Dispersion of the hypersound velocity in aqueous solutions of 4-methylpyridine in the vicinity of a special point concentration

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1. Introduction

A dispersion of high-frequency sound in liquids is widely studied, both theoretically and experimentally, due to significant physical interest to this problem [1]. Method of Brillouin light scattering spectroscopy allows one to study the velocity V and the absorption coefficient α of sound for the frequency f up to $\sim 10^{10}$ Hz. This method was found to be very effective in studying the properties of liquids and binary solutions near their critical points. Binary solutions with a closed phase-separated region, a double critical point, and a special point in x, T plane (x is the concentration, T is the temperature) are poorly studied in spite of they are interesting and important objects for studying phase transitions and critical phenomena [2].

In [3] authors investigated the dispersion of sound velocity in a guaiacol-glycerol (GG) solution with the closed phase-separated region by comparing magnitudes of sound velocity for ultrasonic (2.6 MHz) and hypersonic (12 GHz) frequencies. It was observed that the dispersion of sound velocity below the lower critical temperature of phase separation is 22%, and it depends linearly on temperature. Above the upper critical temperature of phase separation the dispersion is significantly lower, and it also depends linearly on temperature, but with different temperature coefficient.

Experimental data, presented in [2,3], also show that for GG solution peculiarities of sound propagation in the vicinity of the special point temperature are observed in hypersonic region, while no such peculiarities in temperature dependence of the velocity were observed for ultrasound. Accordingly, it is expedient to investigate peculiarities of the dispersion in the region of hypersonic frequencies.

In this paper we briefly report on our preliminary experimental study of the dispersion, which occurs for two different frequencies of hypersound. We also propose a convenient method to determine the magnitude of the dispersion directly from the frequency shift of Brillouin components (BCs) in spectra of light scattering registered at two different scattering angles.

The dispersion of hypersound was studied in aqueous solutions of 4-methylpyridine (4MP). The special point of 4MP-water system corresponds to the concentration of 4MP $x_C \approx 0.06$ mole fraction (m.f.) and the temperature $T_C \approx$

70°C. The dispersion was studied while approaching the concentration of 4MP in the solution to x_C (from the side of higher concentrations) at the temperatures 20 and 70°C.

2. Experimental

We studied the frequency shift $\Delta\nu$ of BCs in 4MP-water solutions in the concentration region $x \geq 0.1$ m.f. for the scattering angles 135° [4] and 45°.

The source of radiation was He-Ne laser. Spectra of scattered light were detected on an experimental setup with a two-pass Fabry-Perot interferometer. To set the scattering angle with a necessary accuracy (error of no more than 0.2°), a cylindrical cell with a solution studied was placed in an octahedral cylinder, composed of cemented optical prisms. To exclude the cylindrical-lens effect, an immersion liquid (with a refractive index close to that of the cylinder) was poured in the gap between the cell and cylinder walls.

For each solution, the spectra of the scattered light were recorded at least four times, and the results of the processing of the spectra were averaged. The error in measuring the BCs frequency shift $\Delta\nu$ did not exceed 1% and 2% for scattering angles 135° and 45°, accordingly.

In the studied solutions the fine structure of spectra at the angles of $\theta_1 = 45^\circ$ and $\theta_2 = 135^\circ$ appears as a result of modulation of the scattered light by hypersonic waves with frequency $f_1 = 2.6 \pm 0.2$ GHz and $f_2 = 6.1 \pm 0.2$ GHz, consequently. Dispersion of sound velocity D in the region of frequencies from f_1 to f_2 ($f_2 > f_1$) can be calculated from the corresponding magnitudes of the sound velocities V_1 and V_2 as follows:

$$D = \Delta V/V = 2 \times (V_2 - V_1) \times (V_2 + V_1)^{-1}, \quad (1)$$

where $V = (V_2 + V_1)/2$ is the average magnitude of the velocity in this frequency region. By taking into account a relation between the hypersound velocity and the frequency shift of BCs [1]

$$\Delta\nu = 2nv_0(V/c) \sin(\theta/2),$$

where v_0 is the exciting light frequency, n is the refractive index, c is the speed of light in vacuum, θ is the scattering angle, we can represent Eq. (1) in the following form:

$$D = 2 \times \left(\frac{\Delta\nu_2}{\Delta\nu_1} - \frac{\sin(\theta_2/2)}{\sin(\theta_1/2)} \right) \times \left(\frac{\Delta\nu_2}{\Delta\nu_1} + \frac{\sin(\theta_2/2)}{\sin(\theta_1/2)} \right)^{-1}, \quad (2)$$

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Fig. 1 Hypersound velocity dispersion D versus reduced concentration $\varepsilon = (x - x_C)/x_C$ in 4MP-water solutions at the temperature $T = 20^\circ\text{C}$. ■, experimental data; □, dispersion in pure water; solid line, smoothing of experimental data; dashed line, extrapolation of the linear part of $D(\varepsilon)$ to $\varepsilon = -1$ (pure water).

Fig. 2 Hypersound velocity dispersion D versus reduced concentration $\varepsilon = (x - x_C)/x_C$ in 4MP-water solutions at the temperature $T = 70^\circ\text{C}$. ■, experimental data; □, dispersion in pure water; solid line, smoothing of experimental data; dashed line, extrapolation of the linear part of $D(\varepsilon)$ to $\varepsilon = -1$ (pure water).

where Δv_1 and Δv_2 are magnitudes of BCs shift in spectra detected at scattering angles θ_1 and θ_2 , consequently.

An advantage of Eq. (2) over Eq. (1) in studying the relative change of hypersound velocity is that the magnitude of dispersion D can be determined directly from BCs shifts. Accordingly, there is no necessity to calculate hypersound velocities on the base of additional measurements of the refractive indexes of solutions in the whole temperature-concentration interval of investigation.

3. Results and discussion

Figures 1 and 2 show experimental magnitudes of D as a function of a reduced concentration $\varepsilon = (x - x_C)/x_C$, which characterizes a degree of closeness of 4MP concentration in the solution (x) to the special point concentration ($x_C = 0.06$ m.f.). Experimental data were obtained for solutions with temperature $T = 20^\circ\text{C}$ (Fig. 1), which is far from the special point temperature ($T_C \approx 70^\circ\text{C}$), and for solutions with temperature $T = 70^\circ\text{C}$ (Fig. 2), which is very close to T_C . Error bars in figures describe the error in the magnitude of D , calculated using the formula (2) with taking into account the error in measuring Δv and inaccuracy of adjustment of the scattering angle θ in each experiment.

One can see that the character of $D(\varepsilon)$ dependence is rather similar in both cases. Decrease of 4MP concentration in solution is accompanied by a monotonic decrease of the dispersion. There is a linear (within experimental errors) part of $D(\varepsilon)$ dependence, and an extrapolation of this part to $\varepsilon = -1$ ($x = 0$) predicts zero magnitude of the dispersion in pure water. This result is in a good agreement with available experimental data on acoustical properties of water.

While approaching the special point concentration we observe a noticeable decrease of the dispersion. In solutions of critical temperature ($T = 70^\circ\text{C}$) in the interval from $\varepsilon = 2.33$ to $\varepsilon = 0.67$ (0.1 m.f. of 4MP) there is a sharp increase of the dispersion, and experimentally observed magnitude of D

at $\varepsilon = 0.67$ exceeds its expectable magnitude more than 20 times.

The dispersion in the region $\varepsilon < 2.33$ (Fig. 2) is very unusual. There is a high level of concentration fluctuations in the vicinity of the special point of a solution, that can, in principle, lead to a change in the sound velocity, and, accordingly, to unusual concentration dependence of the dispersion. However, “critical” mechanisms can contribute noticeably to the sound velocity in the very vicinity of critical point when $\varepsilon < 10^{-2}$ [5]. In our experiment we observe unusual behavior of the dispersion very far from the critical region ($\varepsilon \leq 2$) at the temperature of the special point (Fig. 2). Moreover, the similar picture we observe for solutions with temperature, which is very far from the special point temperature (Fig. 1). These facts, obviously, indicate non-critical nature of the observed phenomenon.

Preliminary results obtained in the present work, allow, we believe, obtaining rich information in the process of further experimental and theoretical studies.

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