VELOCITY OF HYPERSOUND AND DISPERSION OF SPEED OF SOUND NEAR THE CRITICAL STRATIFICATION POINT OF A BINARY SOLUTION OF TRIETHYLAMINE IN WATER

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The measurements of Chynoweth and Schneider [1] have shown that on approaching the critical stratification point of a solution of 44.6 wt.% triethylamine in water (T_c = 17.9°C) the ultrasound velocity v_u at a frequency $f = 6 \times 10^5$ Hz decreases, and the absorption increases, so that the quantity α/f^2 amounts to 10^{-12} cm^{-1} sec^2 (α - amplitude damping coefficient of the ultrasound). According to Semenchenko and Zorina [2], the shear-viscosity coefficient η increases at the critical stratification point of solutions of triethylamine in water by 15 - 20%, and amounts to ~4 centipoise. Consequently, the fraction of ultrasound absorption due to the shear viscosity is $\alpha_\eta/f^2 \simeq 0.4 \times 10^{-15}$ cm^{-1} sec^2, and therefore the observed ultrasound absorption is due entirely to the volume viscosity. Comparison of the data of [1] with the data of Sette [3], who measured ultrasound absorption in the indicated solution at t = 15°C in the frequency range 7.6×10^6 - 52.3×10^6 Hz, has shown that at t = 15°C the critical relaxation frequency of the volume viscosity is $f_c \simeq 3 \times 10^6$ Hz. It was therefore of interest to obtain the spectra of the fine structure of the Rayleigh line in the transition region, and to determine from them the hypersound velocity as well as the dispersion of the sound velocity as a function of the closeness to the critical point; this was done in the present investigation.

The hypersound velocity at $f \sim 0.5 \times 10^{10}$ Hz was obtained from the displacement of the Mandel'shtam-Brillouin components in the spectrum of the thermal scattering of the light. The scattering was excited with an OKG-12 neon-helium laser operating at λ = 6328 Å and having an output power 14 MW. The fine structure of the Rayleigh line for light scattering at an angle $\theta = 90° (\pm 0.5°)$ was obtained with the aid of a Fabry-Perot interferometer with a dispersion region 0.5 cm^{-1} and with multiple-coating dielectric mirrors having a reflection coefficient of 95%. The interference pattern was photographed (Fig. 1).

The temperature of the solution was maintained constant with accuracy not worse than

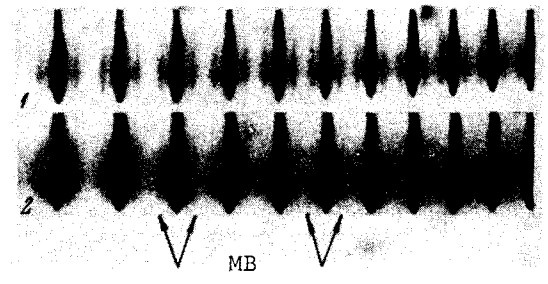

Fig. 1. Thermal Mandel'shtam-Brillouin (MB) scattering in a solution of 44.6% triethylamine (by weight) in water at temperatures 9°C (1) and 17.8°C (2).

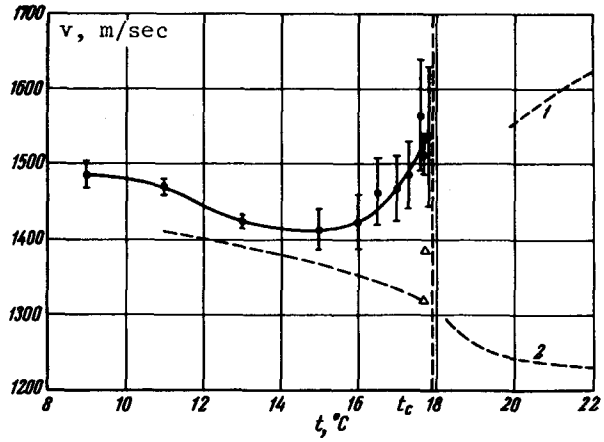

Fig. 2. Hypersound velocity near the critical stratification point of a solution of 44.6 wt.% triethylamine in water (solid curve). The dashed curve shows the ultrasound velocity given in [1] for the same conditions; (1 - water phase, 2 - triethylamine phase).

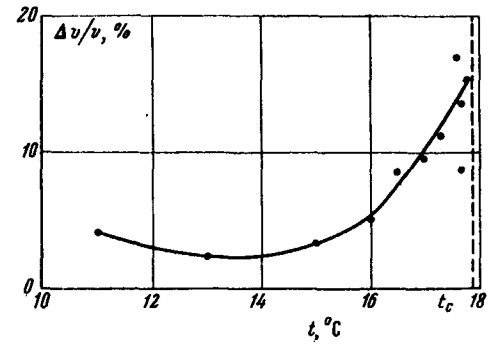

Fig. 3. Sound velocity dispersion near the critical stratification point of a solution of 44.6 wt.% triethylamine in water.

Hypersound velocity v_h and sound-velocity dispersion $\Delta v/v$ near the critical stratification point t_c = 17.9°C of a solution of 4.46 wt.% of triethylamine in water

t, °C	v_u*, m/sec	v_h, m/sec	$\Delta v/v$, %
9	-	1485 ± 18	-
11	1410	1469 ± 10	4.1 ± 0.7
13	1391	1423 ± 7	2.3 ± 0.5
15	1366	1413 ± 27	3.4 ± 2.0
16	1352	1423 ± 35	5.1 ± 2.5
16.5	1343	1463 ± 43	8.6 ± 3.1
17	1334	1468 ± 44	9.6 ± 3.1
17.3	1327	1486 ± 44	11.3 ± 3.1
17.6	1321	1566 ± 72**	17.0 ± 5.0
17.7	1319	1513 ± 27	13.7 ± 1.9
	1386***		8.8 ± 1.9
17.8	1317	1538 ± 92	15.5 ± 6.4

$v = (1/2)(v_h + v_u)$; $\Delta v = v_h - v_u$.

* The ultrasound velocity was calculated from the plot given in [1].

** In two of the many measurement runs made at this temperature, we obtained a value v_h = 1340 ± 40.

*** Two values of the ultrasound velocity are given for this temperature point in [1] (see Fig. 2).

±0.05°C by an ultrathermostat. To obtain thermal equilibrium, each temperature was maintained for not less than 4.5 - 5 hrs (the volume of the solution was approximately 150 cm^3).

The measured value of the refractive index n of the solution at a wavelength $\lambda = 6328$ Å decreased smoothly from n = 1.381 at t = 9°C to n = 1.377 at t = 17.8°C.

The measurement results are shown in the table and in Figs. 2 and 3. The data show that the ultrasound velocity increases on approaching the critical stratification point. We can attempt to explain such a behavior of the hypersound velocity, which is very unusual for critical points, by starting from the relaxation theory of sound propagation in the liquids, as developed by Mandel'shtam and Leontovich (see [4]).*

It is surprising that this simple theory, which employs only one relaxation time τ, gives in our case results close to those observed in experiment. We thus obtain for the sound velocity dispersion $\Delta v/v$ under the condition $\alpha \gg \alpha_\eta$

$$\frac{\Delta v}{v} = \frac{\alpha}{f^2} \frac{v}{4\pi^2 \tau}. \qquad (1)$$

According to the data of [1,3], we have for t = 15°C $\alpha/f^2 = 1360 \times 10^{-15}$ cm^{-1} sec^2 at $f = 0.6 \times 10^6$ Hz and $\tau \simeq 6 \times 10^{-8}$ sec. Hence $\Delta v/v \simeq 7.8\%$, which is close to the value 3.4 ± 2.0% observed for this temperature in our experiment.

According to the data of [1], at a solution temperature t = 17.7°C the value of αf^2 is approximately triple the absorption at t = 15°C. According to our data (see the table) the dispersion of the sound velocity increases by approximately the same factor, in agreement with (1).

From the results obtained in this paper it follows that the increase in the velocity of the hypersound and the growth of the sound-velocity dispersion on approaching the critical stratification point can apparently be attributed to the growth of the volume viscosity and the practically invariant relaxation time of the volume viscosity.

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[1] A. G. Chynoweth and W. G. Schneider, J. Chem. Phys. 19, 1566 (1951).
[2] V. K. Semenchenko and E. L. Zorina, ZhFKh (J. Phys. Chem.) 26, 520 (1952).
[3] D. Sette, Nuovo Cimento 1, 800 (1955).
[4] I. L. Fabelinskii, Molekulyarnoe rassenyanie sveta (Molecular Scattering of Light), Nauka, 1965 [Transl. in prep., Plenum Press].

* A numerical estimate has shown that the possible change in the sound velocity due to the gravitational effect is smaller than the measurement errors listed in the table even in the immediate vicinity of the critical points.