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## NEGATIVE DISPERSION OF HIGH-FREQUENCY SOUND VELOCITY IN AQUEOUS SOLUTIONS OF NON-ELECTROLYTE IN A VICINITY OF THE SINGULAR POINT CONCENTRATION

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*A new method of determination of the hypersound velocity dispersion is proposed. It is based on the direct measurement of the frequency shift of Brillouin components in the light scattering spectra registered at different angles. The concentration dependence of the hypersound velocity dispersion is studied in 4-methylpyridine-water solutions. Negative dispersion is experimentally observed in the region of the singular point concentration.*

*Keywords:* sound velocity, dispersion, Rayleigh scattering, water solution, 4-methylpyridine.

### 1. Introduction

The dispersion of high-frequency sound in liquids is widely studied, both theoretically and experimentally, due to a significant physical interest in this problem [1]. The method of Brillouin light scattering spectroscopy allows one to study the velocity  $V$  and the absorption coefficient  $\alpha$  of sound for frequencies  $f$  up to  $\sim 10^{10}$  Hz. This method was found to be very effective for 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 the  $x$ - $T$  plane ( $x$  is the concentration,  $T$  is the temperature) are poorly studied in spite of they are interesting and important objects for studying the phase transitions and critical phenomena [2].

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

Experimental data [2, 3] also show that, in a GG solution, the peculiarities of a sound propagation in a vicinity of the special point temperature are observed in the hypersonic region, while no such peculiarities in the temperature dependence of the velocity were observed for ultrasound. Accordingly, it is expedient to investigate the 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 dispersion directly from the frequency shift of Brillouin components (BCs) in the spectra of light scattering registered at two different scattering angles.

### 2. Experimental

The dispersion of hypersound was studied in aqueous solutions of 4-methylpyridine (4MP). The singular point of the 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 in the whole range of 4MP concentrations in the solution at temperatures of 20 and 70 °C.

In order to determine the dispersion magnitude, we studied the frequency shift  $\Delta\nu$  of BCs in 4MP-water solutions in the concentration region from 0.005 m.f. to pure 4MP ( $x = 1$  m.f.) for scattering angles of 135° and 90°.

The source of radiation was a He–Ne laser. The 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  $0.2^\circ$ ), a cylindrical cell with the solution under investigation was placed in an octagonal cylinder made of cemented optical prisms. In order to eliminate the cylindrical-lens effect, an immersion liquid (with the refractive index close to that of the cylinder) was poured in a gap between the cell and the cylinder walls.

In each solution, the spectra of the scattered light were recorded at least four times, and the results of processing were averaged. The error of determining the BCs frequency shift  $\Delta\nu$  was no greater than 1%.

In the studied solutions, the fine structure in spectra at the scattering angles  $\theta_1 = 90^\circ$  and  $\theta_2 = 135^\circ$  appears as a result of the modulation of the scattered light by hypersonic waves with the frequencies  $f_1 = 4.6 \pm 0.2$  GHz and  $f_2 = 6.1 \pm 0.2$  GHz, consequently. The sound velocity dispersion  $D$  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:

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

where  $V = (V_2 + V_1)/2$  is the average magnitude of the velocity in this frequency region. With regard for the relation between the hypersonic velocity and the BCs frequency shift [1]

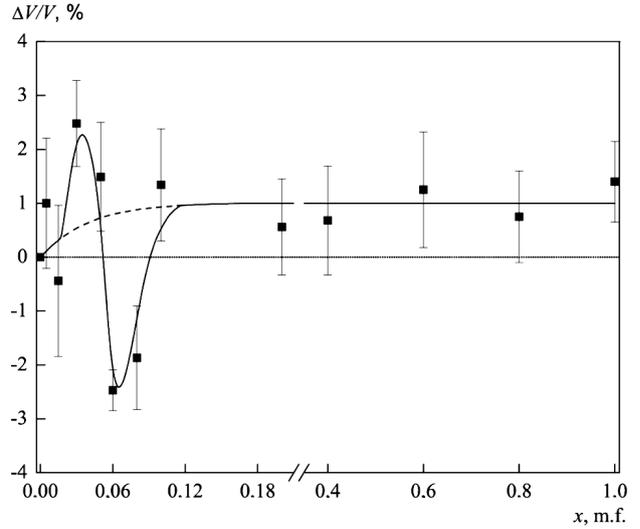
$$\Delta\nu = 2n\nu_0(V/c) \sin(\theta/2),$$

where  $\nu_0$  is the exciting light frequency,  $n$  is the refractive index,  $c$  is the velocity of light in vacuum, and  $\theta$  is the scattering angle, we can represent Eq. (1) in the following form:

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

where  $\Delta\nu_1$  and  $\Delta\nu_2$  are the magnitudes of BCs shifts in the spectra detected at scattering angles  $\theta_1$  and  $\theta_2$ , consequently.

The advantage of Eq. (2) over Eq. (1) in studying the relative change of the hypersonic velocity is that the magnitude of dispersion  $D$  can be determined directly from BCs shifts. Accordingly, there is no necessity to calculate the hypersonic velocities on the base



**Fig. 1.** Dependence of the hypersonic velocity dispersion in a 4MP-water solution on the concentration of 4MP at  $t = 20^\circ\text{C}$

of additional measurements of the refractive indices of solutions in the whole temperature–concentration interval under study.

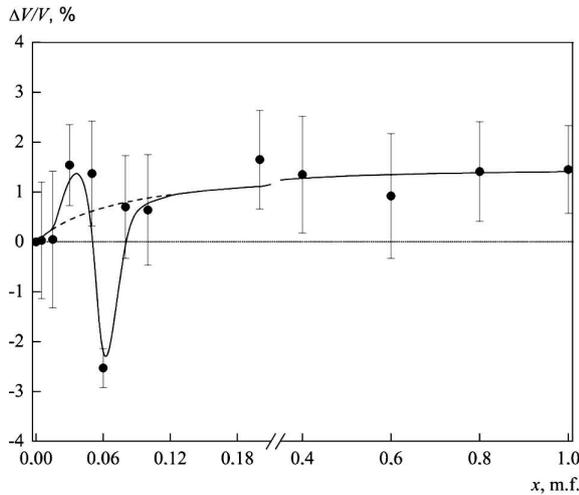
### 3. Experimental Results

The values of dispersion  $D$  in solutions at temperatures of 20 and  $70^\circ\text{C}$  determined from formula (2) are shown in Figs. 1 and 2. Changes of the dispersion in these solutions at variations in the temperature and concentration are atypical and, as far as we know, are observed for the first time.

In pure water,  $D = 0$  [1], and a decrease in the 4MP concentration in solutions is expected to cause a monotonic decrease in  $D$ .

All solutions (except those with 4MP concentrations equal to 0.08 and 0.06 m.f.) had a positive dispersion. The dashed lines in Figs. 1 and 2 show the suggested dependences of  $D$  on the region of low 4MP concentrations. In the solutions with concentrations of 0.08 and 0.06 m.f., the hypersonic velocity dispersion is negative; i.e., it decreases with increasing the frequency. The magnitude of negative dispersion exceeds the experimental error: at  $t = 20^\circ\text{C}$ ,  $D = -1.9 \pm 1.0\%$  and  $-2.5 \pm 0.4\%$  in the solutions with 4MP concentrations equal to 0.08 and 0.06 m.f., respectively.

With the increase in the solution temperature to  $70^\circ\text{C}$ , the magnitude and the sign of dispersion in the solution with a 4MP concentration of



**Fig. 2.** Dependence of the hypersonic velocity dispersion in a 4MP-water solution on the 4MP concentration at  $t = 70\text{ }^\circ\text{C}$

0.06 m.f. are not changed within the experimental error (see Fig. 2), whereas both the magnitude and the sign of the dispersion change in the solution with a 4MP concentration of 0.08 m.f.; at  $t = 70\text{ }^\circ\text{C}$ ,  $D = 0.8 \pm 1.0\%$ .

In the solution with a 4MP concentration of 0.03 m.f., the “excessive” positive dispersion (with respect to the suggested magnitude) is observed.

There are no physical reasons for observing the negative dispersion of the sound velocity in ordinary liquids and solutions. Associated liquid media are a different matter. Vladimirkii [4] and Ginzburg [5] pointed out that the negative dispersion of the sound velocity can be observed in liquids. In [4], the dispersion that is not associated with the relaxation and is related to the intermolecular interaction is considered. In [5], the second approximation of the Navier–Stokes equation is investigated. It is assumed that the absorption is very low; i.e., the effect of viscosities on the dispersion is not actually considered, but rather the effort is aimed to revealing other causes for the dispersion connected with features of the spatial structure of the medium under consideration and thus with the spatial dispersion of the velocity of sound. According to [5], the dispersion can be evaluated by the formula

$$V = V_0 \left( 1 + \frac{2\pi^2 f^*}{V_0^2 \Lambda^2} \right), \tag{3}$$

where  $\Lambda$  is the sound wavelength,  $V_0$  is the low-frequency sound velocity. The sign of the sound dis-

persion in (3) is dictated by the sign of  $f^*$ , which depends on the nature of intermolecular interactions. For example, in a molecular aggregate where the attraction forces act between its particles, i.e.,  $f^* < 0$ , the dispersion found by (3) will be negative [5]. If we assume that  $|f^*| \sim (V_0 r)^2$ , where  $r$  is the distance, at which the molecular interaction is significant (the correlation radius or the diameter of the associated aggregate), formula (3) can be written as

$$\frac{\Delta V}{V} \approx 2\pi^2 \left( \frac{r}{\Lambda} \right)^2. \tag{4}$$

It is known that aqueous solutions of methylpyridines have quite a complicated phase diagram in the three-dimensional temperature–concentration–pressure space. In the temperature region below and above the singular point, these solutions are associated due to the formation of hydrogen bonds of different intermolecular nature. Thus, the conditions, under which the negative dispersion is allowed to exist, are present in the aqueous solution of 4MP.

The diameter of the associated aggregate can be evaluated by formula (4), by using the experimentally observed negative dispersion. Our evaluation of the associated aggregate size was about  $100\text{ \AA}$ , which is in satisfactory agreement with the sizes of the aggregates observed by other methods in other similar solutions. For example, in [6], the sizes of the optical non-uniformity dimensions in aqueous solutions of glycerol at a temperature of  $20\text{ }^\circ\text{C}$  and the glycerol concentrations ranging from 0.031 to 0.055 m.f. were evaluated to be approximately  $70\text{ \AA}$ .

#### 4. Conclusion

In our previous work [7], we observed the negative dispersion, while studying the temperature dependence of the hypersonic velocity in a 4MP solution with the singular point concentration (0.06 m.f.). The results of the present work show that the picture of the sound velocity dispersion in the hypersonic frequency region is more complicated.

Some features of the dependence of the dispersion on the temperature and the concentration of a solution (see Figs. 1 and 2) indicate that their nature is not reduced to only the aforementioned model interaction of sound with molecular (and also model) aggregates.

For example, on the assumption that the negative dispersion in a 0.06-m.f. solution is caused by the in-

teraction of sound with aggregates, the fact that the dispersion is independent of the temperature should be considered as an indication of the stability of these aggregates and their almost constant size at temperatures of 20 and 70 °C. However, it is difficult in this case to explain the fact that a small variation in the ratio of molar fractions of water and 4MP in a solution changes both the sign of the dispersion and its temperature dependence. Figures 1 and 2 demonstrate that the decrease in the 4MP concentration in a solution from 0.06 to 0.05 m.f. leads to the temperature-independent positive dispersion, whereas the increase in the concentration to 0.08 m.f. leads to a strong dependence of the dispersion on the temperature with the inversion of the dispersion sign.

Note another structural feature of the solutions under study and its relationship to the propagation of high-frequency sound. It is known that water molecules can form a 3D network of hydrogen bonds with a coordination close to tetrahedral (see, for example, [7–10]). The incorporation of nonelectrolyte molecules into the network structure can lead to its stabilization (hardening) in a certain concentration range. The network is able to preserve its 3D integrity up to a certain temperature, which depends on the nonelectrolyte concentration [11]. Nonelectrolyte molecules in the network structure can be considered as point defects, which are capable of forming the dislocation lines in the network continuum, with a lifetime corresponding to the hydrogen bond lifetime. The propagation of sound in a medium with dislocations can be accompanied by a resonant-type dispersion of its velocity [12]. The interaction between sound and these inhomogeneities manifests itself, when the sound frequency is close to the resonant frequency of the dislocation motion. In this case, both positive and negative dispersion of sound velocity can be observed [12].

The preliminary results obtained in the present work will allow, we believe, obtaining a rich information during the further experimental and theoretical studies.

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НЕГАТИВНА ДИСПЕРСІЯ  
ШВИДКОСТІ ВИСОКОЧАСТОТНОГО ЗВУКУ  
У ВОДНИХ РОЗЧИНАХ НЕЕЛЕКТРОЛІТУ  
В ОКОЛІ КОНЦЕНТРАЦІЇ  
ОСОБЛИВОЇ ТОЧКИ

Резюме

Запропоновано новий метод для визначення величини дисперсії швидкості гіперзвуку. Метод заснований на вимірі величини частотного зсуву компонент Бріллоена в спектрах світла, розсіяного під різними кутами. Вивчено концентраційну залежність дисперсії швидкості гіперзвуку у водних розчинах 4-метилпіридину. В околі концентрації особливої точки експериментально виявлено негативну дисперсію.