OBSERVATION OF ANOMALOUS DAMPING AND DISPERSION OF HYPERSOUNDS IN A BINARY LIQUID MIXTURE NEAR THE SOLUTION CRITICAL POINT*

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Although the anomalous temperature dependence of attenuation of sound waves in a binary mixture of liquids near its solution critical point has been extensively studied in the ultrasonic region,[1,2] there is so far no measurement in the hypersonic region available in the literature. From a purely phenomenological point of view, the anomalous damping of a sound wave near the critical point may be related to an anomalous increase of the longitudinal viscosity ($\frac{4}{3}\eta+\zeta$, where η is the shear viscosity and ζ is the bulk viscosity) of the mixture.[3] In view of the current interest in anomalies of transport coefficients near the critical point,[4,5] measurement of frequency and temperature dependence of viscosities near the critical point is important in checking the various theoretical conjectures. The attenuation data in the MHz range are generally taken to support a theoretical model suggested by Fixman.[6,7,2] Using high-resolution Brillouin spectroscopy, we have extended this investigation to the hypersonic region (GHz). We have selected the system nitrobenzene plus n-hexane mainly for two reasons: The system has been studied by D'Arrigo and Sette over a fairly wide range of concentrations and temperatures; the ultrasonic data on this particular system seem to fit Fixman's theory rather well over the frequency range 5-95 MHz.[7] It is therefore of interest to see whether the same agreement with theory would persist up to frequencies of several GHz. A preliminary result of this experiment has already been reported.[8]

The monochromatic light source used is a single-mode He-Ne laser (Spectra Physics Model 119) which has an output of 250 μW at $\lambda = 6320$ Å and a linewidth less than 20 MHz over a period of several hours. A pressure-scanning Fabry-Perot spectrometer having 98% reflectivity mirrors and 1.1094-cm Invar spacer (corresponding to 13.51 GHz interorder spacing) is used to analyze the scattered-light spectrum. The effective finesse of the spectrometer is about 70, giving a frequency resolution of 200 MHz. Backscattering geometry is adopted for the following advantages: maximum light-gathering efficiency, minimum line broadening due to a finite collection angle, and minimum contamination from the wing of the central component (Rayleigh scattering), which has an intensity over one thousand times larger than that of Brillouin component near the critical point. The detection system consists of an ITT FW130 photon counting tube followed by a standard pulse counting and discriminating electronics. Samples were prepared from electronic grade nitrobenzene (Eastman Kodak Co., triple distilled) and research grade n-hexane (Phillips Petroleum Co., 99.99 mole %) in a sealed vessel. A separate experiment was carried out to determine the coexistence curve[9] which gives $X_c = 0.42$ (mole fraction of nitrobenzene in n-hexane) and $t_c = 20.20°$ ±0.10°C. These figures are in fair agreement with values given by Sette.[1] The sample temperature is maintained to about ±0.01°C during a complete scan which lasts for about an hour. The temperature stability is believed to be quite adequate for measurement of the Brillouin width and shift.

Data were taken in the following way: The sample was heated up to 30.25°C and shaken for complete mixing before the scan. After a scan, temperature was lowered and enough time was allowed for the sample to reach a new equilibrium. Three typical Brillouin doublets for three different temperatures are shown in Fig. 1. Note that two peaks belong, respectively, to different orders. The peak height corresponds to

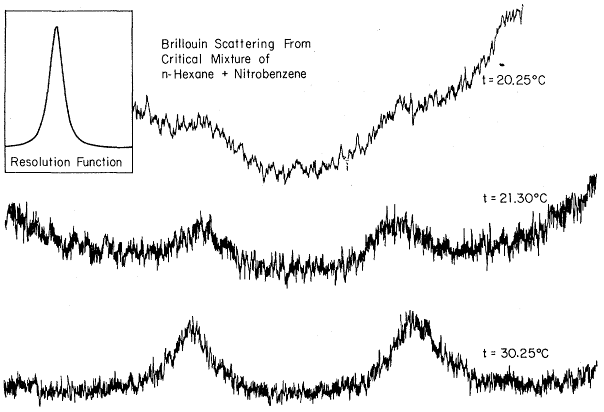

FIG. 1. Typical recorder tracing of the Brillouin doublet for three temperatures. The resolution function of the spectrometer is shown in the upper corner.

about 100 counts/sec. One can see a definite broadening of the peaks as the temperature gets closer to t_c. The Brillouin shift versus temperature is presented in Fig. 2. For the sake of comparison we also include data of pure liquids. It is seen that for the mixture as one comes down toward t_c, the sound velocity increases slightly (like a normal liquid) and then decreases slightly for $t-t_c \leq 1°\mathrm{C}$. We have checked that this is not due to the change in the index of refraction of the mixture. This behavior is qualitatively different from recent measurement on gas-liquid system.[10] To obtain the true linewidth $\Delta\nu_B$, we numerically deconvolute the experimentally measured resolution function (shown on upper left-hand corner of Fig. 1) from the measured Brillouin peak. We assume the true line shape is a Lorentzian and the width thus extracted is good to ±10 %. Figure 3 presents the true width as a function of temperature. We also measured the widths of pure liquids. They do not show appreciable variation over the same temperature range and are about 650 and 290 MHz for nitrobenzene and *n*-hexane, respectively.

From Fig. 3, one can clearly see that there are two contributions to the width $\Delta\nu_B$: a constant or weakly temperature-dependent part which is the concentration-weighted average of linewidths of the two component liquids (shown by dotted line in Fig. 3), i.e., $(\Delta\nu_B)_C = 650\ \mathrm{MHz} \times 0.42 + 290\ \mathrm{MHz} \times 0.58 = 440\ \mathrm{MHz}$, and a strongly temperature-dependent part $(\Delta\nu_B)_a$ which diverges or strongly cusps as t approaches t_c. This behavior is consistent with the measured static shear viscosity.[4]

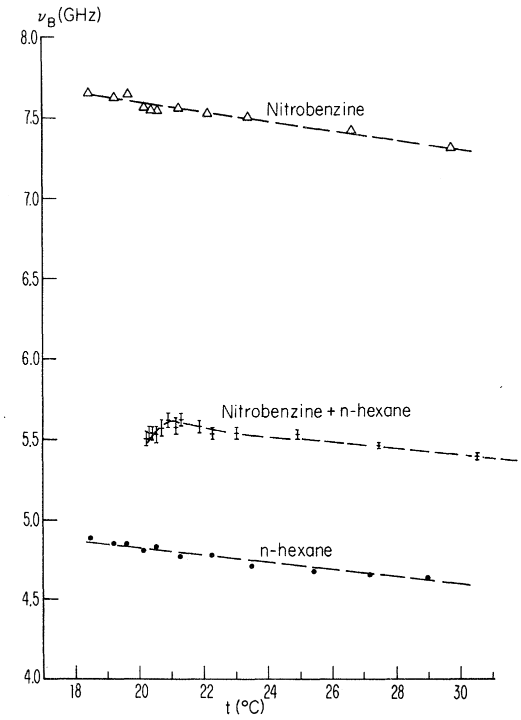

FIG. 2. Brillouin shift versus temperature. The dotted lines are drawn for visual purposes only. The error of the measurement is about 1 %.

If we admit the hydrodynamic description for sound-wave propagation in the solution even in the GHz region, the standard treatment[11,12] gives

$$\Delta\nu_B = \frac{q^2}{2\pi\rho}\left\{\theta(\nu) + \Lambda(\nu)\frac{\gamma-1}{c_P} + D\left(\frac{\partial c}{\partial\mu}\right)_{P,T}\frac{1}{\chi_{s,c}}\left[\frac{1}{V}\left(\frac{\partial V}{\partial c}\right)_{P,T} + \frac{k_T}{c_P}\left(\frac{\partial\mu}{\partial c}\right)_{P,T}\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,T}\right]^2\right\} \tag{1}$$

using the same notation as that of Ref. 11.

It has been shown[4] that the thermal conductivity Λ of a mixture exhibits no anomaly near the critical point, whereas the specific heats become very large. On the other hand, the recent measurements on the quasielastic peak of the mixture[13] and the scaling-law argument of Kadanoff and Swift[14] indicate that the third term is at most weakly divergent with a very small coefficient in front. Therefore, if the temperature is not very close to t_c, the experimentally observed strong divergence is expected to come from the first term. Fixman[6] and Kawasaki and Tanaka[3] have given an expression for the excess frequency-dependent absorption coefficient $\Delta\alpha(\nu)$ which

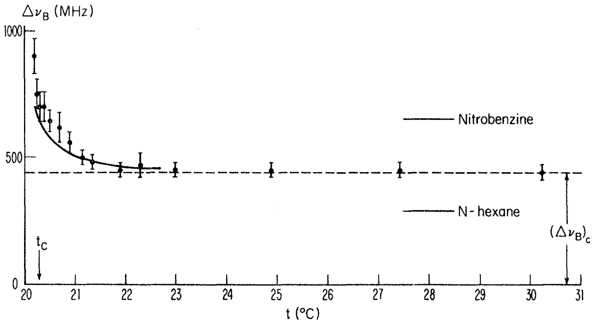

FIG. 3. Width of Brillouin peak versus temperature. The solid line is fit to Fixman's theory. Also indicated are widths for the pure liquids and their weighted averages.

can be related to the excess damping $(\Delta\nu_B)_a = \Delta\alpha(\nu)v_s/\pi$. v_s is the velocity of sound which is proportional to ν_B. Since ν_B is shown to vary less than 2 % over the range of temperature studied, it is safe to regard $(\Delta\nu_B)_a$ as proportional to $\Delta\alpha(\nu)$. We therefore write

$$(\Delta\nu_B)_a = A'I(d), \qquad (2)$$

where

$$d = C'|t-t_c|$$

and $I(d)$ is a known function given in Ref. 6. The solid curve in Fig. 3 is drawn with $A' = 620\times10^6$ sec^{-1} and $C' = 1.20$ deg^{-1}, which is probably the best fit one can do with expression (2). In Fixman's expression both A' and C' are functions of frequency and are given by $A' = A\nu^{3/4}$ and $C' = C\nu^{-1/2}$. If we substitute $\nu = 5.6\times10^9$ Hz as an average frequency of the sound waves being measured, we obtain $A = 3.03$ $\mathrm{sec}^{-1/4}$ and $C = 9.0\times10^4$ $\mathrm{sec}^{-1/2}$ deg^{-1}, which quantitatively disagree with $A = 1.05$ $\mathrm{sec}^{-1/4}$ and $C = 1.936\times10^2$ $\mathrm{sec}^{-1/2}$ deg^{-1} given by Singh[7] et al. from the best fit to the ultrasonic data of D'Arrigo and Sette.[1] It should be noted that expression (2) has a finite value at $t = t_c$, while the experimental width seems to diverge more strongly. The data are not precise enough to test $(t-t_c)^{-\nu}$-type dependence. More precise measurement close to t_c is required to do this analysis. It should be pointed out that, in contrast to sound-absorption measurements, light-scattering experiments give not only the frequency-, but also the wave-vector-dependent transport coefficients. Therefore, the ordinary hydrodynamic theory might need a further extension when the spatial correlation distance in the concentration fluctuations becomes comparable with the acoustic wavelength. For this purpose, the Brillouin width as a function of the scattering angle is also being investigated. The detailed experimental setup and result, together with more refined theoretical analysis, will be reported elsewhere.

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