

**INVESTIGATIONS OF THE HYDRATION OF DEXTRAN USING AN ACOUSTIC METHOD\*****ADAM JUSZKIEWICZ, JADWIGA POTACZEK**

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Measurements of the velocity of ultrasound in alcohol-water solutions of dextran with molecular weights 40 000 and 500 000 in the temperature range of 10-35°C have been made. The values of the hydration numbers have been determined and it has been shown that hydration is independent of the molecular weight of the dextran.

**1. Introduction**

According to the model accepted [1-6] the addition of ethyl alcohol to water causes an increase in the stabilization of the octahedral structure of water because the molecules of alcohol penetrate into the cages of the "open-work" structure of water. Spectroscopic infrared investigations [6-9] have shown that the stabilization of the structure of water by non-electrolyte molecules is connected with the increase of the stability of the hydrogen bonds between the water molecules. The observed order of water is due to the influence of non-polar groups of the non-electrolyte molecules of water; around the non-electrolyte molecules associated molecules of water called non-polar group solvates appear. This type of solvation is defined as second order solvation [10].

It is known that the dependence of the sound velocity and of the adiabatic compressibility on the alcohol concentration for alcohol-water solutions is parabolic. The maxima of the ultrasound velocity curves and the minima of the compressibility curves are dependent on temperature and they shift in the direction of lower concentrations of alcohol with increasing temperature. According to the previously presented considerations [6, 11] the point of maximum

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ultrasound velocity defines the concentration of alcohol at which all the cages of the undestroyed octahedral structure of water are occupied by alcohol molecules. The increase of the non-electrolyte concentration above the maximum value causes a break up of the primitive structure of water. The degree of order of the solution decreases and, as a result of this, the ultrasound velocity decreases. The addition of any solute to the alcohol-water mixtures causes a shift of the peak of the parabola in the direction of lower concentrations of alcohol. This is caused either by a break up of the water structure and the binding of the water molecules by the solute, or by the occupation by the solute molecules of part of the cages (holes) in the water structure. In both instances the proportion of empty cages occupied by alcohol molecules decreases, and the alcohol concentration at which the ultrasound velocity reaches a maximum is smaller. The difference between the concentration of the solute at the velocity maxima of the alcohol-water solution, and the concentration of the reference solution (alcohol-water) is caused by hydration of the solute. The amount of hydration water per number of grams of the solute  $W_x$  can be calculated from the following formula (1)

$$W_x = W_1 - \frac{W_0 A_1}{A_0}, \quad (1)$$

where  $A_0$  and  $W_0$  are the amounts of alcohol and water corresponding to the maximum for alcohol-water mixtures without a solute,  $A_1$  and  $W_1$  are amounts of alcohol and water at the maximum for alcohol-water solutions containing a certain amount of solute and  $W_x$  is the hydration in terms of percentage volume. In the previous paper [11] this method was used for the determination of the hydration of polyethylene glycols having molecular weights 400, 1500, 2000, 15 000 and 20 000. The optimum concentration of macromolecules at which this method gives repeatable results has been determined.

The acoustic and n.m.r. measurements of the longitudinal relaxation times showed that the hydration does not depend on the chain length of the polyethylene glycols tested.

This paper presents results of the measurements of the hydration numbers of dextran with molecular weights 40 000 and 500 000 over a range of concentration from 1.4 g to 17.1 g per 100 g of water in the temperature range 10-35°C.

## 2. Experimental arrangement

The dextran of molecular weight 40 000 used for the investigation was made by "Polfa" and the dextran of molecular weight 500 000 was made by Pharmacia Fine Chemicals AB.

Measurements of the sound velocity as a function of ethanol concentration were performed at 25°C for concentrations of 1.43, 2.68, 4.28, 5.71, 7.14, 8.57, 10.0, 11.43, 12.86, 14.29, 15.71 and 17.14 g per 100 g of water for each dextran.

Moreover, analogous measurements were carried out for 10 percent solutions of both fractions over the temperature range of 10-35°C. The measurements of the sound velocity were made with the system previously described [6, 11] based on the "sing-around" velocity meter. The results of the measurements are presented in Table 1 and in Figs. 1-4.

Table 1. Values of the hydration numbers

$c$ [%]	Dextran 40 000		Dextran 500 000	
	$n_h$ [cm <sup>3</sup> /g]	$\left[ \frac{n_h}{\text{mH}_2\text{O}} \right]$ [m mon.]	$n_h$ [cm <sup>3</sup> /g]	$\left[ \frac{n_h}{\text{mH}_2\text{O}} \right]$ [m mon.]
1.43	0.760	6.8	0.676	6.1
2.68	0.511	4.6	0.511	4.6
4.28	0.340	3.1	0.340	3.1
5.71	0.383	3.4	0.340	3.1
7.14	0.360	3.2	0.321	2.9
8.57	0.370	3.3	0.333	3.0
10.00	0.370	3.3	0.333	3.0
11.43	0.319	2.9	0.287	2.6
12.86	0.340	3.1	0.311	2.8
14.29	0.333	3.0	0.300	2.7
15.71	0.325	2.9	0.279	2.5
17.14	0.325	2.9	0.279	2.5

### 3. Results and conclusions

In Table 1 the values of the hydration numbers for two dextrans are presented. It can be seen from these results that for both weights of dextran above a concentration of 4.28 g per 100 g of water the hydration numbers calculated on the basis of equation (1) are constant within experimental error with a tendency to become lower at the highest concentrations tested. At 25°C over the range of the medium concentrations tested the gram hydration  $n_g$  is equal, respectively, to: 0.366 cm<sup>3</sup>/g for dextran of molecular weight 40 000, and to 0.335 cm<sup>3</sup>/g for dextran of molecular weight 500 000. The contributions of the hydration  $n_i$  calculated from these data in terms of moles of H<sub>2</sub>O per mole of monomer — (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>) are equal to 3.3 for dextran of molecular weight 40 000 and to 3.0 for dextran of molecular weight 500 000.

Figs. 1 and 2 show the graph of ultrasound velocity as a function of ethanol content over the temperature range 5-35°C for water-alcohol solutions without dextran (Fig. 1) and for 10 percent solutions of dextran of molecular weight 40 000 (Fig. 2).

As can be seen in Figs. 1 and 2, the values of ultrasound velocity at the maximum points for water-alcohol solutions of dextran are higher than those

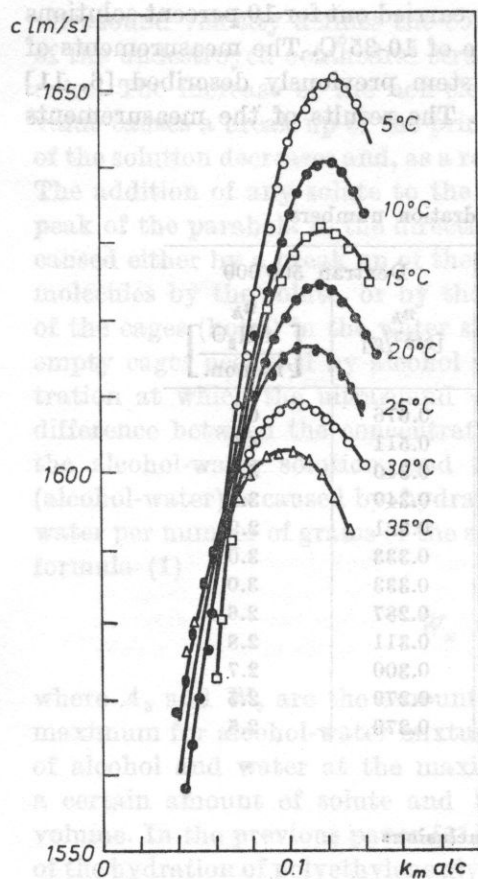


Fig. 1. Propagation velocity of ultrasonic waves as a function of ethanol concentration for a water-alcohol system in the temperature range 5-35°C

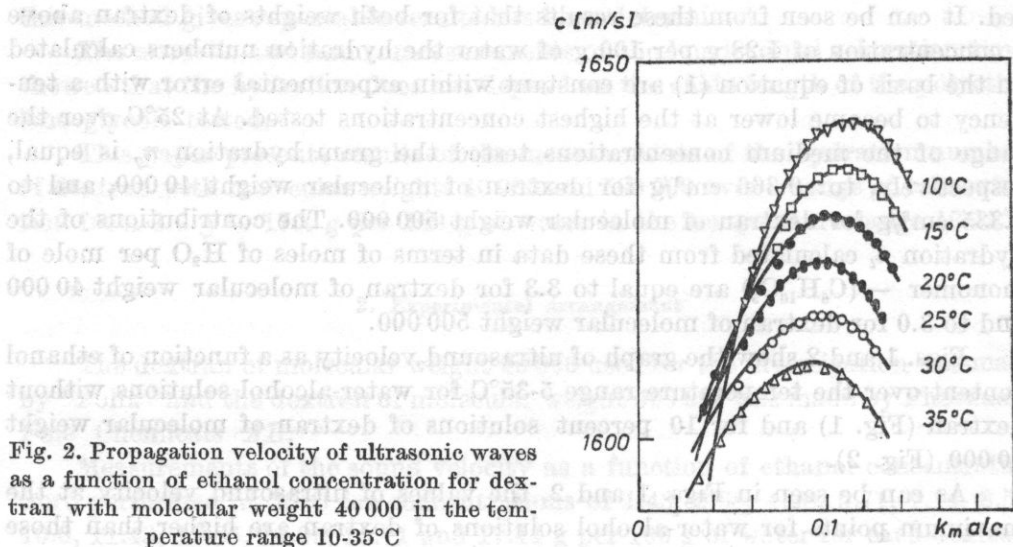


Fig. 2. Propagation velocity of ultrasonic waves as a function of ethanol concentration for dextran with molecular weight 40 000 in the temperature range 10-35°C



at the maximum point for the reference water-alcohol system. An increase in the ultrasound velocity is due to an increase in the order of the solution. In the solutions containing dextran this increase is caused by water molecules which are bound by hydrogen bonds to  $-\text{OH}$  groups of the dextran.

In Fig. 3 the temperature dependence of the number of moles of water per mole of ethyl alcohol at the maximum of ultrasound velocity for the water-

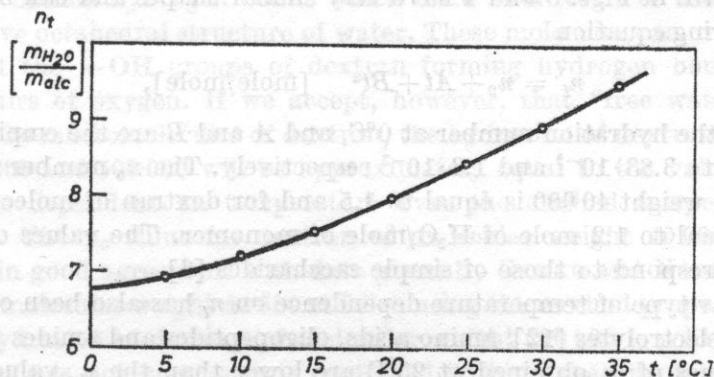


Fig. 3. Number of moles of water per mole of ethanol at the maximum of ultrasound velocity as a function of temperature for a water-alcohol system

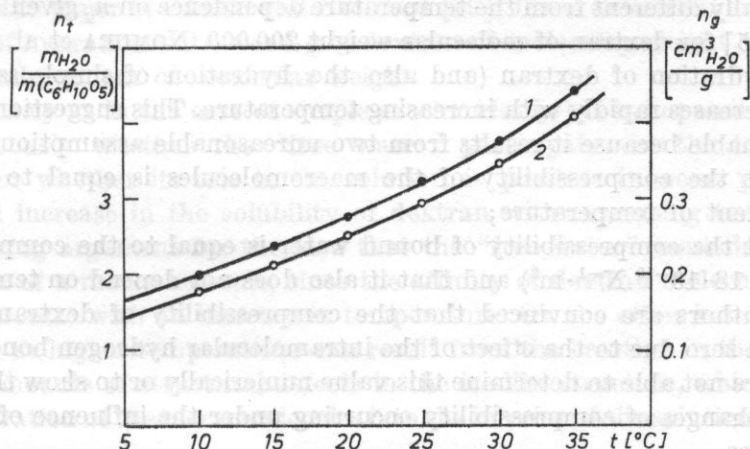


Fig. 4. Hydration numbers  $n_t$  [mole of  $\text{H}_2\text{O}$ /mole of mon.] and  $n_g$  [ $\text{cm}^3/\text{g}$ ] as a function of temperature for dextran with molecular weight 500 000

alcohol mixture is presented. A shift of the maximum of the sound velocity in the direction of lower concentrations of alcohol with increasing temperature, i.e. an increase in the number of moles of water per mole of alcohol, is caused by the partial break up of the cages of the octahedral structure of the water. As

a result of this, the maximum of the ultrasound velocity is reached by the system at a lower concentration of alcohol.

In Fig. 4 the temperature dependence of the hydration numbers  $n_t$  [mole of  $H_2O$ /mole of mon.] and  $n_g$  [ $cm^3/g$ ] for dextran of molecular weight 500 000 is presented. Similar curves  $n_t$  and  $n_g$  were obtained for dextran of molecular weight 40 000.

The curves in Figs. 3 and 4 have very similar shapes and can be described by the following equation

$$n_t = n_0 + At + Bt^2 \quad [\text{mole/mole}], \quad (2)$$

where  $n_0$  is the hydration number at  $0^\circ C$ , and  $A$  and  $B$  are the empirical coefficients equal to  $3.83 \cdot 10^{-2}$  and  $1.3 \cdot 10^{-3}$  respectively. The  $n_0$  number for dextran of molecular weight 40 000 is equal to 1.5 and for dextran of molecular weight 500 000 is equal to 1.2 mole of  $H_2O$ /mole of monomer. The values of  $n_t$  and  $n_0$  obtained correspond to those of simple saccharides [6].

A similar type of temperature dependence on  $n_t$  has also been obtained for solutions of electrolytes [12], amino acids, oligopeptides and amides [13].

The values of  $n_g$  obtained at  $25^\circ C$  are lower than the  $n_g$  value presented by SHIO et al. [14] for dextrin ( $n_g = 0.4 \text{ cm}^3/g$ ) using a slightly different measuring method. The temperature dependence of the values of  $n_t$  and  $n_g$  for dextrans with molecular weights 40 000 and 500 000 presented in this paper is fundamentally different from the temperature dependence on  $n_g$  given by NOMURA et al. [15] for dextran of molecular weight 200 000. NOMURA et al. suggested that the hydration of dextran (and also the hydration of simple saccharides [16-18]) decreases rapidly with increasing temperature. This suggestion seems to be unreasonable because it results from two unreasonable assumptions:

1) that the compressibility of the macromolecules is equal to zero and is independent of temperature;

2) that the compressibility of bound water is equal to the compressibility of ice ( $\beta = 18 \cdot 10^{-10} \text{ N}^{-1} \cdot \text{m}^2$ ) and that it also does not depend on temperature.

The authors are convinced that the compressibility of dextran must be higher than zero due to the effect of the intramolecular hydrogen bonds. However, they are not able to determine this value numerically or to show the character of the changes of compressibility occurring under the influence of temperature changes.

SHIO [14] stated the compressibility of dextrin macromolecules at  $25^\circ C$  to be equal to  $9.2 \cdot 10^{-10} \text{ N}^{-1} \cdot \text{m}^2$ , but this value was determined assuming that the compressibility of the hydration water at  $25^\circ C$  is the same as the compressibility of ice and that neither the compressibility of dextrin nor the compressibility of the hydration water changes with temperature.

It seems to be reasonable that the compressibility of the water in the hydration shells and the compressibility of the macromolecules should increase with increasing temperature. The changes of both compressibilities can give a told

effect markedly exceeding the variation of the compressibility in pure water. If the real numerical values of the compressibility of the hydration water and of the macromolecules were known, it could prove that the dependence of  $n_0$  on temperature has quite a different form.

The increase of the value of  $n_0$  with increasing temperature can be explained by an increase in the number of the molecules of "free water" with partially or completely broken hydrogen bonds which form as a result of the break up of the primitive octahedral structure of water. These molecules can orient themselves around the  $-\text{OH}$  groups of dextran forming hydrogen bonds with free electron pairs of oxygen. If we accept, however, that "free water" does not bind with the macromolecules of dextran, the hydration of dextran of molecular weight 40 000 and 500 000 will be approximately equal to the values of  $n_0$  and will not be dependent on temperature over the studied temperature range of 10-35°C. The  $n_0$  value for dextran of molecular weight 40 000 is equal to 1.5 and is in good agreement with data given by GEKKO and NOGUCHI [19] for dextran of molecular weight 44 500 at 20°C, using the method proposed by SHITO.

The hydration of dextran of molecular weight 500 000 is a little lower but the difference is not great and is contained within experimental error. Apart from the influence of possible branching which can occur in the macromolecule of dextran of higher molecular weight, it can be concluded that the hydration of dextran does not depend on its molecular weight. The same conclusion can be found in the paper of GEKKO and NOGUCHI [19]. These authors showed that the amount of hydration water per 1 g of dextran of molecular weight greater than 2000 is independent of molecular weight.

Similarly as in the case of simple saccharides [6] it is impossible to decide simultaneously whether the "free water" participates in the hydration of dextran or whether its role in the solution is passive. It seems possible that the rapid increase in the solubility of dextran with increasing temperature is a convincing argument for the idea that the "free water" contributes to the hydration of a macromolecule, since the affinity of dextran molecules to water should increase with an increase in temperature. On the other hand, the better solubility at higher temperatures can result from the creation in the solution of greater amounts of structural defects in the ice-like structure, which facilitates the penetration of the macromolecules into the interior of the solution.

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