# Dispersion of the sound speed in water-organic solutions

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Концентрационные и температурные исследования спонтанного мандельштам-бриллюэновского рассеяния света в водных растворах γ-пиколина показали появление отрицательной дисперсии скорости гиперзвука при концентрациях $C \leq 0.2$ молярных долей γ-пиколина. Температурная и концентрационная зависимости величины отрицательной дисперсии связываются с процессом структуризации раствора, достигающей оптимального значения при концентрации $C = 0.06$ молярных долей γ-пиколина.

**Ключевые слова**: γ-пиколин, дисперсия, релаксация объемной вязкости, гиперзвук, время релаксации, водно-органический раствор.

Concentration and temperature studies of spontaneous Mandelstam-Brillouin scattering of light in aqueous solutions of γ-picoline showed the manifestation of negative dispersion of hypersound velocity at concentrations $C \leq 0.2$ mole fractions of γ-picoline. The temperature and concentration dependences of the negative dispersion are associated with the process of solution structurization, which reaches its optimum value at a concentration of $C = 0.06$ mole fractions of γ-picoline.

**Keywords:** γ-picoline dispersion, relaxation of bulk viscosity, hypersound, relaxation time, water-organic solution.

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## I. Introduction. Formulation of the problem

The work is devoted to the description of an experiment on measuring the temperature dependences of the hypersound velocity at different frequencies in water-organic solutions with singular points. Interest in the study of such solutions is due to the following. As is known (see, for example, monograph [1]), there is the class of water-organic solutions in which an anomalously high scattering peak unrelated to molecular scattering is observed in a certain fairly narrow range of concentrations. The physical nature of this peak is currently being actively discussed (see, for example, [2] and references cited in this work). It is believed that the main reason for the appearance of this peak is the appearance of a supramolecular structure in a certain range of temperatures and concentrations. It is necessary to mention the previous works [3-6], in which it has been shown that stable liquid molecular complexes with sizes of 100–200 nm spontaneously arise in aqueous solutions of polar organics, the density of which differs from the density of the surrounding liquid. It has been shown in [7-12] that anomalous light scattering is associated with the formation of a nanodroplet phase in water-organic mixtures.

In this work, a mixture of "water-γ-picoline" is studied. Interest in this particular mixture is due to the fact that in this solution in a certain concentration range there is an abnormally high light scattering peak at a content of γ-picoline ≈0.06 mole fractions (ppm) (see Fig. III.14 in the monograph [1] and comments on this figure). At the same time, in accordance with the literature data (see, for example, [11]), γ-picoline has infinite solubility in water, i.e. the mixture "γ-picoline-water" does not separate at any con-

centration in the entire temperature range at which the liquid mixture exists. The refractive index of γ-picoline at a wavelength of λ = 589.3 nm is 1.5, so it should be expected that in the concentration range for which an anomalous light scattering peak is recorded, a nanodroplet phase enriched in γ-picoline can be observed, and the phase contrast, in this case, will be high enough to study these nanodroplets with a phase microscope, [7-10]; we are currently experimenting with. In addition, in [12-15] it was shown that the Landau-Placek relation $I_\omega / (I_{\omega-\delta\omega} + I_{\omega+\delta\omega})$ where $I_\omega$ – unbiased component intensity, $I_{\omega\pm\delta\omega}$ – the intensity of the displaced components increases with decreasing solution concentration over a wide temperature range. In [16], it was suggested that the increase in $I_\omega / (I_{\omega-\delta\omega} + I_{\omega+\delta\omega})$ is due to an increase in the isothermal compressibility $\beta_T$ with an increase in the water content. This, in turn, may be due to the appearance of stable supramolecular structures (nuclei of the nanodroplet phase) with a decrease in the concentration of γ-picoline; this phase, in accordance with the model presented in [7-10], causes anomalous scattering in an aqueous solution of γ-picoline at its concentration of 0.06 ppm in solution; henceforth, we will call this concentration the critical concentration. This paper presents the results of a study of the frequency dispersion of hypersound velocity in aqueous solutions of γ-picoline in a wide range of temperatures and concentrations; special attention is paid to the concentration region near the critical one.

## II. Experiment

The experimental setup is described in detail in [17]. The spectra of polarized light scattering were studied by using a two-pass Fabry-Perot interferometer. The light scattering angle was ~90° and 135°. The error in setting the angle did not exceed 0.2°. The dispersion region of the interferometer was ⟨0.625 см$^{-1}$ and ⟨0.417 см$^{-1}$⟩. The interference contrast of the pattern reached $4\times10^5$, the sharpness of the interference maxima was 35. The radiation source was a He-Ne laser with a wavelength of 632.8 nm and a power of 115 mW. The shift of the Mandelstam-Brillouin components Δω was measured with an error not exceeding 0.5%. The hypersound velocity $v$ was calculated using the formula:

$$v = \frac{\Delta\omega c}{\omega_0 2n\sin(\theta/2)}, \qquad (1)$$

where $c$ – is the speed of light, $\omega_0$ – is the frequency of the exciting light, $n$ – is the refractive index, θ – is the scattering angle.

## III. Experimental results and discissions

On Fig. 1 (a)–(f) panels show the temperature dependences of the hypersound velocity $v$ for frequencies of 6.2 GHz and 4.5 GHz for pure γ-picoline (panel (a)) and for concentrations of γ-picoline $C$ = 0.4 ppm (panel (b)); $C$ = 0.2 ppm (panel (c)); $C$ = 0.1 ppm (panel (d)); $C$ = 0.06 ppm (panel (e)) and $C$ = 0.05 ppm. (panel (f)). Figure 2 shows the dependence of the area difference $\Delta S$ under the curves for frequencies of 6.2 GHz and 4.5 GHz on the concentration $C$ of the solution.

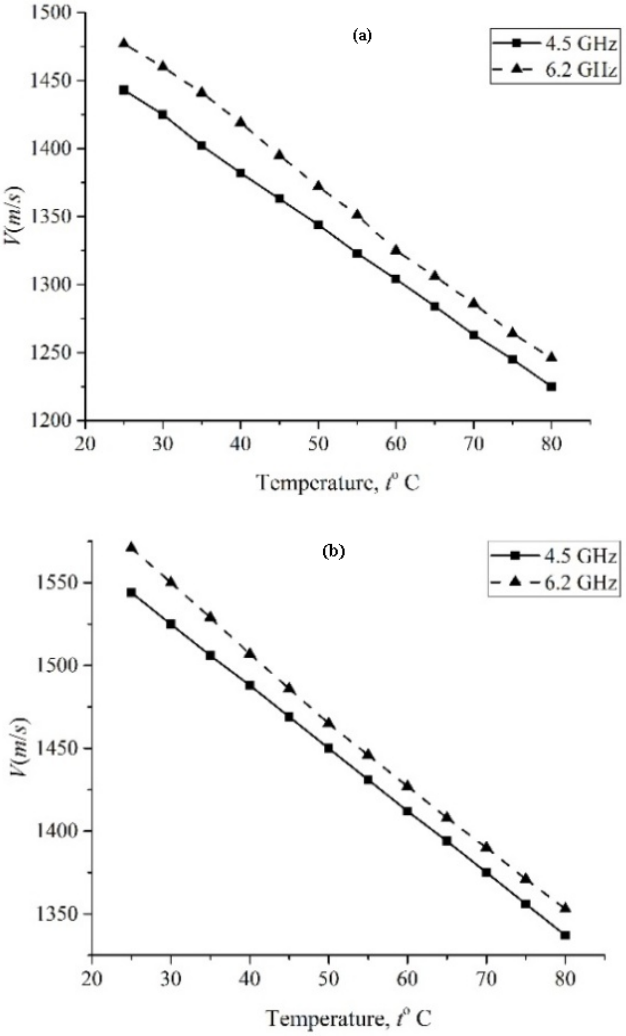



**Figure 1 (a,b).** Dependences of the velocity $v$ of hypersound at frequencies 4.5 and 6.2 GHz on temperature for pure γ-picoline (a), mixture γ-picoline-water at a concentration of γ-picoline 0.4 mole fractions (b).

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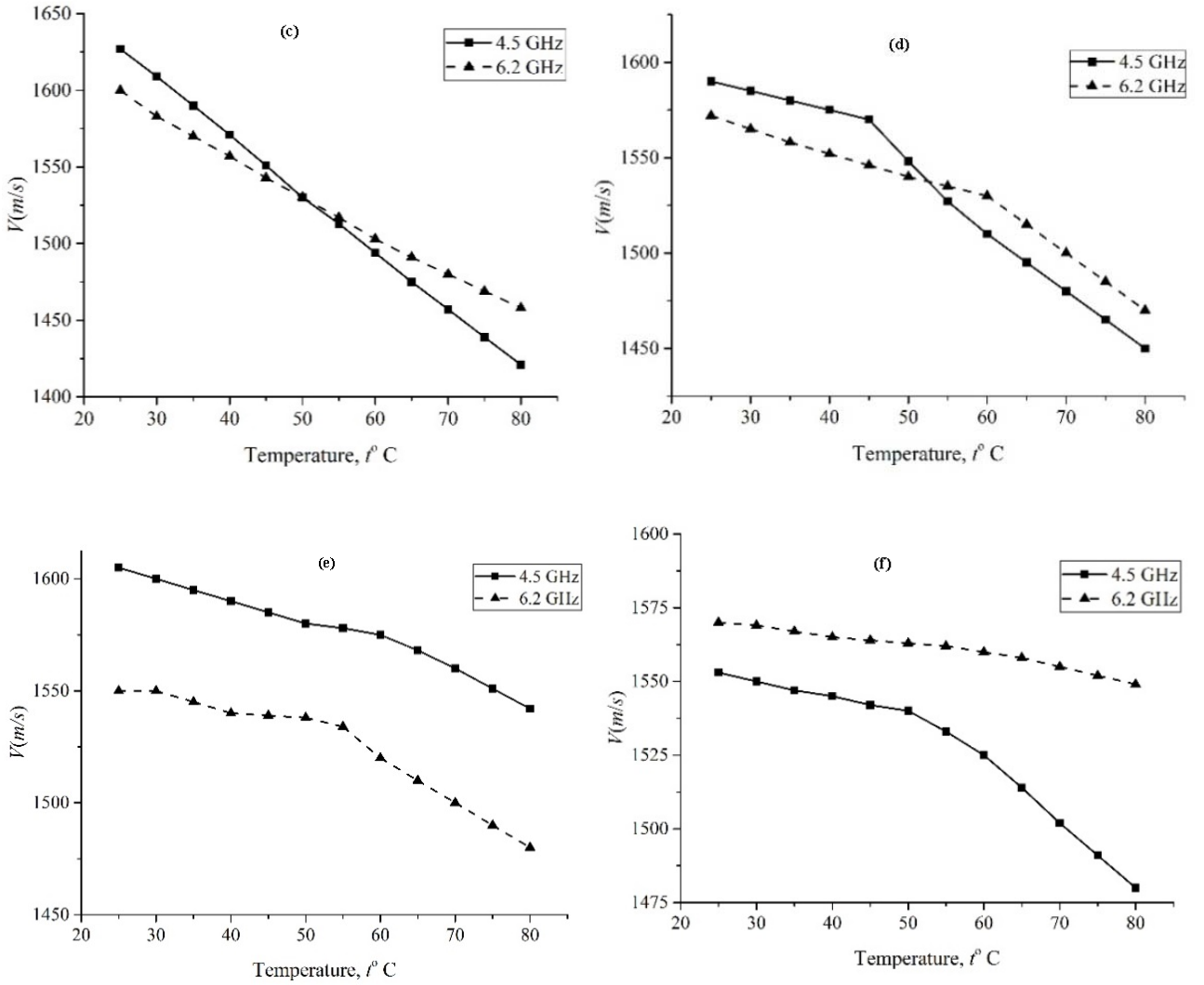



**Figure 1 (c,d,e,f)** (continuation)**.** Dependences of the velocity $v$ of hypersound at frequencies 4.5 and 6.2 GHz on temperature for mixture γ-picoline-water at a concentration of γ-picoline 0.2 mole fractions (c), mixtures γ-picoline-water at a concentration of γ-picoline 0.1 mole fractions (d), mixtures γ-picoline-water at a concentration of γ-picoline 0.06 mole fractions (e), mixtures γ-picoline-water at a concentration of γ-picoline 0.05 mole fraction (f).

As can be seen from Fig. 1 (panels (a) and (b)), the nature of the temperature dependence at the indicated frequencies for pure γ-picoline and 0.4 ppm is approximately the same for both frequencies. Differences appear when the concentration of γ-picoline is $C$ = 0.2 ppm. and 0.1 ppm (panels (c) and (d)). It can be seen that at $t$ > 50°C, there is a positive and at $t$ < 50°C, a negative hypersonic speed dispersion in the frequency interval between 6.2 and 4.5 GHz.

Figure 2 shows the dependence of the area difference $\Delta S = S_{6.2} - S_{4.5}$, where $S_{6.2}$ and $S_{4.5}$ are the areas under the graphs in Fig. 1 for frequencies of 6.2 and 4.5 GHz, respectively, depending on the concentration of γ-picoline. Since $\Delta S$ is the temperature-averaged difference in hypersonic speeds at the specified frequencies, this value can be conditionally considered as a quantitative characteristic of the hypersound velocity dispersion.

In this case, the concentration dependence of $\Delta S$ anticorrelates with the concentration dependence of the scattering coefficient (see [1]): a sharp negative minimum of $\Delta S$ at $C$ = 0.06 ppm. coincides with the position of the scattering peak at the same concentration. Thus, it has been found that the appearance of a

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nanodroplet phase (peak of anomalous scattering) leads to a change in the sign of the dependence $dV/d\omega$, where $V$ – is the hypersound velocity.

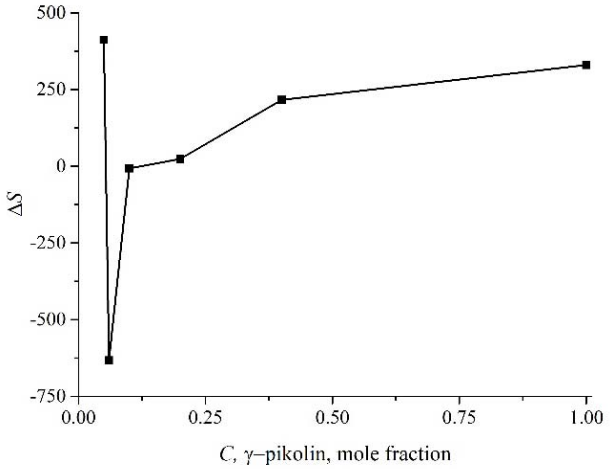



**Figure 2.** Concentration dependence of Δ*S*.

## IV. Conclusions

An analysis of experimental measurements of the speed of high-frequency sound in the gigahertz frequency range in a relatively wide temperature range and the concentration of picoline in aqueous solutions indicates a noticeable change in the thermodynamic states of the solutions. These changes manifest themselves in the form of a difference in the temperature gradient of the velocity at different frequencies, different temperature intervals. This difference allows us to conclude about the implementation of the structural process that occurs in solutions, which in turn is associated with high-frequency dispersion.

In aqueous solutions of γ-picoline, the situation occurs when the bulk viscosity relaxes at a relatively low frequency compared to other aqueous solutions. This led to the fact that at frequencies $f$>4GHz, hypersonic speed dispersion appeared, which was not associated with the processes of relaxation of bulk viscosity. The temperature, concentration, and frequency dependences of the hypersound velocity consistently reflect the following: a) Positive sound velocity dispersion for pure γ-picoline and for a solution with a concentration of $C$=0.4 ppm γ-picoline; b) Positive dispersion for $C$=0.2 and 0.1 ppm γ-picoline for temperature $t$>50°C, negative dispersion for temperatures $t$<50°C; c) For a concentration of 0.06 ppm γ-picoline only negative variance is observed. Such a transformation of the sign of the dispersion can be associated with the process of solution structurization, which begins at a concentration of 0.2 ppm γ-picoline and reaches its maximum value at $C$=0.06 ppmγ-picoline. In parallel with structurization, the thermodynamic state of the solution approaches (ECP) or (LCP) [16].

With a decrease in the concentration of γ-picoline, the solution is closer to the periphery of the closed separation curve, and therefore the influence of the upper critical point and the Lower critical point becomes weaker. With a decrease in the concentration of γ-picoline in water, the process of structurization intensifies and its influence increases to a maximum associated with the optimal number of γ-picoline molecules.

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## Сувли органик эритмаларда товуш тезлигининг дисперсияси

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γ-пиколиннинг сувли эритмларида ёруғликнинг спонтан Манделштамм-Бриллюэн сочилишининг концентрацион ва температуравий тадқиқотлари γ-пиколиннинг $C \leq 0.2$ моляр улушли концентрацияларида гипертовуш тезлигининг салбий дисперсияси пайдо бўлишини кўрсатди. Салбий дисперсия қийматининг температура ва концентрацияга боғлиқлиги γ-пиколиннинг $C = 0.06$ моляр улушли концентрациясида ўзининг оптимал қийматига эришадиган эритманинг структурлашуви жараёни билан боғлиқ деб ҳисобланади.

**Калит сўзлар:** γ-пиколин, дисперсия, ҳажмий ёпишқоқлик релаксацияси, гипертовуш, релаксация вақти, сувли-органик эритма.

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