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## STRUCTURE OF AQUEOUS SOLUTIONS OF 1,2- AND 1,3-PROPANEDIOL INVESTIGATED BY POSITRON ANNIHILATION AND ULTRASONIC METHODS

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The structure of aqueous solutions of 1,2-propanediol and 1,3-propanediol was investigated using adiabatic compressibility measurements and positron annihilation methods. The experimental results are different than those obtained earlier for systems where hydrophobic hydration dominates. There are some evidences for increased rigidity of the water network, which can arise from the formation of hydrogen bonds between diols and water.

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### 1. Introduction

Recently it was shown by us (see the papers cited below) that, for aqueous solutions, the long-lived component of the positron annihilation spectrum exhibits characteristic features around the solution composition corresponding to that of hydrates, if only the solute is hydrophobic or contains a hydrophobic moiety. In such cases, with polar organic solutes, the long-lived component's lifetime passes through a plateau, and its intensity — through a maximum at concentration corresponding roughly to the stoichiometry of the clathrate-like hydrate formed in liquid solution. Moreover, the same stoichiometry could be extracted from the interception point of compressibility isotherms, as it was done in series of aqueous solutions of normal and isomeric short-chained alcohols [1], as well as in the system water + tetramethylurea [2].

Diols, especially of 1,2-type, are of special interest because of possibility of building into the hydrogen-bonded water network. Moreover, those with a well-defined hydrophobic moiety (i.e. again the 1,2-diols) are supposed to form crystalline-like hydrates similar structurally to the clathrates known for many nonelectrolytes, with stoichiometries of these hydrates close to  $X \cdot 17H_2O$  [3] (for

details of clathrate hydrate stoichiometries see also the review of Byk et al. [4]). At present, however, it is not yet clear what kind of water structure is formed around the alkyl groups of diols: ice-I-like, gas-hydrate-like, a structure involving some non-tetrahedral H-bonds, or possibly mixtures of all these, while the contribution of hydrophilic hydration, implied by the existence of two  $\text{OH}^-$  groups in the solute's molecule has not been known yet. It is known, however, that the effect of the existence of two hydroxyl groups in the molecule of ethylene glycol on structure of water leads to prevailing hydrophilic hydration [5].

In their classical paper, Frank and Evans [6] concluded that the large negative entropies of dissolution of apolar solutes (in particular gases) in water could be explained by the formation of "microscopic icebergs" around the solute molecules. This concept was extended later by Frank and Wen [7] to explain the singular heat capacity behaviour of tetraalkylammonium salts in water (short-lived clusters of water molecules are in equilibrium, and exchange rapidly with monomers). This idea was later supported by the occurrence of clathrate hydrates for many apolar solutes and organic electrolytes [8].

In this paper aqueous solutions of 1,2-propanediol,  $\text{HOCH}_2\text{-CH(OH)-CH}_3$ , and 1,3-propanediol,  $\text{HOCH}_2\text{-CH}_2\text{-CH}_2\text{OH}$ , were investigated using independently the sound velocity and positron annihilation methods. The main goal was to study whether the solutes under tests form inclusion-type hydrates in liquid aqueous mixtures.

## 2. Experimental

### 2.1. Chemicals

1,2-Propanediol (Riedel de Haën, purum) and 1,3-propanediol (Fluka AG, purissimus) were used without further processing. Water was doubly distilled. Solutions were prepared by weighting.

### 2.2. Positron annihilation measurements

The annihilation measurements were carried out at room temperature (approx.  $20^\circ\text{C}$ ) with a standard measuring device based on the "fast-slow" coincidence technique as described elsewhere [9]. Solutions were refluxed with nitrogen before the measurements to remove oxygen dissolved in the samples. The obtained spectra were resolved using POSITRONFIT program.

### 2.3. Sound velocity measurements

The ultrasonic velocity was measured at five temperatures close to, respectively, 15, 20, 25, 30, and  $35^\circ\text{C}$  (measured with an accuracy of  $\pm 0.01^\circ\text{C}$ ) with an accuracy of  $\pm 0.1$  m/s using a "sing-around" equipment (apparatus Ecolab MPFU, Kraków, Poland). The details of the apparatus and measurement techniques applied in this study are given in Ref. [10]. The temperature dependences of sound velocity were approximated using second-order polynomials to obtain the sound speed values at  $15\text{--}35^\circ\text{C}$  with  $5^\circ$  intervals.

### 2.4. Density measurements

Densities were measured at temperatures the same as sound velocity using a vibrating tube densitometer type Ecolab MG-2 (Kraków, Poland). The accuracies of the densities are better than  $\pm 0.05 \text{ kg/m}^3$ . Further processing of the data was similar to that described above for the sound velocities.

## 3. Results and discussion

### 3.1. Acoustic measurements

The adiabatic compressibility coefficients  $\beta$  were calculated from the Laplace formula  $\beta = (c^2 d)^{-1}$ , where  $c$  is the ultrasonic velocity and  $d$  is the density of the liquid.

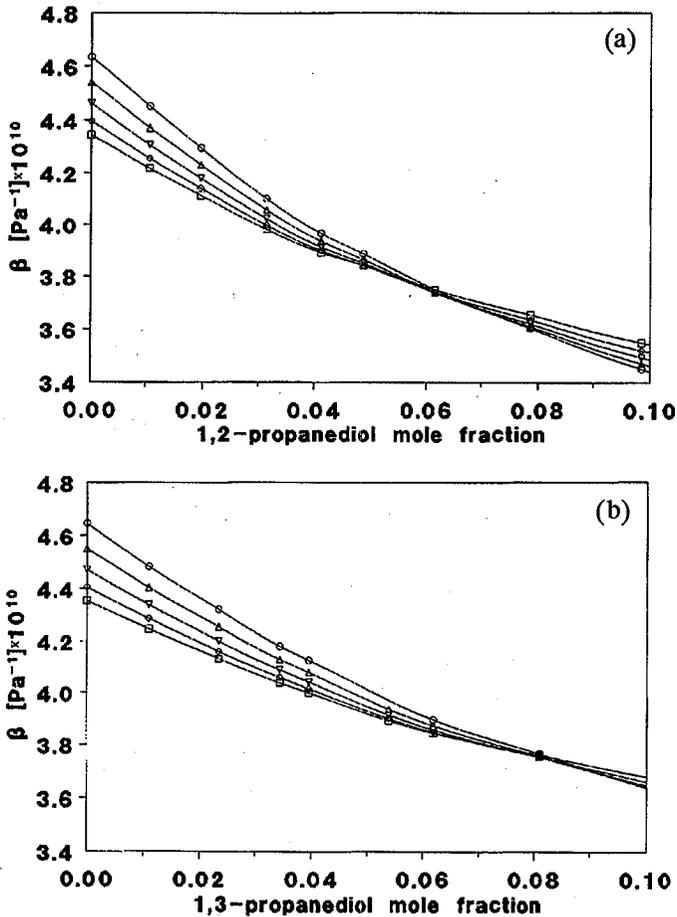


Fig. 1. Adiabatic compressibility coefficients vs. mole fraction of 1,2-propanediol (a) and 1,3-propanediol (b) in water:  $\circ$  — 15°C,  $\triangle$  — 20°C,  $\nabla$  — 25°C,  $\diamond$  — 30°C,  $\square$  — 35°C.

Figures 1a and b show the concentration dependence of the compressibility coefficient in the systems under test for different temperatures.

The concentrations corresponding to the intersections of compressibility isotherms decrease with temperature (in the temperature range studied) and can be observed at the solute mole fractions between 0.07 (at 35°C) to 0.045 (at 15°C) for water + 1,2-propanediol and between 0.085 (at 35°C) to 0.06 (at 15°C) for water + 1,3-propanediol.

The hypothesis of Endo [11] states that the intersection of the compressibility isotherms is situated at a concentration strictly corresponding to the stoichiometry of clathrate hydrates (if formed). In the case of the title systems the concentrations corresponding to the intersection are not constant, suggesting that in the systems under investigation hydrophilic hydration dominates: see for example the results for water + ethylene glycol [5]. It is also worthy to notice that, in both cases, the compressibility reaches at the intersection a value of  $\beta \cong 3.75 \times 10^{-10} \text{ m}^2/\text{N}$ , which is considerably lower than that of solid clathrates, determined by von Stackelberg et al. [12] (for the type II clathrate hydrates  $\beta$  is approx.  $4 \times 10^{-10} \text{ m}^2/\text{N}$ ). Such lowering of the  $\beta$  value at the intersection means that only a partial hydrophobic hydration of the solutes occurs in the systems investigated (see for example the results for the system water + tetramethylammonium chloride [13]). Thus, ultrasonic results give no evidence for formation of clathrate-like hydrates in liquid phase.

### 3.2. Positron annihilation

The experimental lifetime spectra were resolved into three components, each characterised by its lifetime ( $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ ), and intensity ( $I_1$ ,  $I_2$ , and  $I_3$ ). Note that  $I_1 + I_2 + I_3 = 100\%$ . The number of components was chosen arbitrarily, basing only on the quality of the fitting, while only the long-lived one ( $\tau_3$  and  $I_3$ ), attributed to *ortho*-positronium annihilation, is of interest for further discussion. The short-lived components are caused by many different annihilation mechanisms and their more detailed analysis seems impossible. It should be strongly noted, however, that our calculations yielded almost the same character of the concentration dependence of the long-lived parameters, while the short-lived ones were often losing a physical sense when assuming more than two components.

The obtained lifetimes of the long-lived component  $\tau_3$ , plotted vs. concentration of 1,2-propanediol and 1,3-propanediol are shown in Fig. 2a, while the corresponding intensities  $I_3$  are shown in Fig. 2b. For comparison, our previous results obtained for water + ethanol mixtures [14] are included in these figures (dashed lines).

The system water + ethanol was chosen as a typical hydrophobic one, where hydrate structures are undoubtedly formed in a liquid phase. In the vicinity of the concentration corresponding to the stoichiometry of clathrate hydrates (corresponding to ethanol mole fraction of  $\cong 0.05$ ), the lifetime of the long-lived component  $\tau_3$  passes through a plateau, while intensity  $I_3$  — through a flat maximum. None of these features are observed in the title system; however, below the intersection concentration ( $x = 0.03$ ) the long-lived component  $\tau_3$  parameter behaves

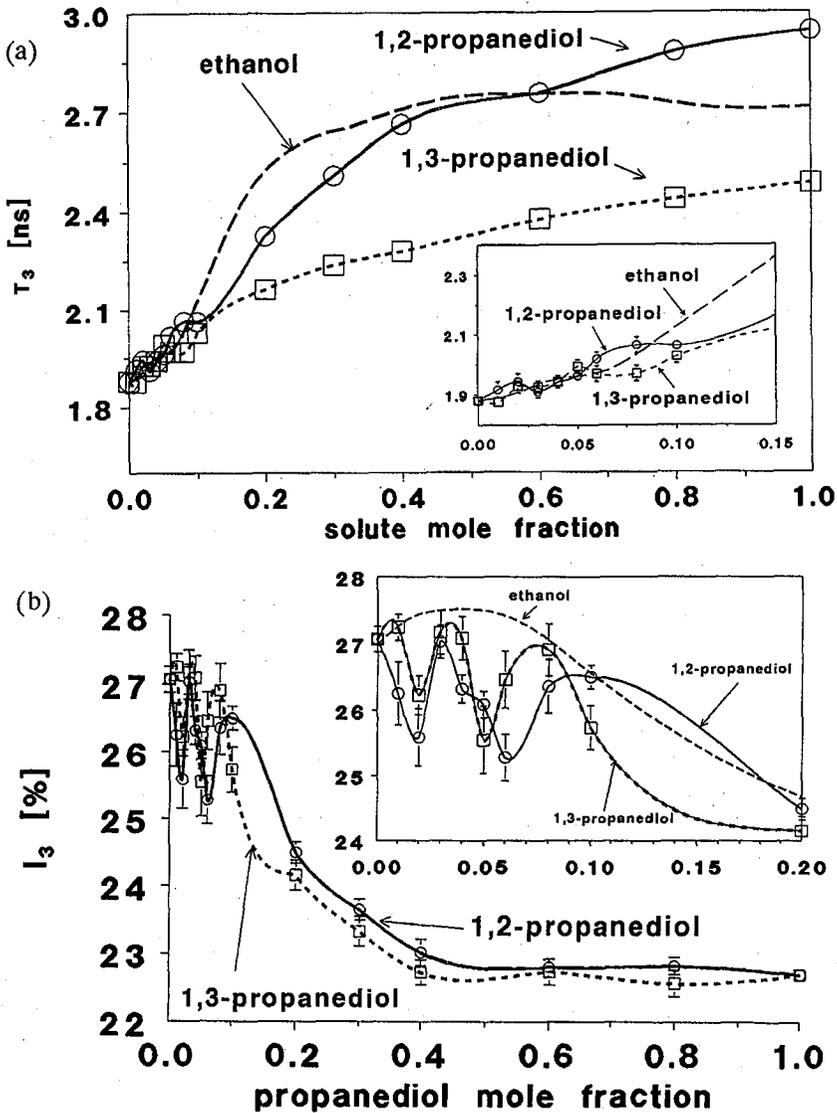


Fig. 2. Lifetimes (a) and intensities (b) of the long-lived component of annihilation spectra vs. 1,2-propanediol and 1,3-propanediol concentration in water (room temperature). Broken line: the results for aqueous solutions of ethanol [14].

very similar to the system water + ethanol and at  $x = 0.03$  there is a sharp change in the concentration dependence of the  $I_3$  parameter.

The interpretation which can be drawn from positron annihilation results is substantially similar to that arising from acoustic measurements given above. A comparison with the system water + ethanol shows that in the region of low

concentrations of diols (below  $x = 0.1$ ), the  $I_3$  parameter is lower in the case of propanediols than in aqueous ethyl alcohol solutions. This fact could be understood assuming a lower number and/or size of empties in the water network in the case of propanediols, which should be true if no clathrate hydrates are formed. On the other hand, the  $\tau_3$  parameter should detect rather the changes in rigidity of the water framework than the number and size of cages. Thus, rigidity of the structure possibly changes similarly in the case of ethanol and diols, although the mechanism of this increasing rigidity could be different (ethanol: formation of clathrate-like hydrates, diols: three-dimensional H-bonds between water and solute).

The complicated dependence of  $I_3$  on concentration of diols observed in low contents of the solutes is not clear and needs further investigations. It can be, however, caused by rapidly changing entropy and enthalpy of the surface formation. Recently it was found that these parameters are not monotonous even in the case of such simple solutes like ethanol [15] or *n*-propanol [16]. While, according to the "bubble" model of the pick-off annihilation [17, 18] the long-lived parameters of annihilation spectrum of a liquid depend strongly on the surface tension of the medium, the above should be reflected in the observed concentration dependences of  $\tau_3$  and  $I_3$ .

#### 4. Conclusions

The ultrasonic results (concentration dependences of compressibility) suggest dominating hydrophilic character of hydration. The concentration dependences of positron annihilation parameters (lifetimes and intensities of the long-lived component of annihilation spectrum) are different from those determined for the known clathrate-forming polar organic solutes, but suggest increasing rigidity and a decreasing number of empties in the structure when the solute is added (the cage-building).

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