

Temperature anomaly, due to structural changes, of the properties of a stratified solution

F. V. Bunkin, M. A. Davydov, G. A. Lyakhov, K. F. Shipilov, and T. A. Shmaonov

Institute of General Physics, USSR Academy of Sciences

(Submitted 7 July 1983)

Zh. Eksp. Teor. Fiz. **86**, 963–966 (March 1984)

Anomalies were observed in the temperature dependences of the frequency shift of the proton magnetic resonance, of the hypersound velocity, and of the refractive index of a stratified aqueous solution of γ -collidine. An explanation that connects the anomalies with a change of the structure of the short-range order in this solution is proposed.

1. A very strong anomaly of the optical properties was observed earlier¹ in an aqueous solution of γ collidine. One of the mirrors of the laser cavity used in that reference was a cell filled with the solution and irradiated by an external laser pulse. A giant radiation pulse was generated in the system at a temperature $T = \tilde{T} \approx 40^\circ \text{C}$. The effect had a pronounced threshold of the priming laser intensity.

Anomalies in the thermodynamic parameters of aqueous solutions were also observed earlier (see, e.g., Ref. 2). To clarify the mechanism of the phenomenon observed by us we investigated the basic physical properties of an aqueous solution of γ collidine in the temperature range from 20 to 70° C. We obtained the temperature dependence of the chemical frequency shift $\Delta\nu$ of the proton magnetic resonance (PMR), of the hypersound velocity, and of the refractive index at ruby-laser wavelength.

2. The PMR spectra were recorded with a Tesla 6897 instrument at magnetic-field intensity 14 kG and modulation frequency 60 MHz. The temperature of the working mixture of the apparatus in which the collidine layer was placed was maintained within $\pm 0.5\%$. The corresponding values of γ -collidine concentration were determined by the stratification curve (Fig. 1).³

At the end points of the investigated temperature range, the PMR spectrum contains two distinctly separated lines near the frequency of the proton from the OH^- group. With changing temperature, these lines come closer and merge

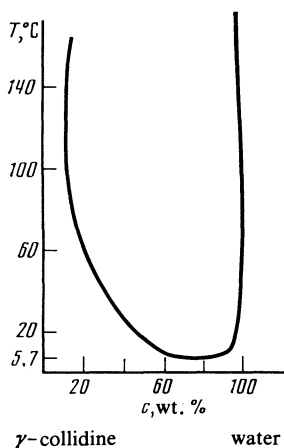


FIG. 1. Phase diagram of water + γ collidine solution.

into one at $T \approx 40^\circ \text{C}$ (Fig. 2). Reduction of the results yields for the $\Delta\nu(T)$ dependence two straight lines with slopes that differ by a factor of two. The line with the larger slope describes the temperature shift of the proton from the OH^- group of free water.

3. The refractive index n of the solution was measured with a standard refractometer whose prism temperatures were maintained constant within $\pm 0.3^\circ \text{C}$. n has a maximum at $T \approx 41^\circ \text{C}$; the experimental $n(T)$ dependence is approximated by a parabola (curve 2, Fig. 3). This differs greatly from the calculated dependence (curve 1, Fig. 3) obtained by adding the molecular refractions.

The measured solution density ρ revealed no anomalies of the $\rho(T)$ dependence; the density varies linearly with T (line 3, Fig. 3), thus confirming the simple law of addition of partial densities.

4. The hypersound velocity v was determined by measuring the shift $\Delta\nu$ of the backward stimulated Mandel'stam-Brillouin scattering (SMBS). The SMBS was excited in the solution with a ruby laser and amplifier (approximate pulse duration 30 nsec, energy on the order of $8 \times 10^{-2} \text{ J}$). The SMBS spectrum was recorded with a Fabry-Perot interferometer having a base $l = 1 \text{ cm}$. The cell with the solution was thermostated in the same temperature range accurate to $\pm 0.5^\circ \text{C}$. Under the experimental conditions only the first Stokes component of the SMBS was excited. The calculation was in accord with the known relation

$$v = c \frac{\Delta\nu}{\nu} \frac{1}{2n}$$

(c is the speed of light), and for $v(T)$ we used the experimental

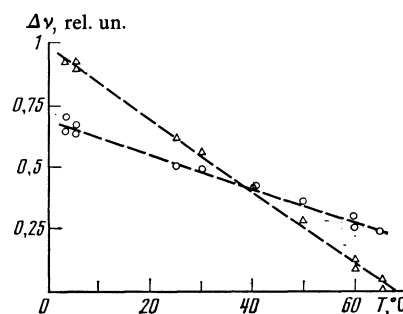


FIG. 2. Temperature dependence of the chemical shift of the PMR for the lines of the OH^- group.

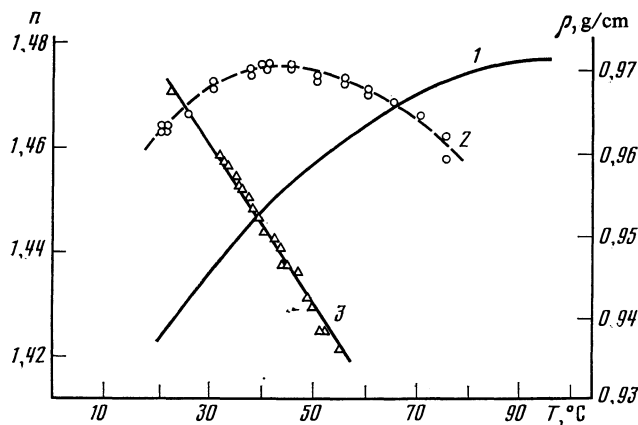


FIG. 3. Dependence of the refractive index (2) and of the density (3) of the collidine layer on the temperature. Curve 1—theoretical $n(T)$ dependence in the additive model.

values shown in Fig. 3 (curve 2). Numerical reduction of the data for $v(T)$ yields the change of the derivative $\partial v/\partial T$ at $T \approx 42^\circ\text{C}$ (Fig. 4).

5. The results described above pertain to microscopic properties of the solution that differ substantially, but the magnetic, optical, and acoustic parameters all reveal singularities in one and the same narrow temperature interval near $\tilde{T} \approx 40^\circ\text{C}$. This points to a thermodynamic origin of the obtained anomalies, and permits in turn to conclude that at $T \approx \tilde{T}$ the quasicrystalline short-range structure of a two-component liquid is transformed in the same manner as in pure water at $T = 4^\circ\text{C}$ (maximum sound velocity).

This conclusion relates the generation of a short light pulse, observed in Ref. 1, with the substantial change, in this region, of the refractive index and of the light-scattering cross sections (small-angle opalescence of the priming laser wave and stimulated 180-degree scattering of the amplified radiation by this wave). At the same time an increase takes place in the reflection coefficient R of the distributed mirror, whose role is played by the cell with the solution, viz., $R \propto W$ (W is the energy of the priming pulse). The threshold dependence of the feedback on T and W is now understandable.

The results of Sec. 2 admit of two most probable interpretations. The splitting of the PMR line for the OH^- group outside the transition region can be attributed to the hydrogen bonds between the water and γ -collidine molecules (the γ -collidine molecule has a dipole moment $\approx 2\text{ D}$ with a negative charge near the nitrogen atom). The PMR-frequency shift is proportional to the change of the internal magnetic field in the medium. The coalescence of the two investigated

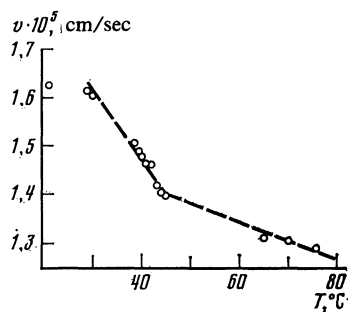


FIG. 4. Variation of hypersound velocity with temperature in the collidine layer of the solution.

lines means that the protons of the OH^- group which are neighbors (in a probabilistic sense, of course) of the collidine molecules, land at $T \approx \tilde{T}$ in exactly the same environment as the protons that enter only into hydrogen bonds that are typical of water. The numbers of the water and collidine molecules per unit volume at $T \approx \tilde{T}$ are in a ratio 3: 1, in accord with the phase curve of Fig. 1. Together with the PMR data, this points to a high probability of formation of tetrahedral complexes. The notion of formation of such statistical structural complexes explains why n has an extremum at the point \tilde{T} and why the $v(T)$ curve has a break. The obtained anomaly is analogous in a certain sense to the anomaly of the properties of water at $T \approx 37^\circ\text{C}$ (minimum specific heat). The experimental results of Ref. 1 can then be attributed to formation of a temperature grating (and hence, to spatially-periodic modulation of the refractive index) on account of interference between the priming and amplified light waves. This grating serves furthermore as a mirror for the underexcited ruby amplifier (stimulated temperature scattering).

If further experiments decide in favor of this second interpretation, we shall have thus a highly sensitive optical method of observing smooth anomalies of thermodynamic parameters in binary solutions.

The authors are grateful to M. A. Anisimov for helpful discussions and to O. N. Shumilov for assistance with the PMR measurements.

¹F. V. Bunkin, M. A. Davydov, N. P. Kitaev, *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **37**, 147 (1982) [*JETP. Lett.* **37**, 178 (1983)].

²M. A. Anisimov, V. S. Esikov, V. M. Zaprudskii, *et al.*, *Zh. Strukt. Khim.* **18**, 835 (1977).

³*Spravochnik po rastvorimosti* (Solubility Handbook), V. V. Kafarov, ed., Nauka, Vol. 1, Book 1, p. 503.

Translated by J. G. Adashko