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ULTRASONIC VELOCITY MEASUREMENTS OF HYDRATION NUMBERS OF SUGARS IN ALCOHOL-WATER SOLUTIONS*

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This paper describes a method for finding the hydration numbers of electrolytes and non-electrolytes based on ultrasound velocity measurements in a mixed ethanol-water solvent. The hydration numbers of sugars such as: glucose, mannose, arabinose, xylose, saccharose and lactose were determined. Interpretation of the results obtained on the basis of the theory of "specific hydration" for sugars was presented.

1. Introduction

Ultrasonic interferometry can be a useful instrument for investigation of the hydration of substances in an aqueous environment. The advantage of this particular method of hydration number determination is its great simplicity. The first method of determining the hydration number using ultrasonic velocity and density measurements was proposed by PASSYNSKY about forty years ago [1, 2]. PASSYNSKY assumed that the decrease of solution compressibility is connected with the strong compression of water in an ionic field and that this decrease of compressibility in solution is due to hydration. He found the following expression for determining the hydration numbers of molecules in an aqueous solution:

$$n_h = (1 - \beta_T/\beta_T^0)\frac{100-x}{M_0}\frac{M_2}{x}, \tag{1}$$

where β_T and β_T^0 are the isothermal coefficients of compressibility of the solution and solvent respectively, x is the weight percentage of the solute, M_0 is the molecular weight of the solvent and M_2 is the molecular weight of the solute.

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All of the remaining methods using ultrasonic measurements for the determination of hydration numbers are based on this expression [3-8]. In deriving this expression PASSYNSKY assumed that an ion, together with its hydration shell, is incompressible. The other authors assumed ionic incompressibility, but the compressibility of the water in the hydration shell they assumed to be equal to the compressibility of free water. The incompressibility of an hydrated ion can only be valid for small ions such as: Mg^{2+} and Li^{+}. In the case of larger ions the electric field of these ions interacting with water molecules changes widely and the local compressibility of the water molecules in the hydration shells also changes ($0-4.5\cdot10^{-10}N^{-1}\,m^{2}$) [9]. For molecules of non-electrolytes and macromolecules the situation is still more complicated because besides the necessity of taking into consideration the compressibility of the water in the hydration shell, the compressibility of the solute itself has to be considered also. It has generally been believed that the small molecules of nonelectrolytes are incompressible and the compressibility of the hydration water is equal to the compressibility of normal ice [3, 4]. Thus, the hydration numbers of electrolytes and nonelectrolytes obtained by different authors on the basis of different assumptions cannot be relied upon because the possibility of experimental verification of these assumptions does not exist. For these reasons the method of measurement of hydration numbers which was first proposed by YASUNAGA at al. [10, 11] was used. This method gives valid results for electrolytes as well as for non-electrolytes and macromolecules. Using this method the hydration of the molecules can be determined by ultrasonic velocity measurements in alcohol-water solutions. It is known that the dependence of the ultrasonic velocity as a function of alcohol concentration in water-alcohol mixtures is parabolic, and the maximum is precisely defined for each temperature.

The addition of any given substance causes the maximum to shift in the direction of smaller alcohol concentration. The difference between the abscissae of the maxima of the curves obtained is caused by the molecules of the solute bonding part of the water.

With this assumption we have

$$\frac{A_0}{W_0} = \frac{A_1}{W_1 - W_x} = \text{const}, \tag{2}$$

where A_0 and W_0 are the amounts of alcohol and water corresponding to the maximum for alcohol-water mixtures without solute, and A_1 and W_1 are the amounts of alcohol and water at the maximum for alcohol-water solutions containing a certain amount of solute. W_x in this equation is the amount of water bound to the solute.

In a previous paper [12] the hydration numbers of polyethylene glycols of different molecular weights were determined using the method described above.

2. The structure of alcohol-water solutions

The addition of small amount of a non-electrolyte to water causes stabilization of the structure of the water [13, 14]. Stabilization of the structure of water implies effects connected with the passage of non-electrolyte molecules into the cages of this structure. According to DANFORD and LEVY [15] the structure of the water (particularly its short-range order) ought to be considered as a defective ice structure with partly filled cages. In the structure of ice every cage is surrounded by six water molecules. Thus every molecule neighbours with three cages and the number of cages in the structure of ice is equal to half the number of molecules. In water some of the molecules form a skeleton of cages and some fill up the cages. The presence of non-electrolyte molecules in the cages leads to a decrease in the translational mobility of the water molecules In effect it causes a decrease in the selfdiffusion coefficient of water, and change of the kinetic and equilibrium properties of a solution. For alcohol solutions an anomal dependence of some of the properties of the solution can be observed within the concentration range of 0.03 to 0.2 mole fraction of alcohol [16-18].

3. Investigation in alcohol-water solutions using infra-red spectroscopy and ultrasonic measurements

In Fig. 1 the results of measurements of ultrasonic velocity in alcohol-water solutions at 25°C (curve *1*) and the shifts of the valence-deformation band of water $\nu_\delta + \nu_{OH}$ with the maximum at 5180 cm^{-1} (curve *2*) are presented. Measurements of the ultrasonic velocity were performed using the "singaround" method described below and the spectroscopic measurements were made using infra-red spectrometer of high resolution Digilab produced by U.S.A.

As can be seen from Fig. 1 the ultrasonic velocity increses at first, reaches a maximum at a concentration $k_{mol} = 0.106$ and then decreases. On the curve of $\Delta\nu_{max}$ as a function of alcohol concentration an increase in the shift of the studied absorption band in the concentration range 0-0.1 k_{mol} is observed, and for the higher concentrations this shift is constant and independent of alcohol concentration up to $k_{mol} \sim 0.4$ [19]. Previous infrared spectroscopic investigations [19, 20] showed that the stabilization of the structure of water by non-electrolyte molecules is connected with an increase of the stability of the hydrogen bonds between the water molecules. This effect is reflected in the shift of absorption bands in the direction of lower frequencies. The observed order of water is due to the influence of non-polar groups of non-electrolyte molecules on 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 [21].

Mathematical analysis of the shift of the absorption band at 5180 cm^{-1}, assuming a Gaussian character for the contour of this band, allowed the determination of the mean number of water molecules in the non-polar group solvate. For ethyl alcohol it equals 6 ±1 [19] and 7 ±1 [20] at 20°C and it decreases with increasing temperature.

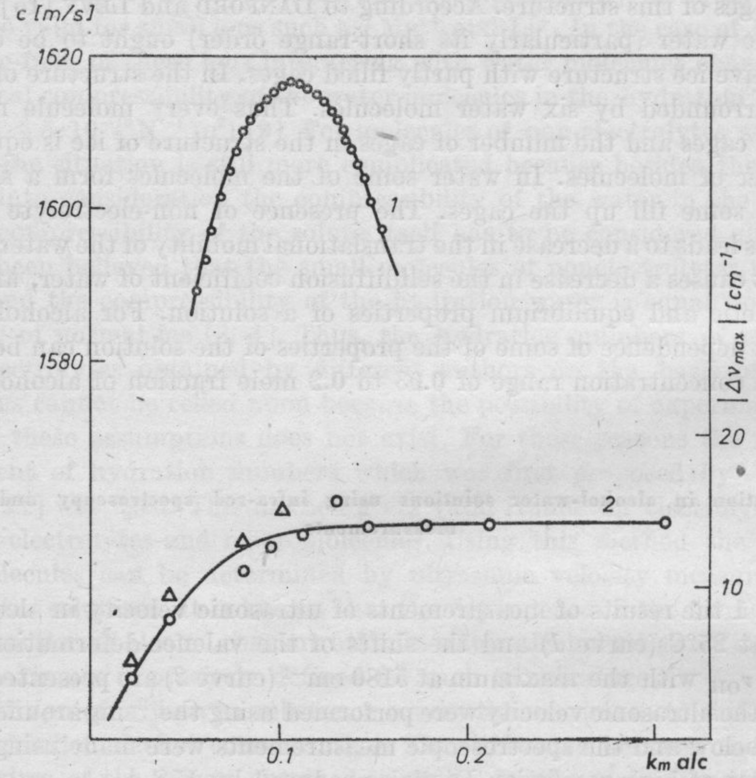

Fig. 1. Ultrasonic velocity (*1*) and the shift of the valence-deformation band of absorption of water with the maximum at 5180 cm^{-1} (*2*) versus k_{mol} of alcohol for an ethanol-water system

It is known that the maxima on the ultrasonic velocity curves (minima on the compressibilty curves) shift in the direction of lower concentrations with increasing temperature. This is caused by a decrease in the "open-work" structure of water with increasing temperature. The number of empty cages ("holes") which can be occupied by alcohol molecules decreases and the amount of "free" water molecules increases. Assuming that at 0°C all the water molecules occur in an ice-like skeleton it can be presumed, with a high probability, that the concentration at which the ultrasonic velocity maximum at 0°C occurs defines the number of molecules surrounding the non-polar molecule. Due to the impossibility of defining this concentration at 0°C with satisfactory accuracy (the error of the velocity measurement ought not to exceed 2 cm/s) ultrasound velocities at higher temperatures were determined.

In Fig. 2 the results of our measurements in ethanol-water solutions in the temperature range 5-35°C are presented. As can be seen in Fig. 2 the ultrasound velocity maximum shifts in the direction of lower concentrations of alcohol. The number n (mole/mole) of water molecules per alcohol molecule were determined at the maximum points in the investigated temperature range and are graphically presented in Fig. 3.

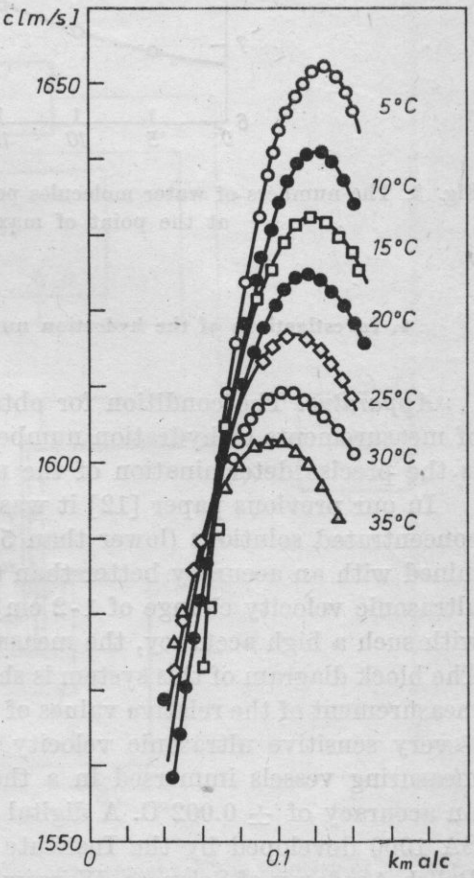

Fig. 2. Ultrasonic velocity versus k_{mol} of alcohol in the temperature range 5-35°C for the ethanol-water system

Extrapolating to a temperature of 0°C a value of $n = 6.6$ was obtained. The results obtained are in good agreement with the results of infrared measurements. Theoretically at 0°C n should be equal to 6 for a perfect ice crystal lattice of ice (octahedral structure). However, due to the occurence of defects in the water structure (Frenkl and Schoottky defects), the number of empty cages is less and $n > 6$.

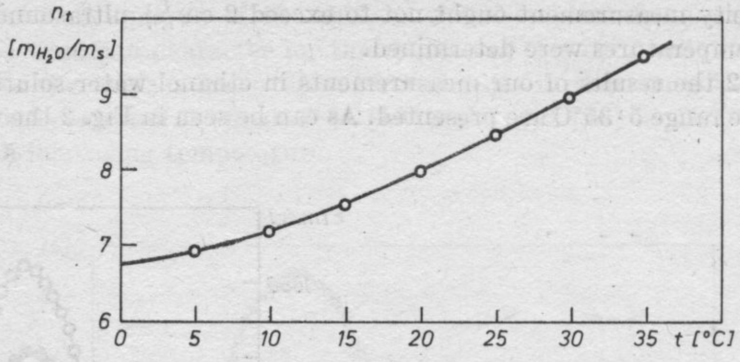

Fig. 3. The numbers of water molecules per alcohol molecule as a function of temperature at the point of maximum ultrasonic velocity

4. Investigations of the hydration numbers of sugars in alcohol-water solutions

Apparatus. The condition for obtaining reproducible and authentic results of measurements of hydration numbers from ultrasonic velocity measurements is the precise determination of the maximum point.

In our previous paper [12] it was shown that in the case of not too highly concentrated solutions (lower than 5%) the maximum point should be determined with an accuracy better than 0.2 ml of alcohol which corresponds to an ultrasonic velocity change of 1-2 cm/s. In order to perform the measurements with such a high accuracy, the measurement system described below was used. The block diagram of this system is shown in Fig. 4. Such a good accuracy in the measurement of the relative values of the ultrasonic velocity was obtained with a very sensitive ultrasonic velocity meter, with the construction of suitable measuring vessels immersed in a thermostat, with thermostatic control with an accuracy of ± 0.002°C. A digital velocity meter of the "sing around" type SA 1000 developed by the Institute of Fundamental Technological Research, Polish Academy of Sciences, Warsaw, was used for the ultrasonic velocity measurements. The change of the last figure on the wave meter display gives, depending on the measuring vessel used, a change in velocity of the order of 0.5-1 cm/s. A cylindrical measuring vessel of stainless steel which has a small coefficient of expansion (50 mm diameter) was immersed at a constant level in the thermostat. The termostat had a 25 dcm^3 capacity, double walls and was powered and controlled by a temperature regulator of the type 650 and power unit of the type 651 developed by UNIPAN, Warsaw. The regulator and the power unit are part of a microcalorimeter produced by that firm. The regulator and the power unit are automatically controlled by a resistance platinum sensor of type 2100 s-3 wire-100ohm of English production. The temperature in the measuring vessel was controlled by the same kind of resistance sensor with an accuracy of ± 0.001°C. The thermostat was cooled by water from a second thermostat in which the temperature of the thermostating water was 2-3°C lower than the temperature of the water in the main thermostat. With the aim of assuring the stability of the "sing-around" velocity meter, the wavemeter and the regulator, the environmental temperature was held constant (21 ± 1°C).

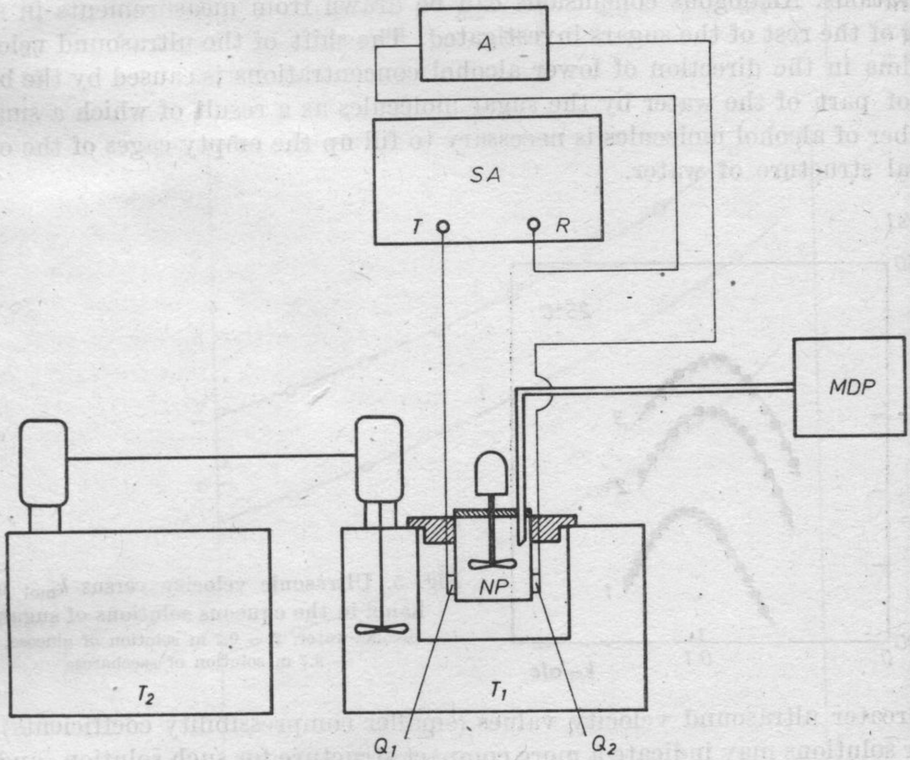

Fig. 4. Block diagram of the apparatus used for the measurement of the velocity of the ultrasonic waves

Procedure. Hydration number measurements of sugars such as: glucose, mannose, arabinose, xylose, saccharose and lactose were performed over a temperature range of 10-40°C. Furthermore, hydration number measurements of sugars as a function of concentration were performed at 25°C. The range of concentrations investigated was 3-25 % wt. for glucose and saccharose, and 3-8 % wt. for the remaining sugars.

The results of these measurements are presented in Tables 1 and II and also graphically in Figs. 5 and 6.

Results and discussion. In Fig. 5 the curves of ultrasonic velocity as a function of ethanol concentration, expressed as molar fractions for glucose (curve *2*) and saccharose (curve *3*) solutions having concentrations of 0.7 mole of sugar per 1000 g of water, are presented. As can be seen from the graphs, the ultrasonic velocities in ethanol-water solutions of glucose and saccharose are greater by 20 - 30 m/s than the velocities in alcohol-water solutions without sugar (curve *1*). Simultaneously the maximum velocity points occur at lower alcohol concentrations. Analogous conclusions can be drawn from measurements in solutions of the rest of the sugars investigated. The shift of the ultrasound velocity maxima in the direction of lower alcohol concentrations is caused by the binding of part of the water by the sugar molecules as a result of which a smaller number of alcohol molecules is necessary to fill up the empty cages of the octahedral structure of water.

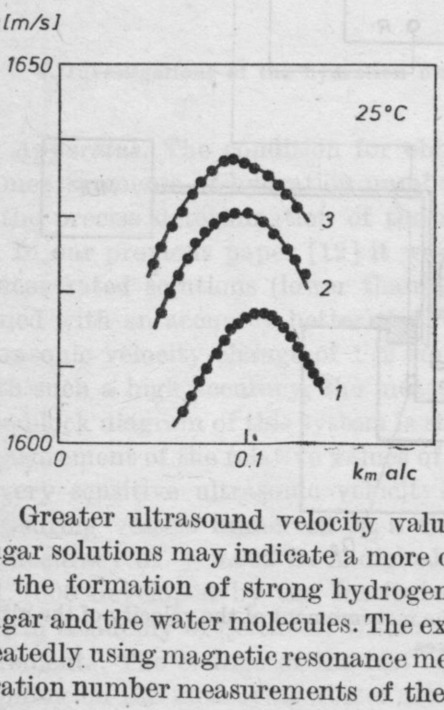

Fig. 5. Ultrasonic velocity versus k_{mol} of ethanol in the equeous solutions of sugars
1 – alcohol-water, *2* – 0.7 m solution of glucose, *3* – 0.7 m solution of saccharose

Greater ultrasound velocity values (smaller compressibility coefficients) for sugar solutions may indicate a more compact structure for such solution and also the formation of strong hydrogen bonds between the hydroxyl groups of the sugar and the water molecules. The existence of such bonds has been confirmed repeatedly using magnetic resonance methods [22 - 24]. In Table 1 the results of hydration number measurements of the investigated substances at 25°C and their dependence on concentration expressed in weight per cent are presented.

From the above data it can be seen that in the concentration range of 3 - 25 % wt. of glucose and saccharose, and 3 - 8 % wt. of the other sugars, the hydration numbers (within experimental error) are not dependent on concentration. The results of hydration number measurements of glucose and saccharose and their dependence on temperature from 10 - 40°C are presented in Fig. 6. Similar curves were obtained for the remaining sugars. As can be seen from Fig. 6 the temperature dependencies of the hydration numbers of glucose (2) and saccharose (3) are of the same type as the temperature dependence (1) of the number

Table 1

Concentration (% of weight)	Glucose	Mannose	Arabinose	Xylose	Lactose	Saccharose
3	4.7	4.8	4.0	4.0	8.0	7.4
5	5.2	4.9	4.0	4.1	8.3	7.2
6	5.2	5.1	3.9	4.1	8.2	7.0
8	5.1	5.1	3.9	4.0	8.1	7.0
20	4.9					6.8
25	4.9					6.8

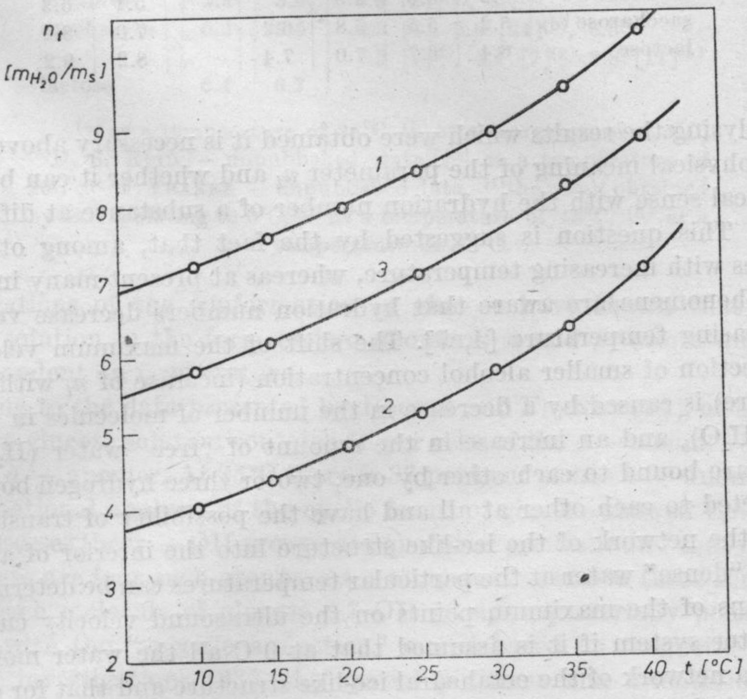

Fig. 6. The numbers of water molecules n_t per mole of solute as a function of temperature at the points of maximum ultrasonic velocity
1 – ethanol, *2* – glucose, *3* – saccharose

of moles of water for each mole of ethyl alcohol at the maximum velocity points (Fig. 3).

The curves in Fig. 3 and 6 can be described by the following equation

$$n_t = n_0 + At + Bt^2 \tag{3}$$

where n_0 is the hydration number at 0°C, and A and B are empirical coefficients equal to $3.83 \cdot 10^{-2}$ and $1.3 \cdot 10^{-3}$ respectively.

The numerical values of n_0 and $n_{5°C}$ calculated on the basis of the above equation, and the values of n_t obtained for the particular sugars at different temperatures are presented in Table 2.

Table 2

	n_0	$n_{5°C}$	$n_{t°C}$				
			10	15	20	25	35
glucose	3.4	3.7	4.0	4.4	4.8	5.2	6.4
arabinose	2.2	2.5				4.0	5.2
xylose	2.3	2.6	3.0			4.1	
mannose	3.3	3.6	3.9			5.1	6.3
saccharose	5.2	5.5	5.8	6.2		7.0	8.2
lactose	6.4	6.7	7.0	7.4		8.2	9.2

In analysing the results which were obtained it is necessary above all to consider the physical meaning of the parameter n_t and whether it can be identified in a physical sense with the hydration number of a substance at different temperatures. This question is suggested by the fact that, among other things, n_t increases with increasing temperature, whereas at present many investigators of these phenomena are aware that hydration numbers decrease very quickly with increasing temperature [4, 7]. The shift of the maximum velocity point in the direction of smaller alcohol concentration (incerase of n_t with increasing temperature) is caused by a decrease in the number of molecules in the ice-like skeleton $(H_2O)_b$ and an increase in the amount of "free" water $(H_2O)_d^*$ whose molecules are bound to each other by one, two or three hydrogen bonds, or are not connected to each other at all and have the possibility of translating from a node of the network of the ice-like structure into the interior of a cage. The amount of "dense" water at the particular temperatures can be determined from the locations of the maximum points on the ultrasound velocity curves in an alcohol-water system if it is assumed that at 0°C all the water molecules are present in a network of the octahedral ice-like structure and that for each molecule of ethyl alcohol there are six molecules of water. If the amount of "dense" water occuring at the particular temperatures is subtracted from the values obtained for n_t, the same number n_0 is obtained, as was earlier defined as the hydration number at 0°C and which is found by extrapolation of the n_t dependence to 0°C.

Is it possible therefore to assign to the values of n_0 the physical meaning of hydration number?

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* Consistent with the expressions used in previous papers [23, 26] water occuring in the ice-like structure is expressed as "bulky" – $(H_2O)_b$ and "free" water as "dense" – $(H_2O)_d$.

Based on contemporary knowledge of the structure of sugar solutions and the comparison of the results obtained with literature data (Table 3), the answer to this question should be affirmative.

Table 3

	n_0	$n_{5°C}$	Literature data
glucose	3.4	3.7	3.5 [4](a), 3.7 [24](b), 2.7(c), 4.0 [25], 5.0 [22], 4.5 [3](d), 3.5 [11](h)
arabinose	2.2	2.5	3.5 [4]
xylose	2.3	2.6	2.3 [4]
mannose	3.3	3.6	3.9 [24](b), 3.7(e)
saccharose	5.2	5.5	3.8 [4], 6.6 [24](b), 6.5(e) 5.3 [7](f), 4.1 [7](g) 3.8 [11](h)
lactose	6.4	6.7	

(a) at a temperature of 25°C, (b) at a temperature of 5°C, (c)D. S. REID – unpublished data, (d) at a temperature of 20C°, (e) F. FRANKS – unpublished data, (f)the result obtained by extrapolating to 0°C, (g) at a temperature of 15°C, (h) at a temperature of 25°C.

Investigations of the conformation of glucose have shown that it occurs in a water solution in the form of two anomers: α and β, whose quantitative ratio is dependent on temperature.

According to the data presented by BOCIEK and FRANKS [24], at a temperature of 5°C a glucose solution contains 68 per cent of the β – anomer and 32 per cent of the α – anomer. At 25°C there is 37 per cent of the α – anomer.

Conformational analysis of the cyclic forms of glucose showed that the α – anomer possesses theer –OH groups at equatorial positions and that in the β – anomer, there are four such groups. At a temperature of 5°C there remains therefore for each molecule of glucose 3.7-OH groups equatorially positioned. In agreement with the "specific hydration" model based on magnetic resonance and X-ray investigations [23], the spatial positions and orientations of the equatorial –OH groups eases the hydration interaction of these groups with water molecules. If it is assumed that only the equatorial –OH groups of the sugar are hydrated, from SUGGETT's data [24] indicates that each group is hydrated by one water molecule. At a temperature of 5°C the hydration number of glucose given by SUGGETT is 3.7 and is equal to the average number of equatorial –OH groups per molecule of glucose. As can be seen from Table 3, an identical value was obtained from ultrasonic measurements of glucose at 5°C. At 0°C, n_0 is smaller and is equal to 3.4 m H_2O/m of sugar. For the remaining sugars investigated the values of n_0 which were obtained were approximately equal to the number of equatorial –OH groups. In reference to the "specific hydration" model of sugars the n_0 parameter is, therefore, the hydration number of the given sugar at a temperature of 0°C, which, it is proposed, should be called the absolute hydration number. The values of n_0 which were obtained for glucose and xylose correspond to the data obtained by SHIIO [4] at a temperature of 25°C using a slightly different method of determining the hydration numbers from the ultrasonic measurements. In order to produce an expression for the hydration number, Shiio assumed that the compressibility of sugar is equal to zero and the compressibility of the water in the hydration shell is equal to the compressibility of normal ice ($\beta = 1.8 \cdot 10^{10}\ \mathrm{m^2N^{-1}}$).

Both of these assumptions can be verified experimentally. However it seems that the second assumption, particularly, is more probable at a temperature of 0°C and that at higher temperatures the compressibility of the hydration water is certainly larger. As the temperature increases the compressibility will increase to the compressibility of pure water. Thus the hydration number values obtained by SHIIO are close to the values of n_0 obtained in this paper. If this discussion is accepted, then the rapid decrease of the hydration numbers of sugars with increasing temperature observed by many authors is probably only an apparent effect, and in reality the hydration numbers do not decrease with a temperature increase. If the participation of "free" water in the hydration of sugars is not taken into consideration, the above conclusion finds confirmation in the investigations which were conducted. The hydration number values which were obtained over a temperature range of 10-40°C are approximately equal to the absolute hydration number n_0.

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