Light Scattering and Pseudospinodal Curves: The Isobutyric-Acid-Water System in the Critical Region*

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Intensity and linewidth measurements of light scattered by the isobutyric acid in water system are reported for various equilibrium states in the critical neighborhood of the temperature-concentration diagram. By extrapolation of these data to zero scattering angle and then to (unrealized) states below the phase separation temperature one may determine a common "pseudospinodal curve" $T_{sp}(X)$ described by $T_c - T_{sp}(X) \sim |X - X_c|^{1/\beta^\dagger}$ where X is the concentration, and we find $\beta^\dagger \simeq 0.37 \pm 0.04$. As expected on the grounds of the homogeneity hypotheses, the value of $\beta^\dagger$ is essentially the same as the previously observed value of the exponent β for the coexistence curve. Empirical equations of the form $I_{C,0}^{-1} \propto [T - T_{sp}(X)]^\gamma$ and $D \propto [T - T_{sp}(X)]^{\gamma^*}$ are used to effect the extrapolations to determine $T_{sp}(X)$. Here $I_{C,0}$ and D are the extrapolated zero-angle scattering intensity and the diffusion coefficient, while γ and γ^* are corresponding critical exponents. We show theoretically, however, that a value $\beta^\dagger \neq \frac{1}{2}$ is inconsistent with the general validity of these empirical formulas, which should thus be discarded as over-all representations of the variations of D and $I_{C,0}$. A tentative test is made of a more general scaling equation for $I_{C,0}$ by a convenient plot. Moderate success is obtained. The measurements confirm the exponent values $\gamma = 1.24 \pm 0.03$ and $\gamma^* = 0.67 \pm 0.03$. The distinction between pseudospinodal curves, determined by extrapolation from stable thermodynamics states, and a true spinodal curve which (if it exists) can only be observed by measurements on metastable states, is emphasized.

1. INTRODUCTION

Recent developments in laser self-beating spectroscopy[1] have enabled us to study the transport properties and correlation effects of time-dependent concentration fluctuations of binary liquid mixtures in the neighborhood of the critical mixing point. In this paper we report extensions of the previous experiments[2-4] for the system isobutyric acid in water, including intensity and linewidth studies along the critical isotherm and on the coexistence curve. In addition, we present some considerations concerning the so-called "spinodal curve" of this system.

According to the Ornstein-Zernike and the Debye theory[5,6] of critical opalescence, the relative scattered intensity due to concentration fluctuations of a binary critical mixture is approximated by the relation

$$I_C \propto \left(\frac{C}{n}\frac{dn}{dC}\right)^2 \frac{T/T_c}{(T/T_c) - 1 + \frac{1}{6}K^2 l^2}, \quad (1)$$

in which C denotes the concentration and n is the index of refraction of the mixture. As usual T_c

is the critical mixing temperature, l is the Debye interaction parameter, while $K = (4\pi/\lambda)\sin(\frac{1}{2}\theta)$ where λ is the wavelength of light in the medium and θ is the scattering angle. Although the experimentally observed K^2 dependence of the scattered intensity is well represented by this formula, we do *not* find a linear relation between $\lim_{K \to 0} I_C^{-1}$ and $T - T_C$;[3,4] rather at the critical solution concentration we have

$$\lim_{K \to 0} I_C^{-1} = I_{C,0}^{-1}(T) = \left(\frac{\partial \mu}{\partial C}\right)_{P,T} = f(\tau - 1)^\gamma, \quad (2)$$

where μ is the chemical potential, while $\tau = T/T_c$, f is a constant related to the osmotic coefficient, and γ is the usual critical exponent. According to the classical theory, $\gamma = 1$, although it may be noted that Debye[5] himself used the van der Waals gas only as an example; in fact $\gamma \neq 1$ is not inconsistent with the K^2 dependence he predicted for critical mixtures.[6,7] We shall not employ the more general scattering formula introduced by Fisher,[6] which entails the extra exponent η to describe the K dependence at T_C, because within

the limits of our experiments, which do *not* include the most immediate neighborhood of the critical mixing point, we have found that $\eta \simeq 0$.

The linewidth Γ of quasielastically scattered light for critical mixtures has been predicted by Fixman[8] and Felderhof[9] to behave as

$$\Gamma \approx DK^2(1 + \tfrac{1}{6}K^2L^2), \tag{3}$$

where D is the diffusion coefficient and $L^2 \approx l^2/[(T/T_c) - 1]$. The previous experimental results[3,4] indicate that at the critical solution concentration one should more generally write

$$\Gamma \approx \alpha^*(\partial\mu/\partial C)_{P,T}K^2[1 + b\xi_\Gamma^2 K^2], \tag{4}$$

where

$$\lim_{K \to 0} \Gamma/K^2 = D(T) = \alpha^*(\partial\mu/\partial C)_{P,T} \approx d(\tau - 1)^{\gamma^*}, \tag{5}$$

in which α^* is a transport coefficient and the constants d, b, and γ^* can be determined by the experiments. As usual we may express the temperature dependence of the correlation lengths by the relations

$$\xi_\Gamma \propto (T - T_c)^{-\nu_\Gamma} \quad \text{and} \quad \xi_s \propto (T - T_c)^{-\nu_s},$$

where ν_Γ and ν_s are the corresponding exponents. The subscripts Γ and s denote determinations from linewidth and intensity studies, respectively. Although the correlation ranges ξ_Γ and $\xi_s[=(\tfrac{1}{6})^{1/2}L$ if $\nu_s = \tfrac{1}{2}]$ should have a similar physical meaning as well as the same order of magnitude, we have introduced the constant b in (4) to allow for possible differences in the apparent molecular interaction ranges between intensity and linewidth measurements should the situation demand it. In fact this additional complication turns out to be unnecessary because we have found that the molecular interaction ranges deduced from intensity and linewidth studies are quite comparable for binary liquid mixtures of small molecules even though there may be some difference between ν_s and ν_Γ.

2. SPINODAL AND PSEUDOSPINODAL CURVES

In order to describe the behavior of the thermal diffusivity with density and temperature for SF$_6$, Benedek[10] has recently proposed an extension of Eq. (5) by introducing the so-called "spinodal curve" which is generally supposed to represent the limits of stability of the metastable, uniform one-component phase. We have examined a futher extension of his formulas to the two-component system of isobutyric acid and water,[4] in an attempt to describe *both* the linewidth and the intensity measurements in the critical region. The proposed extended versions of (2) and (5) are simply

$$D(X, T) \approx d[\tau - \tau_{sp}(X)]^{\gamma^*} \tag{6}$$

$$\text{and} \quad I_{C,0}^{-1}(X, T) \approx f[\tau - \tau_{sp}(X)]^{\gamma}, \tag{7}$$

$$\text{where} \quad \tau_{sp}(X) = T_{sp}/T_c$$

is the reduced temperature on the assumed spinodal curve at mole fraction X of one component.

As shown below, analysis of our somewhat preliminary data does indeed seem to indicate that Eqs. (6) and (7) provide fair representations of the available experimental facts. However, a closer theoretical examination reveals that such a postulated form may imply stringent and unrealistic restrictions on the equation of state. If indeed the spinodal curve exists we may suppose it has the form

$$T_c - T_{sp}(X) \approx A|X - X_c|^{1/\beta^\dagger} \tag{8}$$

as $X \to X_c$, where A is a constant and we have introduced the exponent $\beta^\dagger$ in the event that $\beta^\dagger$ is not equal to β, the corresponding exponent describing the coexistence curve. Then the expression (7) for the reciprocal zero-angle intensity may be transformed to

$$I_{C,0}^{-1}(X, T) \approx (f/T_c^\gamma)(T - T_c + T_c - T_{sp})^\gamma$$

$$\approx (f/T_c^\gamma)[(T - T_c) + A|X - X_c|^{1/\beta^\dagger}]^\gamma. \tag{9}$$

Now let us consider the expansion of $I_{C,0}^{-1}(X, T)$ in powers of $(X - X_c)$ at some fixed temperature in the single-phase equilibrium system *above* $T_c (\Delta T = T - T_c > 0)$. We evidently have from (9) the result

$$\frac{1}{I_{C,0}(X, T)} \approx \frac{f}{T_c^\gamma}(\Delta T)^\gamma \left(1 + \frac{A}{\Delta T}|X - X_c|^{1/\beta^\dagger}\right)^\gamma$$

$$= \frac{f}{T_c^\gamma}(\Delta T)^\gamma \left(1 + \frac{A\gamma}{\Delta T}|X - X_c|^{1/\beta^\dagger} + \cdots\right). \tag{10}$$

Now on very general grounds we expect the function $I_{C,0}(X, T)$ (and hence its reciprocal) to vary perfectly smoothly, and indeed even analytically, with the concentration difference $X - X_c$ at finite positive $T - T_c$.[11] In particular, $I_{C,0}(X, T)$ should have a Taylor series expansion in powers of $X - X_c$ above T_c (which would be at least asymptotic[11]). It follows from (10) that $\beta^\dagger$ should have

a value equal to the reciprocal of an even integer such as $\frac{1}{2}$ or $\frac{1}{4}$. Indeed $\beta^\dagger$ should really be equal to $\frac{1}{2}$, since a smaller value, such as $\beta^\dagger = \frac{1}{4}$, would imply that the quadratic term in $X - X_c$ should vanish identically leaving only a quartic term. This is most implausible[11]; in principal, this point could be checked experimentally by making measurements above T_c at a number of concentrations close to X_c. In practice, of course, it is difficult to vary the mole fractions in controlled small increments at constant temperature.[12]

The above considerations regarding the value of $\beta^\dagger$ apply equally to the diffusion coefficient, and to the thermal diffusivity in a one-component system.[13] Indeed for SF_6 Benedek did estimate $\beta^\dagger$ to be about $\frac{1}{2}$. On the other hand, from the viewpoint of the homogeneity or scaling hypotheses[14,15,7] we should certainly expect that, if a spinodal curve exists, it is described by $\beta^\dagger = \beta$.[16] For the isobutyric-acid–water (IBW) system we know that β is rather close to $\frac{1}{3}$,[3] and our own data, if extrapolated at fixed X using (6) and (7), yield $\beta^\dagger \simeq \beta$ (see below). As demonstrated above, a value $\beta^\dagger \simeq \frac{1}{3}$ implies through Eqs. (6) and (7) a nonsmooth and nonanalytic variation of $I_{C,0}(X, T)$ and $D(X, T)$ above T_c. (Specifically, the fourth derivative would be divergent or discontinuous at $X = X_c$.) This is unacceptable[11] and we conclude that (6) and (7) are inconsistent with a "spinodal curve" having an exponent $\beta^\dagger$ close to $\frac{1}{3}$. (In any event, the opposite conclusion would be sufficiently startling that much stronger evidence than direct numerical fits to these equations would be needed to support it.) Conversely if we found $\beta^\dagger = \frac{1}{2}$ at the same time as $\beta = \frac{1}{3}$, Eqs. (6) and (7) would be satisfactory as regards smoothness and analyticity but the implications regarding the homogeneity and scaling hypotheses would be rather drastic.

Finally, we note that our whole discussion so far has concerned *stable* homogeneous equilibrium states and the *extrapolation* of their properties, via. Eqs. (6) and (7), into regions of the phase diagram where the stable thermodynamic state is one of inhomogeneous two-phase equilibrium. A true spinodal curve, on the other hand, as contemplated by van der Waals and his school, relates to an actual *metastable* homogeneous extension of the single-phase equilibrium states beyond the point where, in complete equilibrium, phase separation should have taken place. In a one-component system, it is traditionally supposed that as such a metastable isotherm or isochore is followed, the compressibility will increase until it becomes infinite at some point which then locates the spinodal curve. An infinity of the compressibility implies mechanical instability and further prolongation of the isotherm or isochore would necessarily result in immediate collapse into separated phases. In

the case of a two-component system, $(\partial \mu / \partial C)_{P, T}$ would become infinite on the spinodal curve and material instability (i. e., chemical phase separation) is implied. Now the ease of producing a homogeneous metastable state varies from system to system although reproducible metastable states seem difficult to generate near critical points. But, in any case, it is by no means obvious that a metastable isotherm or isochore even when experimentally realized, need approach a point of over-all mechanical or material instability. On the contrary it seems not improbable, in view of present knowledge of nucleation phenomena, that the lifetime for the decay of the metastable state through a local inhomogeneous process or homogeneous fluctuation, will decrease rapidly to unobservable, sublaboratory times at a point on the (average) isotherm or isochore where the compressibility [or $(\partial \mu / \partial C)_{P, T}]$ is still quite finite. If this is indeed the case the spinodal curve could not be observed (and its definition would be purely a matter of convention).

Experiments designed to investigate these points by attempting to realize metastable states near a spinodal curve, are certainly worthwhile. We wish to stress, however, that to our knowledge such studies of metastable states near a critical point have not been made. In the present experiments (and those of Benedek[10]) only equilibrium states have been observed; phase separation always took place below the appropriate temperature $T_p(X)$. Accordingly, it would be preferable to call the locus $T_{sp}(X)$ determined by extrapolation of equilibrium data below $T_p(X)$ using Eqs. (6) and (7), a "pseudospinodal" curve. Such a terminology does not prejudice the question of the existence of a true spinodal curve. Equally if a true spinodal curve does exist, its identity or nonidentity with the extrapolated form is not taken for granted. More generally one might consider extrapolations using postulated equations with more satisfactory analytic features such as might be generated by scaling and homogeneity analyses.[12,14,15,17] In general, different pseudospinodal curves might be found depending on the property studied and on the assumed equation. It is clear, however, to reiterate, that measurements of equilibrium states such as ours and Benedek's cannot answer questions about the true spinodal curve.

3. EXPERIMENTAL

The system, isobutyric acid and water, was selected for study because the coexistence curve $T_p(X)$ had been determined previously[3] and light scattering experiments had already been performed at two different concentrations.[2-4] The isobutyric acid (IB) (Fisher certified reagent

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grade) was purified by preparative gas chroma-tography and then fractionally distilled. De-ionized and doubly distilled water was used as the second component. The intensity of scat-tered light was measured in two photometers with different optical geometry and at two dif-ferent wavelengths, $\lambda_0 = 435.8$ nm and 632.8 nm. Measurements at the Hg line were carried out in the photometer[18] with an angular range ex-tending from $11°$ to $140°$. The temperature of the sample cell could be controlled to within $0.001°$.

Both scattered intensity and quasielastic Ray-leigh linewidth measurements were made at the 632.8 nm wavelength using the laser homodyne self-beating spectrometer which has been de-scribed elsewhere.[2] In most of the present work, we have used a dc excited laser with an output power of $20-25$ mW. Our spectra were obtained either with a General Radio 1900A wave analyzer with a low pass filter, or with a spectrum analy-zer using a Varian C-1024 time averaging com-puter.

4. TREATMENT OF DATA

The experimental data were handled as follows: All intensity readings were corrected for densi-ty, dust, and attenuation and then related to a scattering standard (Cornell 60) in order to com-pare our results from different samples in the presence of slight changes of the incident light intensity from day to day. We were not able, however, to compare scattered intensities mea-sured in different photometers at different wave-lengths directly, except by superimposition of the scattering curves using K as the appropriate variable. For a given temperature and concen-tration, we first extrapolated each set of inten-sities or linewidths to zero scattering angle. De-tails concerning this procedure have been given in previous work.[2-4]

We shall analyze the data first by assuming that Eqs. (6) and (7) are valid, since these equa-tions provide a way of determining $\beta^\dagger$. Fig. 1(a) shows a plot of the zero-angle extrapolated recip-rocal scattered intensity $I_{C,0}^{-1}$ versus the tem-perature distance from the phase separation temperature T_p. The measured points can be represented by the equation

$$I_{C,0}^{-1} = f[(T/T_p) - 1 + t_s]^\gamma , \tag{11}$$

in which the constants may be determined either graphically, or numerically by a least-squares method. The data taken at $\lambda_0 = 632.8$ nm together with results from $\lambda_0 = 435.8$ nm and at other con-centrations are summarized in Table I. In Fig. 1(b) a similar plot shows the temperature de-pendence of D as fitted to the formula

$$D = \lim_{K \to 0} \Gamma/K^2 = d[(T/T_p) - 1 + t_\Gamma]^{\gamma *} , \tag{12}$$

where the appropriate parameters d, $\gamma *$, and t_Γ are also presented in Table I.

First, we may note that the fitted exponents γ and $\gamma *$ do remain relatively constant with chang-ing concentration. Second, although the tem-perature dependence of the reciprocal intensity $I_{C,0}^{-1}$ and the diffusion coefficient D differ con-siderably $(\gamma * \neq \gamma)$, Figs. 1(a) and 1(b) demon-
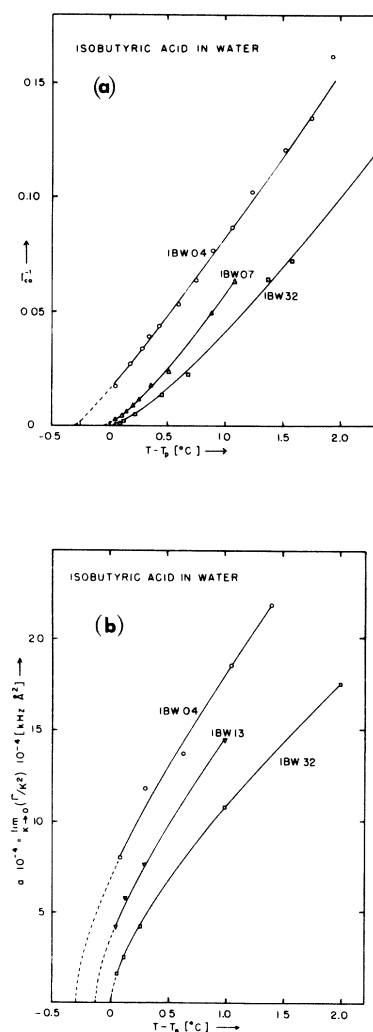

FIG. 1. (a) Reciprocal scattered intensity extrapolated to zero angle for isobutyric acid in water versus $T - T_p$. The curves represent functions of the form $I_{C,0}^{-1}$ $= f[(T/T_p) - 1 + t_s]^\gamma$ with the parameters listed in Table I. (b) Plot of $a = \lim_{K \to 0} \Gamma/K^2$ as a function of $T - T_p$. The curves represent functions of the form $a = d[(T/T_p) - 1 + t_\Gamma]^{\gamma *}$ with the parameters listed in Table I.

TABLE I. Values of $T_p - T_{sp}$, the exponents γ and γ^*, and the coefficient d [see Eqs. (11) and (12)].

Sample IBW	Mole fraction IB acid	$t_s \cdot T_p$ [°C]	γ	$d \times 10^{-6}$ [kHz Å²]	$t_\Gamma \cdot T_p$ [°C]	γ^*
04	0.0906	0.30	1.2_6	6.8_5	0.30	0.6_7
05	0.0966	0.12				
07	0.102	0.045	1.3_0			
32	0.114	~ 0	1.24	4.8_2	~ 0	0.68
12	0.130_9	0.045				
13	0.140_5	0.13_3	1.2_7	6.0	0.13_3	0.6_7
25	0.161_5	0.45	>1.1			

strate that, to within the limits of error of our measurements, an extrapolation of *either* curve at a given concentration intersects the temperature axis at the *same* point. In other words, we observe that $t_s = t_\Gamma$. This is remarkable since, as noted above, one might well have expected different pseudospinodal curves to characterize the intensity and the diffusion coefficient. In any event since for a given concentration the extrapolated values of t_s and t_Γ coincide to within a fairly small experimental error, we can construct the pseudospinodal curve explicitly by subtracting $T_p t_s$ or $T_p t_\Gamma$ from the phase separation temperature $T_p(X)$. [Again it should be emphasized that this construction rests on the assumed empirical formulas (6) and (7) and need not tell us anything about any true spinodal curve.] In order to characterize the shape of the pseudospinodal curve in the neighborhood of the critical mixing point we employed a logarithmic plot of the temperature differences

$$\Delta T_{sp} = (T_c - T_p) + |t_{s,\Gamma}| T_p$$

versus concentration differences. A relation of the form

$$\Delta T_{sp} \propto (X_2' - X_2'')^{1/\beta^\dagger}, \tag{13}$$

where X_2 represents the mole fraction of the second component of the binary system, could be fitted by a least-squares calculation with $1/\beta^\dagger = 2.7 \pm 0.3$. (The superscript primes and double primes refer to the right and the left half of the region under the coexistence curve.) In Fig. 2 the dashed curve represents a fit of our extrapolated points by Eq. (13) assuming, for convenience, $1/\beta^\dagger$ to be 3. The concentration differences can also be expressed in terms of $X_2' - X_c$, and $X_2'' - X_c$ corresponding to two branches of one curve; one finds only slightly different coefficients on each side of the critical mixing point. The solid line represents the coexistence curve as the best fit of the experimental studies reported in a previous paper.[3] These measurements are only preliminary and bear an uncertainty of about 5% in

the exponents and 0.03–0.05° in the temperature constants for $t_s T_p$ and $t_\Gamma T_p$.

We have previously reported intensity and linewidth studies at the critical solution concentration[3] and at one additional concentration.[4] Now we will discuss measurements along the critical isotherm. A plot of the reciprocal scattered intensity extrapolated to zero angle at the critical temperature versus the molar concentration X_2 of IB is shown in Fig. 3(a) and a similar plot of $D = \lim_{K \to 0} \Gamma / K^2$ versus X_2 is in Fig. 3(b). The reciprocal scattered intensity extrapolated to zero angle was found to be approximately proportional to $(X_2' - X_2'')^{2.85}$ along the critical isotherm. Although we have not explicitly corrected the intensity
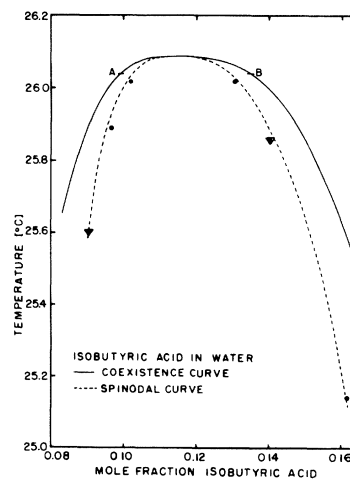
FIG. 2. Coexistence and pseudospinodal curves for the system isobutyric acid and water. The solid curve represents earlier phase-separation-temperature determinations (Ref. 3) and has the form $\Delta T = 10^3 |X_2' - X_2''|^3$ °C. Dashed curve is the pseudospinodal curve of the form $\Delta T_{sp} = 2.3_7 \times 10^3 |X_2' - X_2''|^3$ °C and connects the experimental points obtained by extrapolation of intensity (filled circles) or linewidth (triangles) measurements.

values for the concentration dependence of the refractive index, we estimate that the appropriate correction of the exponent would be less than 10–15% i.e., about ±0.40, by using Eq. (1) and the Lorentz-Lorenz relation. A similar treatment of our linewidth data in Fig. 3(b) gives approximately $D \propto (X_2' - X_2'')^{1.75}$ In linewidth studies along the critical isotherm corrections due to the concentration dependence of the refractive index become less important. Points A and B in Fig. 2 indicate the location of the addi-

tional linewidth experiments made with a sample (IBW 32) at the critical solution concentration but below its critical solution temperature. These linewidth results were found to be consistent with our usual measurements in which we approached the phase separation temperatures from higher temperatures at fixed concentrations.

5. RESULTS AND DISCUSSION

Now along the critical isotherm, $T = T_c$, the analog of Eq. (9) for D has the form

$$D = (d/T_c^{\gamma^*})(X_2' - X_2'')^{\gamma^*/\beta^\dagger} .$$

More generally from a homogeneity or scaling assumption we would similarly find that

$$D \propto (X_2' - X_2'')^{\gamma^*/\beta^\dagger}, \quad (T = T_c). \tag{14}$$

With the observed values $\gamma^* \simeq 0.67$, and $1/\beta^\dagger \simeq 2.7$, we find $\gamma^*/\beta^\dagger \simeq 1.8$ which compares quite favorably with the directly determined exponent of 1.75 indicated in Fig. 3(b). This is evidence in favor of the scaling of the diffusion coefficient $D(X, T)$. Similarly, we can obtain a relation for the extrapolated zero-angle scattered intensity. Assuming that the exponent γ remains fixed in Eq. (9) and that changes in the coefficient f are relatively small, one concludes that along the critical isotherm one should have

$$I_{C,0}^{-1} \propto (X_2' - X_2'')^{\gamma/\beta^\dagger}, \quad (T = T_c). \tag{15}$$

Again this result follows much more generally from the usual homogeneity or scaling assumptions for $I_{C,0}(X, T)$.[7] Indeed in standard notation, and with $\beta^\dagger = \beta$, this result simply expresses Widom's exponent relation $\delta - 1 = \gamma/\beta$.[7,14] Now with the observed values $\gamma \simeq 1.24$ and $1/\beta^\dagger \simeq 2.7$ [see Table I] we find $\gamma/\beta^\dagger \simeq 3.3$, a value somewhat higher than the value 2.85 estimated directly from the data shown in Fig. 3(a). (The lower limit $1/\beta^\dagger \geq 2.4$ gives $\gamma/\beta^\dagger \geq 2.98$.) In view of the lack of corrections for the variation of refractive index and the relatively large value of the exponent, we do not regard this discrepancy as significant. We do, however, have reasonable confidence in the precision of the experimentally determined values of γ and γ^*.

The linewidth measurements on the coexistence curve have been made by approaching the phase separation temperatures from the homogeneous region (as indicated in Fig. 1) and also by making measurements below the phase separation temperature in the two-phase region. Points A and B in
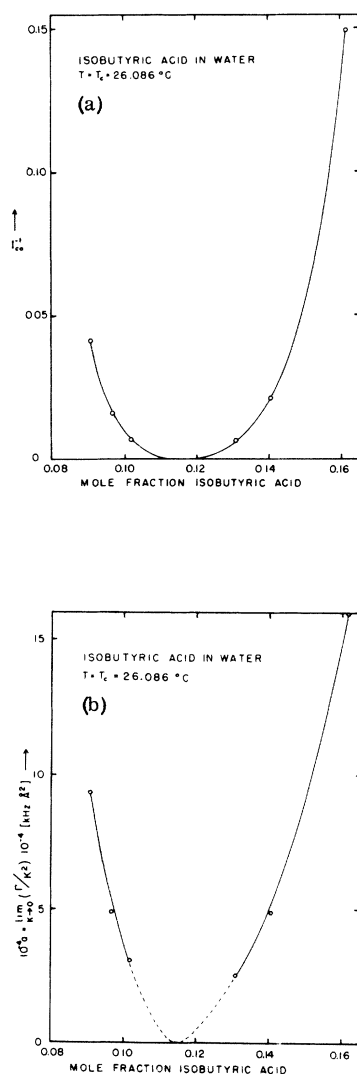

FIG. 3. (a) Zero-angle reciprocal scattered intensity $I_{C,0}^{-1}$ at the critical isotherm as a function of concentration. (b) Plot of $a = \lim_{K \to 0} \Gamma/K^2$ at the critical isotherm as a function of concentration.

Fig. 2 gave an observed D of about 3.2×10^4 kHz Å^2. Alternatively, D may be computed from Eq. (6) with the result

$$D = 1.3_2 \times 10^5 (T_p - T_{sp})^{\gamma^*} \simeq 2.8 \times 10^4 \text{ kHz Å}^2.$$

The agreement is surprisingly good in view of the small temperature distances between ΔT_{sp} and ΔT. For the IBW-13 sample with $T_p - T_{sp} = 0.133°$ (Table I), we obtain a computed D at T_p of

$$D = 1.3_2 \times 10^5 (0.133)^{0.67} \simeq 3.4 \times 10^4 \text{ kHz Å}^2,$$

which also agrees well with the measured D of 3.4×10^4 kHz Å^2 [as shown in Fig. 1(b)]. We remark that we have used T/T_p as the reduced temperature in the equations because, experimentally, we can determine the phase separation temperature of the sample under investigation more precisely (to within $0.001°$) than the deviation from the critical solution temperature (which is only observable directly for $X = X_c$).

The previous measurements on the coexistence curve and the above analysis based on Eqs. (6) and (7) indicate that $\beta \geq \frac{1}{3}$ and $\beta^\dagger > \frac{1}{3}$, although within the error limits of our experiments it is still possible to maintain that $\beta^\dagger = \frac{1}{3}$. We are, however, inclined to believe that both β and $\beta^\dagger$ are some 10% larger than $\frac{1}{3}$. Nevertheless, if we accept Eqs. (6) and (7) as valid for the determination of the pseudospinodal curve and thence of $\beta^\dagger$, there is no doubt that $\beta^\dagger$ (like β) is less than $\frac{1}{2}$. Conversely, as our data have unambiguously led us to $\beta^\dagger \simeq \frac{1}{3}$, it follows from the arguments developed in Sec. 2 that we should discard Eqs. (6) and (7) as a complete representation of the critical opalescence in the homogeneous phase, since even though our present measurements have not been sufficiently extensive or precise to demonstrate the inconsistency directly, the implications regarding the behavior across $X = X_c$ for $T > T_c$ are not acceptable.[11,12]

It is worthwhile to attempt, tentatively, a more general test of the homogeneity and scaling laws with our data. If we follow the initial approach of Green and co-workers[15] we might plot $I_{C,0}^{-1}/ (\tau - 1)^\gamma$ versus $(X - X_c)/(\tau-1)^\beta X_c$. Then the scaling relation takes the form[7]

$$I_{C,0}^{-1} = (\tau - 1)^\gamma Y^\pm [(X - X_c)/|\tau - 1|^\beta X_c], \qquad (16)$$

where the two branches $Y^+(w)$ and $Y^-(w)$ have to match as their argument $w = (X - X_c)/|\tau - 1|^\beta X_c$ approaches infinity, or, in other words as the critical temperature is approached $(\tau \to 1)$ at fixed $X \neq X_c$. An alternative approach, which avoids separate branches joined only at $w = \infty$, is to write

$$I_{C,0}^{-1} = \Delta x^{\gamma/\beta} W[(\tau - 1)/\Delta x^{1/\beta}] \qquad (17)$$

with $\Delta x = (X - X_c)/X_c$. We may then plot, say,

$$S = \frac{aI_{C,0}^{-1}}{aI_{C,0}^{-1} + \Delta x^{\gamma/\beta}} \quad \text{versus} \quad U = \frac{\tau - 1}{\tau - 1 + \Delta x^{\gamma/\beta}}, \qquad (18)$$

where a is some conveniently chosen constant. Such a plot is shown in Fig. 4. The critical isochore $(\Delta x = 0, \ T > T_c)$ will now be represented by the point $(1, 1)$ in the (S, U) plane. The point at $U = 0$ represents the critical isotherm while the coexistence curve corresponds to the point $U = U_{min}$. Superimposition of the values of $I_{C,0}^{-1}$ at different compositons for $X \leq X_c$ could be accomplished with a reasonable degree of precision by assuming, for simplicity, the values $\gamma = \frac{5}{4}$ and $\beta = \frac{1}{3}$. [Since only relative intensities are available at each concentration the constant a in (18) had to be treated as an adjustable parameter.] As evident from Fig. 4, however, the data for $X > X_c$ (in particular, the squares denoting the 13.09% IB solution) do not appear to scale well with the same values of γ and β. We have not investigated this point more closely; it may be associated with the slope of the rectilinear diameter of the coexistence curve and consequent asymmetry, as visible in Fig. 2. For a more stringent test of the scaling hypothesis it would be desirable to have more extensive data particularly for concentrations closer to critical. By the same token the nine observations made in the linewidth studies are insufficient for even a rough test of the corresponding scaling hypothesis

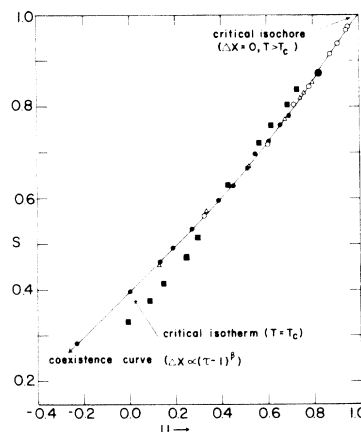$$D(X, T) = \Delta x^{\gamma^*/\beta} Z[(\tau - 1)/\Delta x^{1/\beta}]. \qquad (19)$$

FIG. 4. A scaling plot of the scattering intensity in terms of the variables $S = S(I_{C,0}, X)$ and $U = U(X, T)$ as defined in Eq. (18). The values $\gamma = \frac{5}{4}$ and $\beta = \frac{1}{3}$ have been assumed. Filled circles, hollow triangles, hollow circles, and filled squares represent 9.06, 9.66, 10.2, and 13.09 mole % of isobutyric acid in water, respectively.

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[1]N. C. Ford, Jr., and G. B. Benedek, Phys. Rev. Letters 15, 649 (1965).

[2]B. Chu, Phys. Rev. Letters 18, 200 (1967); J. Chem. Phys. 47, 3816 (1967).

[3]B. Chu, F. J. Schoenes, and W. P. Kao, J. Am. Chem. Soc., 90, 3042 (1968).

[4]B. Chu and F. J. Schoenes, Phys. Rev. Letters 21, 6 (1968).

[5]L. S. Ornstein and F. Zernike, Physik. Z. 19, 134 (1918); 27, 761 (1926); P. Debye, in Non-Crystalline Solids, edited by V. D. Frechette (John Wiley & Sons, Inc., New York, 1960); J. Chem. Phys. 31, 680 (1959); see also B. Chu, Molecular Forces; Based on the Baker Lectures of Peter J. W. Debye (John Wiley & Sons, Inc., New York, 1967).

[6]M. E. Fisher, J. Math. Phys. 5, 944 (1964).

[7]M. E. Fisher, Rept. Progr. Phys. 30, 615 (1967).

[8]M. Fixman, Pontifica Academia Scientiarum Scripta Varia 31 on the Molecular Forces (Pontifical Academy of Science, Vatican City, Italy, 1966), p. 329.

[9]B. U. Felderhof, J. Chem. Phys. 44, 602 (1966).

[10]This so-called spinodal line has been studied for SF_6 by G. B. Benedek, in Polarisation Matiè et Rayonnement, Livre de Jubilé en l'honneur du Professeur A. Kastler (Presses Universitaires de Paris, France, 1968).

[11]The principal point at issue here is the existence (i.e., finiteness) of, say, the first four or five derivatives of $I_{C,0}(X, T)$ with respect to X or equivalently via (2), of the first six or seven derivatives of the free energy with respect to concentration. In the case of a lattice model of a binary solution (see, e.g., the review Ref. 7) these derivatives can be constructed explicitly for $X = X_c$ as power series in $1/T$ and are found to be well-defined and finite. Furthermore, as regards the even derivatives, they are nonvanishing. Such series have been rigorously proved convergent and, in addition, the analyticity of the free energy in X (as well as in T for sufficiently high T) has been strictly proved: See G. Gallavotti, S. Miracle-Sole, and D. W. Robinson, Phys. Letters 25A, 493 (1967); J. L. Lebowitz and O. Penrose, Commun. Math. Phys. 11, 99 (1968); and the review: J. L. Lebowitz, Ann. Rev. Phys. Chem. 19, 389 (1968). There is very little reason to doubt the existence of the derivatives for more realistic continuum systems. This is so even if some subtle, infinite-order essential singularity existed along $X \approx X_c$ above T_c, as sometimes suggested [see M. E. Fisher, Physics 3, 255 (1967)]; in such a case the corresponding Taylor series would only be an asymptotic expansion. Of course, all the standard approximations like the van der Waals equation, the Bethe-Guggenheim approximation, and other models like the spherical model (see, e.g., Ref. 7) lead to complete analyticity above T_c.

[12]On the other hand, in the case of a magnetic system the corresponding measurements, i.e., varying the magnetic field and hence the magnetization, continuously at fixed $T > T_c$, are straightforward and the existence and nonvanishing of the derivatives is readily confirmed: see, e.g., J. S. Kouvel and J. B. Comly, Phys. Rev. Letters 20, 1237 (1968); J. T. Ho and J. D. Litster, ibid. 22, 603 (1969); J. Appl. Phys. 40, 1270 (1969).

[13]Although from a fully rigorous statistical mechanical standpoint even the existence of such transport coefficients, let alone their differentiability, is very hard to prove. Nevertheless an experimental check on the existence of the derivatives at X_c is still possible.

[14]B. Widom, J. Chem. Phys. 43, 3898 (1965).

[15]M. Vicentini-Missoni, J. M. H. Levelt-Sengers, and M. S. Green, Phys. Rev. Letters 18, 1113 (1967); 22, 389 (1969).

[16]This result, of course, is consistent with a van der Waals treatment (in which $\beta^\dagger = \beta = \frac{1}{2}$). It is also a feature of the analysis of B. W. Davis and O. K. Rice, J. Chem. Phys. 47, 5043 (1967), which allows the possibility $\beta^\dagger = \beta = \frac{1}{3}$. Their analysis, however, is open to the strong objection that it assumes power series expansions about the critical point itself.

[17]See also B. Josephson Proc. Phys. Soc. (London) (to be published); P. Schofield, Phys. Rev. Letters 22, 606 (1969).

[18]B. Chu, Rev. Sci. Instr. 35, 1201 (1964).