SHEAR VISCOSITY OF THE BINARY SYSTEM ANILINE-CYCLOHEXANE NEAR THE CRITICAL POINT*

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(Received 11 February 1969)

The shear viscosity of the system aniline-cyclohexane has been measured for a mixture at the critical concentration. Above the critical temperature the experimental points are well fitted over three decades by a logarithmic law. A discussion of the relevance of this result on some recent theoretical work is also included.

In this Letter we wish to report recent measurements on the behavior of the shear viscosity in the binary system aniline-cyclohexane at the critical concentration above the critical temperature. Measurements have been made with an Ubbelohde capillary-flow viscosimeter. In order to avoid contamination of the mixture during measurements, the viscosimeter has been modified to work in an inert-gas atmosphere. The bath temperature has been controlled up to 0.01°C, and temperature measurements have been made with a mercury thermometer calibrated with a Leeds and Northrup platinum-resistance thermometer. Both components have been doubly distilled and purity tested thus determining the coexistence curve. The value obtained for the critical temperature, 29.84°C, is a little higher than that reported by Atack and Rice[1] which is 29.59°C. According to these authors this fact would indicate that small impurities (quite probably water) are still present in the mixture. On the other hand the value of the critical concentration, 44% mole fraction of aniline, agrees quite well with that reported by these authors.

Previous measurements[2,3] of the viscosity of binary mixtures have clearly indicated that this quantity shows an anomalous behavior near the critical consolute temperature. However, none of these works reports sufficient data to allow a quantitative comparison with the predictions of recent theoretical works.[4-8] In particular, it appears to be very interesting to establish the temperature dependence of the viscosity at the critical concentration above the critical temperature.

Our results are summarized in Figs. 1 and 2. As far as Fig. 1 is concerned, one must observe

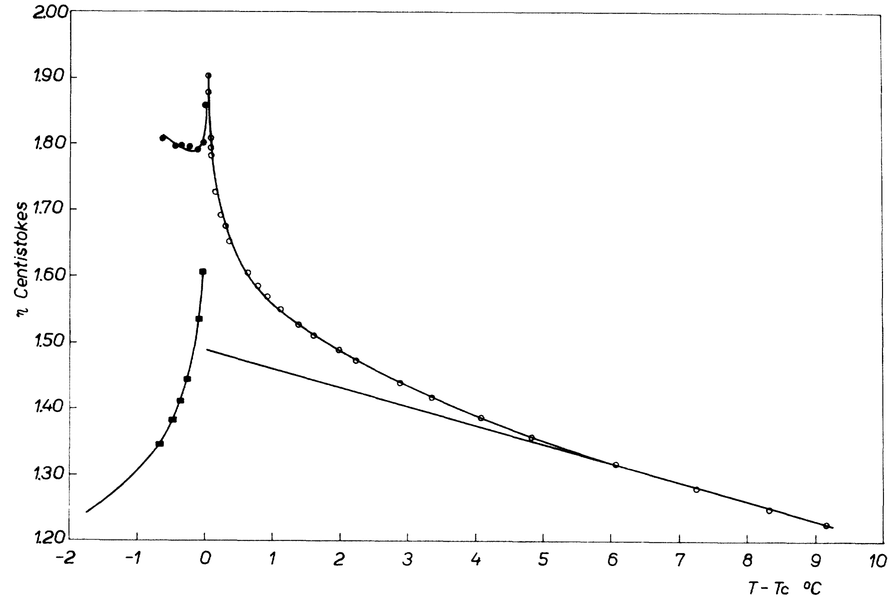

FIG. 1. Kinematic viscosity versus $T-T_c$. The straight line represents normal behavior in this restricted range of temperature. The lower curve below T_c refers to the phase with the greater concentration of cyclohexane.

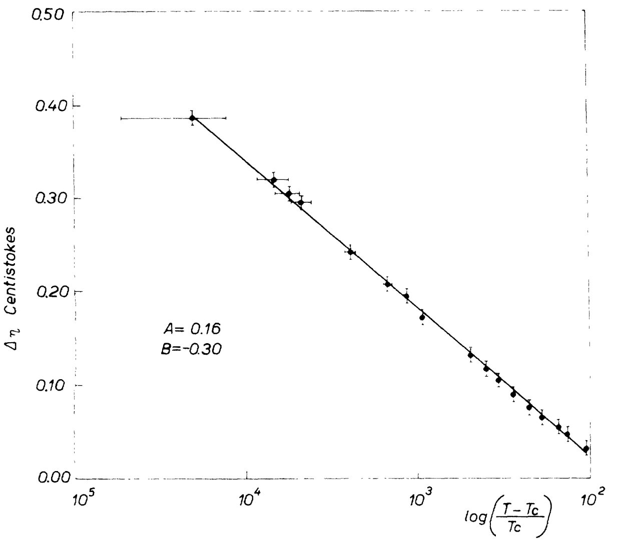

FIG. 2. Excess kinematic viscosity versus $\ln[(T-T_c)/T_c]$.

that points taken below the critical temperature refer to different concentrations, and there are not enough to get quantitative conclusions. We will report subsequently the results of a detailed experimental study including mixtures of different concentrations. As is shown in Fig. 2 the points above the critical temperature are quite well fitted over three decades by a logarithmic law

$$\Delta\eta = -A\ln[(T-T_c)/T_c]+B, \tag{1}$$

where $\Delta\eta$ is the excess shear viscosity, $A=0.16$, and $B=-0.30$. This is a new result and the remaining part of this Letter is devoted to a discussion of its relevance to the above-mentioned theoretical work.

The first attempt to explain the anomalous behavior of the viscosity near the critical consolute temperature has been made by Fixman.[4] His basic assumptions can be more easily understood in terms of the general formulation given by Kawasaki.[6] The relevant results of this approach can be written down as follows:

$$D\Delta\eta \sim \xi^{-1}, \tag{2}$$

$$D \sim \xi^{-2}, \tag{3}$$

where D is the diffusion coefficient and ξ the correlation length for concentration fluctuations. Since ξ diverges as $(T-T_c)^{-\nu}$ and $2\nu=\gamma$,[9] Eqs. (2) and (3) lead to a rather strong singularity for the viscosity which is in contrast to our experimental results.

In an attempt to explain this breakdown of the theory, the first hypothesis one can make is that this is a consequence of using the ideas of Ornstein and Zernike to evaluate correlation functions. Indeed, one must expect this estimate to be correct only for a system with very long-range interaction potential. Moreover, the calculation of Deutch and Zwanzig[7] seems to indicate that the behavior predicted by Eqs. (2) and (3) is to be expected for a van der Waals mixture. However, this is quite probably not the case. We can suggest a very simple argument to show that a relation in agreement with Eq. (2) must be expected between the viscosity and diffusion coefficients. Let us consider inside the mixture a region of linear dimensions ξ. Particles inside this region are strongly correlated and we must expect that under the influence of an external force F they move together with a mean velocity $\bar{v}$ given by Stokes' relation

$$F \sim \eta\xi\bar{v}. \tag{4}$$

This gives for the mobility b the expression

$$b=\bar{v}/F \sim 1/\eta\xi. \tag{5}$$

on the other hand, we can make use of Einstein's relation

$$D=K_BTb \tag{6}$$

to conclude that

$$D\eta \sim \xi^{-1} \tag{7}$$

in agreement with Eq. (2).

In order to derive Eq. (3) a further, stronger assumption must be introduced. To appreciate this point we recall that the diffusion constant D is the product of the Onsager kinetic coefficient α and the thermodynamic susceptibility[10] $(\delta\mu/\delta c)_T$:

$$D=\alpha(\delta\mu/\delta c)_T. \tag{8}$$

Therefore, taking into account that $(\delta\mu/\delta c)_T \sim \xi^{-2}$, Eq. (3) follows if we assume that α is well behaved near the critical point. This would be in agreement with the conventional theory of critical slowing down[11] but it is much more doubtful than the general relation (2). Indeed, recent measurements performed by Chu and Shoenes[12] of the quasielastic Rayleigh linewidth in the mixture of isobutyric acid and water have provided indications that the Onsager coefficient α diverges in the critical region like ξ. If we assume the validity of Eq. (2), then our measurements provide a completely independent confirmation of this result. In Kawasaki's approach mentioned above, Eq. (3) is an almost direct consequence of the assumption that energy and concentration are the only macroscopic variables whose Fourier components must be included in the expansion of the microscopic fluxes. Then Eq. (3) follows quite simply from the time-reversal property of these variables.[6,11]. If we accept the validity of the expansion procedure, our results seem to indicate that other variables beside concentration and energy must be introduced. In this respect the recent work by Swift[8] and Kadanoff and Swift[13] are very interesting. There are two main differences between Kadanoff and Swift's and Kawasaki's methods. First, they estimate correlation functions with the aid of the "scaling-law" idea. As we have discussed above, this does not represent a substantial improvement of the theory. In our opinion the most important difference between the two approaches is that Kadanoff and Swift in their perturbation theory take into account the entire set of densities of the conserved additive quantities. This method has been directly applied only to the liquid-gas critical point. The relevant results for mixtures have been obtained by Swift[8] simply by establishing an analogy between transport process in binary mixtures and in simple fluids. According to this analogy diffusion corresponds to heat conduction in simple fluids and therefore α corresponds to the thermal conductivity λ. As far as the shear viscosity is concerned, his conclusions are that it has at most a logarithmic divergence. This prediction is in agreement with our experimental results.

Finally, we must mention that in a series of recent papers[14] Kawasaki has suggested that near the critical point certain modes of motion that usually have been considered to be microscopic begin to slow down enormously. As a consequence, new dynamical variables beside the original macroscopic variables must be introduced to account for all the anomalies of the transport coefficients. However no prediction on this basis has been made for binary mixtures.

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*Work supported by Consiglio Nazionale delle Ricerche, Rome, Italy.

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PLASMA DENSITY MEASUREMENT BY ION-BEAM PROBING*

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(Received 23 December 1968)

The collisional dissociation of a beam of energetic H_2^+ ions provides a localized and rapid measurement of plasma density and perturbation of plasma density, yet leaves the plasma undisturbed.

In some fields important quantities are hard to measure, and plasma physics is such a field. The physicist who wants to measure plasma density, for instance, finds himself caught on the horns of a dilemma: Either he can make a measurement with low spatial resolution on an undisturbed plasma by using microwaves, interferometers, or similar techniques which measure a line integral of the density, or else he can make a high-resolution measurement using Langmuir