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L.M. SABIROV, D.I. SEMENOV
Physics Department, Samarkand State University
(15, University Blvd., Samarkand 140104, Uzbekistan; e-mail: denis.samarkand@gmail.com)

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DIFFERENT STRUCTURAL STATES OF 4-METHYLPYRIDINE–WATER SOLUTIONS: EXPERIMENTAL STUDY OF THE ADIABATIC COMPRESSIBILITY AT THE HYPERSONIC FREQUENCY

The behavior of the adiabatic compressibility β_S with variation in the temperature t and the concentration x in the aqueous solution of a nonelectrolyte is experimentally studied from the fine structure of the spectra of light scattering. The sign inversion of the derivative of the adiabatic compressibility with respect to the concentration $d\beta_S(x)/dx$ and temperature $d\beta_S(t)/dt$ is observed. In the temperature-concentration phase diagram, the inversion points determine the lines of transition from the solution structure characterized by a nondisturbed continuous network of hydrogen bonds to the disturbed one, and, further, to the structure with fragmentary network.

Keywords: Rayleigh scattering, water solution, 4-methylpyridine, adiabatic compressibility.

1. Introduction

Experimental studies of the fine structure of Rayleigh scattering spectra in aqueous solutions of 4-methylpyridine (4MP) in a wide range of variations in the temperature and the concentration show that the kinetic regularities of the frequency shift of the Brillouin components (BCs) can be explained by a reconstruction, which occurs in the solution with variation in its temperature or by variation in the nonelectrolyte concentration in water [1, 2].

The critical points separating solutions with substantially different structural organizations of components are found in the temperature-concentration phase diagram. In a particular region of temperatures and concentrations, the hydrogen bond network in the solution retains its continuous three-dimensional integrity. In the region of concentrations $x > x_0$ (at a fixed temperature) or temperatures $t > t_0$ (at a fixed concentration), the hydrogen bond network is fragmentary.

One of the parameters closely connected with the structure of the liquid is the compressibility. The experimental values needed for calculations of the adiabatic compressibility by the Newton–Laplace equation ($\beta_S = 1/V^2\rho$, where V is the speed of sound, and ρ is the density) can be easily measured to a high accuracy. Therefore, the determination of this quantity and characteristics that are the derivatives of it (excess molar adiabatic compressibility, partial adiabatic compressibility [3]) is quite a common method for studying the structure of solutions [4].

To find the limits for the existence of a continuous hydrogen bond network in 4MP-water solutions, we investigated the adiabatic compressibility β_S in a wide range of variations in the solution temperature (10 to 80 °C) and in the 4MP concentrations in water (1 to 0.005 mole fraction (m.f.)).

2. Experimental

Spectra of Brillouin scattering were measured, by using an experimental setup with a double-pass Fabry–Perot interferometer. The angle of light scattering was 90°. The error in setting this angle did not exceed 0.2°. At this geometry of the experiment, the interferometer dispersion region was 0.625 cm^{-1}, the interference pattern contrast was 5×10^4, and the sharpness of fringes was 35. As a radiation source, we used a He–Ne laser operating at a wavelength of 632.8 nm with a power about 15 mW. The error in the measurement of the BCs frequency shift $\Delta\nu$ was no greater than 1%.

The solutions were prepared, by using pure grade 4MP and redistilled water. The uncertainty in the concentration of 4MP in solutions did not exceed 10^{-4} m.f. The solutions prepared were purified by triple distillation. After the purification, the samples of solutions were sealed in cylindrical glass cells at a negative pressure. The cell with a sample was placed in a thermostat, whose electronic scheme allowed the temperature stabilization with an accuracy better than $\pm 0.1\,^\circ$C.

The values of β_S were calculated on the basis of the measured BC shift $\Delta\nu$ by the formula

$$\beta_S = \frac{1}{\rho}\left(\frac{2n\sin(\theta/2)}{\lambda_0\Delta\nu}\right)^2, \tag{1}$$

where λ_0 is the wavelength of the exciting light, ρ is the density, n is the refractive index, $\Delta\nu$ is the BC shift, and θ is the light scattering angle. These calculations involved the densities of aqueous solutions of 4MP measured in [5, 6] and the refractive indices n measured by us.

3. Experimental Results

In our previous work [7], we discussed the experimental results obtained for the adiabatic compressibility of 4MP-water solutions in the region of concentrations $x \geqslant 0.1$ m.f. It was shown that an increase in the solution temperature leads to a monotonic increase in β_S. The highest compressibility is observed in pure 4MP. A decrease in the nonelectrolyte concentration in water leads to a decrease in the adiabatic compressibility. Figure 1 demonstrates the isotherms of the $\beta_S(x)$ dependence for temperatures of 25, 45, and 65 °C calculated from the data on the BCs frequency shift for the scattering angle 90°. The magnitude of BCs shift in this scattering geometry is governed by the modulation of the scattered light by elastic thermal waves (hypersound) with the frequency ~4.8 GHz.

The shape of the $\beta_S(x)$ dependence appreciably varies with temperature. At low temperatures, β_S varies nonmonotonically with decreasing the concentration of the solution and passes through a minimum at a certain concentration. As the temperature increases, the position of the minimum in the $\beta_S(x)$ dependence shifts to the region of lower concentrations, and the minimum itself becomes less distinct. Finally, at high temperatures, the minimum in the isotherms of the $\beta_S(x)$ dependence disappears, and β_S is seen to decrease monotonically with decreasing the concentration.

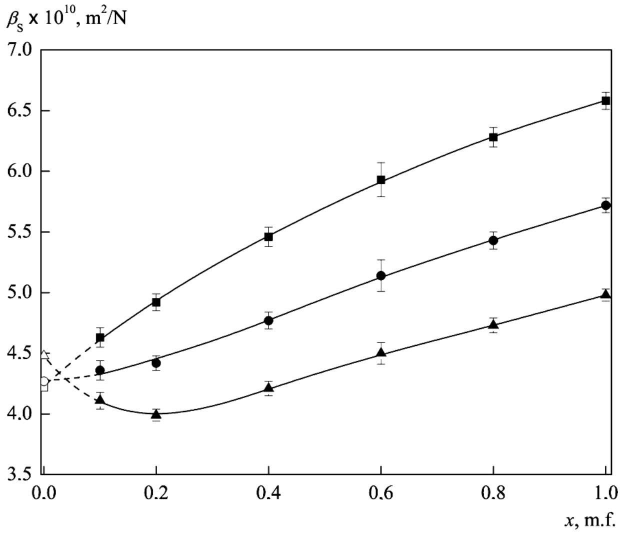

Fig. 1. Isotherms of the concentration dependence of the adiabatic compressibility $\beta_S(x)$ of 4MP-water solutions ($x \geqslant 0.1$ m.f.) at a hypersonic frequency: experimental data ▲ – 25 °C, ● – 45 °C, ■ – 65 °C; dashed lines – extrapolation of $\beta_S(x)$ to $x = 0$ (pure water); Δ, ○, and □ – adiabatic compressibility of pure water at the corresponding temperatures

In the region $x < 0.1$ m.f., we observe experimentally a nonmonotonic dependence of β_S on the temperature of the solution. At low concentrations of 4MP, β_S varies nonmonotonically with rising the temperature of the solution and passes through a minimum at a certain temperature. As the concentration increases, the position of the minimum in the $\beta_S(t)$ dependence shifts to the region of lower temperatures. Figure 2 shows the $\beta_S(t)$ dependences in solutions of low 4MP concentrations and pure water determined from the experimental data on BCs shift.

From the entire set of experimental data on β_S in the whole range of investigated temperatures and concentrations of 4MP-water solutions, it follows that the sign inversion of the derivative of the adiabatic compressibility with respect to the concentration and the temperature is observed in the $\beta_S(x)$ and $\beta_S(t)$ dependences. The inversion points (i.e., $d\beta_S(x)/dx = 0$ and $d\beta_S(t)/dt = 0$) are presented in Fig. 3.

The extrapolation of the position of the minimum of $\beta_S(x)$ to pure water ($x = 0$) predicts the presence of some “critical” temperature $t \approx 48\,^\circ$C in water. This temperature is in good agreement with the results of works [8, 9], where, on the base of comparative analysis of the temperature dependences of the shear viscosities of water and argon, the au-

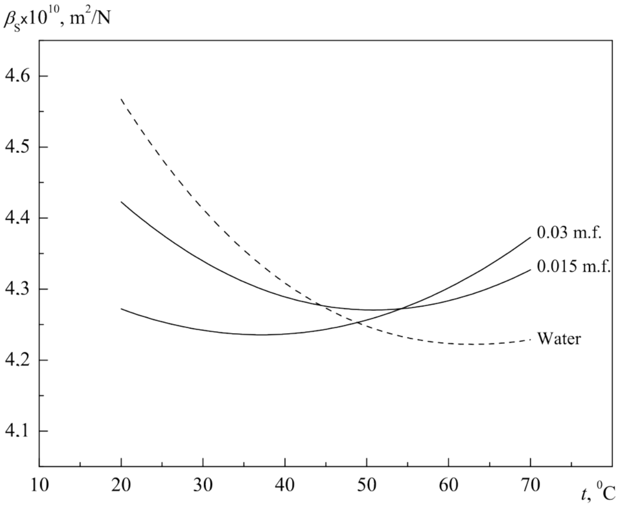

Fig. 2. $\beta_S(t)$ dependences in 4MP-water solutions in the region of low concentrations

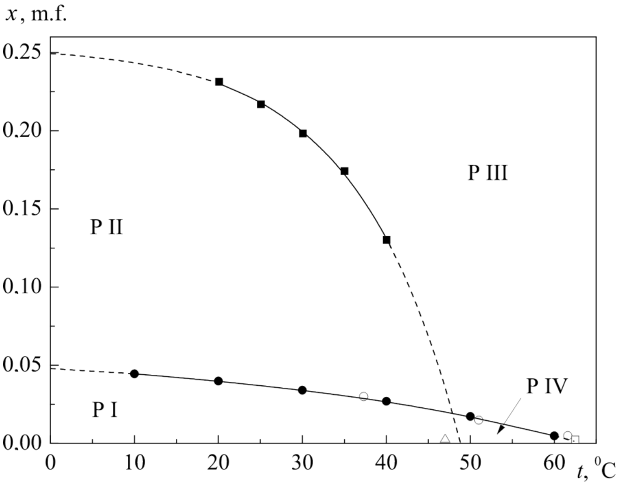

Fig. 3. Set of the sign inversion points ($d\beta_S/dx = 0$, ■; $d\beta_S/dt = 0$, •) in 4MP-water solutions: Δ – temperature of the continuous H-bond network destruction in water according to [8, 9], □ – temperature of the minimum of the adiabatic compressibility in water; solid lines – experimental data smooth; dashed lines – extrapolation of the experimental data to higher/lower temperatures. P I – $d\beta_S/dx < 0$, $d\beta_S/dt < 0$; P II – $d\beta_S/dx < 0$, $d\beta_S/dt > 0$; P III – $d\beta_S/dx > 0$, $d\beta_S/dt > 0$; P IV – $d\beta_S/dx > 0$, $d\beta_S/dt < 0$

thors made conclusion on the destruction of the 3D-continuous H-bond network in water at temperatures above ~47 °C. Accordingly, the line of sign inversion points of $d\beta_S(x)/dx$ shows a boundary of existence (in the "temperature-concentration" coordinates) of the 3D-continuous H-bond network in water and aqueous 4MP solutions.

The line of $d\beta_S(t)/dt = 0$ inversion points in Fig. 3 reflects, obviously, a boundary of existence of a nondisturbed H-bond network in 4MP-water solutions with tetrahedral configuration similar to pure water.

4. Conclusions

The analysis of the β_S variation in a wide range of temperatures and concentrations allows us to define four areas (phases) with different states of 4MP-water solutions (Fig. 3).

In Phase I (P I), which occupies a rather narrow concentration interval, the rise of the solution temperature (at a fixed concentration) or the rise of the solution concentration (at a fixed temperature) is accompanied by the monotonic decrease of β_S. In other words, the derivatives $d\beta_S(x)/dx$ and $d\beta_S(t)/dt$ are negative in Phase I.

In Phase II (P II), the rise of t (at $x = \text{const}$) leads to the monotonic increase of β_S, but the increase of x (at $t = \text{const}$) is accompanied by the decrease of β_S, i.e., $d\beta_S/dt > 0$ and $d\beta_S/dx < 0$.

In Phase III (P III), the rise of t (at $x = \text{const}$) and x (at $t = \text{const}$) is accompanied by the monotonic increase of β_S, i.e., $d\beta_S/dt > 0$ and $d\beta_S/dx > 0$.

Together with the above-mentioned three phases, there is the fourth phase (P IV) in 4MP-water solutions, where the compressibility (at a fixed temperature) is increased with the concentration ($d\beta_S/dx > 0$), but it is decreased (at a fixed concentration) with rising the temperature ($d\beta_S/dt < 0$).

The obtained experimental results show that, in the region of low concentrations and temperatures, the implantation of nonelectrolyte molecules into the matrix of the water H-bond network occurs without any significant disturbance of the network (P I in Fig. 3). The structure of the solution in this temperature–concentration interval is similar to the structure of pure water. The decrease in the compressibility with rising the concentration testifies to the stabilizing (strengthening) influence of nonelectrolyte molecules on the solution structure due to two effects: 1) the implantation of nonelectrolyte molecules into accessible cavities of the H-bond network without the disturbance of its tetrahedral configuration, and 2) the expulsion of nonelectrolyte molecules by the H-bond network into places of its thermal defects. Obviously, in this temperature–concentration region, the hydrophobic interaction between the water and nonelectrolyte molecules plays the determining role.

With rising the concentration of nonelectrolyte molecules, the H-bond network is deformed, but it preserves its 3D integrity (P II in Fig. 3). In this temperature–concentration region, the stabilization of the network (decrease of the compressibility) still occurs, but, obviously, due to the change of the intermolecular interaction from the hydrophobic to hydrophilic one. Under conditions of the concurrence for the H-bond formation, a possibility of 4MP molecules to form H-bonds with water molecules starts to play a rising role.

With the further rising of the concentration of nonelectrolyte molecules, the continuous H-bond network in the solution is destroyed (fragmented) that leads to an increase in the solution compressibility (P III in Fig. 3). The degree of defragmentation increases with the temperature or concentration of solutions.

Increasing the temperature leads to an increase in the thermal deformation of the network. That is why the process of its destruction starts at a less nonelectrolyte concentration. In other words, the “critical” concentration of the minimal compressibility of the solution shifts toward lower concentrations with rising the temperature of the solution. This shift is reflected in the temperature–concentration behavior of the minimum of the adiabatic compressibility (Fig. 3).

However, in 4MP-water solutions, there is one phase (P IV in Fig. 3), where the continuous network of H-bonds is absent, but the solution structure preserves features of pure water (decrease of the compressibility with rising the temperature). In this temperature–concentration region, the number of nonelectrolyte molecules in the solution is rather high to save the integrity of the H-bond network as a whole, but their presence provides a local stabilizing influence on network’s fragments. This rather narrow temperature–concentration interval should be considered to be the area of the “clusterized” state of solutions, if we mean the term “cluster” to be a spatial region of water-like coordination of water molecules due to the stabilizing influence of nonelectrolyte molecules.

The transition from one phase to another one can be realized either by a variation of the solution temperature (at a fixed concentration) or by a variation of the solution concentration (at a fixed temperature).

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Л.М. Сабіров, Д.І. Семенов

РІЗНІ СТРУКТУРНІ СТАНИ РОЗЧИНІВ 4-МЕТИЛПІРИДИН–ВОДА: ВИВЧЕННЯ АДІАБАТИЧНОЇ СТИСЛИВОСТІ НА ЧАСТОТІ ГІПЕРЗВУКУ

Резюме

За спектрами тонкої структури розсіювання світла експериментально вивчено поведінку адіабатичної стисливості β_S водних розчинів неелектроліту при зміні температури t і концентрації x. Виявлено інверсію знака похідної адіабатичної стисливості за концентрацією $d\beta_S(x)/dx$ і за температурою $d\beta_S(t)/dt$. На фазовій діаграмі в координатах “температура–концентрація” сукупність точок інверсії визначає лінії переходів від структури розчину, що характеризується наявністю недеформованої суцільної сітки водневих зв’язків до деформованої сітки і, далі, до структури з фрагментованою сіткою.