has a thermal expansion about twice as great as that of the solidlike component.

If water possesses a characteristic structure as described in the previous paragraphs, then it would be expected that any surface submerged in liquid water would be likely to perturb the structure in the liquid layer near the interface (Fig. 6). The surface could be that of a small molecule such as glucose or butanol in aqueous solution; it could be the surface of a colloidal particle or polymer molecule; it could even be the internal surface of a water swollen gel such as a wet cellulose fibre. Whatever the nature of the surface, the equilibrium between the solidlike and fluidlike components of water would be expected to be changed in the vicinity of the surface.

The original theory of Némethy and Scheraga⁽⁸⁾ was derived particularly for the treatment of the case of hydrophobic surfaces such as the aliphatic chains of the higher alcohols.⁽²¹⁾ The authors proposed that the ice-like quality of water is enhanced adjacent to a hydrophobic surface because the energy of interaction between hydrogen bonded water molecules and a hydrophobic surface is less than that between unbonded water molecules and such a surface. The formation of the well-known clathrate compounds between water and molecules such as methane or chloroform⁽²²⁾ can be regarded as special cases of structure forming by hydrophobic surfaces. In terms of the current theory of Lentz, Hagler and Scheraga⁽²⁰⁾ we can assume that hydrophobic surface will increase the proportion of the solidlike component of water near the interface.

Some solutes are believed to decrease the structure in water. The most well-known of structure breakers are certain ionic species such as K^+ or NO_3^{-} .⁽¹¹⁾ However, some nonelectrolytes such as urea and formamide have also been classed as structure breakers.^(4, 23) Such molecular surfaces would be expected to cause an increase in the proportion of the fluidlike component

of water near the interface. Later in the paper we shall discuss the effect of the cellulose surface on the structure of water in the light of the concepts described above.

The thermal expansion of cellulose and related materials

In previous reports^(1,3) we have described the measurement of the thermal expansion of cellulose in the dry and in the water-wet state. For experiments with dry cellulose we made pellets with tool-steel dies using large pressures. Mercury was used as the confining liquid and the standard procedures for precision dilatometry were adopted. For wet cellulose, we used pulp suspensions of a few percent consistency with water as the confining liquid.

Let us define the specific volume, V_o , of the dry cellulose simply by

$$V_0 = \frac{1}{\rho_0}$$
 (1)

where ρ_0 is the density of a highly pressed pellet of milled cellulose fibre. The apparent specific volume, ϕ_2 , in an aqueous slurry may then be defined by

$$\phi_2 = \frac{(1/\rho_{12}) - [(1 - W_2)/\rho_1]}{W_2} \quad . \quad . \quad . \quad (2)$$

in which ρ_{12} is the 'density' (weight divided by volume) of the mixture, W_2 is the weight fraction of cellulose in the slurry and ρ_1 is the density of water. For ease of graphical comparison we compute the relative specific volume $(V_o)_{rel}$ and the relative apparent specific volume $(\phi_2)_{rel}$ from

and

$$(\phi_2)_{\rm rel} = \frac{(\phi_2)_T}{(\phi_2)_{\,\rm 0^{\circ}\,c}}$$
 (4)

in which the subscript T corresponds to the temperature at which the parameter was determined.

Very early in the work it became apparent that the volume/temperature relationship for dry cellulose was different to that for wet cellulose. This is indicated by the marked differences in the slopes of the plots of $(V_o)_{rel}$ and $(\phi_2)_{rel}$ vs. temperature shown in Fig. 7. If the thermal expansion coefficients are calculated at 4° C,⁽³⁾ we see from Table 2 that the value of dV_o/dT is about one third of that of $d\phi_2/dT$. Similar results were obtained with other types of cellulose. This behaviour must be considered a substantial anomaly in a property as fundamental as the change of volume with temperature.

In seeking an explanation of the difference between the thermal expansion of dry and aqueous cellulose, we are led to consider whether or not this effect is due to the polymeric or fibrous nature of the substrate. Perhaps the porous



Fig. 7— $(V_0)_{rel}$ and $(\phi_2)_{rel}$ vs. temperature for cellulose, crystalline glucose, glycerol and t-butanol.^(3, 4) (There is a typographical error in Table 1, reference 3. The value of A_2 for wood pulp (aqueous) should be -0.0377 (not -0.3767) × 10⁻⁴)

structure of the fibre in some way causes the difference. Perhaps it is related to the cellulose chain molecule. To answer these questions a comparison was made between the thermal expansion of dry crystalline glucose and the apparent thermal expansion of glucose in aqueous solution. From the graphs of $(V_o)_{rel}$ vs. *T* in Fig. 7 we see that in the dry state crystalline glucose behaves in a manner rather similar to that of cellulose. However, $(\phi_2)_{rel}$ shows a very marked increase with *T* and, as seen from the results in Table 2, $d\phi_2/dT$ for glucose is about 17 times as great as dV_o/dT .

The results for glucose indicate clearly that the difference between the thermal expansion in the dry and the water-wet state is due to the interaction of the carbohydrate molecule with the aqueous medium. The question then arises as to whether or not the effect is due to some special feature of the carbohydrate molecule—perhaps some spatial arrangement of —OH groups which allows a specific interaction with the molecules of water. In order to test this, dV_o/dT and $d\phi_2/dT$ were measured for glycerol⁽⁴⁾ and as shown in Fig. 7 the anomaly persists for this polyol as well. The data in Table 2 show that the apparent thermal expansion in water is about the same as that of glucose but the thermal expansion of the pure liquid is, expectedly, somewhat higher than the value found for crystalline glucose.

The results, therefore, indicate that the original observations on wood pulp fibres are not peculiar to cellulose but are merely a special case of a more general phenomenon. Apparently, for compounds rich in —OH groups, $d\phi_2/dT$ is much larger than dV_o/dT . It is not unreasonable to assume that this effect is somehow related to the interaction of the surface of such molecules with liquid water.

Interaction of a cellulose surface with liquid water

In the previous section we have shown that a molecule rich in —OH groups appears to have a remarkably high thermal expansion coefficient when dissolved in water. This behaviour is true also for cellulose even though the fibre is not dissolved but only immersed in the liquid. Earlier in the paper we saw that the thermal expansion of the fluidlike component of water is twice as high as that of the solidlike component. It is therefore likely that the large apparent thermal expansion of cellulose in water is due to the increase in the proportion of the fluidlike component of water at the cellulose/water interface. Thus we are proposing that the cellulose surface acts as a structure breaker by reducing the solidlike component of water near the surface.

A rough estimate of the extent of this effect may be derived from the values of the thermal expansion coefficient at 4° C given in Table 2. If we assume that $d\phi_2/dT - dV_o/dT$ ($T = 4^\circ$ C) is due entirely to the thermal expansion of the perturbed layer we have

$$W_{u} = \frac{d\phi_{2}/dT - dV_{0}/dT}{dV_{f}/dT} \quad (T = 4^{\circ} C) \qquad . \qquad . \qquad (5)$$

in which W_u is the weight of water in the perturbed layer per unit weight of glucose and dV_f/dT ($T = 4^\circ$ C) is the thermal expansion of the fluidlike component at 4° C. From the data in Tables 1 and 2 we can calculate W_u to be 0.9 g/g for glucose.

By substitution of the appropriate values in equation (5) we can calculate W_u for the sulphite pulp to be 0.17 g/g which is in the range of the values of bound water determined by other methods.^(24, 25)

It should be emphasised, however, that the values of the 'hydration' determined as above are not precise but merely serve to indicate that the analysis leads to a reasonably acceptable value for the quantity of water bound to a cellulose surface in an aqueous medium.

The value of 0.17 g of destructured water per gram of sulphite pulp is considerably less than the value of 0.9 g/g obtained for glucose. The mole weight per —OH in glucose is 36 compared with 54 for cellulose. Moreover, some of the cellulose hydroxyl groups are inaccessible to liquid water while, presumably, all five of the —OH groups on glucose will be in contact with the liquid. Thus, assuming that the destructuring effect of an —OH group is the same regardless of whether it is on a glucose molecule or on a cellulose surface, we

would expect that W_u would be higher for glucose. As described in several previous publications^(1, 3, 5, 7) a simple extension of this reasoning permits the determination of the accessibility of the —OH groups on cellulose to liquid water from the volume/temperature behaviour of a pulp suspension.

By assuming a fairly simple picture of the molecular arrangement in the perturbed layer we can estimate its extent from the distribution of cluster species given by Lentz, Hagler and Scheraga.⁽²⁰⁾ If we assume that,

- 1. the distribution of non-rigid clusters associated with the —OH groups on cellulose is the same as that computed by Lentz, Hagler and Scheraga⁽²⁰⁾ for liquid water (i.e., number of H₂O molecules in dimer:trimer:star pentamer = 5:6:5) and,
- 2. every accessible —OH group on the cellulose is a terminal group of a non-rigid cluster and forms part of the chain,

we can show that, on average, 1.9 water molecules are linked by hydrogen bonds to each accessible hydroxyl of the cellulose surface. The surface of cellulose in water can be envisaged as a collection of —OH groups hydrogen bonded to water molecules to give mainly two- or three-oxygen chains with the occasional star pentamer, also hydrogen bonded. Rigid ring structures, though existing further away from the surface, will not, in fact, be hydrogen bonded to the surface —OH groups. A pictorial representation of this effect is shown in Fig. 8. It is interesting to note that the value of 0.9 g/g for W_u for glucose corresponds to 1.8 moles of water destructured per mole of —OH groups. The agreement between this figure and the value of 1.9 as calculated above provides support for the concept illustrated in Fig. 8.



Fig. 8—Conceptual drawing of the perturbed layer produced in the liquid adjacent to a cellulose surface immersed in water

Component	H-Bonds per H ₂ O	Weight fraction	Specific volume (ml/g)	Thermal expansion (ml/g° C)
Water Solidlike Fluidlike	0·9 1·0 0·7	0·83 0·17	1.00 1.03 0.88	0 0·0004 0·0009

TABLE 1—H-BONDS PER WATER MOLECULE, WEIGHT FRACTION, VOLUME AND THERMAL EXPANSION OF THE SOLIDLIKE AND FLUIDLIKE COMPONENTS OF LIQUID WATER AT 4° C

As shown in Table 1, the number of hydrogen bonds per water molecule in the solidlike component is greater than in the fluidlike component. Therefore, we would expect that the number of water-water hydrogen bonds per water molecule will be decreased in the perturbed layer. If the water molecules in the perturbed layer are in non-rigid clusters linked to the —OH groups in the cellulose chain and if the distribution of the non-rigid cluster species is the same as given by the LHS theory, then it can be shown that the number of water-water hydrogen bonds per water molecule in the perturbed layer is about 0.5 which is considerably less than the value of 0.9 for the unperturbed liquid. This provides support for the observation by Carles and Scallan⁽²⁵⁾ that the cellulose surface causes hydrogen bonds in the water to be broken. It should be noted, however, that there are also about 0.5 hydrogen bonds per water molecule formed between water molecules and the —OH groups on the cellulose.

If $d\Phi_2/dT$ is expected to be greater than dV_o/dT for structure breakers then the reverse should be true for structure formers. With its large hydrocarbon group and single —OH, t-butanol is recognised as a strong structure former in aqueous solution.^(4, 11, 26, 27) As shown in Fig. 7 and Table 2 the thermal expansion of liquid t-butanol is much greater than the apparent thermal expansion of t-butanol in aqueous solution. In fact, at 4° C, $d\phi_2/dT$ for t-butanol at 1 per cent concentration is negative suggesting that the volume/

Material	dV_0/dT (ml/g°C)	$d\phi_2/dT$ (<i>ml/g</i> °C)
Cellulose* (sulphite pulp)	0.00006	0.00021
Glucose†	0.00005	0.00086
Glycerol [†]	0.00035	0.00094
t-Butanol†	0.00168	-0.00024

TABLE 2—VALUES OF dV_0/dT AND $d\phi_2/dT$ AT 4°C FOR VARIOUS MATERIALS

* The consistency of the pulp suspension was 8 per cent by weight.

The concentrations of glucose, glycerol and t-butanol in aqueous solution were all about 1 per cent by weight.

temperature relationship is affected not only by the low thermal expansion of structured layer on the surface of the molecule but also by the melting of the structured layer to increase the proportion of the denser fluidlike component. Note that a component of $d\phi_2/dT$ for the carbohydrate could also be due to a decrease in W_u with temperature. Such an effect was taken into account in the original treatment by Ramiah and Goring.⁽¹⁾ However, its inclusion made necessary a calculation of W_u from the loss of volume in mixing crystalline glucose with water. Neal and Goring⁽⁴⁾ showed that $V_o - \phi_2$ is a poor indicator of the effect of a solute on the structure of water and therefore in the present work we prefer to compute W_u from $(d\phi_2/dT - dV_o/dT)$ by means of equation (5).

At this stage it should be pointed out that several authors have used volume/temperature relationships in aqueous solutions to characterise a solute with respect to its effect on the structure of water. Wada and Umeda⁽²⁶⁾ showed that the monohydric alcohols increased the temperature of maximum density (TMD) of water in contrast to most electrolytes which lowered the TMD. The increase in the TMD has been related to the enhancement of water structure by Armitage, Blandamer, Morcom and Treloar,⁽²⁸⁾ by Darnell and Greyson,⁽²⁹⁾ and by Kuppers.⁽²⁷⁾ The temperature dependence of the apparent volume of a solute in aqueous solution has been used as an indicator of structural interaction by Gopal and Siddiqi⁽³⁰⁾ and by Hepler.⁽²³⁾ Neal and Goring⁽⁴⁾ and Kuppers⁽³¹⁾ have shown that a simple, quantitative relationship can be derived between the solute induced shift in the TMD and the temperature dependence of the apparent volume. Thus there is a fair amount of previous literature concerning the relationship between thermal expansion and structure in aqueous systems. As far as we know, however, Ramiah and Goring⁽¹⁾ were the first to apply these concepts to the cellulose/ water interface.

A final word might be said here concerning anomalous water or 'polywater'. In the mid-sixties Derjaguin⁽³²⁾ announced that by condensing water in fine quartz capillaries, it could be obtained as a viscous liquid with properties very different to those of ordinary water. This material was envisaged to be a stable polymer of water (hence polywater) and was studied both theoretically and experimentally by scores of scientists all over the world. The polywater episode began soon after we had proposed that —OH containing surfaces were structure breakers. We therefore considered clean glass to be a structure breaker rather like cellulose and would have predicted that water would be de-polymerised rather than be polymerised by a glass surface. We were therefore very sceptical of polywater and suspected that it was caused by impurities such as silicone grease contaminating the apparatus.^(32, 33) Polywater eventu-

ally turned out to be an aqueous solution of impurities, much to our relief, since the properties found for polywater were not at all consistent with the concept that hydropholic surfaces such as those of cellulose and glass were water structure breakers.

Concluding remarks

THE main conclusion of the present paper is that a cellulose surface in contact with liquid water will reduce the structure in the layer of water molecules adjacent to the surface. In terms of the recently published theory of Lentz, Hagler and Scheraga,⁽²⁰⁾ the hydroxyl groups on the cellulose are hydrogen bonded to water molecules to give a layer of dimers, trimers and star pentamers attached to the surface. Farther away in the liquid, rigid pentamer and hexamer ring structures predominate. Thus the cellulose surface is seen to be bonded to and to comprise part of a fluidlike layer about one or two water molecules thick.

It should be noted that the present treatment predicts the almost complete absence of unbonded water molecules in the perturbed layer. In the previous work the perturbed layer was envisaged as being made up entirely of unbonded water molecules. This is the major difference between the current concept and the original proposal by Ramiah and Goring⁽¹⁾ and it arises from the application of the new cluster model for water developed by Scheraga and his co-workers.

The author is very aware of the serious limitations of the analysis given in the present paper. In the first place, liquid water may not be best represented by a mixture model or by a cluster model in which case the argument falls apart from the beginning. Even if such models turn out to give a realistic picture of the structure of water, there is no guarantee that the model developed by Lentz, Hagler and Scheraga⁽²⁰⁾ will be the correct one. Furthermore, the application of macroconcepts such as volume and thermal expansion to domains which are of molecular dimensions is questionable and to attempt to derive numerical values for such parameters is probably inadmissible. Nevertheless, the author feels that the concept of cellulose as a water structure breaker, with all its flaws and uncertainties, is about as good as we can do at the present state of development of the theories of liquid water.

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Transcription of Discussion

Discussion

Dr A. H. Nissan Frank and Wen's theory I think is getting very well established. Némethy and Scheraga have confirmed their prediction with respect to hydrophilic and hydrophobic solutes. But supposing that I said to you, Dr Goring, that cellulose does not apply to this, I am going to be the devil's advocate and say that cellulose is not glucose. Being a long molecule it has other thermodynamic parameters which do not appear in small molecule solids. Supposing I said this to you, that we know cellulose is hydrogen bonded within itself and to each other, but when water comes in it breaks down these hydrogen bonds, we know that too. But many new degrees of freedom are thereby created for vibration, rotation and partial translation. And it is because of these that we get a higher thermal expansion for cellulose in water than when it is dry. Whether the structure of water is changed or is not changed is not related to the phenomenon. How would you teach me otherwise?

Goring What we really need to do here is some more experiments. I can suggest one which I haven't vet done; that is to study a polymer which is not as hydrophylic as cellulose, e.g. a polymerised alcohol; and then get water against its surface and to see whether its behaviour is opposite to that of cellulose. I think this would answer your question. I see though a rather clear parallel between the behaviour of cellulose and glucose. In fact the parallel is to clear that we have been able to use it to calculate accessibilities of various celluloses. The accessibility is calculated from the thermal expansion data and the values seem to fit in well with other methods. Maybe you are right. I don't know, although I must say I don't see phenomenologically too great a difference between the behaviour of glucose molecules in solution and a cellulose surface immersed in water. From the point of view of thermal expansion, I don't see that there will be free volume effects in a water swollen cellulose fibre qualitatively different from those in a glucose molecule or a cellobiose molecule, or a starch molecule dissolved in water; yet for all of these we have observed the same effect.

Under the chairmanship of Dr H. Corte

Discussion

Dr M. B. Lyne I would like to ask a question about the rate of this phenomenon of structure breaking of water by cellulose. If a fully bleached kraft handsheet is taken as representing cellulose, one finds if one drops water on its surface that there is a wetting time in the order of milliseconds. Would you venture to explain part of this time of wetting as being due to the rate of establishing equilibrium of 'broken' water or as you call it, the broken structure of water near the cellulose surface ?

Goring I think this is an attractive possibility. It would be interesting if this were the case, but the sorts of times that fall out of the theories are fairly small. Structures are supposed to have lifetimes of about 10^{-11} seconds. In other words they are appearing and disappearing at this rate, so that I would expect that the equilibrium would be reached very quickly indeed, in times much shorter than milliseconds.

Prof. H. W. Giertz I have a suggestion to make for the further discussions. That is that the speaker should make sure they mean cellulose or hemicellulose. I think the discussion between Nissan and Goring was a little misleading because they are speaking about cellulose but I think they mean hemicellulose. You remember that Rånby, when he isolated microfibrils by hydrolysis where no hemicellulose was present, characterised these microfibrils as hydrophobic whereas hemicellulose is amorphous and swells in water. In the future we should make it very clear whether we mean the crystalline microfibrils or the amorphous and swollen hemicellulose.

Goring I think that is a good point. What happens with hemicellulose is that it is very highly swollen and the proportion of hydroxyl groups that are exposed to liquid water, of course, is greater. However, cellulose itself, albeit that parts of it might be hydrophobic, must have hydroxyl groups exposed to water when it is wet. We have done experiments with cotton and got the same effect as with pulp. With cellophane we also get the same effect. The difference is the intensity of the effect related to the accessibility of the cellulose. I think that this phenomenon is not particular to cellulose. It happens with a cellulose surface against water; it happens with hemicellulose surfaces; it happens with the surface of a glucose molecule; it occurs with the surface of a glycerol molecule; in fact any surface rich in hydroxyl groups will give you thermal expansion behaviour that we have observed and I think that it is more general than simply for the cellulose molecule.

Dr A. de Ruvo How important is the structure? For example we know that

interaction between water and cellulose is mainly due to hydrogen bonding. How important are different structures, for the swelling of the cellulose. If you have for example changes of 100 units or 5 units that is mainly a change in entropy and the entropic difference wouldn't give so much influence as I would see it on the free energy of swelling. So how important is the structure with regard to different swelling values of cellulose?

Goring That is a very good question but I am not going to attempt to answer it. I think that what you are saying is that these effects are rather subtle. Water is water and we know the way it behaves empirically. Certainly, we have many empirical concepts to explain the behaviour of aqueous systems. So, what use is this knowledge? All I can say is I don't know. Liquids in general are a mystery and water is still perhaps the biggest mystery of all; as such it is a challenge and it is very large part of our industry; and I think we should know as much as it is possible to know about it. But with respect to the application of these concepts in papermaking; we'll have to see.

Mr B. A. Nazir I would like to add that the structure of water in the vicinity of cellulose surface would probably affect the interaction of fibres with each other or the interaction of other additives with fibres. This is important in floc formation of fibres in papermaking or the rentention of other additives. In predicting the various possible interactions one has to take the repulsive forces due to restructuring of water into account, in addition to the van der Waal's and Coulombic forces.

Goring Yes, I agree with you and I think that water structure and the behaviour of liquid water with cellulose fibres could have applications at the wet end of a paper machine. It is in this area that these subtle effects may be important.