

and KPSS to CsPSS. The dependence of ΔG_D^n , ΔH_D^n , and ΔS_D^n on the temperature and the nature of the counterion is consistent with the one observed with the experimental quantities of dilution ΔG_D , ΔH_D , and ΔS_D (Table I). It appears therefore that it is also associated with the already described structural effects of the counterions.

In conclusion, it has to be emphasized that due to the known deficiencies of the cell model all values of coulombic and non-coulombic contributions reported in Table II should be considered only as first approximations. We believe, however, that the relative order of noncoulombic contributions with respect to the type of

the counterion and their trends with temperature clearly indicate the importance of counterion-solvent interactions in determining enthalpies and entropies of dilution of aqueous polyelectrolyte solutions.

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Coexistence Curve of Methanol-Isooctane

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The coexistence curve of the binary fluid mixture methanol and isooctane (2,2,4-trimethylpentane) was determined by precisely measuring the refractive index both above and below the upper critical consolute point. Thirty-five two-phase data points were obtained on three compositions to determine the location of the critical point: critical temperature = 42.38 °C and critical composition = 33.2% by mass methanol. The simple scaling relationship $n_u - n_L = Bt^\beta$ determined the critical exponent $\beta = 0.323 \pm 0.009$ and the amplitude $B = 0.090 \pm 0.001$, where $t = (T_c - T)/T_c$ is the reduced temperature. Correction-to-scaling terms were not needed to describe the data taken over 3 decades in reduced temperature.

Introduction

The substantial recent interest in critical phenomena in a multitude of physical systems has been built upon concepts of scaling and universality that developed from studying second-order phase transitions in fluid systems. Wilson¹ provided a comprehensive framework in renormalization group theory that has been used by many others to predict relationships among exponents, the values exponents should have when they belong to different universality classes, and relationships among the amplitudes of thermodynamic phenomena. Although renormalization group theory does not predict the location of the critical point, all systems behave similarly once they are close to their own critical point.

The predictions for the exponents have been well verified in liquid-gas and in binary fluid mixtures, both of which belong to the same universality class (three-dimensional Ising model). The amplitude predictions from two-scale-factor universality have been confirmed in a few systems but violated in others. Several reviews discuss²⁻⁵ the present status of experiments and theory.

In order to determine amplitudes and exponents, it is essential to be near the critical point. The coexistence curve provides the location of the critical point and is the first experiment that must be conducted on a system. The shape of the coexistence curve also provides information on the critical exponent β and amplitude B_0 , since, for simple scaling, the difference in a generalized order parameter, x , between the upper and lower phases goes as a power law in reduced temperature $t \equiv (T_c - T)/T_c$.

$$\Delta x \equiv x_u - x_L = B_0 t^\beta \quad (\text{simple scaling})$$

The critical exponent, β , is predicted to be 0.325 ± 0.0015 from renormalization group theory⁶ applied to a 3-D Ising model and

0.328 ± 0.003 from series expansion.⁷ In liquid-gas systems the order parameter is the density;^{3,4} for binary fluid mixtures the proper order parameter is still uncertain although many favor volume fraction since this gives^{3,4,8} a more symmetric Ising-like coexistence curve. By volume fraction we mean the volume of one component divided by the actual volume of the phase it occupies. Others have defined volume fraction as the volume of one component divided by the sum of the components' volumes in that phase.^{8,9} The latter definition is equivalent to the former only if there is no volume change on mixing.

The experimental study of binary liquid mixtures has several advantages over liquid-gas systems. Many binary liquid mixtures have a critical point at atmospheric pressure, a critical temperature close to room temperature, and (usually) small gravity effects. Also, simple scaling appears to hold for relatively large reduced temperatures.^{3,4} Since both liquid-gas and liquid-liquid systems belong to the same universality class, the information gained by studying one can be applied to the other.

The coexistence curve of a binary liquid mixture can be measured by several techniques.⁵ The two that are relevant to this work are the following: (1) A set of different composition vials are put in a water bath with the height of the menisci determining the degree of miscibility and, hence, the coexistence curve.^{5,10} (2) One sample is prepared and the refractive index can be used to determine the composition of each phase at various temperatures.^{11,12}

The last method is the one utilized in the investigation reported here. It has an advantage over the first method because the refractive index is a precise, nonintrusive probe that can measure the properties of a single sample of fixed composition. Investigating one sample also avoids the problem of preparing multiple

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samples without introducing differing amounts of impurities that affect the critical temperature.^{13,14} The measurement of the refractive index in each phase at the same temperature allows the shape of the coexistence curve to be precisely determined.

When the refractive index is used to determine the volume fraction of a phase, three assumptions are normally made. First, it is assumed that the refractive index itself does not have an anomaly close to a critical point. Measurements and predictions^{15,16} show any such anomaly to be less than 100 ppm, which is below the resolution in this experiment.

The second assumption is that the extension of the Lorentz–Lorenz relation^{11,17,18} to binary liquid mixtures is valid. The Lorentz–Lorenz relation has been tested in pure fluids near a critical point and found to hold within 1%;^{5,19} deviations close to critical could be due to any combination of gravity effects, thermal gradients, or a breakdown of the Lorentz–Lorenz relation. A very recent, direct experimental test²⁰ of the Lorentz–Lorenz relation in the near-critical binary fluid mixture isobutyric acid and water has verified the Lorentz–Lorenz relation within experimental error (0.5%) when the volume loss upon mixing is taken into account.

The final assumption is the additivity of volume, which assumes no volume loss (or gain) upon mixing. Reeder et al.⁹ studied a binary liquid mixture, nitroethane and 3-methylpentane, where additivity of volume did not hold and found the critical exponent β to be independent of the choice of order parameter. We have reanalyzed Greer's density data⁸ on isobutyric acid and water and found β to be independent of the definition of volume fraction;²⁰ however, the amplitude B increased by 45% when the volume loss on mixing was included in the definition of the volume fraction. The amplitude B can provide an indirect test of the Lorentz–Lorenz and additivity of volumes assumptions as shown recently by Housessou et al.¹⁸ They found B to vary less than 3–4% in the system methanol–cyclohexane as a result of these two assumptions.

With the three assumptions discussed above, the difference in refractive index between the two phases is proportional to the difference in volume fraction between the phases:¹¹ $\Delta n = K\Delta n$. From measurements on pure methanol and isooctane, the proportionality constant K was calculated to be a constant 16.08 ± 0.09 over the range of temperatures investigated here. Until the proper order parameter is established for binary liquid mixtures, the order parameter choice is still somewhat arbitrary. Volume fraction gives more symmetric coexistence curves and Ising exponents.^{3,4,20} The refractive index data reported here could be transformed into volume fractions; however, we prefer to report the raw data and note that the information (T_c , ϕ_c , β , and B) obtained in the analysis is equivalent.

This experiment uses refractive index techniques to investigate the coexistence curve of the binary fluid mixture methanol–isooctane. This mixture's coexistence curve has not been precisely measured before yet provides a good system for future impurity investigations.¹⁴

Experimental Section

The fluids used were spectral-grade methanol (J. T. Baker's Photorex) and isooctane (Eastman Kodak), used without further purification. The fluids were transferred in a drybox under a nitrogen atmosphere to prevent water contamination. Three different compositions were prepared and measured: 37.42%, 34.99%, and 32.70% by mass methanol. The first two samples

TABLE I: Refractive Indices in the Upper and Lower Phases of the Binary Fluid Mixture Methanol–Isooctane^a

T , °C	n_u	n_L	$T_c - T$, °C	run
44.107	1.3647	1.3510	0.991	1
44.999	1.3605	1.3537	0.099	1
45.008	1.3605	1.3541	0.090	1
44.865	1.3615	1.3530	0.233	1
42.741	1.3671	1.3487	2.357	1
42.299	1.3677	1.3484	2.799	1
43.368	1.3659	1.3493	1.730	1
43.380	1.3659	1.3490	1.718	1
43.663	1.3653	1.3497	1.435	1
44.644	1.3630	1.3516	0.454	1
35.291	1.3751	1.3457	9.807	1
34.639	1.3757	1.3458	10.459	1
36.324	1.3741	1.3457	8.774	2
38.325	1.3723	1.3461	6.773	2
39.331	1.3713	1.3463	5.767	2
40.337	1.3700	1.3467	4.761	2
41.347	1.3691	1.3476	3.751	2
42.357	1.3674	1.3479	2.741	2
43.367	1.3657	1.3487	1.731	2
44.399	1.3634	1.3502	0.699	2
34.119	1.3734	1.3455	8.536	3
38.348	1.3689	1.3466	4.316	3
39.941	1.3665	1.3476	2.726	3
40.913	1.3648	1.3479	1.757	3
41.902	1.3630	1.3500	0.769	3
42.151	1.3622	1.3506	0.544	3
42.218	1.3618	1.3509	0.509	3
42.426	1.3610	1.3517	0.303	3
42.712	1.3593	1.3541	0.055	3
42.740	1.3585	1.3541	0.031	3
42.761	1.3583	1.3542	0.021	3
42.769	1.3582	1.3545	0.015	3
42.721	1.3597	1.3532	0.091	3
42.324	1.3622	1.3509	0.502	3
42.855	1.3567	1.3567	-0.171	3

^aData were taken on three compositions: 37.42% (run 1), 34.99% (run 2), and 32.70% (run 3) by mass methanol. The critical temperature T_c for runs 1 and 2 was 45.098 °C while it was 42.38 °C in the third sample when the cell was filled. A small drift (14 mK/day) in T_c for run 3 was also observed and is used to form ($T_c - T$).

were prepared from different bottles than the third and in a drybox that could not be sealed as well. The 32.7% composition was found to be very close to the critical one of 33.2% by mass. Each composition was sealed in a prism-shaped cell that had a volume of 7.3 cm³ including a 1-cm³ nitrogen bubble to maintain the pressure close to atmospheric.

An aluminum, prism-shaped cell¹² was used to seal each of the first two samples (37.42% and 34.99%) in turn and allow the refractive index to be measured in each phase. The fluids were sealed with Teflon o-rings and plug. The temperature control and monitoring for these samples were the same as previously described.¹² Modifications were made prior to taking data on the last composition (32.70% by mass methanol) to improve the experiment. The cell was gold plated and Kalrez o-rings were used to seal the sample, which was prepared in a drier drybox. The cell remained sealed over a 4-month period as determined from subsequent weighing of the fluids used. This cell's temperature was controlled with an ac bridge using a ratio transformer and lock-in amplifier. A temperature-controlled thermostat surrounded the cell as before. The temperature of the cell was monitored with a Leeds & Northrup potentiometer sensing a Thermometrics ultrastable thermistor, which was calibrated on the international practical temperature scale of 1968 to 0.01 K. Temperature resolution was ± 0.2 mK with control of ± 1 mK over 24 h.

The bulk refractive index was determined in each phase from measurements of the minimum deviated angle of the 632.8-nm He–Ne laser light bending through the prism-shaped samples of fluid. The undeviated angle and the prism angle were also measured. Angles were read with a Gaertner spectrometer to a precision of 30 s of arc, which provided a resolution in refractive index of ± 0.00015 .

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The procedure for taking a data point and calculating the refractive index is the same as reported previously.¹²⁻¹⁴ No gravity effects³ were observed in this system. The lower phase completely wets²¹ the upper phase in the 37.42% and 34.99% samples, while no wetting was observed in the sample closest to the critical composition.

Results

Data were taken on three separate compositions over 3 decades in reduced temperature: $3 \times 10^{-5} < (T_c - T)/T_c < 3 \times 10^{-2}$. The refractive index data are shown in Table I. Different critical temperatures were observed in the samples taken before plating the cell and the sample taken afterward. The critical temperature in the first two samples was found to be 45.098 °C while the third (32.7%) sample was 42.38 °C. The difference is attributed to water impurities in the first two samples. Such impurities substantially alter T_c but have little effect on the critical composition, ϕ_c , critical exponent, β , or the amplitude of the coexistence curve, B .^{13,14}

In addition, a small drift (14 mK/day) in the critical temperature was detected in the 32.7% sample, where the critical temperature could be approached more closely. It is speculated that this constant drift is due to absorbed impurities in the Kalrez o-rings which gradually came into the system. This drift rate was used to determine T_c for each point in the third sample. The drift was too small to affect ϕ_c ; $T_c = 42.38$ °C is taken as the extrapolated T_c when the cell was filled. The refractive index data on the 32.7% sample were taken over a 3-week period; the critical temperature drift rate was determined over a 3-month period.

The average of the upper and lower phase refractive indices represents the diameter of the coexistence curve. This diameter was linear for this system as it is in most systems.^{3,22,23} The diameter can be extrapolated to the critical temperature to give a refractive index $n_c = 1.3563 \pm 0.0002$ corresponding to the critical composition. By taking the difference in refractive index between the one phase and the diameter at the critical temperature and by using the Lorentz-Lorenz relation, one can calculate the correction to the prepared composition (32.70% by mass methanol).¹¹ The critical composition is just the sum of this correction and the prepared composition. This procedure gives $\phi_c = (33.2 \pm 0.5)\%$ by mass methanol, or $(30.3 \pm 0.5)\%$ by volume methanol.

The shape of the coexistence curve is expected, to leading order, to be

$$\Delta n \equiv n_u - n_L = Bt^\beta$$

which is the simple scaling result. In binary mixtures, simple scaling is generally observed^{3,4} to hold for reduced temperatures, t , less than 10^{-2} . When further from the critical temperature, additional "correction-to-scaling" terms^{3,4} are often needed to explain the experimental data. The 35 data points taken on the three compositions for this system are shown in Figure 1 and listed in Table I. These data were divided into two sets (runs 1 and 2 and run 3) and were analyzed with a properly weighted linear least-squares fit²⁴ to the simple scaling relationship $\Delta n = Bt^\beta$. The critical temperature was determined from the best fit of simple scaling to each data set. These critical temperatures are used to determine the $(T_c - T)$ column in Table I; the small drift rate in the third run is also included.

The parameter values β and B were found to be independent of the data set fit by simple scaling. These fits are shown in Table II along with the best fit to the combined sets of data. The value of the critical exponent β is thus 0.323 ± 0.009 and $B = 0.090 \pm 0.001$, where the errors are 3 times the standard deviation determined from the statistical fluctuation in the data. Simple scaling fitted the data with none of the systematic deviations

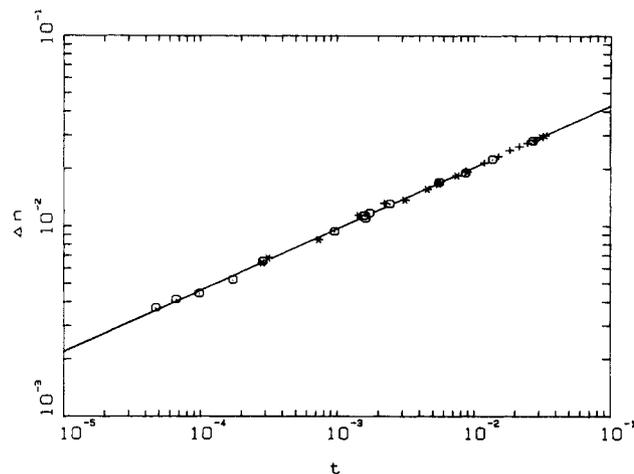


Figure 1. A log-log plot of the difference in refractive index between the upper and lower phases ($\Delta n = n_u - n_L$) test its dependence on the reduced temperature $t = (T_c - T)/T_c$. The (*) and (+) data points are from the first two samples while the (O) data points are from the third sample of methanol-isooctane. If simple scaling holds, then the points should fall on a straight line of slope β . The line through the points is the best fit to simple scaling and gives $\beta = 0.323 \pm 0.009$ and $B = 0.090 \pm 0.001$.

TABLE II: Data in Table I Fit by the Simple Scaling Relationship. $\Delta n = Bt^\beta$, where $t = (T_c - T)/T_c^a$

run	B	β	χ^2/N
1, 2	0.0907 ± 0.0006	0.322 ± 0.004	0.67
3	0.0894 ± 0.0006	0.324 ± 0.005	0.14
1, 2, 3	0.0903 ± 0.0005	0.323 ± 0.003	0.61

^a The critical temperature was allowed to vary to minimize the reduced χ^2 : χ^2/N (see ref 24). The errors in the parameters are one standard deviation as determined from the fits.

characteristic of correction terms.

Discussion

Our value of the critical exponent $\beta = 0.323 \pm 0.009$ agrees well with theoretical predictions^{6,7} ($0.322 < \beta < 0.328$) and with other experimental determinations^{3,4} ($0.315 < \beta < 0.328$). The critical composition, $\phi_c = 33.2\%$ by mass methanol, and temperature, $T_c = 42.38$ °C, are consistent with preliminary data we took by using meniscus heights to map out the coexistence curve.¹⁰ The value of B is particularly important now, since two-scale-factor universality predicts a universal relationship between B , the amplitude of the correlation length ξ_0 above T_c , and the amplitude of the osmotic compressibility χ_0 . The latter two amplitudes, ξ_0 and χ_0 , can be determined from a light scattering experiment as done recently^{25,26} on other systems.

Our amplitude $B = 0.090 \pm 0.001$ compares quite favorably with the amplitude found¹⁰ for this same system using meniscus heights to determine the coexistence curve. Following Housessou et al.,¹⁸ who did an indirect test of the Lorentz-Lorenz relation in the system methanol-cyclohexane, the value of B from the refractive index technique done here can be compared to B determined from meniscus heights, which are directly related to volume fractions. With $K = 16.08 = \partial\phi/\partial n$, the meniscus height study¹⁰ provides a value of $B = 0.088 \pm 0.003$, which agrees well with our value.

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