

Frequency shift of Rayleigh line fine structure components in a water solution of 4-methylpyridine as a function of temperature, concentration, and light scattering angle

N.F. Bunkin, V.S. Gorelik, L.M. Sabirov, D.I. Semenov, Kh.S. Khaidarov

Abstract. The frequency shift $\Delta\nu$ of the fine structure components of Rayleigh light scattering in 4-methylpyridine water solutions is studied in the ranges of 1–0.1 mole fraction concentrations and temperature 10–80 °C. The laws of $\Delta\nu$ variation at different light scattering angles are discussed from the viewpoint of solution structural reorganisation under the varying temperature and concentration of nonelectrolyte in water. Existence of a continuous hydrogen-bond net in the solutions is experimentally proved in a certain range of temperatures and concentrations.

Keywords: Rayleigh scattering, fine structure, water solution of 4-methylpyridine.

1. Introduction. Formulation of the problem

Study of linearly polarised spectrally decomposed light in some nonlaminating solutions shows that there exist binary solutions, in which the scattering intensity strongly increases while approaching some concentration and temperature (see [1] and the references therein). Such solutions are, for example, water solutions of pyridine or its methyl derivatives (picolines). The maximum in the concentration dependence of the light scattering intensity resides at low concentrations of nonelectrolyte [~ 0.1 mole fraction (m.f.) for pyridine and 0.06–0.09 m.f. for methyl pyridines]. As the temperature increases, the light scattering intensity in solutions with such concentrations does not vary monotonically but has a maximum (~ 60 °C for pyridine, ~ 70 °C for 4-methylpyridine, and ~ 80 °C for 3-methylpyridine). The scattering indicatrix of 3-methylpyridine water solutions is characterised by noticeable asymmetry [2] at the concentration of 0.06 m.f. and temperature of approximately 70 °C. It is assumed that at such concentrations and temperatures, water solutions of pyridine and methylpyridines are most close to the laminating critical point and the increase in the light scattering intensity is due to developed concentration fluctuations [1]. This assumption agrees, in particular, with the fact that a substitution of a part of H₂O molecules for D₂O [3–5], variation in pressure [6], or addition

of a small amount of NaCl [7] result in the origin of a closed laminated domain in these solutions.

Study of ultra-acoustic parameters of water solutions of methylpyridines [8–10] shows that isotherms of the adiabatic compressibility of the solutions intersect around the concentration of ~ 0.04 m.f. The authors explain such temperature independence of the solution compressibility at certain concentrations by the increased rigidity of the solution structure when methylpyridine molecules become embedded to the hydrogen-bond net formed by water molecules. In studying hyperacoustic parameters of the 3-methylpyridine water solution (0.06 m.f.), the authors of [11] found that the sound velocity decreases in a narrow range of hypersound frequencies, which allowed them to assume that the solution structure may strengthen due to the production of clathrate-like associates. The possible origin of molecular associates in these solutions is confirmed by the investigations on neutron scattering at small angles [12, 13], quasi-elastic neutron scattering and NMR [14], and by the results of quantum-mechanic calculations [15] and computer simulation [16]. It seems natural to assume that the structural features of water solutions of nonelectrolytes are mainly determined by the structure of pure water and specificity of interaction between water molecules and molecules of dissolved substance. The ability of water molecules to form a continuous three-dimensional hydrogen-bond net [17, 18] is the factor responsible for a series of interesting physical phenomena revealed in water solutions at small (at most 0.1 m.f.) concentrations of nonelectrolyte in water. The water structure should play a substantial role at higher nonelectrolyte concentrations as well. However, in the range of mean concentrations the relationship between the water structure and various physical properties of the solutions is less pronounced and worse investigated.

Presently, light scattering is one of the most informative methods for studying finest processes occurring in liquids [19]. The laws of the integral scattering intensity variation in water solutions are well studied [1, 20, 21]. Nevertheless, there is actually no information on spectral characteristics of the scattered light in these solutions in a wide range of temperatures and concentrations. The aim of the present work is to study the temperature dependences for the fine structure components of Rayleigh light scattering (Mandelstam–Brillouin components MBC) $\Delta\nu$ in water solutions of 4-methylpyridine (4MP) at various concentrations of nonelectrolyte.

2. Experimental

Spectra of scattered light were detected on an experimental setup with a two-pass Fabry–Perot interferometer. The scattering angles were 135° and 90°. The error of adjusting the

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scattering angle was at most 0.2° . The free spectral range of the interferometer was 0.714 and 0.625 cm^{-1} at 135° and 90° , respectively. The contrast of the interference pattern was 5×10^4 . The source of radiation was a 632.8-nm , 15-mW He–Ne laser. The error of determining the MBC frequency shift was no greater than 0.5% . In preparing the solutions we used 4MP samples of pure grade. Optically pure components of the solution were obtained by triple distillation. The solution samples were sealed in glass cylindrical cells at a pressure lower than the atmospheric one. The sample cell was placed into a thermostat controlled by the electronic scheme enabling temperature stabilisation with the accuracy better than $\pm 0.05^\circ\text{C}$. The scattering spectra of pure 4MP and its water solutions at the concentrations $x = 0.8, 0.6, 0.4, 0.2$, and 0.1 m.f. were studied in the temperature range $T = 10\text{--}80^\circ\text{C}$.

At the scattering angle of 135° , in the whole investigated range of concentrations we obtained linear (within the experimental error) dependence of the shift $\Delta\nu$ on temperature T measured in Celsius scale at a fixed solution concentration x . With a temperature fall, $\Delta\nu$ increases regardless of the solution concentration; however, the rate of the $\Delta\nu$ increase (the temperature factor of shift) differs in solutions with different concentrations. A similar behaviour of $\Delta\nu$ is observed at the light scattering angle of 90° . Figure 1 shows the results of measuring $\Delta\nu$ for the solutions with the concentrations 0.8 and 0.1 m.f. at the scattering angles of 90° and 135° . One can see that at lower concentration of 4MP in water the temperature dependence of the MBC shift becomes less pronounced. The shift temperature factor, remaining negative and constant in the whole temperature range at each concentration of solution, reduces (by absolute value) as the concentration of nonelectrolyte in water falls. At a greater light scattering angle, the frequency MBC shift increases for all investigated solutions. For example, in the solutions with the concentrations 0.8 and 0.1 m.f. the ratio $\Delta\nu_{135}/\Delta\nu_{90} \sim 1.3$ remains constant in the whole range of temperatures under study.

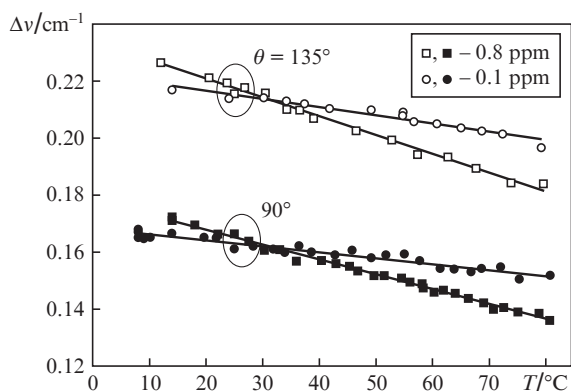


Figure 1. MBC shift versus temperature at the solution concentrations of 0.8 and 0.1 m.f. and scattering angles of 90° and 135° .

Figure 2 presents the temperature factor of the MBC shift $d(\Delta\nu)/dT$ versus concentration for the scattering angles of 90° and 135° . The temperature factor of the MBC shift depends on both the solution concentration (at fixed light scattering angle) and scattering angle (at fixed concentration). The ratio of the temperature factors for the scattering angles of 135° and 90° is ~ 1.3 in the whole range of investigated concentrations. The dependence of the shift temperature factor $d(\Delta\nu)/dT$

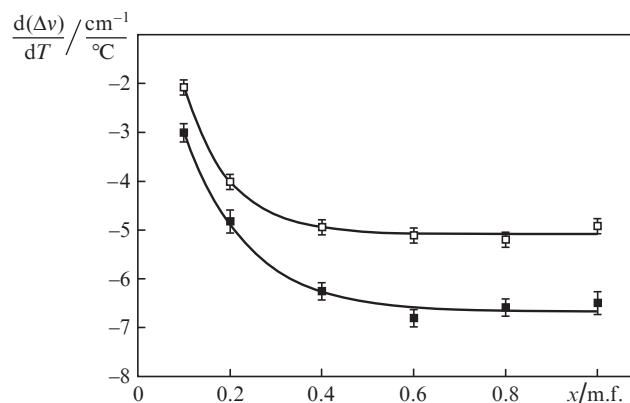


Figure 2. Temperature factor of the MBC shift versus 4MP concentration in water at the scattering angles of 90° (■) and 135° (□).

on the solution concentration x is well described by the expression

$$\frac{d(\Delta\nu)}{dT} = A_1 \exp\left(-\frac{x}{B_1}\right) + C_1, \quad (1)$$

where

$$A_1 = 8.5 \times 10^{-4} \text{ cm}^{-1}/\text{deg}; B_1 = 9.67 \times 10^{-2} \text{ m.f.}; \\ C_1 = -5.1 \times 10^{-4} \text{ cm}^{-1}/\text{deg} \text{ for the scattering angle of } 90^\circ$$

$$\text{and } A_1 = 7.7 \times 10^{-4} \text{ cm}^{-1}/\text{deg}; B_1 = 13.8 \times 10^{-2} \text{ m.f.}; \\ C_1 = -6.7 \times 10^{-4} \text{ cm}^{-1}/\text{deg} \text{ for the scattering angle of } 135^\circ.$$

In both the cases $\Delta\nu$ is measured in cm^{-1} and x is measured in mole fractions.

It is known that the existence of a fine structure of the Rayleigh line is caused by the presence of pressure adiabatic fluctuations in a liquid, which propagate through the medium in the form of elastic (Debye) waves [19]. The effect of scattered light modulation by these waves (independently predicted by Mandelstam and Brillouin) leads to a change in the frequency of the scattered light $\Delta\nu$, which can be written [19] in the form

$$|\Delta\nu| = 2n\nu_0 \frac{V}{c} \sin \frac{\theta}{2}, \quad (2)$$

where ν_0 is the exciting light frequency; n is the refractive index; V is the sound velocity; c is the speed of light in vacuum; θ is the scattering angle. According to (2) the variation in the MBC shift with temperature may be related to either the sound velocity in medium or the temperature dependence of the refractive index. At a constant concentration x the dependence $n(T)$ in the solution is similar for all scattering angles. Hence, the observed difference in the temperature factors of the MBC shift at the scattering angles of 90° and 135° is the evidence of a different temperature dependence of sound velocity at the frequencies corresponding to these scattering angles (~ 4 and 6 GHz, respectively). Thus, the revealed laws of variation of the MBC shift temperature factor makes us assume that in the investigated range of temperatures and concentrations the propagation velocity of sound depends on its frequency (sound velocity dispersion).

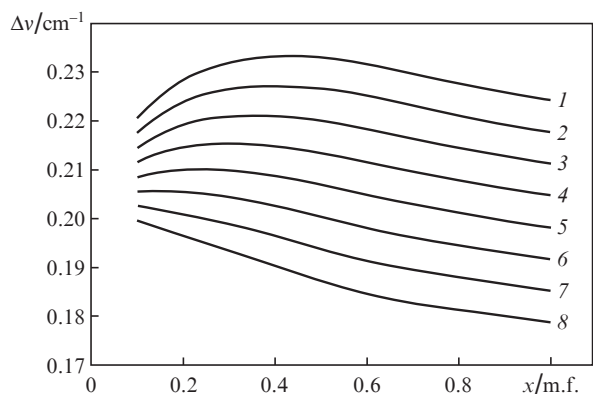


Figure 3. Isotherms for the MBC shift versus 4MP concentration in water at the scattering angle $\theta = 135^\circ$ and temperature $T = 10$ (1), 20 (2), 30 (3), 40 (4), 50 (5), 60 (6), 70 (7), and 80°C (8).

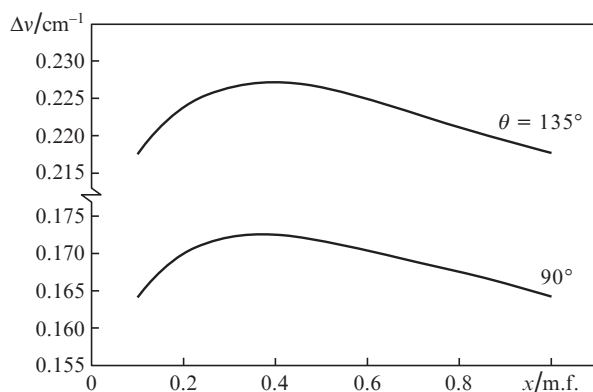


Figure 4. Isotherms for the MBC shift versus 4MP concentration in water at the scattering angles $\theta = 90^\circ$ and 135° and temperature of 20°C .

The linear approximation parameters for the experimental dependence $\Delta\nu(T)$ at various concentrations were used for drawing isotherms $\Delta\nu(x)$ (see Fig. 3). In Fig. 4, the isotherms $\Delta\nu(x)$ for the scattering angles 90° and 135° at the temperature of 20°C are shown for comparison. One can see that the curves $\Delta\nu(x)$ corresponding to the studied scattering angles are similar.

It follows from (2) that at a constant temperature and solution concentration the ratio of shifts $\Delta\nu_1$ and $\Delta\nu_2$ for two scattering angles θ_1 and θ_2 is determined as follows:

$$\frac{\Delta\nu_1}{\Delta\nu_2} = \frac{V_1 \sin(\theta_1/2)}{V_2 \sin(\theta_2/2)},$$

where V_1 and V_2 are the sound propagation velocities at the frequencies corresponding to the scattering angles θ_1 and θ_2 . For the scattering angles 135° and 90° the ratio of MBC shifts can be written in the form

$$\frac{\Delta\nu_{135}}{\Delta\nu_{90}} = 1.3066 \frac{V_{135}}{V_{90}}.$$

In the absence of the sound velocity dispersion ($V_{135} = V_{90}$) the ratio of MBC shifts should be equal to 1.3066. In the case of a positive sound velocity dispersion in a medium ($V_{135} >$

V_{90}) the ratio will be greater than 1.3066; correspondingly, at a negative dispersion ($V_{135} < V_{90}$) the ratio should be less than 1.3066. An analysis of the experimental data shows that the ratio $\Delta\nu_{135}/\Delta\nu_{90}$ in the investigated solutions is within the range 1.312–1.332, which makes us conclude that the dispersion of the hypersound velocity is positive in the frequency range 4–6 GHz and the whole investigated range of temperatures and concentrations.

The sound velocity dispersion $\Delta V/V$ (where $\Delta V = V_{135} - V_{90}$ and $V = (V_{135} + V_{90})/2$) is related to the frequency shift of MBC by the expression

$$\frac{\Delta V}{V} = 2 \frac{(\Delta\nu_{135}/\Delta\nu_{90}) - 1.3066}{(\Delta\nu_{135}/\Delta\nu_{90}) + 1.3066}.$$

Calculations show that the dispersion depends on neither solution temperature, nor concentration of nonelectrolyte and varies within the limits from 0.4% to 1.9%. The existence of the hypersound velocity dispersion in water solutions of 4MP and the laws of its variation with temperature and concentration are of independent interest. However, a more thorough study and discussion of this phenomenon are beyond the scope of this work.

It follows from Fig. 3 that appearance of the dependence $\Delta\nu(x)$ substantially changes with temperature. At low temperatures and a reducing concentration of 4MP in water $\Delta\nu$ varies nonmonotonically passing a maximum at some concentration x_{\max} of the solution. At higher temperatures, the position of the maximum shifts to lower concentrations and the maximum itself becomes less pronounced. Finally, at high temperatures the maximum on the isotherms $\Delta\nu(x)$ vanishes and the MBC shift monotonically increases with decreasing the solution concentration. Figure 5 shows the concentrations x_{\max} for various temperatures. The dependence $x_{\max}(T)$ is well described by the expression

$$x_{\max} = A_2 \exp\left(-\frac{T}{B_2}\right) + C_2, \tag{3}$$

where $A_2 = -0.0258$ m.f.; $B_2 = -24.05^\circ\text{C}$; $C_2 = 0.4554$ m.f. According to (3), in pure water ($x_{\max} = 0$) the maximum MBC shift should correspond to the temperature $T \sim 69^\circ\text{C}$.

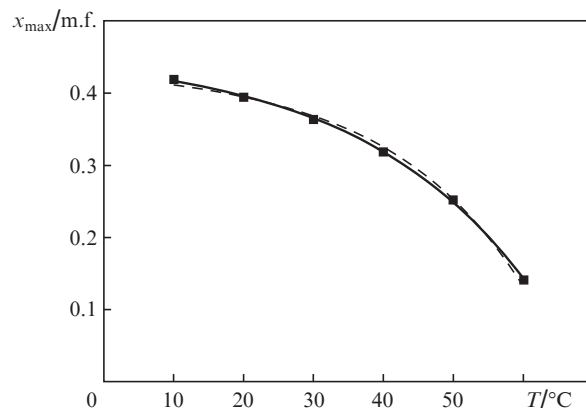


Figure 5. The 4MP concentration, which corresponds to the maximal MBC shift, versus temperature: experimental data for the scattering angle of 135° (■), a calculated curve for the scattering angles of 135° (solid line) and 90° (dotted line).

3. Discussion of results

Experimental investigations of water acoustic parameters reveal the absence of the sound velocity dispersion in the whole range of ultrasonic frequencies and the hypersonic frequencies up to the frequency of $\sim 10^{10}$ Hz [19, 22]. Correspondingly, Eqn (3) can be used for calculating the MBC shift in water by using well known values of the ultrasound propagation velocity. Using tabulated data for the sound velocity and refractive index in water [23], we calculated by formula (2) the MBC shift for the scattering angle of 135° and the exciting radiation frequency corresponding to the wavelength of a 632.8-nm He–Ne laser in the temperature range 10–80°C. An analysis of the function $\Delta\nu(T)$ for water shows that the shift $\Delta\nu$ reaches a maximum at the temperature $T = 68.5^\circ\text{C}$, which well agrees with the value obtained from (3).

The coincidence of maxima positions on the isotherms $\Delta\nu(x)$ for the scattering angles 135° and 90° (Fig. 5) is worthy of notice. Such a coincidence is not accidental and testifies that the spectra of the fine structure of the Rayleigh line taken at various scattering angles contain information concerning the process, the nature of which is related to changes in the structure organisation of solution components under varying concentration and temperature.

In a solution with some concentration x of nonelectrolyte, the MBC shift (at a fixed scattering angle and excited radiation frequency) is determined by the refractive index and velocity of hypersound propagation (2). By using the expression for the adiabatic compressibility $\beta_s = (\rho V^2)^{-1}$, one can rewrite (2) in the form

$$\Delta\nu(x) = \frac{2\nu_0}{c} \sin \frac{\theta}{2} \frac{n(x)}{\sqrt{\rho(x)} \sqrt{\beta_s(x)}}, \quad (4)$$

where ρ is the material density. According to the literature data available [10] the density of pure 4MP at 20°C is 954 kg m^{-3} and the refractive index is 1.499. Being dissolved by water to the nonelectrolyte concentration of 0.1 m.f. the solution density monotonically grows to 995 kg m^{-3} and the refractive index falls to 1.399. According to (4) the MBC shift in this case should monotonically rise to approximately 10%. Hence, the observed maximum on the isotherm $\Delta\nu(x)$ (Fig. 4) can be only explained by the presence of a minimum on the isotherm $\beta_s(x)$. The shift of the maximum of isotherms $\Delta\nu(x)$ to lower concentrations under the elevated temperature (Fig. 5) is related to the corresponding shift of the minimum of adiabatic compressibility isotherms.

At a temperature of 20°C for pure water we have $\rho = 998.2 \text{ kg m}^{-3}$, the ultrasound velocity is $V = 1484 \text{ m s}^{-1}$ [23] and, correspondingly, adiabatic compressibility is $\beta_s = 4.6 \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$. Because the velocity dispersion is absent, this parameter remains unchanged in the range of hypersound frequencies as well. For pure 4MP a calculation by expression (4) yields for the scattering angle of 135° (the sound with the frequency of $\sim 6 \text{ GHz}$) $\beta_s = 4.7 \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$. Thus, in the range of hypersound frequencies the adiabatic compressibilities of water and 4MP at a temperature of 20°C are actually equal. Hence, at this temperature the general picture of the behaviour of the solution compressibility under varied 4MP concentration is as follows. Gradual addition of water to pure 4MP ($\beta_s = 4.7 \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$) leads to monotonic reduction of the solution compressibility; the reduction continues until the 4MP concentration reaches a certain critical value, at which

the solution is characterised by the least compressibility as compared to solutions of higher or lower concentrations. Further reduction of the 4MP concentration in water leads to a monotonic increase in the solution compressibility up to the compressibility of pure water ($\beta_s = 4.6 \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$).

There are two remarks concerning the above consideration. First, due to the limited range of investigated concentrations our results cannot qualify the compressibility behaviour in solutions with the 4MP concentration lower than 0.1 m.f. Second, for solutions at the same temperature the positions of the maximum for function $\Delta\nu(x)$ and minimum for function $\beta_s(x)$ are obviously separated in the concentration scale. With the above given estimates of the contributions made by the refractive index and solution density into the dependence of shift $\Delta\nu$ on concentration we may assert that the minimum of the adiabatic compressibility resides at lower concentrations than the maximum of the MBC shift. Hence, the results presented in Fig. 5 only qualitatively illustrate the temperature dependence of the concentration corresponding to the minimum of solution adiabatic compressibility. A more correct determination of this dependence requires temperature-concentration measurements of the refractive index and solution density.

4. Conclusions

We may assume that the revealed specific behaviour of the MBC shift (and, respectively, of the adiabatic compressibility) as a function of temperature and concentration is determined by the substantial role, which a structure of pure water plays in water solutions. Unusual water properties are related to structural features of its molecule and to specificity of intermolecular interactions. Unfortunately, the latter is not yet clarified [24, 25] and we suggest only some qualitative considerations concerning the effects observed in our experiments.

At a fixed temperature when the intensity of the molecule heat motion remains constant, a gradual increase in concentration, i.e., penetration of nonelectrolyte into the water hydrogen-bond net cavities results in strengthening of the bond and, consequently, reduces the solution compressibility. The compressibility falls until the 3D-integrity of the hydrogen-bond net is kept, i.e., until a certain critical concentration of nonelectrolyte molecules in water is reached. Overrunning the critical concentration results in that the continuous hydrogen-bond net disintegrates (becomes fragmented). A further increase in the nonelectrolyte concentration leads to progressing fragmentation of the net and, hence, to a monotonic growth of the solution compressibility.

At a higher temperature the intensity of heat motion of both water and 4MP molecules rises and, respectively, the disintegration of the net starts at lower concentrations. Therefore, as the temperature increases, the critical concentration corresponding to the minimal compressibility of solution shifts to lower concentrations. This shift is revealed in our experiments on the temperature-concentration behaviour of the maximum of the MBC shift (see Fig. 5).

In Fig. 5, the curve representing the shift of maximum $\Delta\nu$ in the temperature-concentration coordinates reveals variation in the position of the minimal solution adiabatic compressibility. Thus, this curve may be considered as a boundary separating the solutions with substantially distinct structural organisations. Below the curve, the hydrogen-bond net in the solution keeps its three-dimensional integrity at all temperatures and concentrations, whereas above the curve the net is

to some extent fragmented. The degree of the net fragmentation depends both on the solution temperature and concentration.

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