ULTRASONIC INVESTIGATION
OF
"Pseudo-STABLE" STRUCTURE IN WATER MIXTURES

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Abstract

The velocity of ultrasound and the density were measured in some mixture of water and non-electrolytes in the temperature range 288-308 K. Based on the results obtained, adiabatic compressibilities were calculated from Laplace's equation. The dependence of the compressibility upon concentration indicates the formation of a pseudo-stable liquid structure which we tried to compare with the solid clathrate and other structure.

Introduction

The velocity of ultrasounds in the mixtures of water and organic compounds

The investigations of the ultrasonic waves propagation velocity provide possibilities to calculate the coefficient of adiabatic compressibility in accordance with Laplace's equation (1):

$$\beta_a = \sqrt{\frac{1}{\rho c^2}} \qquad (1)$$

where: c - the velocity of ultrasonic wave, ρ - density
of the liquid.

According to previous investigations, characteristic of this magnitude, when plotted as a function of non-electrolyte concentration in water, is the common point of its isotherms intersection [1, 2, 3, 10 - 14]. The presence of this point was attributed by Endo [10 -12] to the formation of clathrate-like structures. The author assumed the concentration corresponding to the zero temperature coefficient of adiabatic compressibility:

$$\left(\frac{\partial \beta}{\partial T} = 0 \right) \qquad (2)$$

to be equivalent to the concentration of liquid clathrate-like hydrates. This resulted from the assumption that compressibility could be expressed as the sum:

$$\beta = \beta_\infty + \beta_{st.}$$

where: β_∞ & $\beta_{st.}$ are instantaneous (related with the compressibility of molecules as such and the distance between them) and structural compressibility, respectively.

At this concentration, both components of compressibility are independent of temperature.

In the case of aqueous solutions of non-electrolytes, structural compressibility is assumed to be related with the changes in the molecular structure, accompanying the breaking of intermolecular hydrogen bonds and resulting from periodic changes caused by the ultrasonic wave.

Anomalous properties of aqueous solutions of non-electrolytes are most frequently attributed to hydrophobic interactions, resulting either from the structure of water in the closest neighbourhood of hydrophobic radicals at low concentrations, or from the establishing of equilibrium between the molecules. The former case is ascribed to the plateau on the absorption curve, α/f^2(f), [4, 5, 10 - 12] and the common point of the intersection of isothermal lines on the plots of β(x) [10 - 12], and the latter - to relaxation phenomena [6, 7] and the minima of isotherms.

There are two different interpretations of the relation β(x): the first one was advanced by Baumgartner and Atkinson [2, 3], and the second one by Endo [10 - 12] who related the point of the intersection of compressibility isotherms with the formation of pseudoclathrate structures, while Baumgartner and Atkinson attributed it to the existing minima of the compressibility isotherms.

The theory of Endo describes the structure of the liquid at the point of the intersection of compressibility isotherms, comparing it either to one of the known solid clathrates or to other clathrate-like structures containing the solute molecules freely distributed in a spatial structure corresponding to pure water.

Such an interpretation seems adequate for aqueous solutions of 1,3- and 1,4-dioxane [13,14]. Hence, the existence of a region where β is independent of temperature might be assumed to be an indicator of the formation of the clathrate structure. Then, the compressibility at the intersection point of curves β(x) determines the elasticity of the lattice of water molecules, i.e. the instantaneous compressibility (4):

$$\frac{\partial \beta}{\partial T} \approx \frac{\partial \beta_\infty}{\partial T} \qquad (4)$$

The stoichiometry of clathrate-like structures formed in the solution need not necessarily correspond to the concentration at the intersection point of isotherms, β, since: a) part of gaps may be vacant, b) condition (2) may not be fully satisfied in the temperature range investigated c) hydration of dimers or larger systems cannot be excluded.

Structure of clathrates

The formation of aqueous structures with participation of hydrophobic or hydrophilic substances of part of solute molecules in water was already suggested in the 1940-ies [15], whereas the formation of gaseous hydrates was later confirmed by Frost [16]. Hydrates formed by saturation of water with gases or gas mixtures create non-stoichiometric systems. Such a stabilizing

effect is described by the use of a guest-host model. The organic molecule fills in the free space in the construction skeleton of water (the clathrate structure). In pure water, this space is occupied, at least in part, by monomeric water molecules [20, 8].

Many organic compounds form clathrate structures in the solid state by the interacting with the aqueous structure which plays the role of a "host". The guest molecule stabilizes the clathrate structure. This is how we try to explain some interesting properties of two-component mixtures of dioxanes and water. The crystalline lattice of water which is not stabilized by the "guest" is metastable, thus differing from the crystalline lattice of ice.

Measuring apparatus

The propagation velocity was measured using two methods, i.e. by means of an MPFU ECOLAB meter (determination of an averaged time of passing through the sample by an acoustic signal with a frequency of 1-10 MHz between the transmitting and receiving transducers) and by Eggers' method [9].

The density of the liquid was measured using an MG-2P microprocessor density meter. The results of measurements were displayed in absolute units: density with an accuracy of $10^{-5} g/cm^3$.

The error in the temperature measurement was +0.02 K.

Results and discussion

Mixtures of non-electrolytes and distilled water were prepared by weighting. The density and passage times were measured as a function of temperature for more than 10 mixtures of them with water in the whole concentration range for temperatures from 283 to 308 K at intervals of about 5 K. The results obtained from measurements are usually shown as functions of the propagation velocity of an ultrasonic wave versus temperature, and as the adiabatic compressibility coefficient versus temperature and concentration of organic substances.

The propagation velocity grows with temperature for mole fractions starting from 0.02 to 0.15, depending on the substances having a first maximum.

The plots representing the dependence of the adiabatic compressibility coefficient determined from Laplace's formula are decreasing functions for mole fractions from 0.02 to 0.15. The values of the coefficient also decrease reaching minima. At low concentration there exist a common point of intersection of isotherms. Then one can assume that the adiabatic compressibility coefficient is independent of temperature. For higher mole fractions, marked discrepancy between the values of the adiabatic compressibility coefficient is observed in the case of all isotherms (strong temperature dependence).

The presence of the minimum manifests the formation of stable structures in all mixtures.

Summary and conclusions

The plots of the ultrasonic wave propagation velocity display maxima, whereas those of the adiabatic compressibility coefficient have minima in the temperature range examined for the mixtures.

In the case of many aqueous mixtures of nonele-ctrolytes, characteristic of the isotherms of the adiabatic compressibility coefficient is a common intersection point near the low concentration of mole fraction.

According to earlier papers of Frank et al. [15], Yashkitsev et al. [20], Buslaeva [8], Endo [10 - 12], Ernst et al. [14], Gliński et al. [17], Linde et all [13, 18, 19], it is possible that liquid clathrate structures are formed in the mixtures of nonpolar compounds. But it is rather more probable formation of the pseudo-stable structure with lower quantities of molecules.

For some of the measured mixtures the minima or inflexion points occur at higher concentrations (the mole fraction higher than 0.5. This, however, has not been elucidated yet and is presumed to result from the formation of some structures.

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