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INVESTIGATIONS OF THE HYDRATION OF POLYETHYLENEGLYCOLS USING AN ACOUSTIC METHOD

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Measurements of the velocity of ultrasound in alcohol – water solutions of polyethylene glycols with molecular weights 400, 1500, 2000, 15000 and 20000 at a temperature of 25 ± 0.1°C have been made and the values of the hydration numbers defined by the YASUNAGA method.

1. Introduction

The YASUNAGA method for the determination of hydration, is one of several known methods based on acoustic measurements. One of the first methods which subsequently provided the basis for further investigations was PASSYNSKY's method [1], with the aid of which it is possible to evaluate the hydration of electrolytes and non-electrolytes

$$h = \frac{(1-\beta/\beta_0)(1-g)}{g}, \tag{1}$$

where h is the hydration in terms of grams of solvent per gram of solute, β and β_0 are the adiabatic compressibilities of the solution and solvent respectively, and g is the number of grams of the solute dissolved in 1 gram of solution.

In deriving this expression, PASSYNSKY did not consider the compressibility of the solute. Such a simplification can only be valid for electrolyte solutions and for small solute concentrations.

An interesting modification of PASSYNSKY's method was made by ERNST and JEŻOWSKA-TRZEBIATOWSKA [2] in the determination of the hydration numbers of some uranyl salts in an aqueous-organic mixture. To determine the hydration of uranyl sulphate and uranyl nitrate they used PASSYNSKY's standard method while in the case of solutions of the same salts in a mixed water-dioxsan solvent they stated the following formula for the hydration number:

$$n_h = \frac{c_1}{c_2} + \frac{c_3 \Phi k_3 - 10^3 \beta}{c_2 \overline{V}_1^0 \beta_1^0}, \tag{2}$$

where c_1, c_2, c_3 are the concentrations of water, electrolyte and dioxsan, respectively, in moles per l of solution, Φk_3 is the apparent molar compressibility of dioxsan in solution, β and β_1^0 are the adiabatic compressibilities of the solution and of water, respectively, and $\overline{V}_1^0$ is the volume of water.

Generally speaking, Φk_3 in this formula depends on the composition of the solvent and the concentration of the electrolyte, in order to determine these values and to evaluate the hydration numbers, use has been made of a special procedure involving the introduction of an organic constituent into the solution.

Another method of determining the hydration numbers was proposed by Shiio [3, 4] using the dehydration properties of such liquids as ethyl alcohol or acetone.

The methods described above require a knowledge of the adiabatic compressibilities, and thus involves the necessity of the measuring both the sound velocity and the density of each solution.

In the method developed by Yasunaga for the determination of hydration only the measurement of the velocity in the alcohol-water solutions is necessary. It is known that the dependence of the sound velocity on the alcohol concentration for alcohol-water mixtures is parabolic, its maximum being precisely defined for each temperature [5]. The addition of any substance causes a shift of the peak of the parabola in the direction of lower concentrations of alcohol. 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

$$\frac{A_0}{W_0} = \frac{A_1}{W_1 - W_x}, \tag{3}$$

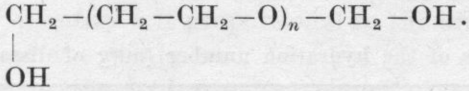
where A_0 and W_0 are the amounts of alcohol and water corresponding to the maximum for alcohol-water mixtures without solute, A_1 and W_1 are amounts of alcohol and water at the maximum for alcohol-water solutions containing a certain amount of solute and W_x is the hydration in terms of percentage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

This paper presents measurements of the propagation velocity of ultrasound in alcohol-water solutions of polyethylene glycols with five different molecular weights over a range of concentrations from 1.4 g to 14.3 g per 100 g of water.

The investigations were aimed at determining the hydration of polyethylene glycols by Yasunaga's method and also the optimization of the concentration of macromolecules for which this method gives reproducible results. The investigations involved measurement of the propagation velocity of ultrasound using a "sing-around" method at a frequency of 10 MHz and at a temperature of 25 ± 0.01°C.

2. Experimental arrangement

All the materials used for the investigation of polyethylene glycol were made by BDH Chemicals Ltd. Measurements of the sound velocity as a function of ethanol concentration were performed for axis concentrations: 1.43, 2.86, 5.71, 8.57, 11.43, 14.29 g per 100 g of water for each polyglycol of the form



$$\underset{\displaystyle OH}{\underset{|}{CH_2}}-(CH_2-CH_2-O)_n-CH_2-OH.$$

Apparatus. The measurements of the sound velocity were made with the system shown in the block diagram of Fig. 1.

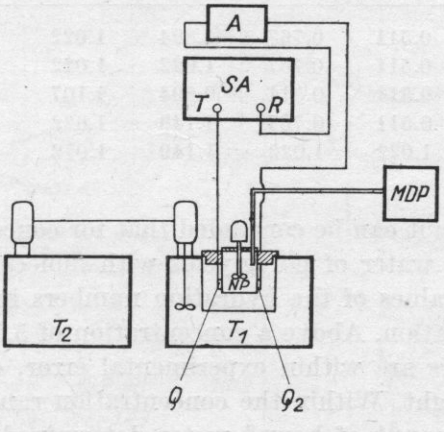


Fig. 1. Block diagram of the apparatus used for the measurement of the velocity of ultrasonic wave

A – ultrasonic wave velocity meter of the type SA 1000, developed by the Institute of Fundamental Technological Research, Polish Academy of Sciences, Warszawa, which enables a measurement of relative velocity to be made with an accuracy of up to 2 cm s, A – high frequency resistance attenuator, MDP – small-dimension metering pump, type 355 A developed by UNIPAN, Warszawa, which monitors the flow of ethanol into the measuring vessel with an accuracy of up to 0.02 ml, T_1 and T_2 – thermostat systems type NBE/NBER made in GDR, which ensure constant temperature in the measuring vessel with an accuracy of ± 0.01 °C, and NP – measuring vessel with agitator and transmitting and receiving transducers Q_1 and Q_2

3. Results and conclusions

Figure 2 shows the graph of ultrasonic velocity as a function of ethanol content for polyethylene glycol of molecular weights 400 and 20000, with a marked shift of the parabola in the direction of smaller ethanol concentration with increasing content of the substance examined.

On the basis of Yasunaga's formula

$$W_x = \frac{W_1 - A_1 W_0}{A_0}, \tag{4}$$

where W_x is the hydration for a certain amount of the substance examined, and the other symbols have the same meaning as in formula (3). The total hydration of all the polyglycols at six concentrations has been calculated and then converted into 1 g of solute.

Table 1 shows the values of the hydration numbers for polyglycols with molecular weights 400, 1500, 2000, 15000 and 20000 for concentrations ranging from 1.4 to 14.3 g per 100 g of water.

Table 1. Values of the hydration number (ml/g of dissolved substance)

Polyethylene glycol	c[g/100 g H_2O]					
	1.43	2.86	5.71	8.71	11.43	14.29
400	0.511	0.767	0.894	1.022	1.149	1.175
1500	0.511	0.767	1.022	1.022	1.149	1.124
2000	0.511	0.511	0.894	1.107	1.149	1.175
15000	0.511	0.767	1.149	1.022	1.149	1.226
20000	1.022	1.022	1.149	1.072	1.149	1.226

From these results it can be concluded that for concentrations in the range 1.4-5.7 g per 100 g of water of polyglycols with molecular weights 400, 1500, 2000 and 15000 the values of the hydration numbers increase with increasing of polyglycol concentration. Above a concentration of 5.7 g per 100 g of water, the hydration numbers are within experimental error, constant and independent of molecular weight. Within the concentration range 1.4-5.7 g per 100 g of water, the total amount of bound water determined from the shift of the parabola varies between 0.8-5 ml. The minimum dose of alcohol that causes perceptible changes in the shift of the maximum point of the parabola is 0.2 ml and this gives an equivalent amount of bound water of about 0.6 ml.

Thus, if the total amount of water bound per unit amount of solute is smaller than 6 ml, the determination error is higher than 10%, and the obtained results are barely trustworthy.

At concentrations of 1.4-5.7 g per 100 g of water the determination error considerably exceeds 10%, and at the lowest concentration examined is almost as high as 60%, so that the results obtained in this concentration range cannot be taken into consideration.

For confirmation of our conclusions, measurements of the time longitudinal relaxation time T_1 of water solutions of polyethylene glycols in the above-mentioned concentration range have been made in the Radiospectroscopy Establishment of the Physics Institute, Jagiellonian University, Kraków. The measurement were performed with a pulse spin echo apparatus, operating at a proton resonance frequency of 25 MHz by three method 180-90-180, at constant temperature of 22°C.

The relation between the longitudinal relaxation time T_1 for water solutions of macromolecules and their concentration is described by the linear equation [6, 7, 8, 9]

$$\frac{1}{T_1} = \frac{1}{T_{1w}} + kc, \tag{5}$$

where T_1 is the longitudinal relaxation time and T_{1w} the relaxation time of pure water, while the quantity k is proportional to the amount of water bound within the molecules of the solute.

The water found in the hydration envelopes of the macromolecules is less mobile than the free water which is not bound to the macromolecules. The relaxation process of the molecules of unbound water is therefore considerably faster than that of water bound within the molecules of the solute. When it is assumed that the interchange between molecules of free and bound water is very rapid, a shorter relaxation time for the solution in comparison with that of pure water can be observed.

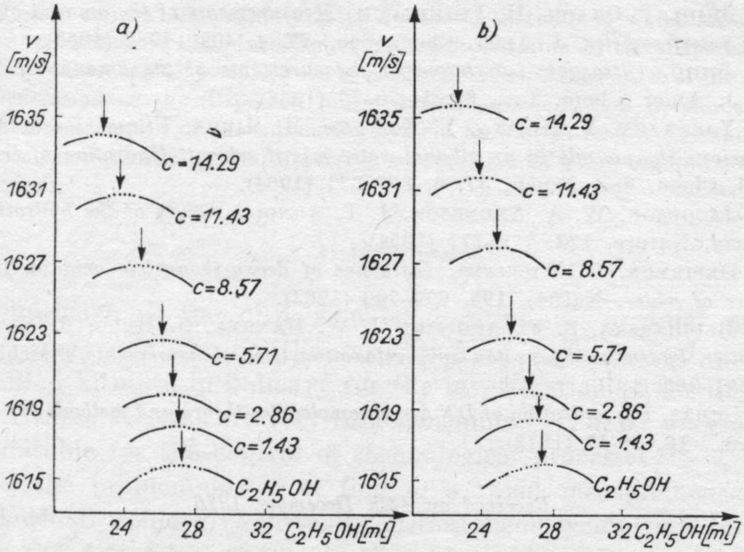


Fig. 2. Propagation velocity of ultrasonic waves as a function of ethanol concentration for ethylene polyglycol with molecular weight 400 and 20000

The results for the longitudinal relaxation time T_1 for water solutions of polyethylene glycols with molecular weights 400, 1500, 2000, 15000 and 20000, over a concentration range from 4 to 10% by volume, have shown that the relaxation time does not depend on the chain length of the polyethylene glycols tested. From this it results, in agreement with the results of the ultrasonic measurements, that the amount of bound water does not depend on the molecular weight of the polyethylene glycols, but only on their concentration in the solution.

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