X-Ray Analysis of Intermolecular Interactions in Water Solutions of 2-Propanol

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The results presented in this work confirm the specific structural properties of water solutions of 2-propanol at low concentrations, discovered earlier by other methods. The mean least intermolecular distance for pure alcohol, its water solutions at different molar concentrations, and for pure water, have been determined from the angular distributions of X-ray scattering. The concentration dependence of intermolecular distances revealed an extremum for the concentration $X = 0.01$ which can be interpreted as due to the clatrate structure of water. This structure remains only for solutions of low concentrations of 2-propanol and is altered at concentrations higher than 0.04 molar fraction.

KEY WORDS: X-ray diffraction, intermolecular interactions, water solutions.

1. INTRODUCTION

The present work has been stimulated by discovery of specific structural effects in water solutions of 2-propanol in low concentrations detected by the thermodynamic [1, 2], spectroscopic [3, 4, 5], dielectric [6], optical [7] methods, ultrasound absorption [8, 9] and positron annihilation [10]. Diffraction patterns of liquids provide only information on the so-called short-range order of atoms and molecules. The short-range arrangement is characterized by the values of the distance between the nearest molecules determined by the so-called radii of coordination spheres and a number of molecules in subsequent coordination spheres around one molecule chosen as central. The radius of the first coordination sphere is the mean value of the least intermolecular distance in the liquid. It is denoted by $\bar{R}$ and can be obtained directly from the experimental curve of the scattered radiation intensity. The intensity of the scattered radiation can be expressed by the following formula taking into account both inter and intramolecular effects [11]:

$$I^{\text{theor.}} = F_i^2 + F_a^2 \left[\bar{N} (\sin s\bar{R})/s\bar{R} \right], \qquad (1)$$

where F_i and F_a are the intra and intermolecular scattering factors, respectively, while $\bar{N}$ is the coordination number and $s = 4\pi \sin\vartheta/\lambda$, λ is the wavelength, and 2ϑ is the scattering angle. So, as follows from Eq. (1), the angular distribution of the scattered

radiation intensity $I^{\text{theor.}}$ is determined by the function "$\sin(s\bar{R})/s\bar{R}$". The first maximum of this function corresponds to the first maximum in the experimental curve of the scattered intensity $I_{eu}(\vartheta)/N$, in electron units per unit of composition. Since this maximum appears for $s\bar{R} = 7.73$, we can write the following formula to find the mean approximate value of the least intermolecular distance as:

$$\bar{R} = 7.73/s_{\text{max}} - 0.3, \tag{2}$$

where $s_{\text{max}} = 4\pi\sin\vartheta_{\text{max}}/\lambda$. The correction factor that must taken into account for molecular liquids is determined by the external factor of molecular scattering F_a which shifts the maximum of the $\sin(s\bar{R})/s\bar{R}$ dependence on the scattered radiation intensity.

2. EXPERIMENTAL

Intensity of radiation scattered by a layer of the studied solution was determined by the transmission method [12, 13] using a typical X-ray diffractometer adapted for measurements of liquids. The number of pulses in a chosen period of time was calculated and thus obtained pulse density was recorded. The monochromatic MoKα radiation, $\lambda = 0.71069$ Å, was used. The samples of 2-propanol were obtained by recrystallization of anallytically pure alcohol and the water used as a solvent was three times distilled. The value of molar concentration, molar mass and density of the aqueous solutions of 2-propanol and of pure water und pure alcohol are given in Table 1.

The structural formulae in inverted commas, Table 1, describe the so-called effective molecules in the solution calculated according to the equation [14]: "effective molecule" $= \Sigma\ x_i$ molecule$_i$, where x_i is the molar fraction of the i-th molecule.

Table 1 Values of the molar concentration, molar mass and density for pure water, aqueus solutions of 2-propanol and pure alcohol.

Formula of chemical compound	Molar concentration X	Molar mass $[10^{-3}\ Kg/Mol]$ M	Density $[10^3\ Kg/m^3]$ ρ
H_2O	0.00	18.015	0.9982
"$C_{0.03}H_{2.06}O$"	0.01	18.436	0.9913
"$C_{0.06}H_{2.12}O$"	0.02	18.857	0.9847
"$C_{0.09}H_{2.18}O$"	0.03	19.278	0.9783
"$C_{0.12}H_{2.24}O$"	0.04	19.698	0.9723
"$C_{0.15}H_{2.30}O$"	0.05	20.119	0.9665
"$C_{1.50}H_{5.00}O$"	0.50	39.056	0.8349
$CH_3CH(OH)CH_3$	1.00	60.096	0.7860

3. RESULTS

From angular distribution of the scattered radiation intensity, Fig. 1, we obtained the mean least intermolecular distance for pure alcohol, its mole concentration $X = 0.50$;
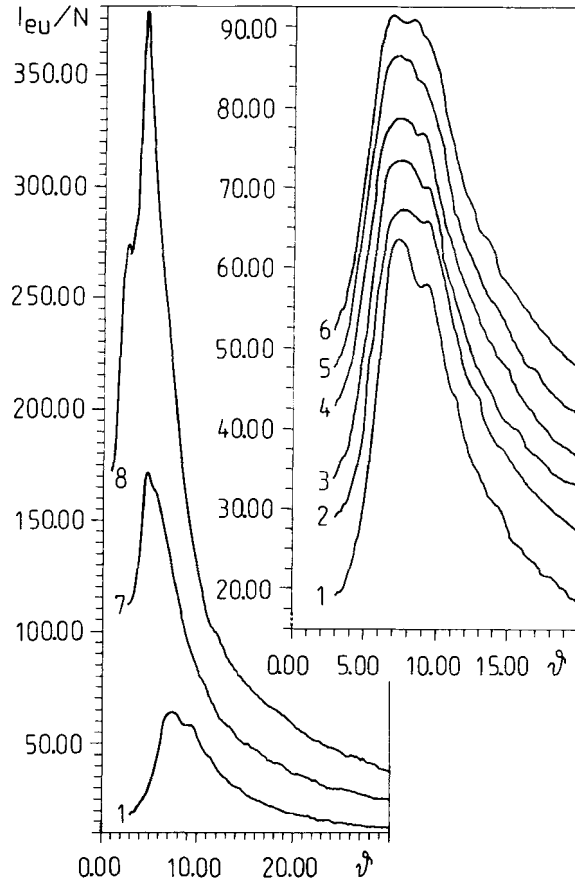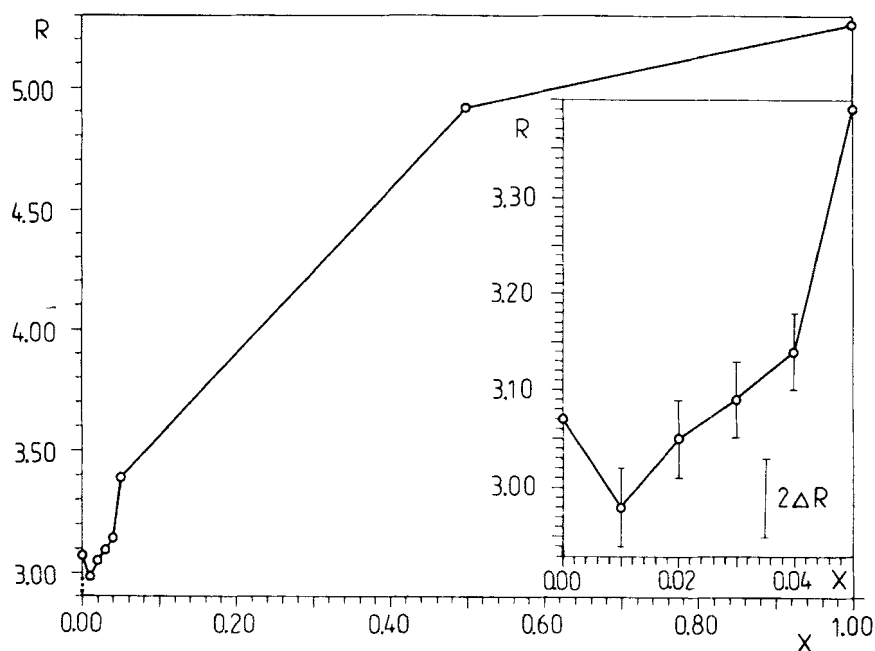
Figure 1 Mean angular distributions of the scattered radiation intensity for: 1) pure water and 8) pure 2-propanol and for its solutions in water: 2) $X = 0.01$, 3) $X = 0.02$, 4) $X = 0.03$, 5) $X = 0.04$, 6) $X = 0.05$, 7) $X = 0.50$.

0.05; 0.04; 0.03; 0.02; 0.01 and pure water, Table 2. These values are: 5.27 Å; 4.92 Å 3.39 Å; 3.14 Å; 3.09 Å; 3.05 Å; 2.98 Å and 3.07 Å.

The intermolecular distance of 3.07 Å obtained for pure water is in good agreement with literature data [15]. The character of the angular distribution of the intensity of scattered radiation for molar fractions 0.01, 0.02 and 0.03 resembles that for pure water, Fig. 1, however, the main maximum for pure water at $\vartheta = 7.455°$ is much clearer. The side maximum at $\vartheta = 9.400°$ characteristic for the tetragonal structure of ice, remains at this position only for a molar fraction of 0.01. For higher concentrations it is shifted towards smaller angles and for 0.04 its position is ambiguous. The positions of the main maxima on the angular distribution of intensity for molar fractions of 0.05 and 0.50 (Fig. 1) are significantly shifted with respect to the main maximum for pure water. For a molar fraction of alcohol of 0.50 the curve resembles the one obtained for pure alcohol but is significantly shifted with respect to it, Table 2.

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Table 2 The position of the first maxima in the experimental curve and the mean value of the least intermolecular distances.

X	Position of the maxima		Mean least intermolecular distances
	$\vartheta_{max}[°]$	$\vartheta[°]$	$R \pm 0.04$ [Å]
0.00	7.455	9.400	3.07
0.01	7.650	9.400	2.98
0.02	7.500	9.300	3.05
0.03	7.400	9.000	3.09
0.04	7.300	–	3.14
0.05	6.800	–	3.39
0.50	4.805	–	4.92
1.00	4.500	–	5.27

Figure 2 The values of the mean least intermolecular distances for various molar concentrations of 2-propanol in water.

Since the positions of the experimental maxima of the curves of the intensity distribution were determined with an accuracy of $\Delta\vartheta = \pm 0.001°$, the mean value of the absolute error in the calculation of the mean intermolecular distance $\bar{R}$ equation (2) is $\Delta\bar{R} = \pm 0.04$ Å.

4. CONCLUSIONS

A decrease in the mean intermolecular distance, relative to that in in pure water, to a value of 2.98 Å for the molar concentration of 0.01, Figure 2 and Table 2, is most probably accounted for by the clatrate structure of water, which has been suggested earlier [10, 16, 17]. The water molecules arranged into clatrates may form ordered complexes. In such complexes they are bonded through hydrogen bonds whose lengths vary from 2.77 Å to 2.94 Å [15]. If such a complex is made by e.g. 12 water molecules then a cavity may appear inside it. At a sufficiently low molar concentration, molecules of alcohol can penetrate into the cavity inside the ordered complexes of clatrate structure without damaging it. It is possible beacause the radius of an alcohol molecule $r = 2.44$ Å [18] is shorter than the distance from the centre of the cavity to the centres of the oxygen atoms forming a complex [15, 19]. As a consequence, the packing of the molecules in solution increases and the mean molecular distance decreases becomes less than in pure water (Table 2). However, it cannot be excluded that after penetration of alcohol molecules into the cavities the ice-like structure of water is changed into a lattice of dodecahedrons where greater cavities can occur [16]. With increasing concentration of alcohol, from 0.02 to 0.04 molar fraction, mean intermolecular distances increase subsequently by 0.07 Å; 0.11 Å and 0.16 Å with respect to the distance $\bar{R} = 2.98$ Å, for 0.01 molar fraction. This increase is, however, rather small, as it amounts to less than 10%, whereas for the alcohol concentration of 0.50 mole fraction it reaches 65%. In conclusion we can say that when a concentration of 2-propanol is low, water molecules successfully defend themselves against interference of alcohol molecules into their clatrate structure. For the alcohol concentration higher than $X = 0.04$ molar fraction, the clatrate structure of water begins to get modified as is manifested by the dis-appearance of the side maximum, for $\vartheta = 9.400°$, typical of the structure of pure water [19]. In such circumstances the mean intermolecular distance increases up to 5.27 Å for pure alcohol which is consistent with the mean radius of its molecule. The presence of a local extremum in the intermolecular distance indicates that the clatrate structure of water gets damaged in the solutions with 2-propanol of mole concentrations above 0.04.

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