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ISOTHERMAL COMPRESSIBILITY NEAR THE SOLUTION'S PECULIAR POINT

Using the Mandelstam–Brillouin spectrum of scattered light, the velocities of hypersound with frequencies of 6.2, 4.8, and 2.6 GHz in three aqueous solutions of non-electrolytes have been determined in a wide temperature interval. The ratio of the central triplet line intensity to the intensity of the Mandelstam–Brillouin components (the Landau–Placzek ratio) is calculated as well. The corresponding temperature dependences of the adiabatic and isothermal compressibilities and the coefficient of volumetric expansion are plotted. The adiabatic compressibility value was found to depend on the angle of scattered light.

Keywords: Mandelstam–Brillouin light scattering, Landau–Placzek ratio, isothermal compressibility, adiabatic compressibility, coefficient of volumetric expansion.

1. Introduction

There is a class of solutions, which, irrespective of the concentration of their components, can be mixed only at a certain pressure value or if a third component is added. The aqueous solutions of methylpyridine are an example. At normal atmospheric pressure $P_H = 10^5$ Pa, methylpyridine and water are in a mixed state [1]. However, if the pressure P becomes much lower or greater than P_H, those solutions demonstrate a tendency to the stratification. Other types of mixtures, such as solutions of glycerin with guaiacol [2], form a closed stratification region, if a third component is added.

The aqueous solutions of methylpyridine are characterized by a specific temperature behavior. The specific feature consists in that the homogeneous solutions are in the thermodynamic equilibrium only at the normal pressure P_H and a certain temperature t_0. The latter is usually called the temperature of the solution's peculiar point. As a rule, the temperature t_0 has the same value for all concentrations and can be evaluated, if the upper and lower temperatures of the closed stratification region are known.

For the aqueous methylpyridine solutions, the peculiar point temperature is located within an interval of 45–55 °C. In Fig. 1, the temperature dependences of the line intensity corresponding to the Rayleigh light scattering in the aqueous solutions of γ-picoline with concentrations of 0.2, 0.1, and 0.06 mole fractions are depicted. From the figure, one can see that the intensity maximum for the upper critical temperature at a γ-picoline concentration of 0.06 mole fraction takes place at $t \approx 35$ °C, whereas the corresponding maximum for the lower critical temperature is observed at $t \approx 62$ °C. The peculiar point t_0 is located near a temperature of 50 °C.

One of the important parameters that characterize the liquid structure is the liquid compressibility. This quantity is related to the sound propagation velocity. The adiabatic compressibility is mainly determined by the velocity of sound wave propagation, whereas the isothermal compressibility is connected with the Landau–Placzek ratio. Experimental results obtained for the ultrasonic and hypersonic propagation velocities in liquids and solutions, including those which had undergone stratification [3,4], showed that the adiabatic compressibility, as well as the sound velocity, does not have specific deviations larger than 3–4% even near the critical and peculiar points in liquids and solutions.

The isothermal compressibility β_T is related to the adiabatic compressibility β_S via the known expression

$$\frac{\sigma^2 T}{\rho C_P \beta_S} = \frac{\beta_T}{\beta_S} - 1, \tag{1}$$

where σ is the coefficient of volumetric expansion, T the absolute temperature, ρ the density, and C_P the heat capacity at a constant pressure. The adiabatic compressibility

$$\beta_S = \frac{1}{\rho V^2}, \tag{2}$$

where V is the sound velocity. At the same time,

$$L\,\frac{\sigma^2 T}{\rho C_P \beta_S} = \frac{I_C}{2I_{\mathrm{MB}}}, \tag{3}$$

where L is a constant that is very close to unity in many cases, I_C the intensity of the central line of the Rayleigh triplet, and I_{MB} the intensity of the Mandelstam–Brillouin components [5]. Hence, we obtain the relation

$$\frac{I_C}{2I_{\mathrm{MB}}} = \frac{\beta_T}{\beta_S} - 1. \tag{4}$$

For liquids and solutions far from the phase transition temperature, the values of β_T and β_S are of the same order of magnitude. Near the phase transition temperatures, the peculiar solution points, and the stratification temperatures of binary liquids, the quantity $\frac{I_C}{2I_{\mathrm{MB}}}$ increases, and this behavior is responsible for the growth of the β_T-values.

Very often, however, the growth of I_C is associated with the multiple light scattering. The contribution of this process is difficult to distinguish from the total increase of I_C. In this case, while estimating the value of β_T, it is necessary to adequately account for possible distortions of the I_C-values by contributions from the multiple light scattering. The Landau–Placzek ratio makes it possible to calculate not only β_T, but also the related coefficient of volumetric expansion σ. Really, by denoting $\frac{I_C}{2I_{\mathrm{MB}}} = I$ and using Eq. (2), we obtain

$$\sigma = \sqrt{\frac{I C_P}{V^2 T}}. \tag{5}$$

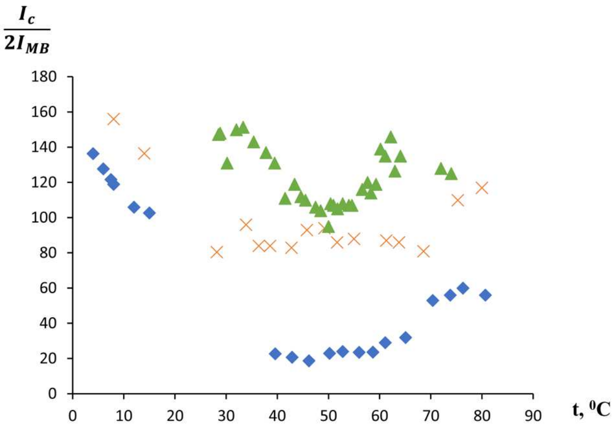

Fig. 1. Temperature dependences of the Landau–Placzek ratio $\frac{I_C}{2I_{\mathrm{MB}}}$ for the aqueous solutions of γ-picoline with concentrations of 0.2 (♦), 0.1 (×), and 0.06 mole fractions (▲)

In work [4], the results of experiments aimed at studying the adiabatic compressibility β_S in low-concentration aqueous solutions of γ-picoline at hypersonic frequencies 4–5 GHz were reported. A pronounced minimum of β_S was detected at a sound frequency of about 4.7 GHz in the vicinity of a γ-picoline concentration of 0.06 mole fraction both at $t = 25$ and 65 °C. The obtained value of β_S was used to calculate the characteristic scale of microscopic inhomogeneities.

At the same time, the temperature behavior of the quantity β_T in solutions with low concentrations is also of great importance. Since the quantities β_S and β_T are related to each other via the Landau–Placzek ratio [see Eq. (4)], our main attention will be focused on the experimental measurements of the quantity $\frac{I_C}{2I_{\mathrm{MB}}}$ in the aqueous solution of γ-picoline with a concentration of 0.06 mole fraction. The obtained data will also allow us to determine the frequency dependence of the quantity β_S in the vicinity of the solution peculiar point.

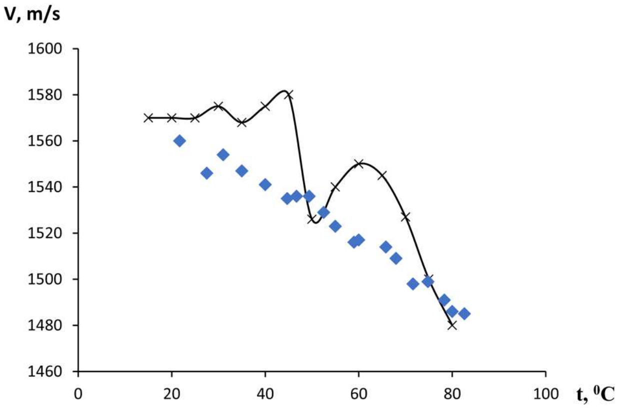

Fig. 2. Temperature dependences of the hypersound velocity in the aqueous solution of γ-picoline with a concentration of 0.06 mole fraction. The hypersound frequencies are 6.2 (♦), and 2.5 GHz (×)

In this work, we evaluate the adiabatic, β_S, and isothermal, β_T, compressibilities, as well as the coefficient of volumetric expansion σ, for an aqueous solution of γ-picoline. For this purpose, we use the temperature dependences of the Landau-Placzek ratio $\frac{I_C}{2I_{\text{MB}}}$ near the peculiar point. The exact values of those parameters will help the elucidation of the physical nature of peculiar points in the aqueous solutions of γ-picoline to be made.

2. Experiments and Their Results

The experimental installation and its parameters were described in work [6]. The spectra of the polarized light scattering were studied making use of a double-pass Fabry–Perot interferometer. The light scattering angle was about 45°. The error of the angle fixation did not exceed 0.2°. The interferometer dispersion was 0.417 cm^{-1}. The contrast of the picture interference reached 4×10^5, and the sharpness was equal to 35. A He–Ne laser with a wavelength of 632.8 nm and a power of 115 mW served as a light source. The shift Δv of the Mandelstam–Brillouin components (MBCs) was measured with an accuracy of 0.5%. The hypersound velocity V was calculated by the formula

$$V = \frac{\Delta v \; C}{2 n v_0 \; \sin\frac{\theta}{2}},$$

where C is the velocity of exciting light, v_0 its frequency, n the refractive index, and θ the scattering angle.

The values of the Landau–Placzek ratio $\frac{I_C}{2I_{\text{MB}}}$ were determined by measuring the areas under the peaks I_C and I_{MB}. The corresponding accuracy of area measurements was close to 15–20%.

The measured quantity β_T is closely related to the intensity of the central component in the Rayleigh triplet. However, this intensity can be distorted by the light scattering at concentration fluctuations. In our case, due to a low concentration of γ-picoline in the aqueous solution, the light scattering at concentration fluctuations was reduced to a minimum value (it was insignificant even at much higher picoline concentrations).

In Fig. 2, the temperature dependences of the velocity of hypersound with frequencies of 6.2 and 2.4 GHz in the aqueous solution of γ-picoline are shown. As one can see from this figure, the obtained dependences differ substantially. The velocity of 6.2-GHz hypersound gradually decreases with the increasing temperature, as it usually occurs in the cases of molecular liquids and ideal solutions. For hypersound with a frequency of 2.6 GHz, the temperature dependence of the hypersound velocity has some peculiarities.

In particular, two maxima and a minimum are observed in a rather narrow temperature interval. The minimum takes place at the temperature $t = 50$ °C, i.e. at the temperature of the peculiar point. From whence, it follows that the thermodynamic instability in a vicinity of the peculiar point is observed for the velocity of hypersound with a frequency of about 2.6 GHz. The origin of the interaction between the sound modes of the medium motion and the modes associated with structural changes has yet to be elucidated with the help of experiments. However, it is possible to calculate the temperature dependence of the compressibility and the coefficient of volumetric expansion, if we take into account the non-trivial temperature behavior of the hypersound velocity at the frequency $f = 2.6$ GHz.

Using the values obtained for the hypersound velocity, the quantity I, and relations (2) and (4), the adiabatic, β_S, and isothermal, β_T, compressibilities were calculated. The coefficients of volumetric expansion for the solution were calculated with the help of formula (5). The heat capacity at a constant pressure, C_P, was obtained making use of the additive formula.

Table 1 demonstrates the values of β_T and β_S calculated from the experimentally obtained values for the sound velocity V and the ratio $\frac{I_C}{2I_{\mathrm{MB}}}$. The values of β_T expectedly exceed the β_S-values by two orders of magnitude, because the Landau–Placzek ratio has a general tendency to grow.

Table 2 contains the values of the coefficient of volumetric expansion σ calculated by formula (5), as well as the corresponding values for pure water, σ_{w}, calculated by the same formula. The calculations were carried out for the same temperatures at which the experimental values of $\frac{I_C}{2I_{\mathrm{MB}}}$ were obtained. It should be noted that, in Table 1, for the quantity $\frac{I_C}{2I_{\mathrm{MB}}}$, there is a minimum of 100 at $t = 50$ °C located between two maxima (155 at $t = 30$ °C and 148 at $t = 62$ °C). This value extends to a wider temperature interval, playing the role of a temperature-independent background. Subtracting this background, we obtained values that characterize the intensity values associated with the upper and lower critical temperatures. Table 2 also contains the values for the coefficient of volumetric expansion for water, σ_w, taken from work [7].

Hence, from the data presented in Table 2, it follows that the coefficient of volumetric expansion of the solution is numerically much larger than σ for pure water. In other words, despite that water dominates in the solution, the value σ of the solution is not determined by the value σ_{w} of water. The coefficient of volumetric expansion of the solution exceeds that of water by 4.5–20 times in the examined temperature interval. Table 2 also demonstrates that the difference $\sigma - 0.023$ also has maximum values at the upper and lower critical temperatures, and those values strongly exceed the value of the coefficient of volumetric expansion of pure water σ_{w}.

Let us consider the value of σ at $t = 50$ °C. According to Fig. 1, the temperature dependence of the quantity $\frac{I_C}{2I_{\mathrm{MB}}}$ contains sections, where it retains constant values: $\frac{I_C}{2I_{\mathrm{MB}}} \approx 20$, 80, and 100 at γ-picoline concentrations of 0.2, 0.1, and 0.06 mole fractions, which corresponds to σ-values of 0.01, 0.02, and 0.023, respectively. Those values do not depend on the temperature and exceed the value of the coefficient of volumetric expansion of water at 50 °C by factors of about 22, 43, and 50, respectively. Such an increase of the coefficient of volumetric expansion, which is connected only with the solution concentration and does not depend on the temperature, gives grounds to suggest that it is not associated with the existence of the solution's peculiar point. Instead, we may assume that such a behavior of the quantity σ for the solution is governed by the structuring processes in aqueous solutions. This hypothesis is supported, in particular, by the fact that the structuring process becomes more intensive with a reduction of the non-electrolyte concentration in water. Perhaps, a γ-picoline concentration of 0.06 mole fraction in water is optimal for the structuring, because changing it in any direction from this value leads to the structuring weakening.

Table 1. **Isothermal, β_T, and adiabatic, β_S, compressibilities at various temperatures**

t, °C	$\frac{I_C}{2I_{\mathrm{MB}}} = I$	V, m/s	$\beta_S = \frac{1}{\rho V^2}$	$\beta_T = (I+1)\beta_S$
28	140	1570	45×10^{-12}	6345×10^{-12}
30	155	1570	45×10^{-12}	7020×10^{-12}
40	130	1580	44.5×10^{-12}	5829×10^{-12}
50	100	1525	47.7×10^{-12}	4817×10^{-12}
60	130	1540	46.8×10^{-12}	6131×10^{-12}
62	148	1550	46.2×10^{-12}	6884×10^{-12}
70	125	1525	47.7×10^{-12}	6010×10^{-12}

Table 2. **Coefficients of volumetric expansion for the aqueous solution of γ-picoline, σ, and pure water, σ_{w}, at various temperatures**

t, °C	T, K	$\sigma = \sqrt{\frac{I\,C_p}{V^2 T}}$	$\sigma - 0.023$	σ_{w}	$\frac{\sigma - 0.023}{\sigma_{\mathrm{w}}}$
28	301	0.028	0.005	0.00028	17.8
30	303	0.029	0.006	0.0003	20
40	313	0.026	0.003	0.00039	7.7
50	323	0.023	0	0.00046	0
60	333	0.0263	0.0033	0.00052	8.3
62	335	0.0278	0.0048	0.00053	9.05
70	343	0.0257	0.0027	0.00058	4.65

From the aforesaid, it follows that the adiabatic and isothermal compressibilities of the aqueous γ-picoline solution measured at the sound frequency $f = 2.6$ GHz reveal a specific behavior in a vicinity of the peculiar point. Such behavior may probably be associated with the interaction of various modes of the medium motion taking place at this frequency.

3. Conclusions

To summarize, in this work, on the basis of experimental measurements, the following results are obtained:

- the temperature dependences of hypersound velocities in the aqueous solution of γ-picoline are determined at frequencies of 6.2, 4.5, and 2.5 GHz;
- a non-trivial behavior of the temperature dependence of the hypersound velocity at a frequency of about 2.5 GHz is revealed;
- the adiabatic and isothermal compressibilities of the aqueous γ-picoline solution at a frequency of about 2.5 GHz are evaluated on the basis of the hypersound velocity values and the value of the Landau–Placzek ratio;
- the temperature dependence of the coefficient of volumetric expansion σ of the solution is calculated on the basis of the Landau–Placzek ratio value; it is found that the values obtained for the aqueous solution of γ-picoline considerably exceed the corresponding values for pure water.

The coefficient of volumetric expansion of the aqueous solutions of γ-picoline depends only on the concentration, but not on the temperature. Its values are associated with the structuring process. The latter becomes stronger with a reduction of the γ-picoline concentration. It is quite possible that this structuring process is closely related to a specific charge formation which, according to work [8], takes place near the peculiar point of the solutions and reflects the existence of a long-term equilibration process in them.

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1. G.H. Schneider. Phase behavior and critical phenomena in fluid mixtures under pressure. *Ber. Bunsen Phys. Chem.* **76**, 325 (1972).
2. K.V. Kovalenko, S.V. Krivokhizha, I.L. Fabelinskii, L.L. Chaikov. Propagation of hypersound and ultrasound in a liquid solution undergoing a phase transition. *Laser Phys.* **13**, 332 (2003).
3. L.M. Sabirov, D.I. Semenov, Kh.S. Khaidarov. Mandelshtam–Brillouin scattering spectra of aqueous solutions of γ-picoline and manifestation of a phase transition of the structural type in these spectra at low concentrations of γ-picoline. *Opt. Spectrosc.*. **105**, 369 (2008).
4. L.M. Sabirov, D.I. Semenov, H.S. Haidarov. Temperature and concentration dependences of the frequency shift of the Rayleigh line fine-structure components in aqueous solutions of γ-picoline. *Opt. Spectrosc.* **103**, 490 (2007).
5. I.L. Fabelinskii, *Molecular Scattering of Light* (Plenum Press, 1968).
6. L.M. Kashaeva, L.M. Sabirov, Ya. Turakulov, T.M. Utarova. Method of simultaneous registration of Mandelstam-Brillouin components at substantially different scattering angles. *Kratk.Soobshch. Fiz.* **5**, 41 (1981) (in Russian).
7. *Reference Book on Hydraulic Resistance.* Edited by M.O. Shteinberg (Mashinostroenie, 1992) (in Russian).
8. L.A. Bulavin, V.Ya. Gotsulskii, N.P. Malomuzh, V.E. Chechko. Relaxation and equilibrium properties of dilute alcohol aqueous solutions. *Izv. RAN Ser. Khim.* **4**, 851 (2016) (in Russian).

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ІЗОТЕРМІЧНА СТИСЛИВІСТЬ В ОКОЛІ ОСОБЛИВОЇ ТОЧКИ РОЗЧИНУ

За допомогою мандельштам–бріллюенівського спектра розсіяного світла визначено швидкості гіперзвуку на частотах 6,2, 4,8 та 2,6 ГГц для трьох водних розчинів неелектролітів у широкому інтервалі температур. Також визначено відношення Ландау–Плачека, а саме відношення інтенсивностей центральної лінії триплету до компонентів Мандельштама–Бріллюена. За допомогою отриманих даних побудовано температурні залежності адіабатичної та ізотермічної стисливостей і коефіцієнта об'ємного розширення. Виявлено залежність адіабатичної стисливості від кута спостереження розсіяного світла.

Ключові слова: мандельштам–бріллюенівське розсіювання світла, відношення Ландау–Плачека, ізотермічна та адіабатична стисливості, коефіцієнт об'ємного розширення.