The Mutual Diffusion Coefficient of Methanol–*n*-Hexane Near the Consolute Point

The composition and temperature dependence of the mutual diffusion coefficient near the liquid-liquid critical point of methanol-*n*-hexane mixtures has been determined by Gouy interferometry. The critical exponent was found to be 0.685. Constant-temperature extrapolation to zero diffusivity located the spinodal curve. Spinodal loci calculated from the NRTL model are inconsistent with the experimentally determined values.

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SCOPE

Mutual diffusion coefficients can be separated into two parts: a mobility or Onsager term and a thermodynamic factor. The mathematical criterion, which defines the spinodal curve and demarcates the unstable region interior to the equilibrium coexistence curve, can be expressed as the loci of points where the thermodynamic factor is identically zero. Classical and light-scattering experiments have shown that the diffusion coefficient goes to zero as the temperature approaches the liquid-liquid critical point at constant critical composition. Although Skripov et al. (1980) concluded that the diffusion coefficient for the methanol–*n*-hexane system vanished at the same rate as the thermodynamic factor, indicating a finite Onsager term, it has been fairly well established by studies on other systems that the Onsager coefficient actually diverges as the critical point is approached. One purpose of this study was to determine the critical exponent in the methanol-*n*-hexane system by a series of temperature-jump-initiated diffusion experiments in a Gouy interferometer. The diffusion critical exponent has significant implications in terms of universality and scaling theories.

The second purpose was to use diffusion coefficient measurements to determine the spinodal curve. Since the diffusion coefficient must be zero at the spinodal, extrapolation of measured diffusivities to zero could be used to determine its location. No methods have heretofore been able to provide spinodal information in liquid-liquid phase-splitting systems. Classical equilibrium studies provide only coexistence information. Nevertheless, the location of the spinodal curve could be extremely valuable in developing and testing liquid mixture models for the Gibbs free energy since it is related to the second derivative with respect to composition, as shown in Eq. 7. Generally, liquid-mixture model parameters are fitted from the solubility or equilibrium concentration information. No other data have been available to test the model at other compositions at the same temperature. The spinodal criterion on the other hand provides additional restrictions that a satisfactory and consistent liquid-mixture model must satisfy.

CONCLUSIONS AND SIGNIFICANCE

Diffusion coefficients were measured in methanol-*n*-hexane mixtures as a function of temperature along the critical composition in a temperature-jump cell using a Gouy interferometer. The critical exponent was found to be 0.685, in good agreement with previous studies on other systems, indicating that the results of Skripov

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et al. (1980) on this system are in error. Diffusion coefficients on this same system were measured as a function of composition at five temperatures, two of which were below the consolute temperature, in a boundary-sharpening cell. The diffusion coefficients were fitted to a polynomial in composition and were well represented by that equation utilizing the temperature dependence found in the critical exponent study. The spinodal curve was then determined from the roots of this equation. Generally, liquid mixture activity information is determined from phase equilibrium measurements. The spinodal method investigated here provides a previously unexploited, unique method for obtaining liquid-mixture activity information in a region inaccessible to phase-equilibrium studies. In this work NRTL model predictions were tested against measured spinodal values. Parameters obtained from measured coexistence data predicted spinodal loci significantly different from measured values. Thus, spinodal compositions can be obtained from diffusion experiments to better define the free energy surface and provide meaningful tests of liquid mixture models in regions where previously no testing could be done.

Introduction

Nonequilibrium thermodynamics indicates that the driving force for molecular diffusion processes is an isothermal gradient of chemical potential (deGroot and Mazur, 1969; Fitts, 1962; Horne 1966)

$$J_i = -\sum_{j=1}^{N-1} \Omega'_{ij} \nabla_T \mu_j, \quad i = 1, 2, \ldots, N-1 \tag{1}$$

where the Onsager coefficients, Ω'_{ij}, can be related to the mutual diffusion coefficients by comparison of the above equation to a generalized form of Fick's law

$$J_i = -\sum_{k=1}^{N-1} D_{ik} \nabla C_k, \quad i = 1, 2, \ldots, N-1 \tag{2}$$

which relates the molar fluxes to molar concentration gradients instead of the actual driving forces of Eq. 1. Equation 2 is convenient to use because concentrations are directly measurable, but Eq. 1 indicates that for highly nonideal mixtures the mole flux is not proportional to just the concentration gradient. In particular, if Eq. 1 is rewritten in terms of the concentration gradient

$$J_i = -\sum_{j=1}^{N-1} \sum_{k=1}^{N-1} \Omega'_{ij} \mu_{jk} \nabla C_k, \quad i = 1, 2, \ldots, N-1 \tag{3}$$

where

$$\mu_{jk} \equiv (\partial \mu_j / \partial C_k)_{T,P,C_{l \neq k}} \tag{4}$$

is often called the thermodynamic factor, then a comparison of Eqs. 2 and 3 yields the relationship between mutual diffusion coefficients, Onsager coefficients, and thermodynamic factors.

As indicated in the above equation, there are $(N-1)^2$ independent diffusion coefficients for an N-component mixture. In general,

$$D_{ik} = \sum_{j=1}^{N-1} \Omega'_{ij} \mu_{jk}, \quad i, k = 1, 2, \ldots, N-1 \tag{5}$$

or for a binary mixture,

$$D_{11} = \Omega'_{11} \mu_{11}, \tag{6}$$

and the diffusion coefficient is seen to be composed of two parts: a mobility or Onsager term and a thermodynamic factor. Measurements of diffusion coefficients in the near-consolute region of liquid mixtures can provide interesting and important information about the diffusion coefficient and its interrelationship with liquid mixture thermodynamic properties. This information can be valuable in development of realistic liquid-mixture free energy models and predictive equations for diffusion coefficients. This is particularly true near the liquid-liquid critical or consolute point.

Liquid-liquid phase equilibrium can be described in terms of stability requirements (Gibbs, 1957; Wisniak, 1983, 1984). At constant temperature and pressure, the propensity for phase splitting is governed by minimization of the Gibbs free energy. For stable solutions,

$$(\partial^2 g / \partial x_2^2) \geq 0. \tag{7}$$

The spinodal curve or mathematical dividing line between stable and unstable states occurs at loci for which the equality in Eq. 7 holds. This condition can be rewritten for a binary mixture in terms of the thermodynamic factor as (Rowlinson and Swinton, 1982)

$$(\partial \mu_1 / \partial x_2)_{T,P} = 0 = (\partial \mu_1 / \partial C_1)_{T,P,C_2} = \mu_{11} \tag{8}$$

Thus, the thermodynamic factor, μ_{11}, appearing in Eq. 6 is zero for a binary mixture everywhere along the spinodal curve including the consolute point. Equation 6 requires that the diffusion coefficient must vanish along the spinodal curve if the Onsager coefficient is finite.

Classical experimental studies by Lorentzen and Hansen (1957), Haase and Siry (1968), Balzarini (1974), and Claesson and Sundelöf (1957) have shown that the mutual diffusion coefficient does approach zero at the critical solution temperature. Light-scattering techniques have further shown that the rate at which the diffusion coefficient goes to zero as the critical temperature is approached from above at constant critical composition is not the same as the rate at which the thermodynamic factor approaches zero (Chu et al., 1968, 1969, 1973, and Burstyn and Sengers, 1982, are a few of many studies). While the thermodynamic factor has been found to approach zero with a critical exponent of nearly $4/3$, the critical exponent of the diffusion coefficient appears to be approximately $2/3$. Equation 6 therefore requires that the Onsager coefficient approaches infinity with approximately a $-2/3$ exponent as the critical point is approached, similar to the behavior of the correlation length (Sengers, 1972; Rowley and Horne, 1979). Skripov et al. (1980), however, determined that both the diffusion coefficient and the thermodynamic factor have critical exponents on the order of unity and that the Onsager coefficient therefore remains finite.

The purpose of this study on the methanol-hexane system was twofold. First, diffusion coefficients were measured as a function of temperature along the critical composition line to resolve the discrepancy between Skripov's results and the general results obtained on other systems. Second, both the binodal curve and diffusion coefficients as a function of composition and temperature were measured to experimentally determine the spinodal loci. Based on Eqs. 6 and 8 in conjunction with known critical exponents, careful diffusion measurements can be used to obtain the spinodal curve, since the diffusion coefficient must be zero there and (effectively) negative in the unstable region. While diffusion measurements cannot be made in the metastable region between the binodal and spinodal curves, Vitagliano et al. (1980) suggested that diffusion measurements made as a function of composition in the homogeneous region could be used to extrapolate to the spinodal curve. Myerson and Senol (1984) recently used a similar procedure to locate the solid-liquid spinodal. This provides the only method known to the authors of experimentally determining the liquid-liquid spinodal curve, and it could be very important in providing data by which liquid-mixture models commonly used to correlate liquid-liquid equilibria could be tested. Usually two adjustable parameters in these models are fitted from the two binodal compositions at a specified temperature. This leaves no indication of how well the model represents the chemical potential at other compositions at the same temperature and leaves untested the use of these models in the calculation of thermodynamic factors. Since the model must satisfy the equality portion of Eq. 7 at the spinodal curve, spinodal data provide a consistency test for these models. As an illustration, spinodal predictions of Renon and Prausnitz's (1968) NRTL model have been compared to those obtained from the measured diffusion coefficients.

Experimental

Methanol–n-hexane mixtures were prepared gravimetrically from Baker-analyzed photrex grade reagents without further purification. Water content, measured with a Karl Fischer apparatus, was found to be 0.02% and 0.01% for pure methanol and n-hexane, respectively. Pure-component densities were measured at 298.15 K with a Mettler-Paar 4.5 digital densitometer and were found to be 0.7866 and 0.6558 g/cm^3, in comparison with literature values (Wei and Rowley, 1983) of 0.7866 and 0.655 g/cm^3 for methanol and n-hexane, respectively.

Binodal or coexistence curve measurements were made by visual observation of the cloud point or separation temperature, T_s, for samples prepared at known compositions. Each sample was introduced into a clean, oven-heated (to remove adsorbed water) vial equipped with a Teflon-coated magnetic stir bar and then quickly frozen in liquid nitrogen. The vials were then evacuated and flame-sealed before allowing the sample to melt. Sealed vials were totally immersed in a bath thermostatically controlled to ±0.005 K. The bath temperature could be slowly increased while magnetically stirring the samples until the single-phase region was reached, and then slowly decreased to observe the cloud point. Replicate runs were made on each sample to insure consistency, and based on the reproducibility of those replicates the uncertainty in measured binodal points is estimated to be less than ±0.01 K.

Diffusion coefficients were measured with a Gouy interferometer. The techniques, theory, and data analysis involved in determination of binary diffusion coefficients from this instrument have been described in the literature (Gosting et al., 1949; Weissberger, 1972; Cussler, 1976; Tyrrell and Harris, 1984). Several improvements over traditional instruments were incorporated in the construction of the Gouy diffusiometer used in this work. A He-Ne laser was used as a light source to provide bright monochromatic illumination of the cell without the use of filters or condenser lenses. Kodak Technical Pan 2415 sheet film was used in place of the awkward glass plates previously used for fringe pattern recording. This was made possible by construction of a vacuum-back film holder to secure the film in a reliable and even manner free of ripples and small displacements. Two new cells were designed for use in conjunction with the diffusiometer. One was a boundary-sharpening, flowing-junction cell similar to that used by Thomas and Furzer (1962); the other was designed for temperature-jump initiation of the diffusion process.

The flowing-junction cell and reference cell were milled in parallel from a solid Teflon block and sealed with compression-fit glass optical windows in the optical path direction. A small hole into the cell was drilled at half-height and the outside tapped for connection of 1/8 in (3.2 mm) OD Teflon tubing for fluid withdrawal to form and sharpen the initial interface. As shown in Figure 1, the cell was mounted in a Plexiglas box into which quartz optical windows have been cemented perpendicular to the optical path. The box served as a thermostatting jacket for the cell into which water controlled to ±0.005 K was circulated from an external constant-temperature bath. Cemented into the lid of the water jacket was a quartz thermometer probe (2.5 in [63.5 mm] immersion depth) and the necessary fill and

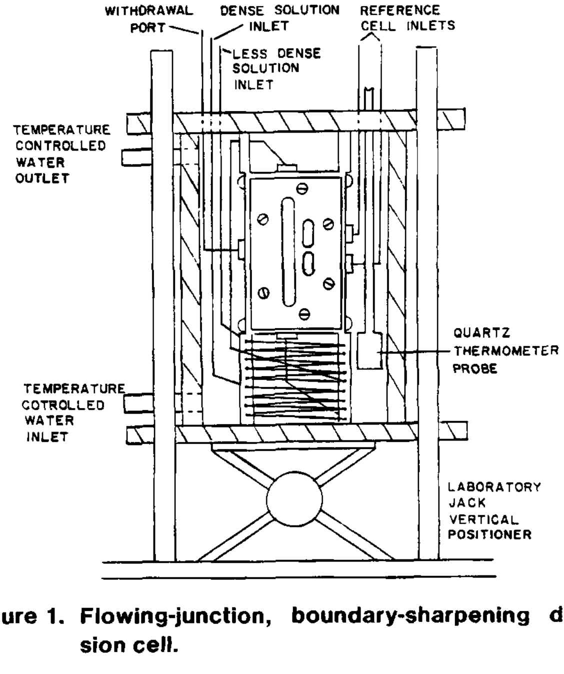

Figure 1. Flowing-junction, boundary-sharpening diffusion cell.

withdrawal lines for operation of the measurement and reference cells. The entire assembly was then fastened to a small laboratory jack that was mounted to a vibration-isolated optical bench. The jack allowed vertical alignment of the cell in the optical path. Boundary formation and sharpening was done with a dual-channel infusion/withdrawal syringe pump. Fluid was withdrawn from the center tap while fluid at the desired upper concentration was infused at roughly half the withdrawal rate into the upper portion of the cell; the volumetric difference between these two rates was infused into the bottom of the cell from a reservoir containing fluid at the desired lower composition. Both the reservoir supplying the lower mixture and the syringe supplying the upper fluid were cothermostatted by means of water jackets maintained at temperatures above their phase-separation temperatures. Fluid infused or drawn into the cell first passed through a coil of tubing inside the main water jacket which served as a heat exchanger. Testing of the diffusiometer was performed by measurement of mutual diffusion coefficients at the same composition and temperature studied by Gosting and Morris (1949) on an aqueous sucrose system; agreement was better than 1%.

A temperature-jump (Lorentzen and Hansen, 1957; Balzarini, 1974; and Rowley and Horne, 1979) cell was constructed to measure diffusion coefficients at the critical composition as a function of temperature above the critical. This cell was jacketed and mounted to the optical bench in a fashion similar to that shown for the boundary-sharpening cell. The cell itself was a Hellma model 111 optical cell fitted with a Teflon stopper. The cell was filled with the critical-composition mixture and a small Teflon-coated stir bar, sealed, and then glued into a Plexiglas sleeve and cemented into the top of the Plexiglas waterjacket. Two constant-temperature baths were connected to the cell jacket through a rapid-switching valve that allowed communication to the cell with one bath at a time while shunting the other back to itself. Thus, the cell could be thermostatted below the consolute temperature, stirred with the magnetic stirrer, allowed to sit undisturbed for 5–6 h to insure complete phase separation at the controlled temperature, and then jumped in temperature to the run conditions above the critical solution temperature by switching the valve to the run bath. The control baths were of large capacity and replacement of fluid in the jacket occurred rapidly relative to experimental time. Compared to the diffusion time scale, the temperature-change time was extremely small as monitored by the quartz thermometer in the jacket. Thermal equilibration was complete, to within the ±0.005 K control accuracy, within 4–5 min depending upon the magnitude of the jump, while 4–5 h were required before sufficient decay of the concentration gradient had occurred to allow photography of the entire fringe pattern on a single film, and 5–6 h more were required for completion of the experiment.

Table 1. Phase-Separation Temperatures at Various Compositions for the Methanol (1)–*n*-Hexane(2) System

T_s °C	X_1	T_s °C	X_1
25.22	0.2440	33.70	0.5619
27.22	0.2626	33.54	0.6071
29.67	0.2985	33.51	0.6242
32.82	0.3493	33.50	0.5998
33.41	0.3762	33.25	0.6513
33.48	0.4520	33.23	0.6452
33.62	0.4227	33.06	0.6568
33.67	0.4328	32.67	0.6823
33.82	0.5026	32.57	0.6820
33.83	0.4997	31.80	0.7067
33.84	0.5291	30.65	0.7288
33.81	0.5574	28.91	0.7529
33.80	0.5452	28.61	0.7566
33.77	0.5805	27.15	0.7721
33.73	0.6154	26.19	0.7795

An advantage of this technique is that the same mixture could then be used in subsequent studies by again thermostatting the fluid below the consolute point, thereby inducing phase separation. Initial concentrations for each run were obtained from the measured binodal curve and the initial temperature at which the critical mixture was thermostatted. Additionally, the initial interface created in this manner is significantly sharper and more stable than that created in boundary-sharpening cells, as monitored by the Gouy fringe patterns, and it remains sharp and stable as long as the cell is maintained at $T < T_c$. A detailed description of the experimental procedure, equipment, and data analysis procedures is available in Clark's dissertation (1984).

Results

Measured values for the binodal curve are listed in Table 1 as separation temperatures at various compositions, and are plotted in Figure 2. The critical temperature was determined to be 33.84°C, which compares favorably with that found by Kiser et al. (1961) of 33.2°C (who also reported other literature values ranging from 32 to 43.8°C). Cornish et al. (1934) found that a 1% water content would raise the critical solution temperature by 10 K, which is the probable cause of most of the higher values reported in the literature. Although the water content of the chemicals used in this study was explicitly analyzed and found to be about 0.01% and care was taken to desorb water from glassware before use, the scatter in the data is probably due to moisture absorption from the air during handling. Because of the large scatter in literature values, the binodal curve and consolute temperature were determined in this study so that the diffusion coefficients were measured relative to the phase envelope

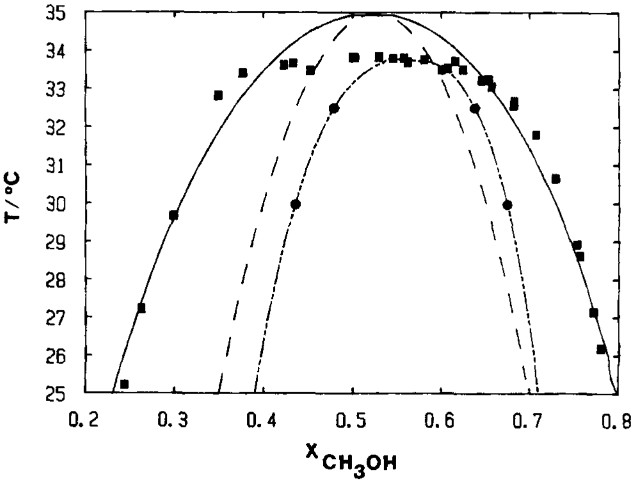

Figure 2. Binodal measurements.

■ measured binodal points; —NRTL correlation of the binodal points; ● spinodal points extrapolated from diffusion study; – – – spinodal from diffusion coefficient smoothing equation; —— NRTL prediction of spinodal.

for the actual mixtures studied; the diffusion results with respect to the critical point are thus independent of any impurities.

The critical solution concentration was found using the known relation

$$T_c - T = A\,|X_1 - X_{1C}|^{\beta} \tag{9}$$

for the coexistence curve and fitting the critical composition. If β is assigned the generally accepted value of $1/3$, the critical methanol mole fraction is found to be 0.5224, as shown in Figure 3; but if β is also treated as an adjustable parameter, the critical composition is 0.5243. However, these values probably have an uncertainty of 0.02 mole fraction due to the extremely flat top of the binodal curve that produces the scatter in Figure 3 as the critical temperature is approached from below. Critical exponents do not change with small amounts of impurities or small deviations from the true critical composition (Scott, 1978). As a consistency check on the critical composition, although less accurate than the direct method, a minimum in the diffusion coefficient with respect to composition was found by fitting the diffusion coefficient results to a fourth-order polynomial in mole fraction. This procedure yielded a value of 0.5621 methanol mole fraction.

The results of the flow cell diffusion studies are shown in Table 2. Diffusion coefficients are reported at average mole fractions for five temperatures, three above and two below the critical solution temperature. Also shown in Table 2 are the initial composition differences across the interface and the total number of fringes obtained from the resultant Gouy interference pattern. All of the results were fitted to the smoothing equation shown in Table 2. As can be seen from the form of this equation, the composition dependence is independent of temperature and can therefore be used to extrapolate values measured at temperatures below the critical (but outside the binodal curve) into the metastable region to determine spinodal points. The spinodal compositions at 32.5°C were found to be 0.4792 and 0.6386 methanol mole fraction, respectively, and those at 30°C were 0.4360 and 0.6744, respectively. Figure 2 shows the determined spinodal loci as well as the spinodal curve calculated over a range of temperatures from the diffusion coefficient smoothing equation.

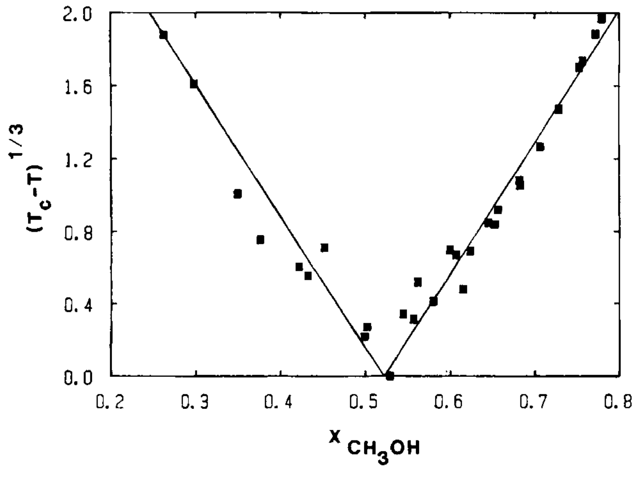

Figure 3. Determination of critical composition of methanol–*n*-hexane mixtures from binodal data.

Table 2. Diffusion Coefficients at Various Compositions and Temperatures for the Methanol (1)-*n*-Hexane (2) System Near the Critical Mixing Point

T °C	X_1	J_m	D 10^{-10} m²/s
40.0	0.0643	89.5	30.84
40.0	0.1245	90.7	19.37
40.0	0.2307	85.5	10.95
40.0	0.4062	67.0	3.751
40.0	0.4979	83.9	2.092
40.0	0.5331	82.1	1.939
40.0	0.5353	55.0	2.154
40.0	0.5610	41.8	1.678
40.0	0.5917	73.9	2.055
40.0	0.6408	56.4	2.867
40.0	0.7276	83.3	4.674
40.0	0.7289	76.6	4.632
40.0	0.8324	65.9	9.986
40.0	0.9135	80.5	18.26
40.0	0.9903	71.0	30.85
37.5	0.2295	93.8	9.806
37.5	0.4067	83.6	3.339
37.5	0.5338	77.6	1.380
37.5	0.5918	85.0	1.299
37.5	0.6884	63.6	2.574
37.5	0.8330	82.8	9.583
34.6	0.1258	79.6	15.89
34.6	0.2289	88.2	8.892
34.6	0.3183	62.1	4.483
34.6	0.4006	71.0	2.052
34.6	0.4541	39.6	1.070
34.6	0.6320	58.1	0.548
34.6	0.7294	74.5	2.891
34.6	0.8627	77.5	11.55
34.6	0.9605	71.5	23.03
32.5	0.1261	82.9	15.34
32.5	0.2283	75.2	8.387
32.5	0.2932	59.6	4.975
32.5	0.7345	65.0	2.506
32.5	0.7665	59.1	4.221
32.5	0.8628	77.7	10.88
32.5	0.9901	76.8	27.45
30.0	0.0680	96.3	22.46
30.0	0.1270	85.5	15.23
30.0	0.2295	93.0	7.377
30.0	0.7645	82.5	3.342
30.0	0.7658	36.1	3.591
30.0	0.7660	60.7	3.411
30.0	0.8328	62.8	7.451
30.0	0.9124	76.0	14.75
30.0	0.9798	83.8	24.41

Results have been fitted to the equation $D = \Sigma_{n=0}^{4} A_n x^n + A_5 \epsilon^{0.68516}$ where $A_0 = 3.2457 \times 10^{-9}$, $A_1 = -1.68497 \times 10^{-8}$, $A_2 = 3.63103 \times 10^{-8}$, $A_3 = -4.1949 \times 10^{-8}$, $A_4 = 2.223 \times 10^{-8}$, and $A_5 = 2.5067 \times 10^{-9}$ to yield D in m²/s.

In a highly nonideal system such as this, the measured diffusion coefficients are not expected to be as accurate as those for the aqueous sucrose test system, but the maximum uncertainty in the results reported here is less than 10% as determined from worst-possible-case analysis. The major source of error is the uncertainty in the fractional portion of the fringe analysis as determined with the iterative scheme of Thomas and Furzer (1962). Additional errors include imperfect initial interface formation, moisture, and the assumption of concentration-indepen-

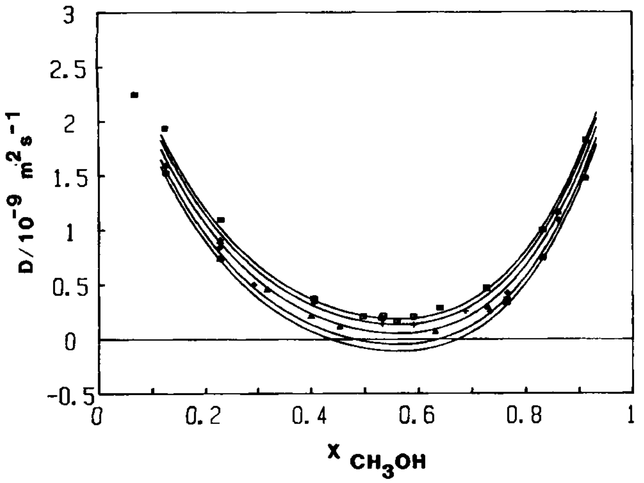

Figure 4. Determination of spinodal from temperature and composition dependence of mutual diffusion coefficient.

▫ 40°C; + 37.5°C; ▲ 34.6°C; ◆ 32.5°C; ■ 30.0°C.

dent diffusion coefficients required by the Gouy analysis procedure; see Figure 4.

The results of the temperature-jump diffusion studies at the critical composition are tabulated in Table 3. A plot of ln D vs. ln ϵ shown in Figure 5 yields a critical exponent of 0.685 ± 0.015 from least squares regression analysis.

Discussion

The critical exponent of 0.685 is in close agreement with current theoretical considerations and measurements performed on other binary systems. Skripov's conclusions appear to be in error. The Onsager coefficient thus diverges with an approximately $-2/3$ critical exponent in this system, roughly equivalent to the divergence of the correlation length.

Development of liquid mixture models is most often based on vapor-liquid equilibrium measurements. However, a more exacting test of a model's ability to predict liquid mixture free energies and chemical potentials is liquid-liquid equilibrium compatibility, for which Rowley and Battler (1984) have shown that equilibrium compositions are extremely sensitive to the shape of the free energy curve. Unfortunately, most models involve two adjustable parameters that must be determined from the two equilibrium compositions. Location of the spinodal curve places two new independent restrictions on the model at each temperature which can then be used for model development or testing of existing models.

Table 3. Temperature Jump Diffusion Measurements: Diffusion Coefficients as a Function of Distance from Critical Temperature at Critical Composition

$T - T_c$ °C	$\epsilon/10^{-3}$	D $10^{-10}\,m^2/s$
4.100	13.36	1.406
2.792	9.09	1.053
1.310	4.26	0.632
1.057	3.44	0.546
0.937	3.05	0.456
0.368	1.20	0.274
0.105	0.34	0.111

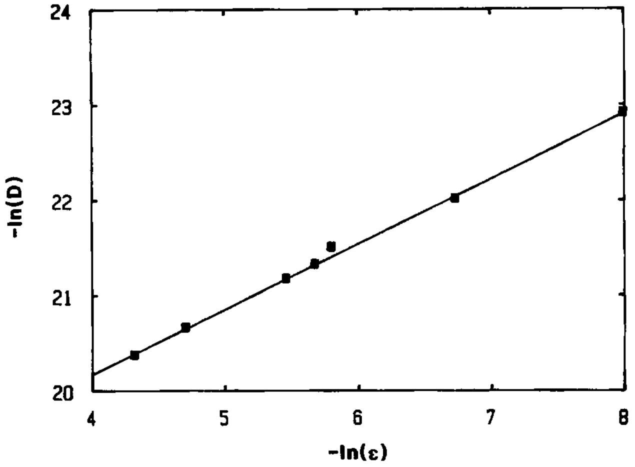

Figure 5. Plot of $-\ln(D)$ vs. $-\ln(\epsilon)$ used to determine critical exponent from temperature-jump study.

■ experimental; — least-squares fit.

As an example of how spinodal data can be used to test existing classical model liquid-liquid equilibrium predictive capabilities, consider the NRTL model developed by Renon and Prausnitz (1968) which has been used considerably for correlation of liquid-liquid equilibria. Model parameters fitted from liquid-liquid equilibrium data have been compiled by Sorensen and Arlt (1979). The latter authors found that the NRTL parameters are not temperature-independent and must be fitted from coexistence data at each temperature. The coexistence curve measurements, interpolated with respect to temperature with a polynomial, were used to directly calculate NRTL parameters from the equilibrium criteria as discussed above (α was set to 0.2); the values obtained are shown in Table 4. These values were then fitted as a linear function of temperature; the coefficients obtained are also shown in Table 4. Note that very near the critical point even a linear temperature dependence is insuf-

Table 4. NRTL Parameters Fitted from Coexistence Data (interpolated with a Polynomial Fitting Equation)

T	X_1'	X_1''	A_{21}/K	A_{12}/K
298.15	0.2435	0.7902	341.11	433.93
299.15	0.2516	0.7821	339.89	430.99
300.15	0.2524	0.7793	343.16	428.70
301.15	0.2679	0.7650	338.67	424.53
302.15	0.2817	0.7519	335.63	420.96
303.15	0.2956	0.7382	333.37	417.10
304.15	0.3121	0.7218	331.04	412.73
305.15	0.3340	0.7001	328.01	407.59
305.65	0.3487	0.6854	326.25	404.31
305.85	0.3559	0.6783	325.33	402.93
306.15	0.3689	0.6655	323.72	400.60
306.45	0.3866	0.6481	321.65	397.83
306.65	0.4044	0.6308	319.59	395.64
306.85	0.4411	0.5960	315.10	393.32
306.90	0.4798	0.5657	304.97	399.49
306.95	0.5400	0.5400	269.66	434.67

The temperature dependence was fitted to $A_{ij} = B_{ij} + C_{ij}T$ where B_{21} = 1,606.53, $C_{21} = -4.2156$, B_{12} = 1,540.70, and $C_{12} = -3.7096$.

ficient. The correlation of the coexistence data (obtained from isoactivity conditions) with these four parameters is shown by the solid line in Figure 2. Once the NRTL parameters were obtained, calculations of the spinodal curve were also made. In this case, the calculations were made using the equality portion of Eq. 7 and a numerical technique. The NRTL-predicted spinodal curve is also shown in Figure 2. Even though the NRTL parameters were obtained at the binodal compositions, there were still significant deviations between measured and calculated spinodal compositions not too far removed from the binodal curve. One should be cautious in using the NRTL model in determining thermodynamic factors (for use in Eq. 6 for example) at conditions away from the binodal. Spinodal compositions obtained from diffusion experiments better define the free energy surface; they are related to the second derivative of the free energy and can be used for liquid mixture model testing and development of more realistic and sophisticated models.

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Notation

A_i = coefficients in smoothing equation of Table 2
A_{ij} = NRTL parameter
B_{ij} = NRTL parameter, Table 4
C_{ij} = NRTL parameter, Table 4
C_k = molarity of component k
D_{ik} = mutual diffusion coefficient of component i driven by a concentration gradient of component k
g = molar Gibbs free energy of the mixture
J_i = mole flux of component i relative to center of volume reference velocity
N = number of components
P = pressure
T = temperature
T_c = consolute temperature
X_i = mole fraction of component i
X_{ic} = critical mole fraction of component i

Greek letters

α = NTRL nonrandomness parameter, set to 0.2 in this work
β = critical exponent for coexistence curve (order parameter)
∇ = gradient operator
∇_T = isothermal gradient $\equiv \nabla - (\partial/\partial T)\nabla T$
ϵ = dimensionless temperature difference $(T - T_c)/T_c$
μ_j = chemical potential of component j
μ_{jk} = thermodynamic factor, Eq. 4
Ω'_{ij} = Onsager coefficient relating flux i relative to center of volume velocity to driving force j. These are related to the more commonly used Onsager coefficients defined with respect to the barycentric velocity by $\Omega'_{ij} = \Sigma_{m=1}^{n-1} \Omega_{im}(\delta_{mj} + \bar{V}_m C_j/\bar{V}_N C_N)$ where δ_{mj} is the Kronecker delta and $\bar{V}_m$ is partial molar volume of component m.

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