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Pseudospinodal curves and scaling of the shear viscosity of binary mixtures in the critical region

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The shear viscosity of binary liquid mixtures shows a weak anomaly in the critical region. Its empirical formula $\eta = \eta_{id}\epsilon_{sp}^{-\phi}$ is used first to determine T_{sp} and found to provide reasonable representations of the experimental results. The relevance of this equation to some current theoretical predictions and the general validity are discussed. In addition, it is shown that the shear viscosity satisfies scaling law relations similar to those previously established for equilibrium properties.

I. INTRODUCTION

The shear viscosity of binary liquid mixtures shows a weak anomaly in the critical region. The anomaly is attributed to the cooperation of the two effects: (i) the anomalous increase in certain large scale fluctuations of macroscopic variables obtained in the flux, and (ii) the anomalous increase in the life times associated with these fluctuations.

Attempts have been made to clarify the mathematical character of the weak anomaly.[1] In 1963, Debye and co-workers first noted that the viscosity anomaly could be represented by an empirical formula[2]

$$\eta = \eta_{id}\epsilon^{-\phi}, \quad \epsilon = T/T_c - 1, \tag{1}$$

where ϕ is the critical exponent, η is the full viscosity, and η_{id} is an ideal shear viscosity in the absence of any critical anomaly. η_{id} was estimated in the original form of Debye and co-workers by the Arrehnius-type equation. It is noted that the form of Eq. (1) satisfies the prediction of scaling laws. This fact suggests that this equation seems to be general. Some current theoretical bases of the empirical equation have recently been given by several authors.[3-6]

According to Kawasaki[3] and Perl and Ferrell,[4] the viscosity anomaly has been established to follow the temperature dependence as the temperature T approaches T_c,

$$\Delta\eta/\eta = A \ln q_D \xi, \tag{2}$$

where $\Delta\eta = \eta - \eta_{id}$, $\xi = \xi_o \epsilon^{-\nu}$ is the correlation length, q_D is a Debye cutoff, and A is a constant ($8/15\pi^2 = 0.054$). The theory[3,4] in its current state cannot discriminate between $\Delta\eta/\eta_{id}$ and $\Delta\eta/\eta$. This point should be noted especially in analyzing the critical viscosity with Eq. (2), as did Sengers.[1] It is easily shown that Eq. (2) can be closely related to Eq. (1); hence, it is concluded that the critical exponent ϕ corresponds to that of the correlation length except a constant factor, i.e., $\phi = (8/15\pi^2)\nu$. In an interesting extention of the mode-coupling equations, Oxtoby and Gelbart[5d] have calculated the shear viscosity numerically, with no adjustable parameters, by including background term in the self-consistent equations.[2] They have shown that q_D in Eq. (2), an adjustable parameter in the original theory, can be approximately identified with

$$q_D \simeq C k_B T / 8\pi\eta_{id} D_{id} \xi_0^2,$$

where C is a constant of order of unity, k_B is the Boltzmann constant, and D_{id} is the background diffusion constant, for example, for a binary mixture. Starting with the self-consistent scheme of Kawasaki,[3] which means a direct approach to the three-dimensional case, Ohta[5a] made an approximate estimate of the exponent ϕ and the validity of the relation has been confirmed. On the other hand, Halperin *et al.*[6] discussed the viscosity anomaly on the basis of the renormalization-group method using an ϵ expansion and arrived at the following equation:

$$\eta \sim \epsilon^{-(1.2/6\pi)\nu}. \tag{3}$$

It is clear that Eq. (3) provides a direct and theoretical basis for Eq. (1) and also $(1.2/6\pi)\nu$ as the exponent ϕ.

Now empirical equation (1) is satisfied not only with the prediction of the mode-coupling (or decoupled) theory but also with that of the renormalization-group method. As a result, in the present paper, it is of no interest to discuss whether the mathematical character of the weak anomaly is logarithmic (or power-law) divergence or not, although several investigators have hitherto discussed this point. Rather it should be noted that the viscosity is expressed as a product of the background component η_{id} and the critical component $\epsilon^{-\phi}$, i.e., as a form of the multiplicative renormalization,[7] which enables us to separate an anomalous viscosity in a polymer solution near the critical point from the apparent normal concentration dependence,[2,8] and to study the critical anomaly in polymer solutions on the same basis as critical anomaly in binary-liquid mixture.[3]

Thus, almost all of the efforts have been expended in analyzing the temperature dependence, and the concentration dependence has not been analyzed in terms of scaling-law relations. In order to describe the behavior of the thermal diffusivity with the density and the temperature for SF_6, Benedek[9] introduced the so-called "spinodal curve," which is generally supposed to present the limits of stability of the metastable uniform one-component phase. This concept has been extended to the two-component system of isobutyric-acid–water, in an attempt to describe both the linewidth and the intensity measurements in the critical region.[10] Further extension to the polymer solution in the critical region[11] has also been done. The extended version of the correlation length proposed in this work is simply written

$$\xi \propto \epsilon_{sp}^{-\nu}, \quad \epsilon_{sp} = T/T_{sp} - 1 \tag{4}$$

where T_{sp} is the pseudospinodal temperature, and hence the extension of Eq. (1),

$$\eta = \eta_{id}\epsilon_{sp}^{-\phi}. \tag{1'}$$

Equation (1′) means that, along each of the noncritical isochores, the viscosity has the same temperature dependence as that of the critical isochore except that the viscosity diverges at a certain temperature (T_{sp}) which lies inside the coexistence curve. At this point, it would be reminded that a theoretical consideration of Chu *et al.*[10] on such a postulated form was made without taking account of the convergence of their expansion. Accordingly, we have no reason to accept their consideration that such a postulated form may imply stringent and unrealistic restriction on the equation of state.

However, it should be noted that a spinodal curve determined with Eq. (1′) is obtained by an extrapolation from stable homogeneous equilibrium states (so-called "pseudospinodal" curve) and then a true spinodal curve can only be observed by measurements on metastable states.

The purpose of the present paper is to show that Eq. (1′) can be used to determine T_{sp} and provides reasonable representations of the experimental results, and to demonstrate that the shear viscosity satisfies scaling-law relations similar to those previously established for equilibrium properties.[12,13]

II. TREATMENT OF DATA

In order to examine the validity of the assumption, the viscosity should be investigated over a wide range of temperature-concentration diagram in the critical region; to establish a firm general statement on this, it is necessary to perform a series of such measurements on various samples. Along this line of thought, the most careful works on binary mixtures have been done with the isobutyric-acid–water,[14] the 3-methylpentane-nitroethane,[15] and the 2,6-lutidine-water systems.[16] In the present paper, data on the isobutyric-acid–water system have been chiefly used for the determination of T_{sp}, because the detailed data of the viscosity near the phase-separation temperatures are available,[14a] the study of light scattering had

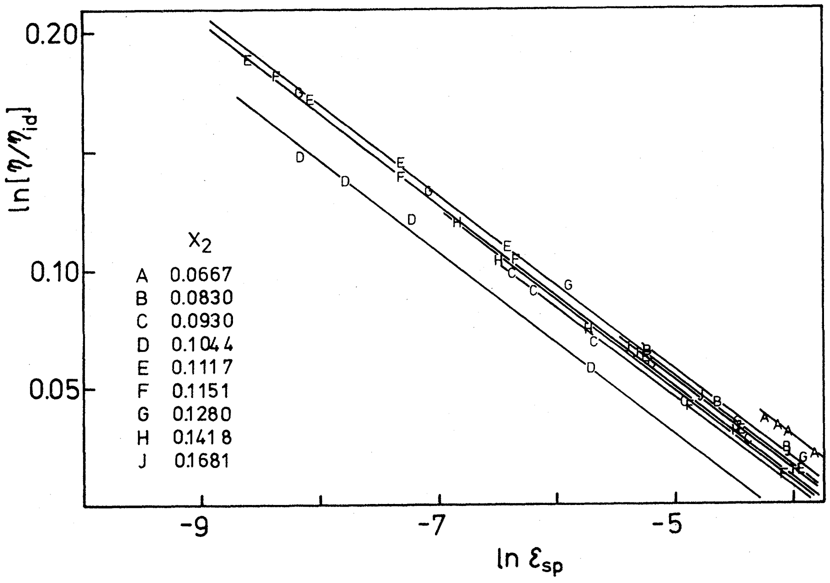

FIG. 1. Plot of $\ln(\eta/\eta_{id})$ vs $\ln\epsilon_{sp}$ for the system of isobutyric acid and water. x_2 is mole fraction of isobutyric acid.

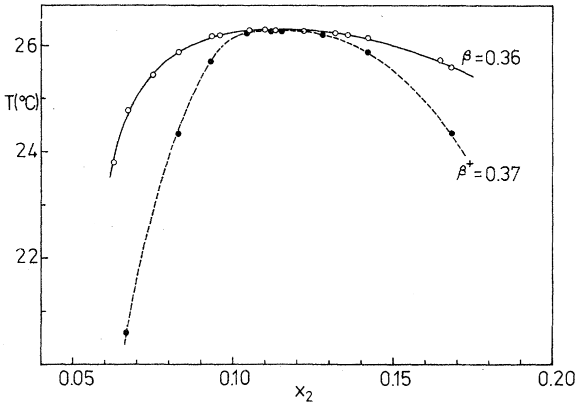

FIG. 2. Coexistence and pseudospinodal curves for the system of isobutyric acid and water. x_2 is mole fraction of isobutyric acid.

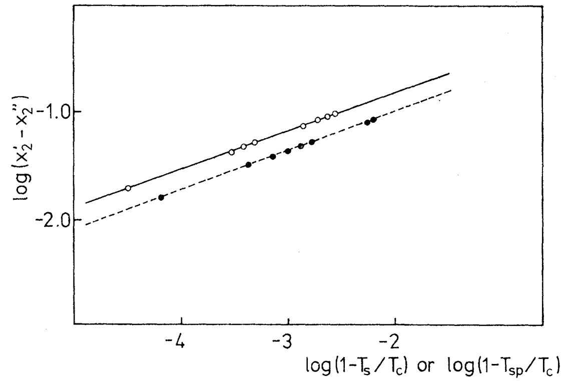

FIG. 3. Plot of $\log_{10}(x_2'-x_2'')$ vs $\log_{10}(1-T/T_c)$. The solid line represents the coexistence curve of Ref. 14a and has the form of $x_2'-x_2''=0.78(1-T_s/T_c)^{0.36}$. Dashed line is the pseudospinodal curve of the form of $x_2'-x_2''=0.54(1-T_{sp}/T_c)^{0.37}$.

also been performed in the critical region,[10] and the comparison between these results is possible. Three systems mentioned above are also analyzed as a test of scaling-law relations.

In interpreting these data, a systematic procedure should be developed for the evaluation of the ideal viscosity, that is, the ideal viscosities for the isobutyric-acid–water and the 3-methylpentane-nitroetane mixtures have been estimated from the Arrehnius equation $\log_{10}\eta_{id}=B/T+C$ and compared with the results obtained by applying the tracer diffusion method.[14b,15a,b] On the other hand, η_{id} of the 2,6-lutidine–water[16b] has been estimated from the rational equation

$$\log_{10}(\eta_{id}/\eta_{id}^0)=[A(T-T_0)+B(T-T_0)^2]/(C+T),$$

where η_{id}^0 is the viscosity at an arbitrary reference temperature T_0, and A, B, and C are constants, because it is not reasonable to apply the Arrehnius equation to this system, that is, this system has a lower critical point at a low temperature and the principal component is almost water, i.e., 94 mol%. As a result, these three systems have almost the same values of the critical exponent ($\phi=0.038-0.040$), whose values are consistent with the theoretical predictions mentioned above, i.e., 0.036 (Refs. 3 – 5) or 0.04 (Ref. 6). It is remarkable that the difference between systems with an upper critical point and systems with a lower critical point has been found mainly in the background viscosity.

Since it can be shown that the exponent ϕ remains constant relatively with changing concentration, Eq. (1′) suggests straight lines of slopes $-\phi$ in plots of $\log_{10}(\eta/\eta_{id})$ vs $\log_{10}\epsilon_{sp}$, as shown in Fig. 1. Pseudospinodal temperatures determined from the data analysis are shown in Fig. 2 with the coexistence curve of Ref. 14a and listed in Table I including the value of ϕ. In order to characterize the shape of the pseudospinodal curve in the neighborhood of the critical mixing point we

TABLE I. Characteristics of the isobutyric-acid–water (IBW) mixture and values of T_{sp} and the exponent ϕ.

Sample IBW	Mole fraction[a] IB acid[b]	T_s (°C)[a]	T_{sp} (°C)	T_s-T_{sp}	ϕ	$\phi_{\text{theoretical}}$
3	0.0667	24.78	20.60	4.18	0.038_4	
4	0.0830	25.88	24.34	1.54	0.038_2	
5	0.0930	26.17	25.70	0.47	0.038_1	
6	0.1044	26.28	26.23	0.05	0.038_4	
7	0.1117	26.30	26.26	0.04	0.038_3	0.036
8	0.1151	26.30	26.26	0.04	0.038_6	
9	0.1280	26.26	26.20	0.06	0.038_3	
10	0.1418	26.15	25.86	0.29	0.038_7	
11	0.1681	25.59	24.34	1.25	0.038_2	

[a] Taken from the experimental data of D. Woerman and W. Sarholz, Ref. 14a. T_s is the phase separation temperature.

[b] IB is isobutyric.

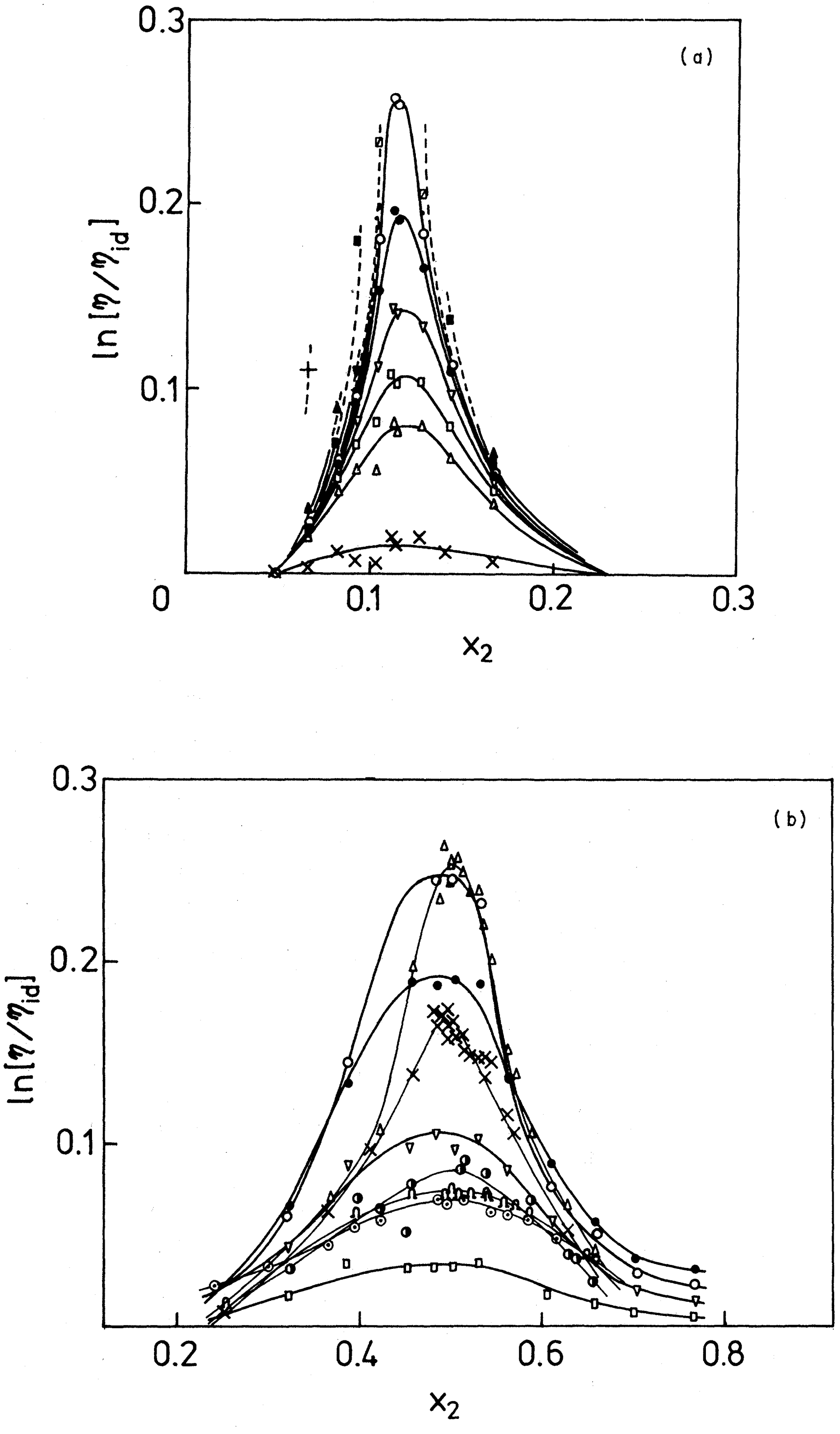

FIG. 4. Plot of (η/η_{id}) vs x_2. (a) The system of isobutyric acid and water (Ref. 14a): $T - T_{sp,\max}$ = 0.01°(○), 0.05°(●), 0.20°(▽), 0.50°(□), 1.00°(△), 5.00°(×), −0.01°(·), −0.05°(⧄), −0.20°(▼), −0.50°(■); −1.00°(▲), −5.00°(+). $T_{sp,\max}$ is the maximum spinodal temperature. (b) The system of 3-methylpentane-nitroethane: $T - T_c$ = 0.044°(△), 0.544°(×), 3.555°(◑), 8.555°(Ω), 13.465°(⊙) (Ref. 15a); 0.083°(○), 0.478°(●), 3.164°(▽), 7.215°(□) (Ref. 15c).

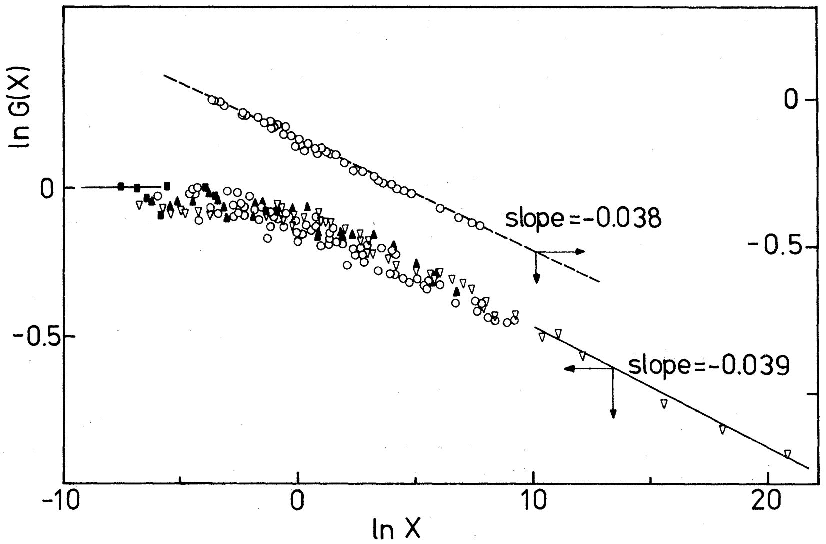

FIG. 5. Scaling plots of the shear viscosity as a function of X: the isobutyric acid and water (○); the 3-methylpentane and nitroethane (▽, Ref. 15a), (▲, Ref. 15c); the 2, 6-lutidine and water (□, Ref. 16a). The broken line and the solid line represent the corresponding scaling plots with $\epsilon_{sp}/|\Delta x_2(sp)^*|^{1/\beta^+}$ and $\epsilon/|\Delta x_2^*|^{1/\beta}$ as X, respectively, and $g(X) = (x_2/x_{2c})^{\phi/2\nu} G(X)$. Here $\Delta x_2(sp)^*$ is Δx_2^* for the pseudospinodal curve.

employed a logarithmic plot of the concentration differences $(x_2' - x_2'')$ versus temperature differences $(1 - T_{sp}/T_c)$ as shown in Fig. 3. A relation of the form

$$x_2' - x_2'' \propto (1 - T_{sp}/T_c)^{\beta^+} , \tag{5}$$

could be fitted by a least-squares calculation with the exponent of the pseudospinodal curve $\beta^+ = 0.37 \pm 0.02$, where x_2 represents the mole fraction of the second component (isobutyric acid) of the binary system. The values of β^+ is in excellent agreement with the value reported by Chu *et al.*[10] for the same system, and also with the exponent of the coexistence curve $(\beta = 0.36 \pm 0.02)$. Consequently, the results show that the homogeneity hypothesis (or scaling assumption) and pseudospinodal generalization are equally demonstrated by the viscosity data as well as the light-scattering data.[10] The viscosity analysis may be recommended because of the facility of the measurement and its applicability even to the system in which the effect of multiple scattering plays an important role.

III. RESULTS AND DISCUSSION

It is worthwhile to attempt a more-general test of the homogeneity and scaling laws with the viscosity data. According to the initial approach of Green and co-workers,[12] the scaling relation takes a form

$$\begin{gathered}(x_2/x_{2c})^{\phi/2\nu}\eta = \eta_{id} |\Delta x_2^*|^{-\phi/\beta} g(X) , \\ X = \epsilon / |\Delta x_2^*|^{1/\beta} ,\end{gathered} \tag{6}$$

where $\Delta x_2^* = (x_2 - x_{2c})/x_{2c}$ and x_{2c} is the mole fraction at the critical concentration. A factor $(x_2/x_{2c})^{\phi/2\nu}$ has been introduced in Eq. (6) in order to account for a small assymmetry in the plots of $\ln(\eta/\eta_{id})$ vs x_2 as shown in Fig. 4. To investigate the assumption of Eq. (6), we calculated the dimensionless quantities $g(X)$ and plotted them as a function of X. In the limit $X \to \infty$, $g(X)$ should approach its asymptotic limit for the critical isochore $\ln g(\infty) = -0.039$. For $X \to 0$, $g(X)$ should approach the value for the critical isochore $\ln g(0) = 0$. The results obtained from systems of the isobutyric-acid–water, the 3-methylpentane-nitroethane, and the 2, 6-lutidine–water are presented in Fig. 5. The data adapted in Figs. 4(b) and 5 seem to be scattered a little. This is because the samples used for measurements were prepared in quite different ways and were of various concentration. Then it can hardly be expected that these data would be explained precisely in terms of the same critical temperature and the same critical concentration. Thus it may be said that these data seem to lie within the allowed precision of the present analysis. It should be noted that the analysis presented here is applicable to all temperatures above and below the critical temperature (the isobutyric-acid–water system) and also to a lower critical point as well as an upper critical point. Figure 5 demonstrates that the reduced shear viscosity data can be represented by a single-valued function $g(X)$ of the scaling parameter X.

Finally, it is remarkable that a simple scaled plot can be obtained when $\epsilon_{sp}/|\Delta x_2(sp)^*|^{1/\beta^+}$ is used instead of $\epsilon/|\Delta x_2^*|^{1/\beta}$ as X, as shown by the broken line in Fig. 5. The plot may be considered as a natural result from the proposed pseudospinodal generalization. In fact, Fig. 1 suggests that such a scaled plot will be already obtained by changing only the shift factors on the vertical or horizontal axis. Further extension to the shear viscosity of a polymer solution in the critical region seems to indicate again the validity of the pseudospinodal generalization.[8] For the general validity on the pseudospinodal generalization, however, it would be more desirable to determine the true spinodal curve by measurements on metastable states and to confirm whether the pseudospinodal curve agrees with the true spinodal one or not. As far as we know such studies have not been made.

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