PHYSICAL REVIEW A VOLUME 15, NUMBER 5 MAY 1977

Static and dynamic viscosities in the binary mixture nitrobenzene–*n*-hexane near a critical point

Yasuhiro Miyake and Yoshinobu Izumi*
Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo, Japan

Ryusuke Kono
Department of Applied Physics, National Defense Academy, Yokosuka, Japan

(Received 28 October 1976)

Ultrasonic shear data are reported for the binary mixture nitrobenzene–*n*-hexane in the homogeneous phase above t_c. The observed dispersions at frequencies of 51 and 3 kHz have been compared with the predictions of a modified form of the Deutch and Zwanzig theory, together with data on the behavior of static viscosity.

I. INTRODUCTION

Although the behavior of dynamic shear viscosity in the critical region of binary mixtures[1-3] has come to the attention of many scientists and the measurements conducted on several systems have been made, as yet no reliable information on the critical slowing down has been reported. Most of the conventional methods for determining viscosity, such as capillary-flow techniques, require or result in pressure changes in the system and tend to obscure the validity of the apparent results. To avoid this difficulty a torsional crystal technique has been employed, which has the great advantage over conventional methods of not producing significant pressure differences in the fluid. Strumpf, Collings, and Pings[1] have measured the viscosity of xenon and ethane in the critical region by the torsion crystal method. They have found no appreciable difference between the static and dynamic viscosities of carbon dioxide in the critical region. This indicates that the viscosity is independent of the shear rate, contrary to the prediction of Botch and Fixman.[4] The contradiction seems to arise from the smallness of critical relaxation times of a component system. In order to survey dynamic critical behavior, the liquid-liquid system (due to its relatively long relaxation time estimated by viscosity) is more appropriate than the gas-liquid system. For this reason, the dynamic shear viscosity in nitrobenzene–*n*-hexane was measured at ultrasonic frequencies. The present article also reports a calculation of the dynamic shear viscosity $\eta'(\omega)$ due to critical fluctuations using the theory of Zwanzig and co-workers,[5,6] which is equivalent to Fixman's derivation, based on the model of a binary Van der Waals mixture compared with the data.

II. THEORY

Botch and Fixman,[4] proceeding from the theory of correlation distribution functions, calculated that the shear rate dependence of viscosity was linked to fluctuations. Their results, however, are not suitable for direct comparison with experimental results.

The starting point of this calculation is a time-correlation-function expression for $\eta'(\omega)$,[7,8]

$$\eta'(\omega)=\frac{1}{Vk_BT}\int_0^\infty e^{-i\omega t}\langle P_{xy}(t)\,P_{xy}(0)\rangle\,dt, \tag{1}$$

where $P_{xy}(t)$ is an off-diagonal element of the total pressure tensor, ω is the frequency, V is the volume of the system, k_B is Boltzmann's constant, and T is the absolute temperature.

Deutch and Zwanzig[6] have separated $P_{xy}(t)$ into a short-range part that includes the kinetic and short-range potential contributions to $P_{xy}(t)$, and a long-range part $P^l_{xy}(t)$, which includes the contribution of long-range intermolecular forces. The only contribution to the critical-excess viscosity $\Delta\eta'(\omega)$ is the $P^l_{xy}(t)$ correlation.

Let $\delta\hat{y}_k$ be the Fourier transform, with wave number k, of the local concentration fluctuations. $\delta\hat{y}_k$ is assumed to follow the diffusion equation

$$\frac{\partial\delta\hat{y}_k(t)}{\partial t}=-D(k)k^2\delta\hat{y}_k(t),$$

neglecting dynamical coupling between temperature and concentration. They have found that the time dependence of $P^l_{xy}(t)$ is given by

$$\langle P^l_{xy}(t)\,P^l_{xy}(0)\rangle=\frac{V}{240\pi^2}\int_0^{k_{\max}}A(k)\,\exp[-2D(k)k^2t]\,dk,$$

$$A(k)=k^2\left(k\frac{\partial\hat{\omega}_k}{\partial k}\right)^2\left(\frac{\hat{\omega}_0}{2T_ck_B}-\frac{\hat{\omega}_k}{2k_BT}\right)^2, \tag{2}$$

$$\hat{\omega}_k=\hat{\omega}_0\lambda^2/(k^2+\lambda^2),$$

where $1/\lambda$ is in the range of long-range interaction, and $D(k)=D(0)(1+k^2\xi^2)$ is the diffusion coefficient. From Eqs. (2) and (1), by straight-forward calculations, one gets

$$\Delta\eta'(\omega)=\frac{1}{240\pi^2 k_B T}\int_0^{k_{\max}} A(k)\frac{1}{2D(k)k^2+i\omega}dk,$$

$$A(k)=\frac{16x'^4}{(x'^2+1)^2}\frac{T_c^2 k_B^2}{(x'^2+\delta T)^2},$$

$$k/\lambda=x',$$

$$\delta T=(T-T_c)/T.$$

A characteristic time for the relaxation process may be the diffusion time for a concentration fluctuation which extends over a region of the correlation length ξ. δT can be replaced with $\epsilon=(T-T_c)/T_c$ in the present case.

Using the power law $\xi=\xi_0\epsilon^{-\nu}$ with $1/\lambda\sim\xi_0$, final equations are given by

$$\Delta\eta'=\frac{A(T)}{D\xi^{-1}}\int_0^{\infty}\frac{x^4}{(x^2\epsilon^{2\nu}+1)^2(x^2+\epsilon^{1-2\nu})^2}\frac{K(x)\,dx}{\omega^{*2}+K^2(x)}, \tag{3}$$

$$\Delta\eta=\frac{A(T)}{D\xi^{-1}}\int_0^{\infty}\frac{x^4}{(x^2\epsilon^{2\nu}+1)^2(x^2+\epsilon^{1-2\nu})^2}\frac{dx}{K(x)}, \tag{4}$$

$$A(T)\equiv T_c^2 k_B/30\pi^2 T,$$

where $K(x)=x^2(x^2+1)$ is the so-called Fixman function, $x=k\xi$, $D=D_0\epsilon^{\nu}$, the reduced frequency $\omega^*=\omega/\omega_D$, and the characteristic frequency $\omega_D=2D\xi^{-2}$. The relaxation time has the form $\tau_D=1/D\xi^{-2}K(x)$, which had been earlier proposed by Mistura and co-workers.[9-11]

III. EXPERIMENT

The torsion crystal techniques for 51 kHz described by Mason[12] were used for dynamic viscosity measurements. The vibration of the crystal is damped by immersing it in a liquid to be measured, and the properties of the liquid in shear may be calculated from the resulting change in the resonant frequency Δf and the half-width Δ of the resonance curve of the crystal, compared with the corresponding values in air (the slight difference of crystal frequency between air and vacuum can be ignored because of the high impedance of the liquid mixture). These quantities are related to the components of the shear mechanical impedance $Z=R+iX$, by the equations $R=\Delta/2\sqrt{2}K$, $X=\Delta f/\sqrt{2}K$,[13] where K is a constant for a particular crystal at a given temperature. The values of K were given by $\Delta f/(\rho\eta\omega)^{1/2}$ and determined from Newtonian liquids. The crystal was connected electrically as the unknown arm of a mutual induction bridge (Ando Electric Co. TR 10). The frequency was determined with an electronic counter which was precise to approximately one part in 10^7. For a frequency source a frequency synthesizer (HP 3320 A) was used.

The quartz cylinder has a length of 3.8 cm and a diameter of 0.5 cm. The quartz crystal was cut, polished, and plated by the Kinsekisha Co. The angle of cut was accurate to 5′. Gold electrodes were placed on the crystal surface by a vacuum deposition technique. The electrodes are carefully oriented so that the center line of each electrode makes a 45° angle to the y axis.

The dynamic viscosity is given by the relation

$$\eta'=2XR/\omega\rho,$$

where ρ is the density of solution.

For lower frequencies of 3 kHz, the 5-cm-long 0.05-cm-thick tuning-fork crystal[14] was used as a transducer. Although the crystal is very thin, the thin side produces a longitudinal wave load. Because of this loading term, the accuracy at 3 kHz is slightly less than at 51 kHz as shown in Fig. 3. (R and X were determined in the usual manner.[14])

The impurities of a sample, no matter how small, greatly affect the value of η' (owing to their conductivity); so the samples had to be very carefully purified. Samples were prepared from reagent grade nitrobenzene and spectro-photometric grade n-hexane. N-hexane was dehydrated by metallic potassium and nitrobenzene in a phosphorus pentoxide over night. Each component was distilled twice. Nitrobenzene was prepared by fractional crystallization.

The critical point in the nitrobenzene–n-hexane system was determined by measuring the precipitation point of the coexistence curve and then observing whether the transmitted beam of a He-Ne laser disappeared or remained. The result is shown in Fig. 1, where at 1 atm the critical temperature is $t_c=19.90+0.02$ °C and critical concentration is $x_c=51.6$ wt.% of nitrobenzene. The value of x_c is consistent with previous data.[11] A critical mixture of $x_c=51.6$ wt.%, prepared with these components, has a critical temperature $t_c=19.8284$

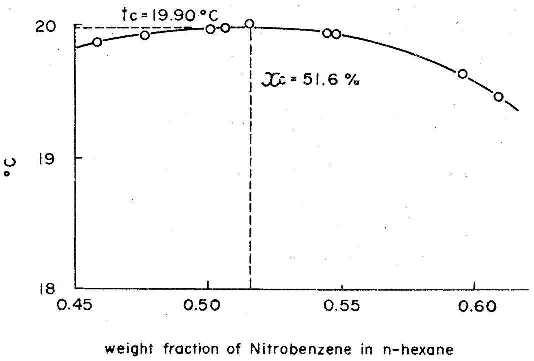

FIG. 1. Coexistence curve of the binary mixture of nitrobenzene and n-hexane.

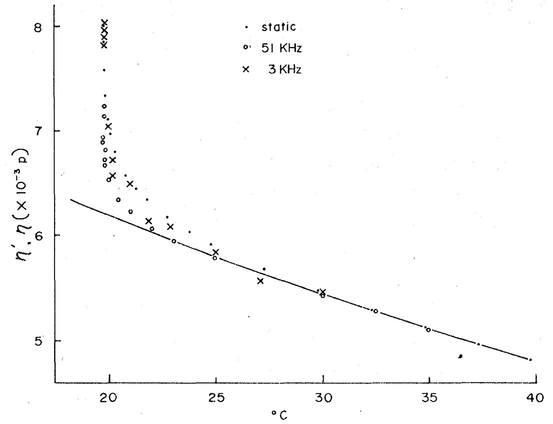

FIG. 2. Static and dynamic viscosities plotted against temperature for a critical mixture (51.6 wt. %) of nitrobenzene–n-hexane. The critical temperature t_c is 19.828 °C.

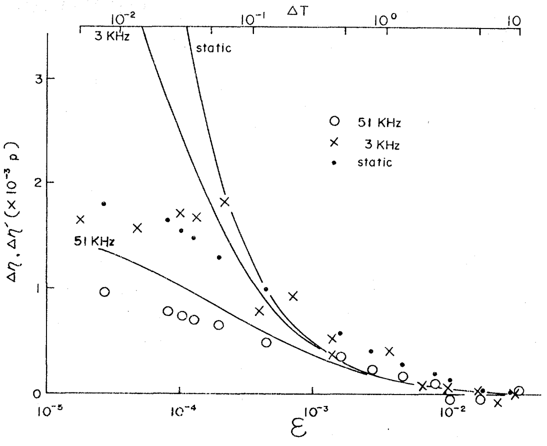

FIG. 3. Anomalous viscosity vs reduced temperature difference $\epsilon = (T - T_c)/T_c$. Solid lines show Eqs. (3) and (4).

± 0.0016 °C. The slight difference in t_c may be due, besides the eventual presence of impurities, to the variations of the concentration of the mixture when poured into the glass cell at about 30 °C.

The crystals for 51 and 3 kHz were separately suspended in two 2-cm-diam. 10-cm-long glass cells, which were tightly sealed by Araldite to avoid concentration change. The change in composition by evaporation during the course of the experiment was less than 0.006% in weight with a fraction of n-hexane. The components were mixed in a dry-nitrogen-gas atmosphere. Each mixture was well stirred before and after it was poured into the ultrasonic cell, and rest periods of more than 40 min were allowed to ensure the establishment of equilibrium in the system before the measurements were made at each temperature. The ultrasonic cell was placed in a water Dewar vessel along with a thermostat which provided a constant temperature within 0.002 °C. The temperature was measured by the quartz thermometer (HP 2801 A). The static viscosity and density were measured by the sealed Ubbelode's viscometer and pycnometer. The value of the density ρ was determined as $\rho = -0.745 \times 10^{-3} t(°\mathrm{C}) + 0.8580$ g/cm^3.

IV. RESULTS AND COMPARISON WITH THE THEORY

The results for the critical mixture are presented in Fig. 2. It is clearly seen that η and η' show a divergence. The dynamic viscosity η' is less than the static viscosity η. The solid line shows the Arrhenius equation, from which η deviates at about 30 °C. The deviation of η' takes place at about 25 °C. The critical excess viscosity is thus determined and plotted against ϵ in Fig. 3.

A comparison of our experimental results with the theory presented in Sec. II requires parameters which cannot be obtained from our measurements. These parameters are the correlation length and the diffusion coefficient obtained by light-scattering experiments. Assuming $\xi = \xi_0 \epsilon^{-\nu}$ and $D = D_0 \epsilon^{\nu}$, one gets the characteristic frequency $\omega_D = 8.01 \times 10^{10}\, \epsilon^2\ \mathrm{sec}^{-1}$ for $\nu = \frac{2}{3}$, employing $\xi_0 = 2.03$ Å and $D_0 = 1.65 \times 10^{-5}\ \mathrm{cm}^2\mathrm{sec}^{-1}$.[11] Because of the unknown value of $k_{\max}$, the thermodynamic coefficient $A(T)$ is a free parameter obtained from the best fit of Eq. (3) with experimental results at 51 kHz. One finds that $A(T) = 2.6 \times 10^{-9}$ (in erg units) is nearly independent of temperature. The quantity $\Delta\eta'(\omega) D \xi^{-1}$ is plotted against ω^* in Fig. 4. Owing to the temperature-dependent parameter ϵ, $\Delta\eta'(\omega)$ over a wide frequency range cannot be reduced to a single curve. The solid line shows the integral in Eq. (3) at 51 kHz; the dashed line, at 3 kHz. It seems that the dynamic data generally follow the prediction of the theory below $\omega^* = 10^2$. Equation

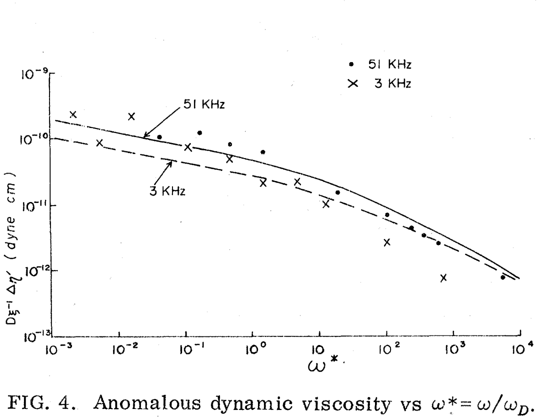

FIG. 4. Anomalous dynamic viscosity vs $\omega^* = \omega/\omega_D$. The solid and dashed lines show the integral in Eq. (3) at 51 and 3 kHz, respectively.

(4) for $\Delta\eta$ is plotted in Fig. 3 as a solid line. The theory predicts the right order of magnitude for $\Delta\eta$ above $\epsilon = 3\times 10^{-4}$, but the temperature dependency of $\Delta\eta$ is quite divergent. The Deutch-Zwanzig theory may be successful when applied to the dynamic viscosity. Below $\epsilon = 3\times 10^{-4}$ or above $\omega^* = 10^2$, the deviation of the theory from the data is large. One source for the deviation probably stems from the inadequacy of the Orstein-Zernik form above $x = 1$, assumed in the derivation of Eqs. (2) and (3) (in addition to the assumption $\gamma = 1$, which should be 1.22 by the scaling law). Other possible sources for the deviation might result from impurities, temperature gradients, or an error in the critical concentration.

The gravitational effect[15,16] is less probable, because no appreciable difference was found between the dynamic viscosities when measured at 51 kHz by a cylindrical crystal placed in the center of the solution, parallel to and then perpendicular to the horizontal over the whole temperature range studied. It seems, as suggested by Sengers[16] that the time needed to establish such a gradient is sufficiently long that in practice measurements are not affected by this effect. Recalling the characteristic frequency for xenon,[17] $\omega_D = 5.38\times 10^{12}\,\epsilon^2$, it can be understood that the dynamic viscosity in a one-component system did not show the critical slowing down at ultrasonic frequencies. A frequency of 38.7 kHz measured in xenon corresponds to about 3 kHz in the present case, where η' is close to η as is seen in Fig. 3.

The sealed-type viscometer was thoroughly immersed to attain a uniform temperature. During the measurement process, the viscometer was rotated in the thermostatic liquid to push the liquid mixture back into the upper reservoir. It has been pointed out[15] that some of the effect may disappear upon stirring the critical mixture to destroy the long-range correlations. These phenomena suggest that the rotation of the viscometer has an effect upon the value of η, thus resulting in unreliable data. Nevertheless, $\Delta\eta$ is well defined by the Kawasaki plot[18] $(\Delta\eta/\eta = -a\ \ln\epsilon + b)$, until it breaks down around $\epsilon = 10^{-4}$. This gives rise to $a = 0.035$, which is nearly equal to the prediction 0.033.

---

*Present address: Centre de Recherches sur les Macromolécules 6, rue Boussingault 67083 Strasbourg Cedex France.

[1] H. J. Strumpf, A. F. Collings, and C. P. Pings, J. Chem. Phys. 60, 3109 (1974).

[2] B. C. Tsai and D. McIntyre, J. Chem. Phys. 60, 937 (1974).

[3] B. C. Tsai, M. Myers, and D. McIntyre, J. Chem. Phys. 58, 4582 (1973).

[4] W. Botch and M. Fixman, J. Chem. Phys. 36, 3100 (1962).

[5] R. D. Mountain and R. Zwanzig, J. Chem. Phys. 48, 1451 (1968).

[6] J. M. Deutch and Robert Zwanzig, J. Chem. Phys. 46, 1612 (1967).

[7] M. S. Green, J. Chem. Phys. 22, 398 (1954).

[8] J. A. McLennan, Phys. Fluids 3, 493 (1960).

[9] L. Mistura and D. Sette, J. Chem. Phys. 49, 1419 (1968).

[10] G. D'Arrigo, L. Mistura, and P. Tartaglia, Phys. Rev. A 1, 286 (1970).

[11] P. Tartaglia, G. D'Arrigo, L. Mistura, and D. Sette Phys. Rev. A 6, 1627 (1972).

[12] W. P. Mason, Trans. Am. Soc. Mech. Eng. 69, 359 (1947).

[13] K. Yamamoto, Y. Yamada, and Y. Wada, Oyo Buturi 27, 98 (1958).

[14] W. P. Mason, *Physical Acoustics and the Properties of Solids* (Van Nostrand, New York, 1958), pp. 54 and 114.

[15] M. Fixman, in *Advances in Chemical Physics*, Vol. VI, edited by I. Prigogine (Interscience, London, 1964), p. 180.

[16] J. V. Sengers, in *Varenna Lectures on Critical Phenomena*, edited by M. S. Green (Academic, New York, 1971), p. 454.

[17] P. E. Mueller, D. Eden, and C. W. Garland, Phys. Rev. A 6, 2272 (1972).

[18] K. Kawasaki, *Critical Phenomena in Alloys, Magnet, and Superconductors*, edited by R. E. Milles, E. Ascher, and R. I. Jaffee (McGraw-Hill, New York, 1971), Part 5, p. 489.