VISCOSITY MEASUREMENTS OF ALCOHOL-WATER MIXTURES AND THE STRUCTURE OF WATER

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In a previous paper,[1] a model of the hydrogen bond was proposed that gave a structure for water differing markedly from others that have been suggested.[2] According to this model, the hydrogen bond would not be located between any two atoms of a given molecular system, as in the case of an ordinary bond, but it would be a *collective bond* linking a number of molecules together and consisting of a ring system of correlated hydrogen bridges. The bond would depend on a simultaneous displacement of the electric charge in each component molecule, all around the ring. If one of the hydrogen bridges of the ring were broken, all the others would break down at the same time.

When this model is applied to water, one finds that each molecule cannot participate in more than two independent collective hydrogen bonds. Several types of molecular aggregates would then be present in the water: e.g., linear chains containing any number of molecules each of which is bound to its neighbor by two hydrogen bridges, or rings of three, four, five, and six molecules, and more complex aggregates made up of a number of rings linked together. These aggregates would not be permanent, as each of them would be able to form further hydrogen bonds, and in the course of a thermal collision some molecules would move from one aggregate to the other, the total number of hydrogen bridges remaining constant.

This model was used primarily to suggest further experiments. First of all we examined the connection between this continuous transfer of molecules between aggregates and the physical properties of water, particularly as it seemed probable that it would affect the value of the viscosity of water. Let us suppose that the viscosity of any liquid is obtained by first putting it into the hollow space between two concentric cylinders, one of which is kept in uniform rotatory motion. An ordered motion of the molecules is then superimposed on their thermal motions, and a velocity gradient is maintained at the expense of the interactions between the molecules of neighboring infinitesimal annular layers of the liquid. In these interactions, a fraction of the kinetic energy of the ordered motion is transferred to the thermal motions, and the viscosity of the liquid arises from this effect.

If, however, the liquid consists of large molecular aggregates, and some molecules can move from one aggregate to another at constant binding energy, then there would be a tendency to maintain the velocity gradient almost without any transfer of energy from the ordered to the thermal motion. In such cases we would expect the viscosity to be lower than in the liquid when resonance transfer of molecules did not take place.

If, somehow, we stop the resonance transfer of water molecules from one aggregate to another, the viscosity should increase and such an experiment will now be described. According to our model, a molecule of a primary alcohol can only be involved in one collective hydrogen bond and Figure 1 shows how methanol and ethanol molecules should normally form dimers. These substances have a fairly

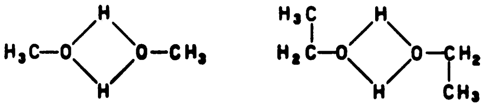

Fig. 1.

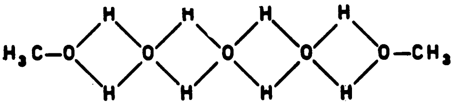

Fig. 2.

large heat of solution when mixed with water, i.e., 8.37 and 10.63 kj per mole solute at infinite dilution, respectively.[3] In a water-alcohol mixture, if the alcohol concentration is low, we can suppose that each molecule of alcohol is bound to a molecular aggregate of water, in a position where it can form an additional hydrogen bond. In this position any binding capacity is saturated and the transfer of water molecules can then no longer take place. An example is given in Figure 2 of the way in which two methanol molecules can prevent resonance transfer by joining the free ends of a linear chain of water molecules through the formation of two hydrogen bonds.

The viscosity of water is 1.0 Cp at 0°C, and that of methanol is 0.6 Cp at the same temperature.[4] If a small quantity of the latter is added to water, the viscosity of the mixture must be higher than that of both components. The broken curve in Figure 3 summarizes a series of viscosity measurements on water-methanol solutions of increasing concentration, using an Ubbelohde viscometer and a thermostat bath at 20 ± 0.01°C. As expected, the curve shows a broad peak at about two methanol molecules per seven water molecules. At this concentration, all hydrogen bonds available in the water at that temperature should be saturated by alcohol molecules. If the alcohol concentration is further increased, the added molecules

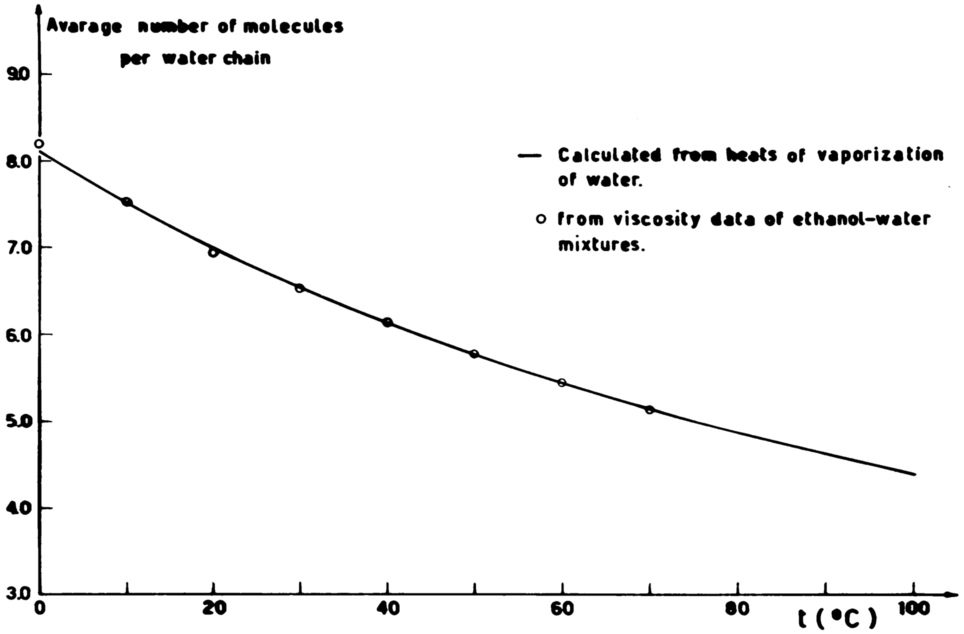

Fig. 3.

cannot join the water molecules and the viscosity of the mixture should decrease toward that of pure methanol.

Let us imagine that all the different types of water molecule aggregates are transformed into linear chains with lengths such that the total number of hydrogen bridges remains constant. Then L, the "mean chain length," can be defined as the mean number of water molecules per linear chain, and making use of this concept, the preceding results can be summarized by saying that L is equal to 7 at 20°C.

In order to confirm these ideas we repeated the experiment, using ethanol in place of methanol, and the results are shown by the continuous curve in Figure 2. This curve also shows a broad peak, the maximum of which again suggests that L equals 7 at 20°C. The two sets of measurements are completely independent and are a first confirmation of the new theory, but the precision is not very high. The position of the maximum of a viscosity curve was deduced from the measurements by interpolation and an error of 0.5 units on the abscissae is not impossible. On the other hand, even if the maxima of the methanol and ethanol curves did not correspond exactly to the same value of L, at the same temperature, there could still be an agreement with the collective model of the hydrogen bond. We assumed that all the alcohol molecules were hydrated before maximum viscosity was reached, and this is justifiable for the alcohols with large heats of hydration. However, a small percentage of alcohol molecules may remain to be hydrated at the time some hydrogen bonds are still available and can cause a displacement of the maximum in either direction, depending on the properties of the two mixed substances and their interactions.

A qualitative confirmation of our interpretation can be obtained by measuring the viscosity of mixtures of water and a substance able to form more than one independent collective hydrogen bond, e.g., a secondary alcohol such as ethylene glycol, or a tertiary one such as glycerol. In these cases the resonance transfer of molecules from one aggregate to another cannot be prevented because the alcohol molecules are simply included in the chains or rings and no saturation of the hydrogen bonds available in water can be obtained. Then the viscosity of the mixtures should not have a peak at any concentration. It should, on the contrary, show a regular transition from the viscosity of the first component to that of the second and this is shown in Figure 4 for ethylene glycol and glycerol. In both cases the heat of hydration is sufficiently large (7.1 and 6.3 kj per mole solute at infinite dilution, respectively[3]) to assume that the single alcohol molecules are effectively hydrated.

We attempted to confirm the above results and their interpretation by performing new experiments not involving viscosity measurements and we therefore considered the heats of vaporization of ice and water from which L can be determined independently. Suppose that the binding energy per hydrogen bridge is the same in ice as in water and that the other interactions between molecules, which do not form stable bonds, in the two cases give a contribution proportional to that of the hydrogen bonds.

The heat of vaporization of ice[5] at 0°C is 675.1 cal-gm^{-1}. Taking into account that part of this is transformed into external work in the passage from ice to saturated steam at 0°C, we can show that only 645.0 cal-gm^{-1} are used to break all the hydrogen bonds joining the molecules of water in the network of ice. Let us

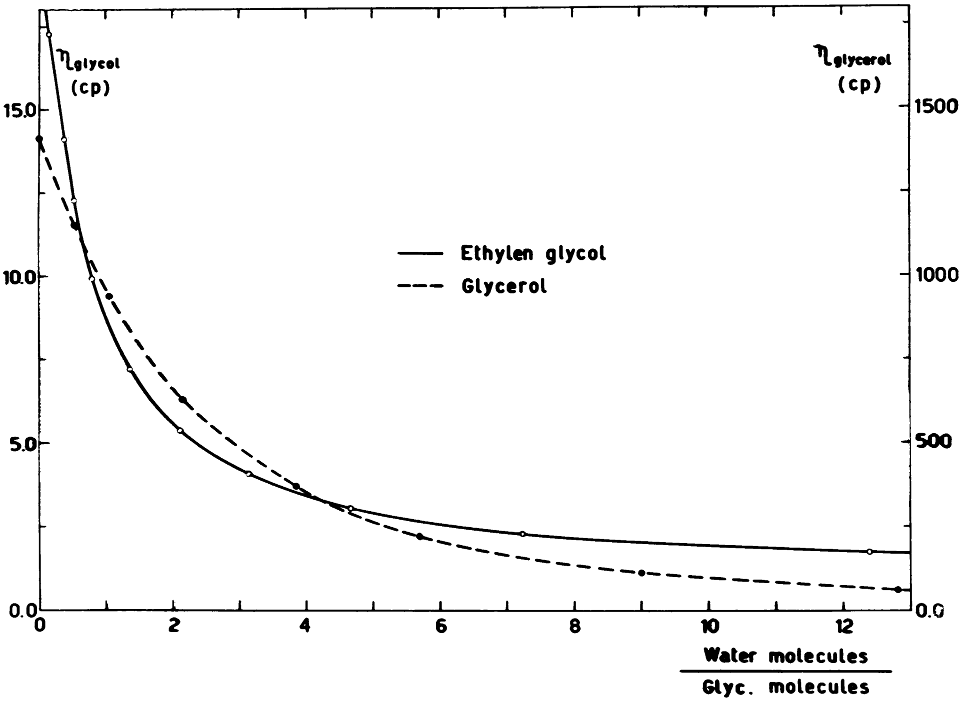

FIG. 4.

now assume that ρ denotes the difference between the heat of vaporization of water at a given temperature, t, and the external work done in the transformation of the liquid into saturated steam at that temperature. We have, then, at t°C

$$L = 1 + \frac{\rho}{645.0 - \rho}.$$

From this formula (at 20°C) we get L equal to 7.0, which is in good agreement with the results of the viscosity measurements on alcohol-water mixtures.

This comparison can be taken further because the heats of vaporization of water at different temperatures are well known,[5] and the viscosities of ethanol-water mixtures of different concentrations were accurately measured, every ten degrees from 0° to 70°C, many years ago.[6] We used the heats of vaporization of water to calculate the continuous curve of Figure 5, giving L as a function of the temperature, and, from the published viscosity measurements, we obtain the eight points indicated by open circles. It will be seen that there is good agreement, even if the concentrations of maximum viscosity are a little uncertain.

In conclusion, it should be stated that the experimental results reported here are not a general confirmation of the collective model of the hydrogen bond. They only demonstrate that a water molecule can be involved in no more than two independent hydrogen bonds, and a primary alcohol molecule in no more than one. These properties can, however, be deduced from the model and they contradict previous theories.

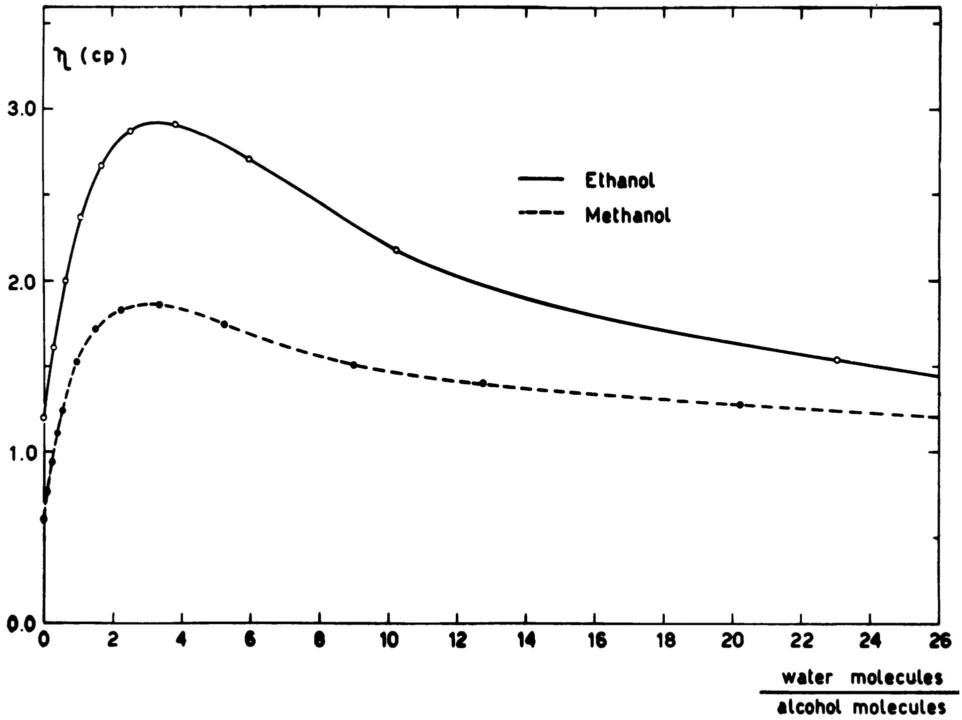

FIG. 5.

Summary.—According to the collective model of the hydrogen bond, the molecules of a primary alcohol can saturate all the bonds available in water in the liquid state, thus preventing the resonance transfer of water molecules from one molecular aggregate to another. Adding to the water a convenient quantity of a primary alcohol, whose heat of hydration is sufficiently large, should make the viscosity of the mixtures higher than that of both components. This statement was experimentally verified for water-ethanol and water-methanol mixtures. In both cases one obtains from the concentration of maximum viscosity $L = 7$ at 20°C, where L is the mean number of molecules per linear chain in water. The same value of L can also be calculated from the heats of vaporization of ice and water. The two methods give results which are in very good agreement, from 0°C to 70°C.

[1] Ageno, M., these PROCEEDINGS, **57**, 567 (1967); Ageno, M., *Rend. Accad. Nazl. Lincei,* **40**, 734–739 (1966).

[2] See for instance: Pauling, L., these PROCEEDINGS, **14**, 359 (1928); Coulson, C. A., *Research* (*London*), **10**, 149 (1957); Nordman, C. E., and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 2077 (1953); Hunter, L., *J. Chem. Soc.*, **1945**, 806 (1945); Pimentel, G. C., and A. L. McClellan, *The Hydrogen Bond* (San Francisco and London: W. H. Freeman and Co., 1960), pp. 203–205.

[3] *International Critical Tables of Numerical Data,* National Research Council (New York and London: McGraw-Hill Book Co., 1929), vol. 5, pp. 148–150.

[4] *Ibid.*, pp. 10 and 11.

[5] *CRC Handbook of Chemistry and Physics* (Cleveland: The Chemical Rubler Co., 1964–65), 46th ed., E_7-E_{12}.

[6] See reference 3, page 22.