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The role of hydrophobic interactions in structure of aqueous nonelectrolyte solutions from positron annihilation measurements

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Abstract
The experimental results of positron annihilation and sound velocity experiments in aqueous solutions of formamide and ethyl alcohol are compared. The concentration dependences of annihilation parameters and of adiabatic compressibility differ significantly for these systems, indicating hydrophobic hydration occurring in the case of water-alcohol system and hydrophilic one in the case of water-formamide.

Introduction
It is very well known fact that presence of non-polar groups in solute molecule leads to hydrophobic association in aqueous solutions [1]. Recently, the series of water - non-electrolyte systems was investigated using two independent methods: positron annihilation and sound velocity (see for example [2-5]). In all the cases hydrophobic hydration leads to formation of hydrates of stoichiometry close to that of known solid clathrate hydrates. However, all the solutes used contained hydrophobic parts and, consequently, only the hydrophobic hydration was possible.

For distinguishing between hydrophobic and hydrophilic hydration it is necessary to compare at least two different aqueous non-electrolyte systems. The systems water-ethanol and water-formamide were chosen. The former system was investigated recently [4] and hydrophobic hydration leading to formation of clathrate-type hydrates in liquid state was found. The latter solute, without any hydrophobic part in its molecule, should behave differently.

Experimental
Chemicals. Formamide (analytical grade, Romil, Great Britain) was used without further purification. Freshly prepared double distilled water was used. Solutions were prepared by weighing.
Positron annihilation measurements. The annihilation measurements were carried out at room temperature (approx. 25°C) with a standard measuring device based on the "fast-slow" coincidence technique as described elsewhere [2].
Sound velocity measurements. The ultrasonic velocity was measured with an accuracy of ±0.1% using a "sing-around" equipment. The details of the apparatus and measurement techniques applied in this study are given in [2].
Density measurements. The calibrated sinker method was used. Calibrations were determined using the known densities of air and water. The reproducibilities were ±0.01 kg/m³.
Experimental results

Sound velocity. The adiabatic compressibility coefficients $\beta$ were calculated from Laplace's equation

$$\beta = (\rho c^2)^{-1}$$

where $\rho$ - density of the liquid, $c$ - sound velocity. The concentration dependence of the compressibility in the low non-electrolyte concentration region for both systems is shown in Fig. 1. The adiabatic compressibility plotted against the mole fraction of formamide shows that there is no common intersection point of isotherms of adiabatic compressibility (the intersection points are shifted with temperature). This result is different comparing with the known aqueous solutions of nonelectrolytes with hydrophobic group, like water-ethanol [4].

Positron mean lifetimes. The numerical treatment gives the positron annihilation parameters $\tau_1$, $\tau_2$ and $I_2$ (see [2] for details). Their concentration dependencies are collected in Fig. 2 for both the systems under investigation.

Fig. 1. Adiabatic compressibility coefficients $\beta$ (in $\text{m}^2/\text{N}\cdot\text{m}^{-1}$) vs. non-electrolyte molar fraction for water-ethanol (lower graph) and water-formamide (upper graph) systems at temperatures: + 15°, Δ 20°, O 25°, + 30° and Δ 35°C.

Fig. 2. Positron annihilation parameters for the systems under investigation: $\tau_2$ (life-time of the long-lived component, in picoseconds, upper) and $I_2$ (intensity of this component, in percent, lower).
In the limits of errors, for the system water-formamide the concentration dependencies of \(\tau_2\) and \(I_2\) in Fig. 2 seem to be smooth. There is no inflection of \(\tau_2\), maximum of \(I_2\) or minimum of \(\tau_1\), which are observed in these systems at the concentrations corresponding to stoichiometry of liquid quasicrystalline hydrates. The results differ significantly from those obtained in the aqueous mixtures of ethanol (and other solutes with hydrophobic group).

**Discussion**

The formation of clathrate hydrates in the aqueous solutions of nonelectrolytes with hydrophobic part of their molecule is well proved now. According to the concept of iceberg formation of Frank and Evans [6] or to that of hydrophobic hydration of Franks [7], the water structure is modified around nonpolar parts of the solute molecule, leading to its increased "crystallinity". Thus, in the vicinity of guest molecule, the water structure is determined mainly by its moieity. The solute molecules are accomodated in the cavities of hydrogen-bonded network, which in pure water are assumed to be occupied by "monomeric" water molecules [8-11].

In the system water-ethanol hydrophobic hydration occurs [4] manifesting as inflection of \(\tau_2=f(c)\) and little maximum in \(I_2=f(c)\) \((c\text{-concentration of non-electrolyte})\) in Fig.2.

However, the system water-formamide does not behave similar. The reason is probably the lack of hydrophobic hydration. Such systems can be structure-breakers, similar to those with hydrophobic hydration occurring [12]. An example of the interpretational problems in water-polar nonelectrolyte systems is the system water-urea. It was concluded [13,14] that urea molecules dimerize in aqueous solutions. On the basis of molecular dynamics simulations, however, this interpretation has been denied [15].

It is worthy noting that for the system water-formamide the compressibility value corresponding to the (not exact) intersection of compressibility isotherms is almost the same \((\beta=40.10^{11}\text{ m}^2/\text{N})\) as for solid clathrate hydrates measured by Stackelberg [16]. However, the solute concentration at this point is too high to assume any solid-like structure of hydrates.

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**References**


