Hypersound propagation near the upper, lower, and double critical points in a liquid solution

K. V. Kovalenko, S. V. Krivokhizha, I. L. Fabelinskiĭ, and L. L. Chaĭkov
P. N. Lebedev Physics Institute, Russian Academy of Sciences, 117335 Moscow, Russia

(Submitted 30 July 1993)
Pis'ma Zh. Eksp. Teor. Fiz. **58**, No. 5, 395–398 (10 September 1993)

The temperature dependence of the hypersound propagation velocity and the width of the Brillouin components (the absorption of hypersound) has been studied near the upper, lower, and double critical points in guaiacol-glycerin solutions with a double critical point. The study was based on Brillouin scattering.

1. Guaiacol-glycerin solutions with a low water content ($\sim 1\%$) have a C,T (concentration, temperature) phase diagram in which there is a small closed region (a loop) in which the components of the solution are stratified. Elsewhere the solution is homogeneous.

On this phase diagram there are upper and lower critical points. The distance between them (along the temperature scale) can be varied easily by varying the concentration of the third component (the water). When there is little water, the upper and lower points merge, forming a double critical point.

There has been little experimental work on systems with a double critical point.[1–5] The theory of Refs. 6 and 7 is capable of describing the phase diagrams of such systems, but there are still some questions which require the solution of a more general physical problem.

Our purpose in the present study was to work from the position and width of the Brillouin components (or "Mandel'shtam–Brillouin components") near the critical points to find distinctive features in the propagation of hypersound in the course of phase transitions in a guaiacol–glycerin solutions. This is the first such study.

2. Brillouin spectra in solutions for which the regions of stratification of the components were at quite different temperatures were recorded on an apparatus with a Burleigh multipass Fabry–Perot interferometer with a DAS-1 multichannel analyzer. The spectra were then analyzed on a personal computer by a special program written by A. Vishnyakov. The scattered light was excited by an ILA-120 single-frequency argon laser with $\lambda = 514.4$ nm. The glycerin and the guaiacol were subjected to a special thorough purification. After filtering with Millipor filters with a pore size of 0.2 μm in a box with a dry, dust-free nitrogen atmosphere, these substances were put in a cylindrical quartz vessel 2.8 cm in diameter with a volume of 18 cm^3.

3. In a solution in which there is a temperature difference $\Delta T = 7.28$ °C between the upper and lower critical points, the hypersound velocity in the homogeneous phase is described by one of two straight lines, which differ in slope, depending on the temperature (Fig. 1). The temperature coefficient of the velocity, dV/dT, for the upper critical point is -6.5 cm/(s · deg), while that for the lower one is -11.6

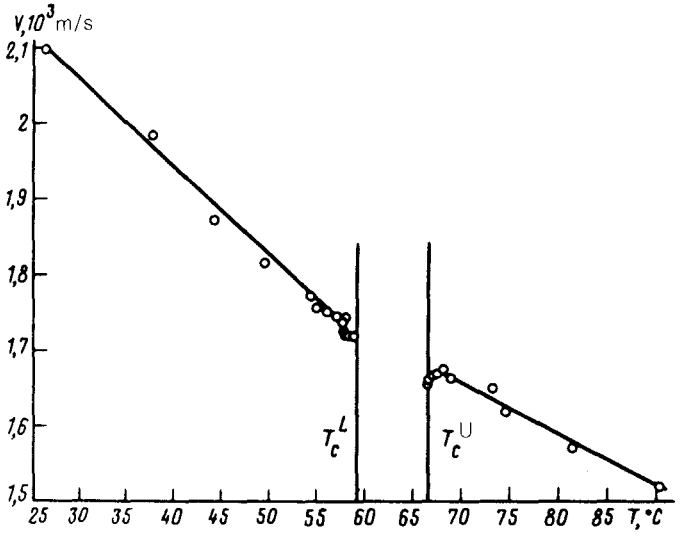

FIG. 1. Temperature dependence of the hypersound propagation velocity in a solution with a stratification region $\Delta T = 7.28$ °C. T_c^L—Lower critical temperature for stratification; T_c^U—upper one.

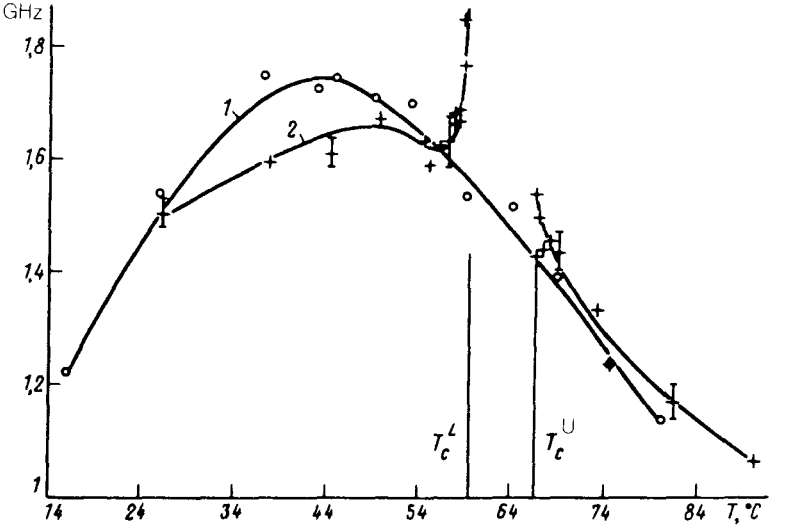

FIG. 2. Temperature dependence of the width of the Brillouin components. *1*, o—"Dry" solution; *2*, + — solution with a stratification region $\Delta T = 7.28$ °C.

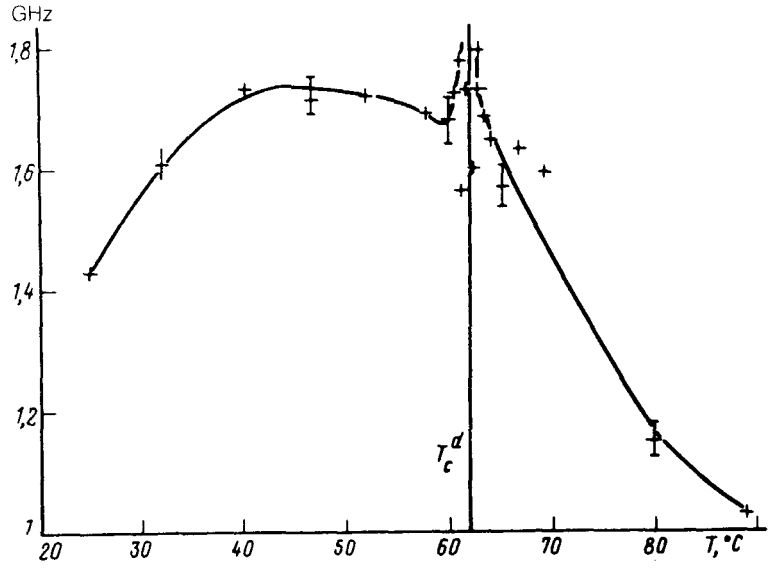

FIG. 3. Temperature dependence of the width of the Brillouin components of a solution with a stratification region $\Delta T = 0.062$ °C.

cm/(s · deg). The temperature coefficient of the velocity near the lower critical point is so large that it is greater than the corresponding coefficients for the individual liquids.[8]

The temperature coefficients of the velocity for the guaiacol–glycerin solutions with various stratification regions, from $\Delta T = 39.52$ °C to $\Delta T = 0.062$ °C in our experiments, were the same for the upper and lower critical temperatures, respectively. The absolute values of the hypersound velocities near the upper and lower critical points are quite accurately the same for all the solutions studied.

In the solutions with $\Delta T = 0.062$ °C we find $dV/dT = 0$ in a narrow temperature interval near the double critical point.

In a "dry" solution, in which there is no stratification region, the temperature dependence of the hypersound velocity is approximately linear, with a temperature coefficient $dV/dT = -11.6$ cm/(s · deg). This is the same as the temperature coefficient near the lower critical point.

4. From the width of the Brillouin components for the solution with $\Delta T = 7.28$ °C we can find the hypersound absorption as a function of the temperature. Figure 2 shows the width of these components versus the temperature. Near the critical points, we clearly see a sharp increase in the width (in the absorption) on a curve with a maximum of the same type as on curve 1, for the "dry" solution without a stratification region. This increase in width is due to a phase transition from a

homogeneous solution to a region in which the components of the solution are separated.

Figure 3 shows the same results, but for a solution with $\Delta T = 0.062$ °C, i.e., essentially for a solution with a double critical point. The nature of the absorption feature near the double critical point is similar to that of the curve in Fig. 2. It is seen against a strong background curve which essentially coincides with the temperature dependence of the width of the Brillouin components of the dry solution.

This study was carried out with financial support from the Russian Basic Research Foundation (code 93-02-14279).

[1] S. V. Krivokhizha, O. A. Lugovaya, I. L. Fabelinskiĭ *et al.*, Zh. Eksp. Teor. Fiz. **89**, 85 (1985) [Sov. Phys. JETP **62**, 48 (1985)].
[2] R. G. Jonston, N. A. Clark, and P. W. Wilzus, Phys. Rev. Lett. **54**, 49 (1985).
[3] S. V. Krivokhizha, O. L. Lugovaya, I. L. Fabelinskiĭ *et al.*, Zh. Eksp. Teor. Fiz. **102**, 115 (1993) [JETP **75**, 62 (1993)].
[4] G. A. Larsen and C. M. Sorensen, Phys. Rev. Lett. **54**, 343 (1985).
[5] C. M. Sorensen and G. A. Larsen, J. Chem. Phys. **83**, 1835 (1985).
[6] J. S. Walker and C. A. Vause, Phys. Lett. **79**, 421 (1980).
[7] J. S. Walker and C. A. Vause, J. Chem. Phys. **79**, 2660 (1983).
[8] L. Bergmann, *Ultrasonics and Their Scientific and Technical Applications* (Russian translation, IIL, Moscow, 1957) (an earlier edition of this book was published in English translation by G. Bell and Sons, London, 1938).

Translated by D. Parsons