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INTERDIFFUSION COEFFICIENT AND DYNAMIC VISCOSITY FOR THE MIXTURE 2,6-LUTIDINE + WATER NEAR THE LOWER CONSOLUTE POINT

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The mixture, 2,6-lutidine + water has a lower consolute point at a temperature of 33.9°C and a lutidine concentration of 2.78 M. The interdiffusion coefficient of this mixture was measured over a wide range of concentrations along the isotherms at 25.00°C and 33.00°C, and over a wide range of temperatures along the critical isopleth. Critical slowing down of diffusion was evident along all three paths. The dynamic viscosity was measured along the isotherm at 25.00°C and along the critical isopleth at temperatures below critical. Along the critical isopleth, the viscosity increased rapidly as the critical temperature was approached. These data are discussed in terms of the cross-over function theory, which is used to connect divergent data near the critical point to smoothly varying data away from the critical point.

Keywords: Diffusion; viscosity; density; diaphragm cell; critical slowing down

1. INTRODUCTION

Two-component immiscible liquid mixtures at atmospheric pressure often have phase diagrams containing a liquid–liquid critical point (consolute point). Sufficiently far away from the critical temperature, the meniscus separating the two liquid phases disappears, and the components become miscible in all proportions. Indeed, there are over a thousand pairs which become miscible above an upper consolute temperature and over a hundred which become miscible below a lower

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consolute temperature [1, 2]. In the one-phase region, the equilibrium thermodynamic, as well as the transport properties, of the mixture are smooth functions of temperature and composition. Sufficiently close to the consolute point, however, certain of these properties display divergent characteristics [3–7]. Although power series developments [8], combining the smooth behavior with the divergent behavior exist, they converge only slowly [9]. A better description can be achieved with a “cross-over” function, which away from the consolute point produces a smooth variation, called the background term, while close to the consolute point produces a divergence, called the critical enhancement [7, 10–18]. Under the usual condition of constant atmospheric pressure, the critical enhancement is a generalized homogeneous function [19] of temperature and composition. The values of the exponents of the temperature and composition variables in this function are universal and can be calculated theoretically on the basis of the 3-dimensional Ising model [18].

In the case of the interdiffusion coefficient, both the background and critical enhancement are proportional to powers of the concentration derivative of the difference in chemical potentials of the two components [20]. Because this derivative goes to zero at the consolute point, both contributions to the interdiffusion coefficient also go to zero there. This behavior has been predicted theoretically, [21–23] and has been demonstrated experimentally in the case of both upper and lower consolute points [24–29]. While Cussler has reviewed early, analytic forms for cross-over functions [30], Sengers and collaborators, [10–16] and Kiselev and collaborators [17, 18] have described improved forms which combine analytic with non-analytic behavior.

In order to calibrate and test the mathematical form to be assumed for a diffusion coefficient cross-over function, diffusion measurements along more than one thermodynamic path are desirable. The most convenient paths from an experimental point of view are: (1) a path with temperature varying and the composition fixed at the critical value (the critical isopleth) and (2) paths with temperature fixed near critical and composition varying (isotherms). Loven and Rice [31] reported that 2,6-lutidine + water has a lower consolute temperature at 33.93°C, and we have confirmed this value. Below, we report interdiffusion data for 2,6-lutidine + water along the critical isopleth and along isotherms at 25.00°C and 33.00°C.

Complete specification of the cross-over function, however, requires also information concerning the viscosity of the mixture [18,20]. Viscosity data taken along the critical isopleth and isotherms at 26.969°C, 29.969°C, and 33.839°C have been collected by Stein *et al.* [32]. We have confirmed their results for the critical isopleth and report here in addition a few observations taken along the isotherm at 25.00°C. We have also found that the data of Stein *et al.* [32] can be readily extrapolated to match our own at 25.00°C.

2. DETERMINATION OF THE CONSOLUTE POINT

The phase diagram of 2,6-lutidine + H₂O has been investigated by Andon and Cox [33]. The diagram is an oval with an upper consolute point, a wide miscibility gap and a lower consolute point at a composition of 28.7 weight % lutidine and a temperature 33.93°C. Our own repeat determination of the lower consolute temperature, which is in good agreement with that of Loven and Rice [31], is shown in Figure 1. Since in measuring diffusion coefficients [34], it is customary to give the concentration in moles L^{-1} , we have used the molar concentration, c , on the abscissa of our phase diagram. The lower consolute point in Figure 1 occurs at a lutidine concentration of 2.78 M and a temperature of 33.9°C.

3. MEASUREMENT OF THE INTERDIFFUSION COEFFICIENT

3.1. Theory of the Diaphragm Cell

The interdiffusion coefficients of solutions of 2,6-lutidine in water were determined using standard, Stokes' design diaphragm cells [34, 35]. A Stokes' cell consists of two-well stirred compartments containing solutions of different composition on opposite sides of a membrane, which is made from a sintered glass disk. The stirring guarantees that the contents of each compartment are uniform, so that mixing is limited to transport through the frit. Because molecular diameters are small as compared to the size of the interstitial spaces between the

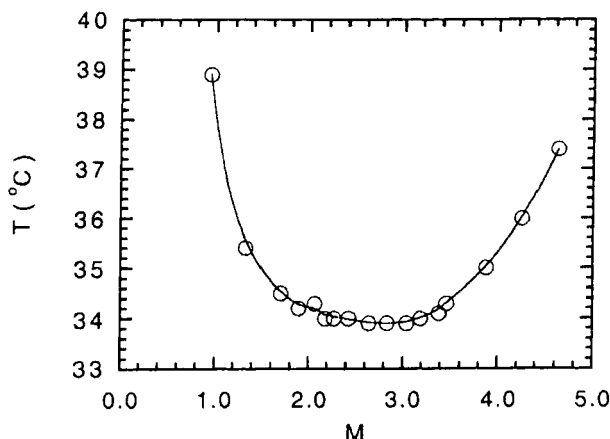


FIGURE 1 Coexistence curve for 2,6-lutidine + water near the lower consolute point. Displayed on the abscissa is the lutidine concentration in moles per liter, M .

sintered glass beads, the diffusive transport within the frit is the same as in bulk solution.

In the absence of a significant volume change upon mixing of the two components, the center of volume within the frit is fixed with respect to the laboratory. Thus, diffusion through the frit can be referred to volume-fixed coordinates. In this reference frame, a two-component solution has but one diffusion coefficient [36].

The diaphragm cell is a relative device, since it involves a cell constant which must be calibrated by analyzing data for a solution whose diffusion coefficient is already known. Once calibrated, however, the cell may be used to determine an unknown diffusion coefficient by following the time relaxation of the concentration difference across the frit. Let t be the time and $c_1(t)$ and $c_2(t)$ be the molar concentrations of one of the components below and above the frit, respectively. If the solution volumes below and above the frit are equal, then the arithmetic mean concentration

$$\bar{c} = \frac{1}{2}(c_1(0) + c_2(0)) = \frac{1}{2}(c_1(t) + c_2(t)) \quad (1)$$

is time-invariant, where $c_1(0)$ and $c_2(0)$ are initial values [37, 38]. In general, the interdiffusion coefficient in a two-component system, $D(c)$,

can be expected to be a function of the concentration, c . In such case, the concentration difference,

$$\Delta c(t) = c_1(t) - c_2(t) \quad (2)$$

and the time are related by

$$t = \frac{1}{\beta D'} \ln \left(\frac{\Delta c(0)}{\Delta c(t)} \right) \quad (3)$$

where $\Delta c(0)$ is the initial value of $\Delta c(t)$. In Eq. (3), β is the cell constant defined by

$$\beta = 2A/\ell V \quad (4)$$

where V is the solution volume of a compartment, and A and ℓ are the cross sectional area and effective thickness of the frit, respectively. The "integral" diffusion coefficient, D' , in Eq. (3) can be represented as a convergent sum of functions of $y = \Delta c(0)/\Delta c(t)$. To lowest order, one has

$$\frac{1}{D'} = \frac{1}{D(\bar{c})} + K f(y) \quad (5)$$

where

$$f(y) = [(y^{-2} - 1)/\ln y](\Delta c(0))^2 \quad (6)$$

and $D(\bar{c})$ is $D(c)$ (the "differential" diffusion coefficient) evaluated at $c = \bar{c}$. The coefficient, K , depends upon both $D(\bar{c})$ and its second derivative [29, 39].

3.2. Diaphragm Cell Calibration

Seven Stokes diaphragm cells with disks sintered from 10 to 16 μm diameter glass beads were operated with equal volumes above and below the frit and with stirring at a rate of 1 Hz in thermostated baths. Each cell constant was calibrated with aqueous KCl at 25.00°C. Initial KCl concentrations for each run were $c_1(0) \approx 0.5 \text{ M}$ and $c_2(0) = 0$. The final values of $c_2(t)$ were determined using a calibrated Radiometer

(Copenhagen) Model CDM 83 conductivity meter, while the final values of $c_1(t)$ were determined by solving Eq. (1) with $\bar{c} = 0.25$ M. The time was measured with an electronic timer. With $D' = 1.840 \times 10^{-5}$ $\text{cm}^2 \text{s}^{-1}$ [40], the value of β was evaluated using Eq. (3). The calibration results are summarized in Table I.

3.3. Techniques for the Measurement of Concentration and Temperature

Each diaphragm cell determination of D' for 2,6-lutidine + water using Eq. (3) required a run lasting approximately four days. Made uncertain only by the aggregate time required to start and stop the experiment, the elapsed time of a run could be measured with the electronic timer to an accuracy of approximately 10 s. The concentrations, $c_1(0)$ and $c_2(0)$, were determined by weighing. The final concentration in the top compartment, $c_2(t)$, was determined by sampling and density measurement using pycnometry, while the bottom concentration was evaluated using Eq. (1).

The temperature during a run was maintained constant using well insulated water baths held isothermal to $\pm 0.001^\circ\text{C}$ using a Philadelphia Thermometer Co. Rotastat Controller. The temperature was determined using a calibrated platinum resistance thermometer read with a Hewlett-Packard model 3458 multimeter with 8-1/2 digits of sensitivity. Mixtures were prepared from Aldrich 99% pure, 2,6-lutidine, once distilled by us, and from water once distilled from a glass system. The water had a residual conductivity of $1.5 \mu\text{S cm}^{-1}$ at 25°C and was deaerated by boiling before use so as to prevent the formation of bubbles in the diaphragm cells.

TABLE I Cell constants

| Cell no. | β (cm^{-2}) |
|----------|------------------------------|
| 1 | 0.144 |
| 2 | 0.153 |
| 3 | 0.185 |
| 4 | 0.219 |
| 5 | 0.236 |
| 6 | 0.252 |
| 7 | 0.278 |

3.4. Evaluation of $D(\bar{c})$

The results of a diaphragm cell experiment are often reported in the form of values of D' vs \bar{c} . To convert these results to values of $D(\bar{c})$, one must use Eq. (5). According to this equation, a plot of $1/D'$ vs $f(y)$ should form a straight line of which the intercept is $1/D(\bar{c})$. For a given value of \bar{c} , application of Eq. (5) requires repeat determinations of $\Delta c(t)$ vs t [29]. In Figures 2 and 3, we show measurements of D' at 33.00°C and lutidine concentrations, $\bar{c} = 2.5$ M and 1.0 M, respectively plotted in this way over a wide range of values of $f(y)$. For both values of \bar{c} , it is clear that the slope, K , is negligible, so that effectively D' can be set equal to $D(\bar{c})$. Consequently, in what follows, we shall report our results in terms of $D(\bar{c})$.

3.5. Diffusion along Isotherms and the Critical Isoleth

The values of the interdiffusion coefficient of 2,6-lutidine + water as a function of concentration along the isotherms at 25.00°C and 33.00°C are listed in Table II and plotted in Figure 4. As a function of \bar{c} , $D(\bar{c})$

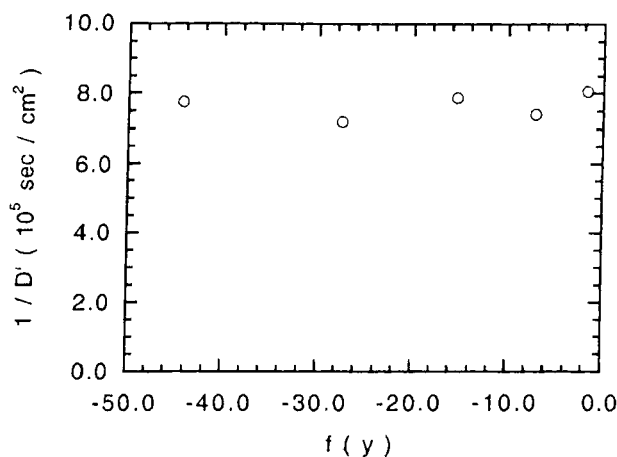


FIGURE 2 Plot of Eq. (5) for 2,6-lutidine + water at 33°C. The mean lutidine concentration in the diaphragm cell is $\bar{c} = 2.5$ M. All other quantities are defined in the paragraph of the text which includes Eq. (5).

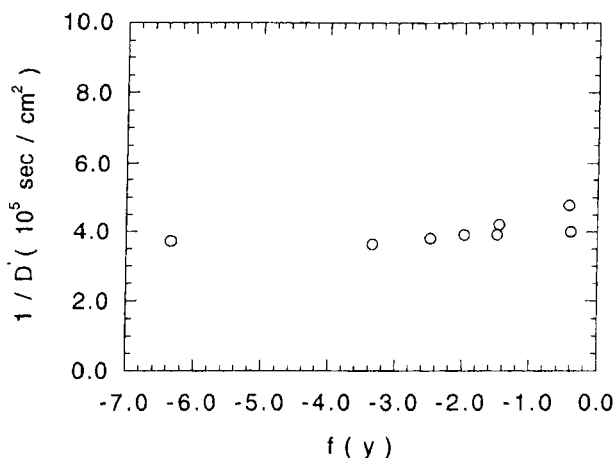


FIGURE 3 Plot of Eq. (5) for 2,6-lutidine + water at 33°C. The mean lutidine concentration in the diaphragm cell is $\bar{c} = 1.0$ M. All other quantities are defined in the paragraph of the text which includes Eq. (5).

TABLE II Interdiffusion coefficient for 2,6-lutidine + water determined along the isotherms 25°C and 33°C. The cells are numbered as in Table I

| 25.00°C | | | 33.00°C | | |
|---------------|---|----------|---------------|---|----------|
| \bar{c} (M) | $D(\bar{c})(10^{-6} \text{ cm}^2 \text{ s}^{-1})$ | Cell no. | \bar{c} (M) | $D(\bar{c})(10^{-6} \text{ cm}^2 \text{ s}^{-1})$ | Cell no. |
| 0.49 | 4.54 | 7 | 0.50 | 5.59 | 6 |
| 0.75 | 4.39 | 2 | 0.75 | 3.88 | 7 |
| 0.90 | 3.36 | 3 | 1.00 | 2.37 | 1 |
| 1.24 | 1.56 | 4 | 1.25 | 2.09 | 3 |
| 1.47 | 2.14 | 6 | 1.50 | 1.42 | 3 |
| 1.74 | 1.26 | 6 | 1.75 | 1.29 | 1 |
| 2.01 | 1.02 | 6 | 2.00 | 0.90 | 6 |
| 2.47 | 1.05 | 4 | 2.15 | 1.06 | 6 |
| 2.73 | 1.14 | 3 | 2.40 | 0.74 | 1 |
| 2.84 | 0.86 | 7 | 2.49 | 0.92 | 7 |
| 3.12 | 0.94 | 3 | 2.54 | 0.77 | 1 |
| 3.45 | 1.22 | 6 | 2.75 | 1.04 | 1 |
| 3.70 | 1.35 | 7 | 2.90 | 0.57 | 1 |
| 3.97 | 1.90 | 2 | 3.15 | 0.82 | 3 |
| 4.43 | 2.49 | 4 | 3.50 | 1.26 | 1 |
| 4.93 | 2.68 | 2 | 4.00 | 1.66 | 6 |
| | | | 4.50 | 2.10 | 3 |
| | | | 5.00 | 3.70 | 2 |

at both temperatures shows a broad minimum near the critical concentration of 2.78 M.

Values of $D(\bar{c})$ determined as a function of temperature along the critical isopleth at $\bar{c} = 2.78$ M are listed in Table III and plotted in

TABLE III Interdiffusion coefficient for 2,6-lutidine + water determined along the critical isopleth at 2.78 M. The cells are numbered as in Table I

| $T(^{\circ}C)$ | $D(T)(10^{-6}cm^2s^{-1})$ | Cell no. |
|----------------|---------------------------|----------|
| 25.0 | 1.65 | 6 |
| 26.0 | 1.88 | 7 |
| 27.0 | 1.99 | 3 |
| 28.0 | 2.09 | 6 |
| 29.0 | 2.15 | 2 |
| 29.5 | 2.22 | 7 |
| 30.2 | 2.34 | 5 |
| 31.0 | 2.33 | 1 |
| 32.0 | 2.40 | 6 |
| 33.0 | 2.51 | 6 |
| 33.2 | 2.60 | 1 |
| 33.4 | 1.99 | 6 |
| 33.6 | 1.71 | 7 |
| 33.7 | 2.17 | 2 |
| 33.8 | 1.98 | 3 |
| 34.0 | 1.90 | 1 |
| 35.0 | 2.50 | 7 |
| 36.0 | 2.77 | 6 |

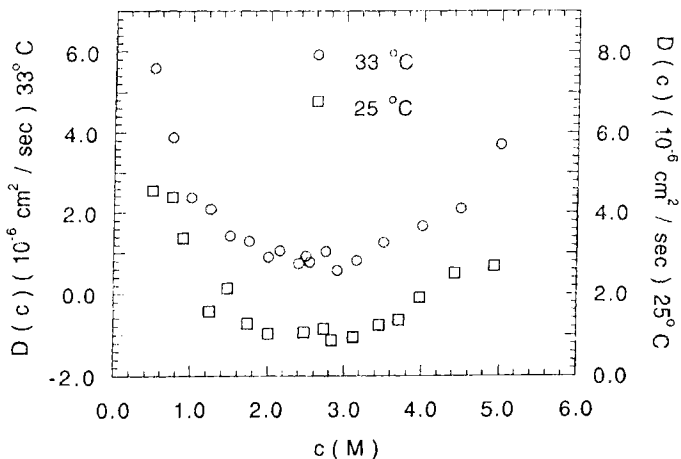


FIGURE 4 Interdiffusion coefficient for 2,6-lutidine + water at 25°C and 33°C as a function of the lutidine molar concentration, c . The critical concentration is 2.78 M.

Figure 5. After a gradual rise, representative of the background, there is a rapid drop starting at about 33°C as the critical point is approached. Above the critical point, $D(\bar{c})$ returns to the background trend established below the critical point.

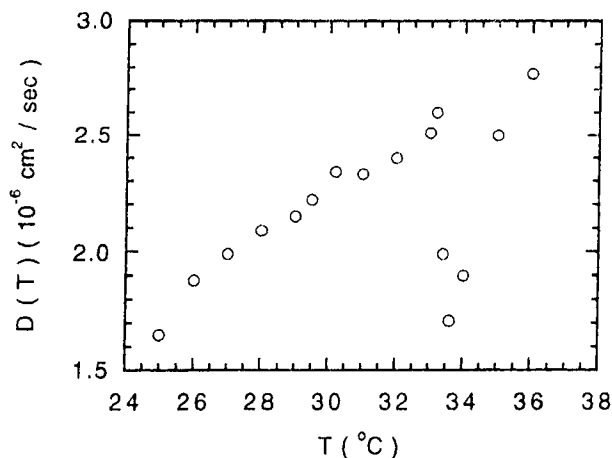


FIGURE 5 Interdiffusion coefficient for 2,6-lutidine + water as a function of temperature at the critical lutidine concentration (2.78 M). The critical temperature is 33.9°C.

4. VISCOSITY

Our measurements of the dynamic viscosity using an Ostwald viscometer were carried out by following the general procedures described by Hardy [41]. In particular, the viscometer was filled and operated at the same temperature and was oriented parallel to gravity using a plumb line. The upper and lower compartments had roughly similar curvature as recommended by Gonçalves *et al.*, so as to reduce the effect of surface tension [42]. Including both Poiseuille and kinetic energy terms in the theory, as summarized by Eq. (6) of Ref. [41], the viscometer was calibrated using water and ethanol [43].

To convert the measured kinematic viscosity, η/ρ , for 2,6-lutidine + water to the dynamic viscosity, η , the density, ρ , was determined by pycnometry. Along the isotherm at 25.00°C, we found that the density data fitted the equation

$$\rho = 0.999 - (4.8 \times 10^{-3})c \quad (7)$$

while along the critical isopleth at $c = 2.78$ M, it fitted the equation

$$\rho = 1.008 - (5.9 \times 10^{-4})T \quad (8)$$

In both equations, ρ , is in the units of g cm^{-3} , while in Eq. (8), the temperature, T , is in $^{\circ}\text{C}$.

In Figure 6, we compare our dynamic viscosity values taken along the critical isopleth with those of Stein *et al.* [32]. In Table IV, we list our dynamic viscosity values measured along the isotherm at 25.00°C . From the figure and the table, it is evident that our data are in good agreement with those of Stein *et al.* [32], and that the two sets can be combined to establish background values for the viscosity.

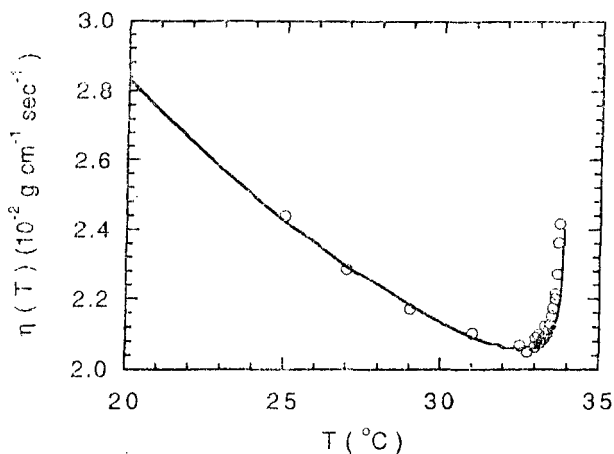


FIGURE 6 Dynamic viscosity of 2,6-lutidine + water as a function of temperature at the critical lutidine concentration of 2.78 M. The critical temperature is 33.9°C . The curve represents the data of Stein *et al.* [32].

TABLE IV Dynamic viscosity of 2,6-lutidine + water at 25.00°C . The values in the second column were measured as described in Section 4. The values in the third column were extrapolated from the data of Table II of Stein *et al.* [32]

| Weight % lutidine | Viscosity (cP) measured | Viscosity (cP) Extrapolated |
|-------------------------|-------------------------------|-----------------------------------|
| 44.98 | 3.916 | 3.89 |
| 45.97 | 3.638 | 3.65 |
| 33.11 | 2.713 | 2.70 |
| 23.99 | 2.066 | 2.10 |
| 10.99 | 1.346 | 1.31 |

5. DISCUSSION AND CONCLUSIONS

Our measured values for the interdiffusion coefficient of 2,6-lutidine + water, as shown in Figure 4 as a function of composition and in Figure 5 as a function of temperature, diminish as the consolute point is approached. This behavior illustrates the concept of "critical slowing down" of diffusion. The data shown in Figure 5 vary with temperature along the critical isopleth in a fashion similar to those of Haase and Siry for triethylamine + water [25, 26], which also has a lower consolute point; namely, below the critical point, they first increase monotonically with increasing temperature before decreasing due to the onset of the "critical slowing down", which occurs over the last few degrees below the critical temperature.

The operational meaning of the diffusion coefficient data shown in Figure 5 at temperatures above critical is as follows: A concentrated solution of lutidine in water corresponding to a point in the one phase region far to the right of the coexistence curve in the phase diagram in Figure 1 was placed in the top compartment of the diaphragm cell, while a dilute solution of lutidine in water corresponding to a point in the one-phase region to the left of the coexistence curve was placed in the bottom compartment. At all times during a diffusion run, the contents of the two compartments remained in their respective one-phase regions, although the value of \bar{c} defined by Eq. (1) was in the two-phase region. The compartments were connected through the frit by a concentration gradient, which was in general non-linear, since the interdiffusion coefficient was a function of concentration [37]. Hence, within some local volume in the frit, the concentration had values corresponding to points in the two-phase region of Figure 1. Because the concentration gradient was steep, however, and because the temperature was not far above critical, the spatial extent of this volume was limited. Consequently, during a run of this type the effective length, ℓ in Eq. (4) passed mostly through regions where there was only one phase in existence. Since our data collected in this way at temperatures above critical fitted smoothly to those taken below the critical temperature, we have included them in Figure 5 and in Table III.

Both along isotherms, as well as along the isopleth, as shown in Figures 4 and 5, respectively, D is an asymmetric function about the

critical value of the independent variable. The asymmetric dependence upon concentration along the isotherms has also been observed in the case of triethylamine + water by Haase and Siry [25] and in the case of succinonitrile + water by Cain *et al.* [29]. Such asymmetry in critical phenomena is not uncommon [44].

Whereas, there are successful theories of the background contribution to the diffusion coefficient near the liquid-vapor critical (plait) point [15, 16, 18], there is as yet no adequate theory of the background contribution near a consolute point. This is due in part to the fact that the molecular theories for both the thermodynamic and kinetic properties of liquid mixtures are incomplete [30, 45]. The data which we have collected, however, could be used to parameterize a semi-empirical background function.

Consider a two-component mixture. Let μ_1 , and μ_2 be the chemical potentials per gram of components 1 and 2, respectively, and let x be the weight fraction of component 1. Define $\mu = \mu_1 - \mu_2$. Near the consolute point of the mixture, the interdiffusion coefficient, D , in the center of mass frame of reference, is given by [20]

$$\rho D \left(\frac{\partial x}{\partial \mu} \right)_{T,P} = \alpha^b + \frac{k T}{6\pi\eta\xi} \left(\frac{\partial x}{\partial \mu} \right)_{T,P} \quad (9)$$

In Eq. (9), T is the absolute temperature, P is the pressure, ρ is the overall mass density, α^b is the background part of the molecular mobility, η is the dynamic viscosity, ξ is the correlation length of the fluctuations in concentration, and k is Boltzmann's constant. At the consolute point, $(\partial x / \partial \mu)_{T,P}$, η , and ξ all diverge toward infinity [16], α^b remains finite, and D must approach zero.

To check the detailed validity of Eq. (9) it is important to be able to evaluate α^b in the vicinity of the consolute point. This might be done empirically first by fitting Eq. (9) to data away from the critical point and solving for α^b and then extrapolating these values to the vicinity of the critical point. Among the measurements away from the critical point which are required to do this are those determining ρ , and η , which we have reported above. The mass-centered diffusion coefficient required by Eq. (9) can be calculated from the volume-centered diffusion coefficient, which we have measured, by using data on the solution density [36]. Light scattering data [46] can be used to evaluate

ξ while any measurement sensitive to the thermodynamic activity, such as the vapor pressure, can be used to evaluate $(\partial x/\partial \mu)_{T,P}$. Once the form of α^b in the critical point region has been thus established, the overall validity of Eq. (9) can be checked by substituting the critical values of the appropriate quantities and checking for equality.

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