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Coexistence curve of methanol + n-heptane: Range of simple scaling and critical amplitudes

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The coexistence curve of methanol + n-heptane has been determined. The difference between the volume fraction ϕ of coexisting phases has been found to be the correct order parameter. The results have been analyzed in terms of two thermodynamic fields, $t=(T-T_c)/T_c$ and $t'=(T-T_c)/T$. While a simple scaling law fits the whole set of results when t' and ϕ are used, it is only valid up to $t \le 8\times10^{-3}$ when t is used with either ϕ or the mole fraction X, and one correction-to-scaling term is needed. The determination of the amplitudes of the correction-to-scaling terms is discussed in detail. The diameter of the coexistence curve has been found to show a $(1-\alpha)$ anomaly when ϕ is used, while a 2β one when X is used. No improvement in the diameter analysis has been attained in terms of a crossover formulation. The pressure dependence of T_c has been measured, the result being used to calculate the amplitude of the isobaric expansion coefficient.

I. INTRODUCTION

Near the critical point (CP) of a fluid mixture, various thermodynamic quantities along special thermodynamic paths vary as power laws with critical exponents which, according to the universality hypothesis, depend only on the symmetry of the Hamiltonian and the dimensionality of the system, and not on its chemical nature or the specific intermolecular potential among its molecules, unless the latter is long ranged.[1] This means that all systems belonging to the same universality class should exhibit the same critical exponents. Pure fluids near the gas-liquid CP, mixtures near liquid-gas or liquid-liquid (LL) CP's, and ferromagnets fall into the universality class of three-dimensional Ising-like systems.

Nevertheless, the simple power laws are exact only asymptotically close to the CP, and in general such a critical region is rather small.[2] To analyze data measured at longer distances from the CP, contributions from the irrelevant operators to the free energy density have to be taken into account, leading to correction-to-scaling terms.[3]

For a binary mixture near an upper-critical-solution temperature (UCST), the shape of the coexistence curve, according to the renormalization group (RG), can be described as[4]

$$\Delta\lambda \equiv \lambda_R - \lambda_L = Bt^{\beta} + B_1 t^{\beta+\Delta} + B_2 t^{\beta+2\Delta} + \cdots , \quad (1)$$

where[5] $\beta=0.325\pm0.001$ and $\Delta=0.50\pm0.02$ are critical exponents; $t=(T-T_c)/T_c$; B, B_1, and B_2 are critical amplitudes; and $\Delta\lambda$ is the order parameter, which is the difference between the compositions of the coexisting phases, R and L referring to both branches of the coexistence curve. Even though for many types of phase transitions the order parameter has been unequivocally identified, this is not the case for LL CP's, and several functions of the composition (mole, volume, or mass fraction) have been used for different binary systems.[6–8]

The RG also predicts that the diameter of the coexistence curve should behave as[4]

$$\frac{\lambda_R+\lambda_L}{2} \equiv d = \lambda_c + A_0 t + A_1 t^{1-\alpha} + A_2 t^{1-\alpha+\Delta} + A_3 t^{1-\alpha+2\Delta} + \cdots , \quad (2)$$

where[5] $\alpha=0.110\pm0.005$ is the critical exponent that describes the divergence of the specific heat at the CP, and λ_c is the critical composition. In principle, Eq. (2) results from the assumption that the correct composition variable has been chosen for the order parameter, and in this case the diameter of the coexistence curve is expected to show a leading $(1-\alpha)$ anomaly. However, it has been shown[6,9] that the diameter will have an additional term with an exponent 2β when a "wrong" choice of the order parameter has been made; thus, as has been previously done,[7] we have added a $A_4 t^{2\beta}$ term to the RG expansion of Eq. (2). The weight of both anomalies might be used to discern the preferred composition variable among different ones. Unfortunately, most frequently the accuracy of the experimental date does not allow one to decide for the $(1-\alpha)$ or the 2β anomalies;[6,9] hence the selection of the right order parameter for mixtures remains, to a good extent, an open question.[10]

Besides the universality of the critical exponents, RG predicts that certain universal relationships hold between the critical amplitudes of different thermophysical properties; thus only two of them are independent for each system (the two-scale-factor universality hypothesis).[11,12] There is substantial experimental support for the validity of such relationships of the amplitudes for the leading (or simple scaling) terms of expansions of the type of Eqs. (1) and (2). Furthermore, there is good agreement between the experimental and theoretical values for those relationships (except for those involving surface tension).[12,13] However, the situation is far from satisfactory for the amplitudes of correction-to-scaling terms.[13]

Several problems affect the experimental determination of the critical amplitudes. The first one is that they are dependent on the value of the critical coordinates, and since especially the critical temperature T_c is strongly affected by impurities,[14] it is recommended to study all the properties using the same sample. In addition, when the critical exponents and critical amplitudes are fitted to experimental data of a property such as $\Delta\lambda$, correlation coefficients close to unity are found between the exponents and the amplitudes. A good example of this can be found in a recent work of Närger and Balzarini[15] (see Table I of Ref. 15) in which changing β from 0.327 to 0.328 leads to changes of 1% in B and 15% in B_1. An additional problem is that the symmetry of the coexistence curve can be different when mole, volume, or mass fractions are used for λ;[7] therefore the importance of the correction-to-scaling terms is different in each case. Finally, although $\Delta\lambda$ has been expanded in terms of t in Eq. (1), Balfour *et al.*[16] have developed an equation of state for pure fluids that also makes use of the Wegner expansion but with $t'=(T-T_c)/T$ as the thermodynamic field. This choice has also been used by Souletie *et al.*,[17–19] concluding that it extends the range of simple scaling to larger values of $|T_c-T|$, thus reducing the weight of the correction-to-scaling terms.

In a recent paper, Singh and Pitzer[20] have analyzed the coexistence of five binary systems near an UCST, concluding that there is evidence supporting a universal value $B_1\simeq 0$ for the amplitude of the first correction-to-scaling term in Eq. (1), which would be consistent with calculations for $s=\frac{1}{2}$ spin systems.[20] For pure fluids B_1 seems also to be universal, although with a different value than for a LL UCST; and it is suggested that $B_1\neq 0$ for LL equilibria near a lower-critical-solution temperature (LCST). These results would imply that even though the three types of systems mentioned belong to the same universality class in the limit $|t|\rightarrow 0$, the approach to critical behavior should be different. Although the calculation for the $s=\frac{1}{2}$ spin system confers strong support to the validity of the $B_1=0$ assumption for liquid mixtures near an UCST, values of $B_1\neq 0$ have been reported for various systems,[8,21–25] and significant discrepancies have been found among the values of B_1 obtained for the same system in different laboratories.[8,12,26–28] Thus, it seems convenient to obtain further experimental evidence on the validity of the assumption of Singh and Pitzer.

Liquid mixtures offer important advantages over pure fluids for studying critical phenomena, like the possibility of choosing systems with CP's near room conditions, thus increasing the accuracy of the measurements, or of reducing gravity-induced gradients to a larger extent than in pure fluids;[9] hence it seems worthwhile to make a further experimental effort to clarify those questions that still remain open concerning LL equilibrium. The aim of the present paper is to obtain data at atmospheric pressure of the coexistence curve of the methanol+n-heptane (MH) system accurate enough as to be able to determine unequivocally the preferred order parameter for this system. The range of validity of simple scaling laws will also be determined, and the leading and first correction-to-scaling amplitudes will be obtained. The system (MH) was chosen because of the following reasons: Some preliminary data[29] indicate that its coexistence curve is not symmetrical when expressed in terms of mole fractions; some C_p data are available for the critical mixture;[29,30] an estimation of the leading amplitude, ξ_0, of the correlation length has been published;[31] and the gravity-affected region has been shown[9,32] to be very small for this system.

The rest of this paper is organized as follows. Section II describes some experimental details. Section III discusses the results for the shape of coexistence curve. In Sec. IV the diameter of the coexistence curve is analyzed. Section V studies the pressure dependence of T_c. Finally, Sec. VI summarizes the results.

II. EXPERIMENT

When measuring transition temperature in the vicinity of a LL CP, special precautions must be taken to prevent effects induced by gravity or by the presence of impurities in the measuring samples.[9] Although, as has been mentioned, the system (MH) seems to have a small gravity-affected region, the sample height was always kept below 2 cm. A mild but constant stirring prevented the formation of gradients. Concerning impurities, they have been shown to have little effect upon critical exponents,[14] but they probably are the main reason for the important discrepancies among the values of T_c obtained for the same system in different laboratories.[33] In particular, MH is a polar-nonpolar system, and water is then expected to cause an important shift in its T_c.[34–36] Consequently, methanol has been purified with a careful drying procedure, described by Ewing *et al.*,[37] which has previously given very good results.[8] Both liquids were kept in a dry nitrogen atmosphere, and over adequate molecular sieves (3 Å for methanol and 4 Å for n-heptane). A single stock of each component was used to prepare all the samples; methanol Fluka puriss., with an initial water content less than 0.05%, and n-heptane Carlo Erba Reagente Puro Erba (RPE), with a water content less than 0.01%.

The samples were prepared in Opticlear glass screw-cap vials, the sealing being accomplished by means of the combined action of a Teflon stopper and a Bakelite cap. This system, similar to that used by Greer and Jacobs,[38] ensures a hermetic closing (no weight loss was detected after long periods of time) and avoids the drastic temperature gradients involved in flame sealing. The liquids were introduced in the vials by means of hypodermic syringes inside a glove box, under dry nitrogen. The composition of the samples was known by weighing in an electronic balance AND ER-120A, with a precision of ±0.05 mg. A Teflon-coated magnet was introduced in each vial to allow stirring during the measuring procedure, preventing the formation of any gradient near T_c or supercooling far from the critical point.

The vial containing the sample is placed inside a water bath in which the temperature can be kept stable to ±1 mK over 20 h periods. The temperature control system is very similar to that described in Ref. 8. The sample, homogeneously illuminated by a set of fluorescent tubes, is observed through a double window and stirred with the help of an exterior magnet. Each point of the coexistence curve represents the transition temperature of one sample. This temperature is the average value of three measurements taken while cooling the sample, since the time required to reach an equilibrium state is much shorter in the one-phase region than in the two-phase region. The phase transition is observed as the appearance of turbidity in the sample.[39] A good illumination and mild stirring ensure the reproducibility of the measurements within experimental error. One sample out of ten was measured a second time after a two week period, and no shift in the transition temperatures was detected; hence any lack of hermeticity in the sample holders was discarded. The advantages and disadvantages of this point-by-point method compared to the one-sample method have been extensively discussed in the literature.[21,27,40] The pressure measurements have been performed with a Cailletet-type apparatus already described in the literature.[8,41]

III. THE COEXISTENCE CURVE

Table I shows the experimental results obtained, from which we have estimated $T_c=(324.008\pm0.001)$ K and $X_c=0.613\pm0.001$, X being the mole fraction of methanol. The equal-volume criterion (which has been recently questioned[42]) for a mixture of such composition supports that estimation. This point will be further discussed below. Table II shows the CP coordinates reported for this system so far in the literature. As can be observed, there is an enormous scattering in the data, most probably due to the existence of humidity in the mixtures, which tends to increase T_c. Our value is in the lowest part of the temperature range shown in Table II. Also for the critical composition the scattering is noticeable. Our results agree strikingly well with those of Klein and Woermann.[30] Figure 1 shows the coexistence curve when $\lambda=X$ [Fig. 1(a)] and when $\lambda=\phi$ [Fig. 1(b)].

In order to calculate the order parameter, the coexistence curve has been divided in two branches with $X<X_c$ and $X>X_c$, respectively. Each branch has been fitted to the following function:[8,22,43]

$$\lambda=C_0+C_1t+C_2t^{1-\alpha}+C_3t^{\beta}\ . \tag{3}$$

Table III shows the characteristics of the fittings, obtained using a regression method based on the maximum likelihood principle.[8] In order to obtain a variance $\chi^2\simeq1$, the following uncertainties have been considered: $\sigma(T)=\pm3$ mK, $\sigma(X)=\pm0.001$, or $\sigma(\phi)=\pm0.001$, X and ϕ being the mole and volume fractions, respectively. In order to calculate ϕ from X, the densities of the liquids in the temperature interval considered in Table I are necessary. They have been taken from the literature, Refs. 44 and 45, for methanol and n-heptane, respectively. No excess volume data are available for this system in the critical region; thus volume additivity has been assumed. Equation (3) contains five adjustable parameters: C_i, $i=0$, 3, and T_c. As can be observed in Table III, the results of both branches lead to the same value of $T_c=324.008$ K, which agrees with the experimental value quoted above. This result, besides confirming the value of T_c, strongly supports the consistency of the experimental data. Equation (3) and the parameters of Table III have been used to

TABLE I. Experimental phase-separation temperatures for the methanol+n-heptane system. The subscript 1 refers to the composition of methanol, X being the mole fraction and ϕ the volume fraction. The left-hand side of the table shows the right branch of the coexistence curve. The right-hand side shows the left branch of the coexistence curve.

T (K)	X_1	ϕ_1	T (K)	X_1	ϕ_1	T (K)	X_1	ϕ_1	T (K)	X_1	ϕ_1
324.008	0.6199	0.3103	321.060	0.7751	0.4875	324.009	0.6055	0.2975	321.170	0.4012	0.1560
324.007	0.6218	0.3120	320.521	0.7825	0.4982	324.008	0.5938	0.2874	321.168	0.4006	0.1557
324.001	0.6270	0.3168	320.384	0.7844	0.5010	324.007	0.5886	0.2830	321.100	0.3999	0.1553
323.999	0.6310	0.3205	320.393	0.7845	0.5012	323.992	0.5862	0.2810	321.020	0.4001	0.1554
324.005	0.6352	0.3245	320.034	0.7883	0.5068	323.989	0.5814	0.2770	320.988	0.3941	0.1522
323.996	0.6389	0.3280	319.747	0.7927	0.5135	323.989	0.5766	0.2371	320.802	0.3927	0.1514
323.998	0.6433	0.3322	319.600	0.7935	0.5147	323.981	0.5758	0.2725	320.706	0.3887	0.1493
323.995	0.6443	0.3332	319.364	0.7952	0.5173	323.944	0.5569	0.2575	320.679	0.3896	0.1498
323.985	0.6511	0.3399	318.746	0.8020	0.5279	323.936	0.5566	0.2572	320.399	0.3838	0.1467
323.963	0.6543	0.3430	318.727	0.8027	0.5290	323.808	0.5353	0.2412	320.322	0.3803	0.1448
323.955	0.6553	0.3440	318.580	0.8033	0.5299	323.750	0.5241	0.2330	319.934	0.3736	0.1413
323.942	0.6587	0.3475	318.185	0.8072	0.5361	323.722	0.5244	0.2332	319.869	0.3699	0.1394
323.915	0.6711	0.3602	316.998	0.8172	0.5524	323.695	0.5210	0.2308	319.614	0.3681	0.1385
323.638	0.6936	0.3844	316.654	0.8200	0.5570	323.631	0.5119	0.2244	319.531	0.3614	0.1351
323.591	0.6988	0.3903	316.484	0.8206	0.5581	323.573	0.5059	0.2203	319.520	0.3620	0.1354
323.331	0.7164	0.4107	316.454	0.8213	0.5592	323.397	0.4927	0.2113	319.964	0.3729	0.1410
323.032	0.7309	0.4284	316.022	0.8232	0.5624	323.386	0.4918	0.2107	318.853	0.3507	0.1297
322.934	0.7336	0.4318	315.760	0.8257	0.5667	323.364	0.4924	0.2111	318.587	0.3441	0.1265
322.843	0.7352	0.4335	315.217	0.8295	0.5732	323.197	0.4801	0.2030	318.466	0.3371	0.1231
322.481	0.7458	0.4474	314.421	0.8345	0.5820	323.113	0.4761	0.2005	318.264	0.3414	0.1252
322.246	0.7530	0.4569	314.216	0.8357	0.5841	323.091	0.4737	0.1989	317.388	0.3268	0.1182
321.500	0.7678	0.4771	313.884	0.8376	0.5875	322.591	0.4505	0.1845	317.174	0.3216	0.1157
321.335	0.7707	0.4812	313.387	0.8399	0.5916	322.522	0.4488	0.1834	316.238	0.3095	0.1101
321.187	0.7725	0.4837				321.799	0.4215	0.1674	315.700	0.3003	0.1059
						321.747	0.4186	0.1657	314.176	0.2755	0.0950

calculate $\Delta\lambda$ and d. For this purpose we have fixed the values of T given in Table I and interpolated the compositions of the two coexisting phases. Vani *et al.*[7] have followed a slightly different procedure for the system acetonitrile+cyclohexane; they used the experimental (T,λ) data point of one branch, and interpolated the point (T,λ') on the other branch. Table IV lists the 94 $(T,\Delta\lambda)$ and (T,d) pairs that were analyzed.

As already mentioned, when studying the order parameter using Eq. (1), T_c, β, and the B's are frequently fitted simultaneously. Although in some cases this procedure offers values of β compatible with the RG prediction $\beta=0.325\pm0.001$,[6,7] the high correlation coefficients among the parameters allow one to obtain several sets of them that lead to similar fits (similar values of χ^2).[46,47] As an example, one of the sets of parameters that fit the whole set of data of Table IV using $\lambda=X$ and simple scaling is $T_c=324.005\pm0.001$ K; $\beta=0.3337\pm0.0005$, and $B=1.795\pm0.004$ ($\chi^2=0.23$). Even though the value of χ^2 indicates that the residuals (experimental $-$calculated values) are compatible with the assumed uncertainties, the value of β is much larger than that given by RG, and that of T_c is smaller than the experimental one. The correlation matrix for the previous parameters is

$$\begin{bmatrix} 1.00 & 0.42 & 0.39 \\ 0.42 & 1.00 & 0.99 \\ 0.39 & 0.99 & 1.00 \end{bmatrix},$$

which clearly shows the very high correlation between β and B, a result comparable to that of Närger and Balzarini.[15] This fact led us to fix the values of the critical exponents in their RG values and to fit only the critical amplitudes. T_c was fixed in its experimental value.

Table V summarizes the results obtained. Fits 1–12 consider $B_i=0$, $i\geq1$, i.e., simple scaling, and $\lambda\equiv X$. The first point to be noticed is that using either t or t' as thermodynamic field does not lead to any noticeable difference with respect to the range of validity of simple scaling. The χ^2 values indicate that simple scaling seems to be valid up to $t\simeq t'\leq 6\times10^{-3}$, which is slightly larger than for pure fluids,[2] in accordance with other results of the literature,[2,15] and similar to the range found for isobutyric acid+water.[28] Fits 13 and 14 of Table V show that including the first correction-to-scaling term, $B_1t^{\beta+\Delta}$, is sufficient to correctly describe the whole set of results ($\chi^2=0.70$ and 0.83, respectively). It has to be noticed that even though B was also fitted, the same value as in fit 5 (the maximum t for which simple scaling is valid) was obtained.

Despite the fact that B and B_1 suffice to describe the data, we have also included B_2 in fits 15–17 in order to il-

TABLE II. Critical-point coordinates of the methanol+n-heptan system according to different authors. X_c is the critical mole fraction of methanol.

T_c (K)	X_c	Year
324.2	0.54	1956[a]
324.4	0.601	1961[b]
324.9	0.619	1965[c]
324.871	0.6135	1973[d]
323.88	0.613	1975[e]
321.50	(0.6135)	1984[f]
324.5	0.588	1986[g]
324.647	(0.6135)	1987[h]
329.27	0.551	1987[i]
324.008	0.613	This work

[a] K. Zieborak, Z. Maczynska, and A. Maczynski, Bull. Acad. Pol. Sci. Cl 3 **4**, 153 (1956).

[b] R. W. Kiser, G. D. Johnson, and M. D. Shetlar, J. Chem. Eng. Data **6**, 338 (1961).

[c] N. I. Chernova, Zh. Fiz. Khim. **39**, 2388 (1965) [Russ. J. Phys. Chem. **39**, 1275 (1965)].

[d] B. Viswanathan, K. Govindarajan, and E. S. R. Gopal, Indian J. Pure Appl. Phys. **11**, 157 (1973).

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[f] J. Balakrishnan, M. K. Gunasekaran, and E. S. R. Gopal, Indian J. Pure Appl. Phys. **22**, 286 (1984).

[g] J. B. Ott, I. F. Hölscher, and G. M. Schneider, J. Chem. Thermodyn. **18**, 815 (1986).

[h] Y. Jayalaxmi, S. Guha, V. C. Vani, and E. S. R. Gopal, Pramana J. Phys. **28**, 269 (1987).

[i] D. Bernabé, A. Romero-Martínez, and A. Trejo, Fluid Phase Equil. **40**, 279 (1987).

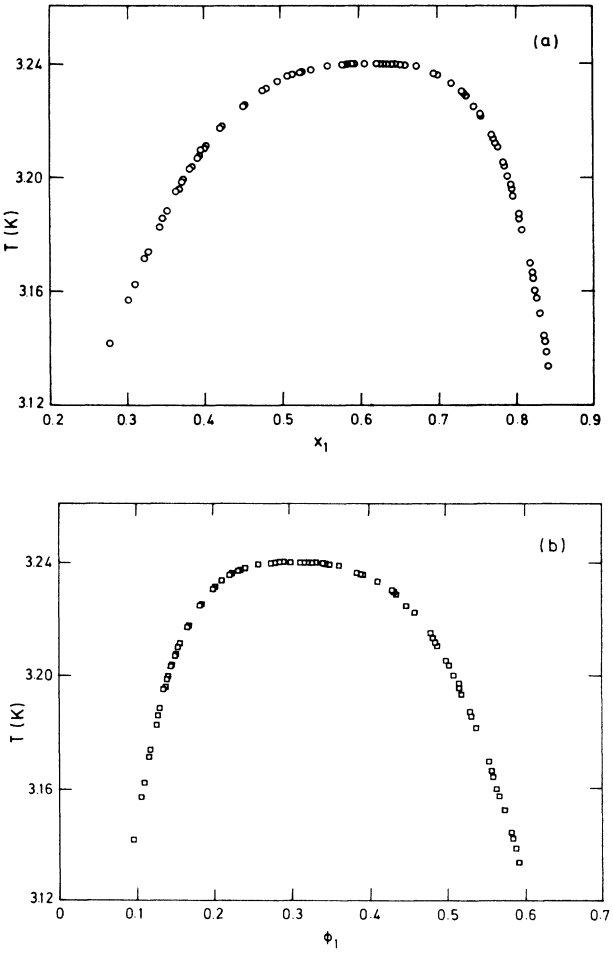

FIG. 1. Coexistence curve of the system methanol+n-heptane. The composition variable is the mole (a) or volume (b) fraction of methanol.

TABLE III. Parameters of the fittings of the two branches of the coexistence curve to Eq. (3), and their estimated uncertainties. n is the number of data points.

Branch	n	T_c	A_0	A_1	A_2	B	χ_ν^2
				$\lambda=X$			
Left	50	324.008±0.004	0.617±0.005	5.06±2.86	−4.61±2.25	−0.892±0.061	2.96
Right	47	324.008±0.002	0.610±0.003	−0.108±1.85	−0.717±1.46	0.810±0.037	2.02
				$\lambda=\phi$			
Left	50	324.008±0.007	0.305±0.003	−0.178±1.55	0.761±1.22	−0.739±0.032	0.97
Right	47	324.008±0.002	0.304±0.003	−5.55±2.02	4.63±1.59	0.764±0.040	2.62

lustrate how delicate the determination of critical amplitudes is when a whole set of experimental data is fitted to Eq. (1). As can be observed, it is possible to obtain several sets of B's that lead to $\chi^2<1$. As an example, the correlation matrix for fit 15 is

$$\begin{bmatrix} 1.00 & -0.96 & 0.89 \\ -0.96 & 1.00 & -0.98 \\ 0.89 & -0.98 & 1.00 \end{bmatrix},$$

which again shows the lack of independence of the parameters, indicating that it is possible to reduce their number in the fit.[46] This can easily be seen by comparing the fits 13 and 16 or 17. In other words, B_2 is not significant from a statistical point of view (Student's t test). However, fits 13–17 point out an important fact. From fits 13 and 17 it can be seen that a change of 0.2% in B leads to changes of 17% in B_1 and 30% in B_2. On the other hand, a comparison between fits 15 and 17 (same B) indicates that the inclusion of B_2 (though not significant) modifies B_1 by 58%. The analysis of the data of Närger and Balzarini for CHF_3 (Ref. 15) leads to similar conclusions. From the previous analysis one can conclude that even though the amplitude of simple scaling can be obtained without difficulty, a careful analysis of the data for different ranges of $T-T_c$ is necessary to obtain the amplitudes of the correction-to-scaling terms. For that purpose, a large number of very precise experimental data are absolutely necessary. The present results warn against the usual practice of fitting the B's directly to the experimental data over a more or less wide t interval.[6,8,12] The high correlation among the parameters also helps us to understand the difficulties found in determining universal ratios for correction-to-scaling amplitudes.[13] Finally, the use of t' instead of t does not change the conclusions, but changes the ratio B_1/B from 0.170 (fit 13) to 0.088 (fit 14).

As already mentioned, Singh and Pitzer[20] have suggested that $B_1\simeq 0$ for binary mixtures near an UCST. Fit 13 shows that a small value of $B_1=0.29\pm0.03$ is obtained for (MH) when only the first correction-to-scaling term is used [note that the B_1 of Singh and Pitzer corresponds to B_1/B in Eq. (1) and Table V]. Addition to the B_2 term, and a free fitting of B, B_1, and B_2 lead to a much larger value of B_1 (fit 15), which is again reduced, when B is fixed according to the simple scaling results (fit 17), to the value $B_1=0.46\pm0.04$. Fit 18 shows the result of fixing $B=1.693$ and $B_1=0$, and fitting B_2; the variance $\chi^2=1.44$ indicates that although the amplitude B_1 of the first correction-to-scaling term may be small, the term itself is not negligible out of the range in which simple scaling can be used. Leaving only B as an adjustable parameter while fixing $B_1=0$, one gets $\chi^2=0.96$ with $B=1.712\pm0.003$ and $B_2=0.98\pm0.15$, which again shows that many sets of parameters manage to fit the whole set of data.

Table V also includes the characteristics of the fittings when $\lambda=\phi$. It is remarkable that the range of validity of simple scaling does not change significantly compared to $\lambda=X$ when t is used as the field ($t\leq 8\times10^{-3}$), but t' extends that range up to $t\leq 3\times10^{-2}$, confirming the conclusions of Souletie *et al.*[17–19] As will be discussed in the next section, $\lambda=\phi$ is the right choice for the order parameter for this system; hence it seems that t' does not change the range of simple scaling when a wrong order parameter is used, but it does for the preferred one. It has to be emphasized that for $\lambda=\phi$, B_1 is closer to zero than for $\lambda=X$, a result which is in agreement with the suggestion of Singh and Pitzer.

IV. DIAMETER OF THE COEXISTENCE CURVE

Table VI shows the results of the fittings of the diameter of the coexistence curve to Eq. (2), while in Fig. 2 it is plotted versus the distance from the critical temperature for both $\lambda=X$ and $\lambda=\phi$. Figures 2 and fits a–c, h, and i show clearly that the diameter of the system (MH) is not rectilinear. Besides resulting in $\chi^2>1$ when $A_i=0$, $i>0$, the value of λ_c is different from the experimental critical composition ($X_c=0.613\pm0.001$, $\phi_c=0.304\pm0.001$). However, the inclusion of a $(1-\alpha)$ or a 2β term suffices to obtain $\chi^2<1$ and a value of λ_c in agreement with the experimental one. Either with $\lambda=X$ or with $\lambda=\phi$, $\chi^2\ll 1$ when $B_1\neq 0$, which probably indicates that the uncertainty in d has been overestimated ($\sigma_d=0.0025$ and 0.0021 for $\lambda=X$ and ϕ, respectively). It can also be observed that from the statistical point of view (Student's t test), once an anomaly has been included, the other correction terms are not necessary. Nevertheless, it is interesting to compare fits g and m. When $\lambda=X$, the ratio $|A_4/A_1|=0.75$, while for $\lambda=\phi$, $|A_4/A_1|=0.006$, which means that for $\lambda=X$ the fits do not allow us to distinguish between $(1-\alpha)$ and 2β anomalies, while for $\lambda=\phi$

the 2β term has a much smaller weight than the $(1-\alpha)$ one. It has been found that most data available in the literature[6,10] do not distinguish between the anomalies, which is unfortunate since RG predicts a $(1-\alpha)$ anomaly when the preferred order parameter is used. Concerning this point, only for the mixture cyclohexane + acetonitrile[7] and for some polymer-solvent systems[24,25] have conclusive results been obtained so far. From Table VI we can conclude that for MH $\lambda=\phi$ is the correct choice, as for the systems mentioned above.

In order to show this point in a clear way, we have fitted the whole set of diameter data to the equation[6]

TABLE IV. Values of the order parameter and the diameter of the coexistence curve of the methanol + n-heptane system, calculated from the compositions of the methanol in equilibrium obtained from Eq. (3) with the parameters of Table III. The subscripts R and L refer to the right and left branches, respectively. The temperatures are those of the experimental points. The points with $T > T_c = 324.008$ K have been neglected.

T (K)	$X_R - X_L$	$(X_R + X_L)/2$	$\phi_R - \phi_L$	$(\phi_R + \phi_L)/2$
324.007	0.0211	0.6139	0.0158	0.3057
324.007	0.0211	0.6139	0.0158	0.0357
324.005	0.0328	0.6132	0.0287	0.3043
324.001	0.0453	0.6126	0.0403	0.3040
323.999	0.0497	0.6125	0.0444	0.3040
324.998	0.0517	0.6124	0.0462	0.3040
323.996	0.0553	0.6123	0.0494	0.3040
323.995	0.0569	0.6122	0.0509	0.3040
323.992	0.0614	0.6120	0.0549	0.3040
323.989	0.0653	0.6119	0.0584	0.3040
332.989	0.0653	0.6119	0.0584	0.3040
323.985	0.0700	0.6117	0.0625	0.3041
323.981	0.0741	0.6115	0.0662	0.3042
323.963	0.0889	0.6109	0.0793	0.3044
323.955	0.0941	0.6107	0.0840	0.3045
323.944	0.1006	0.6104	0.0898	0.3047
323.942	0.1017	0.6104	0.0907	0.3047
323.936	0.1048	0.6103	0.0935	0.3048
323.915	0.1146	0.6098	0.1022	0.3050
323.808	0.1496	0.6079	0.1331	0.3061
323.750	0.1633	0.6071	0.1453	0.3067
323.722	0.1692	0.6068	0.1505	0.3069
323.695	0.1746	0.6064	0.1552	0.3071
323.638	0.1849	0.6057	0.1644	0.3706
323.631	0.1861	0.6056	0.1654	0.3076
323.591	0.1927	0.6052	0.1712	0.3079
323.573	0.1955	0.6050	0.1737	0.3081
323.397	0.2197	0.6031	0.1950	0.3093
323.385	0.2211	0.6030	0.1963	0.3094
323.364	0.2237	0.6028	0.1986	0.3096
323.331	0.2275	0.6025	0.2020	0.3098
323.197	0.2420	0.6013	0.2148	0.3106
323.113	0.2503	0.6006	0.2221	0.3111
323.091	0.2524	0.6004	0.2239	0.3113
323.032	0.2578	0.5999	0.2287	0.3116
322.934	0.2664	0.5991	0.2362	0.3122
322.843	0.2739	0.5984	0.2428	0.3127
322.591	0.2928	0.5965	0.2594	0.3140
322.522	0.2976	0.5960	0.2636	0.3143
322.481	0.3003	0.5957	0.2660	0.3145
322.246	0.3153	0.5941	0.2791	0.3157
321.799	0.3404	0.5912	0.3011	0.3177
321.747	0.3430	0.5909	0.3034	0.3179
321.500	0.3552	0.5894	0.3141	0.3189
321.335	0.3630	0.5884	0.3208	0.3196
321.187	0.3696	0.5875	0.3266	0.3202
321.170	0.3703	0.5874	0.3273	0.3203
321.168	0.3704	0.5874	0.3273	0.3203
321.100	0.3734	0.5870	0.3299	0.3205
321.060	0.3751	0.5868	0.3314	0.3207
321.020	0.3768	0.5866	0.3329	0.3209
320.988	0.3781	0.5864	0.3341	0.3210
320.802	0.3858	0.5854	0.3407	0.3217
320.706	0.3896	0.5849	0.3441	0.3220
320.679	0.3907	0.5847	0.3450	0.3221
320.521	0.3968	0.5839	0.3503	0.3227
320.399	0.4014	0.5833	0.3543	0.3231
320.393	0.4016	0.5832	0.3545	0.3232
320.384	0.4109	0.5832	0.3548	0.3232
320.322	0.4042	0.5829	0.3567	0.3234
320.034	0.4145	0.5814	0.3656	0.3244
319.964	0.4169	0.5810	0.3677	0.3247
319.934	0.4179	0.5809	0.3686	0.3248
319.869	0.4201	0.5806	0.3705	0.3250
319.747	0.4242	0.5800	0.3740	0.3254
319.614	0.4285	0.5793	0.3778	0.3258
319.600	0.4290	0.5792	0.3782	0.3259
319.531	0.4312	0.5789	0.3801	0.3261
319.520	0.4316	0.5789	0.3804	0.3261
319.364	0.4365	0.5781	0.3846	0.3266
318.853	0.4518	0.5757	0.3978	0.3282
318.746	0.4548	0.5752	0.4005	0.3285
318.727	0.4554	0.5752	0.4009	0.3286
318.587	0.4593	0.5745	0.4043	0.3290
318.580	0.4595	0.5745	0.4045	0.3290
318.466	0.4626	0.5740	0.4072	0.3294
318.264	0.4681	0.5731	0.4119	0.3299
318.185	0.4702	0.5728	0.4137	0.3302
317.388	0.4903	0.5694	0.4309	0.3324
317.174	0.4953	0.5685	0.4352	0.3330
316.998	0.4994	0.5678	0.4387	0.3334
316.654	0.5072	0.5664	0.4453	0.3343
316.484	0.5110	0.5657	0.4485	0.3347
316.454	0.5116	0.5656	0.4491	0.3348
316.238	0.5163	0.5648	0.4531	0.3353
316.022	0.5208	0.5639	0.4569	0.3359
315.760	0.5263	0.5629	0.4615	0.3365
315.700	0.5275	0.5627	0.4626	0.3366
315.217	0.5371	0.5609	0.4707	0.3378
314.421	0.5520	0.5580	0.4833	0.3396
314.216	0.5557	0.5573	0.4864	0.3400
314.176	0.5564	0.5571	0.4870	0.3401
313.884	0.5616	0.5561	0.4913	0.3407
313.387	0.5701	0.5544	0.4984	0.3418

TABLE V. Analysis of the shape of the coexistence curve of the methanol+n-heptane system in terms of extended scaling [Eq. (1)]. t refers to those fittings which used $(T-T_c)/T_c$ as the thermodynamic field, while t' stands for $(T-T_c)/T$. Notice that different temperature intervals from T_c have been considered, n being the number of data points included in the fit.

Fit	n	$T_{\min}$	B	B_1	B_2	χ_ν^2
			$\Delta\lambda=X'-X''$			
1t	27	323.573	1.659±0.005			0.42
2t'	27	323.573	1.658±0.005			0.41
3t	35	323.032	1.681±0.004			0.66
4t'	35	323.032	1.680±0.004			0.64
5t	41	322.246	1.693±0.004			0.92
6t'	41	322.246	1.691±0.004			0.86
7t	44	321.500	1.700±0.004			1.14
8t'	44	321.500	1.698±0.004			1.05
9t	51	321.020	1.710±0.003			1.43
10t'	51	321.020	1.707±0.003			1.26
11t	78	318.185	1.725±0.003			1.53
12t'	78	318.185	1.719±0.002			1.20
13t	94	313.387	1.693±0.004	0.29±0.03		0.70
14t'	94	313.387	1.700±0.004	0.15±0.03		0.83
15t	94	313.387	1.623±0.003	1.63±0.05	−5.9±0.2	0.08
16t	94	313.387	$\underline{1.697}$	0.39±0.04	−0.9±0.3	0.64
17t	94	313.387	$\underline{1.693}$	0.46±0.04	−1.2±0.3	0.58
18t	94	313.387	$\underline{1.693}$	$\underline{0}$	1.90±0.08	1.44
19t	94	313.387	1.712±0.003	$\underline{0}$	0.98±0.15	0.96
			$\Delta\lambda=\phi'-\phi''$			
20t	41	322.246	1.502±0.003			0.87
21t	44	321.500	1.507±0.003			1.04
22t	61	320.034	1.519±0.002			1.25
23t'	94	313.387	1.514±0.001			1.07
24t	94	313.387	1.513±0.003	0.08±0.03		0.86
25t'	94	313.387	1.518±0.004	−0.03±0.03		0.79
26t	94	313.387	$\underline{1.517}$	0.15±0.03	−0.8±0.3	0.85

$$d=\lambda_c+A_0t+A_1t^{C_1} \; . \tag{4}$$

Table VII shows the results for $\lambda=X$ and $\lambda=\phi$. When $\lambda=X$, $C_1=0.615\pm0.006$, a value similar to $2\beta=0.650\pm0.002$,[5] while for $\lambda=\phi$ we obtain $C_1=0.90\pm0.03$, very close to $(1-\alpha)=0.890\pm0.009$,[5] which clearly confirms that $\phi_R-\phi_L$ is the best order parameter. For the sake of brevity, we do not include the corresponding analysis using t' as the thermodynamic field, since the results are qualitatively similar to those of t.

There is a final point to be discussed about the results of Table VI. As can be observed, when $\lambda=X$, the addition of new correction terms significantly changes the amplitudes of the previous terms, a result similar to that found for $\Delta\lambda$ in the preceding section. On the contrary, when $\lambda=\phi$, the value of A_1 does not change significantly when A_2 or even A_3 are added, regardless of the fact that these parameters are not statistically significant (fits k and l), which makes us more confident in the determination of A_1 in the present case.

It is well known that the Wegner expansion for thermodynamic properties does not converge properly:[48] thus it is not possible to attain a good description of the system far from the CP using such an expansion. Nicoll and

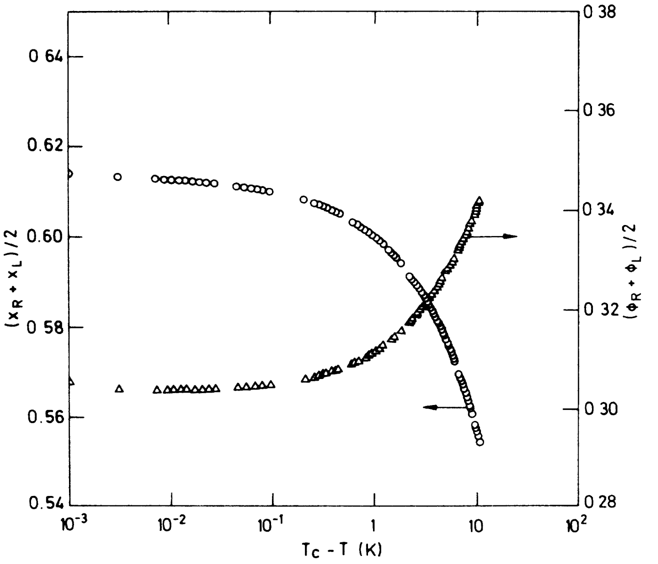

FIG. 2. Diameter of the coexistence curve of the methanol+n-heptane system as a function of the distance to the critical temperature ($\Delta T=T_c-T$). Left- and right-hand side Y-axis scales correspond to $\lambda=X$ (mole fraction, ○) and $\lambda=\phi$ (volume fraction, △), respectively. The composition variable λ refers to concentration of methanol.

TABLE VI. Analysis of the diameter of the coexistence curve of the methanol+n-heptane system in terms of extended scaling [Eq. (2)]. All the fits used the 94 data points, except *c, in which only points with $\Delta T \equiv (T_c - T) > 6$ K ($n = 16$) were considered.

Fit	λ_c	A_0	A_1	A_2	A_3	A_4	χ^2_ν
			$\lambda = X$				
a	0.6074 ±0.0005	−1.85 ±0.04					1.77
b	0.613	−2.16 ±0.04					3.98
*c	0.613	−1.94 ±0.03					1.20
d	0.6127 ±0.0001	5.1 ±0.1	−4.72 ±0.08				0.04
e	0.6127 ±0.0001	12.5 ±0.5	−8.4 ±0.2	−7.6 ±0.4			0.012
f	0.613 ±0.001	24 ±1	−13.3 ±0.5	−32 ±2	45 ±4		0.006
g	0.613	−0.8 ±0.2	0.9 ±0.2			−0.7 ±0.2	0.005
			$\lambda = \phi$				
h	0.3070 ±0.0003	1.23 ±0.02					1.15
i	0.304	1.39 ±0.02					2.13
j	0.3039 ±0.0001	−3.37 ±0.06	3.10 ±0.04				0.016
k	0.3040 ±0.0001	−3.4 ±0.4	3.1 ±0.2	0.06 ±0.45			0.016
l	0.3040 ±0.0001	−3.4 ±0.3	3.12 ±0.03	−0.3 ±0.5	1 ±1		0.016
m	0.304	−3.6 ±0.3	3.3 ±0.2			−0.02 ±0.03	0.016

Albright[49] have developed a crossover theory that links the mean field and the critical regions. According to them, the diameter can be expressed as

$$d = d_1 + d_2 t + d_3 t (y^{-\alpha/\Delta} - 1) + d_4 t (y^{1-\alpha/\Delta} - 1) ,$$

where (5)

$$y^{-1} = 1 + d_5 (t^{-\Delta} - 1) .$$

Equation (5) is nonlinear in the parameters, thus posing an important problem in the determination of the d_i's, since they are strongly dependent upon the initial guesses in the nonlinear regression, and they also depend on the range of t considered. This fact makes it very difficult to assess the reliability of the amplitudes. Table VIII shows some of the results obtained with the crossover formulation. It may be observed that Eq. (5) leads to very good fittings (small values of χ^2_ν) for all the temperature ranges considered, but no regular behavior of the adjusted parameters appeared. Similar results were obtained by Vani *et al.* for cyclohexane+acetonitrile.[7]

The anomaly of the diameter of the coexistence curve has been discussed by Goldstein and Parola[50] for pure fluids, relating it to the many-body correlations and finding a correlation between A_2 and the polarizability of the fluids. Unfortunately, no similar discussion is available for binary mixtures. Alternatively, in some lattice systems the anomaly is originated by the lack of particle-hole symmetry.[9] The anomaly of the diameter has also been discussed by Mulholland *et al.*[51] using a decorated-lattice model.

TABLE VII. Analysis of the anomaly of the diameter of the coexistence curve in the methanol+n-heptane system. Fittings of the whole set of diameter data to Eq. (4).

λ	λ_c	A_0	A_1	C_1	χ^2_ν
X	0.613±0.001	−0.08±0.03	−0.46±0.02	0.615±0.006	0.005
ϕ	0.3040±0.0001	−3±1	3.7±0.6	0.90±0.02	0.016

TABLE VIII. Analysis of the diameter of the coexistence curve of the methanol+*n*-heptane system in terms of the crossover formulation. Notice that different $\Delta T = T_c - T$ ranges have been considered. n is the number of points included in the fit, and $\lambda = X$.

n	$T_{\max}$	d_1	d_2	d_3	d_4	d_5	χ_ν^2
94	324.007	0.6133±0.0001	−0.87±0.01	125±5	9±1	−0.0102±0.0002	0.029
54	321.799	0.602±0.001	−1.36±0.02	1.2±0.3	0.019±0.004	−0.1014±0.0002	0.061
33	319.964	0.6363±0.0002	−0.489±0.0001	27.68±0.08	0.979±0.003	0.0741±0.0004	10^{-8}
16	317.388	0.56±0.09	−1.2±0.5	−4±21	0.07±0.4	−0.15±0.03	0.78

V. PRESSURE DEPENDENCE OF THE CRITICAL TEMPERATURE

We have measured the pressure dependence of the phase separation of a mixture of composition $X_1 = 0.614$ for a pressure range $0.1\ \text{MPa} \le p \le 13.0$ MPa. For $p = 0.1$ MPa the value $T_c = 324.009 \pm 0.003$ K was obtained. This is compatible with the critical temperature considered in Sec. III. Since these experiments were done on a different sample and with a different apparatus than the atmospheric pressure ones, this gives us further confidence about the purification and manipulation procedures. Table IX gives the (T_c, p) results, which were fitted to an equation of the type[8]

$$T_c(°\text{C}) = a + bp(\text{MPa}) + c[p(\text{MPa})]^2 , \tag{6}$$

with $a = 50.819 \pm 0.004$, $b = 0.392 \pm 0.001$, $c = -0.0030 \pm 0.0001$, $\sigma(T(\text{K})) = 0.0027$, $\sigma(p(\text{MPa})) = 0.011$, and $\chi^2 = 2.1$. From this fit a value of $(dT_c/dp)_{p=0.1\ \text{MPa}} = (392 \pm 1)$ mK/MPa is obtained. Sivaraman *et al.*[52] have reported $(dT_c/dp)_{p=0.1\ \text{MPa}} = 220$ mK/MPa for this system, but they used a smaller number of points and assumed a linear fit. When the present results are fitted to a straight line one obtains $dT_c/dp = (355 \pm 1)$ mK/mPa ($\chi^2 = 45$), which is intermediate between our result and that of Sivaraman *et al.* For the methanol+cyclohexane system we have discussed[8] the convenience of using a nonlinear fit.

TABLE IX. Pressure dependence of the phase-separation temperature of a mixture with near critical composition ($X_1 = 0.6139$).

T (K)	P (MPa)	T (K)	P (MPa)
324.285	0.82	326.158	5.83
324.458	1.28	326.252	6.11
324.563	1.56	326.377	6.44
324.667	1.78	326.467	6.73
324.793	2.13	326.535	6.94
324.878	2.36	326.811	7.72
324.975	2.60	327.085	8.51
325.068	2.86	327.194	8.80
325.161	3.09	327.291	9.11
325.276	3.43	327.397	9.44
325.673	4.46	327.497	9.72
325.764	4.72	327.589	9.97
325.867	5.03	327.834	10.71
325.964	5.29	328.061	11.43
326.088	5.63	328.275	12.08

The RG theory predicts that the ratio[39]

$$R_\xi = \xi_0 \left[\frac{T_c A}{k_B (dT_c/dp)} \right]^{1/3} \tag{7}$$

takes the universal value $R_\xi = 0.270 \pm 0.001$, where ξ_0 is the leading (simple scaling) amplitude of the correlation length, and A that of the isobaric expansion coefficient, $(1/V)(\partial V/\partial T)_p$, which can also be related to C, the amplitude for the isobaric heat capacity, through

$$A = \frac{C(dT_c/dp)}{T_c} . \tag{8}$$

Using $T_c = (324.008 \pm 0.001)$ K and $(dT_c/dp) = (392 \pm 1)$ mK/MPa, and the value $C = (10.3 \pm 0.7) \times 10^{-3}\ \text{J cm}^{-3}\,\text{K}^{-1}$ calculated by Klein and Woermann[30] from data of Viswanathan *et al.*,[29] Eq. (8) yields $A = (1.25 \pm 0.08) \times 10^{-5}\ \text{K}^{-1}$, which is very similar to the values of A reported for the system methanol+cyclohexane $[(0.86\text{–}2.5) \times 10^{-5}\ \text{K}^{-1}]$.[8,53]

VI. CONCLUSIONS

The coexistence curve of methanol+*n*-heptane has been measured in the near critical region. The results have been analyzed in terms of extended scaling equations, and show that the difference of volume fractions of the coexistence phases is the correct order parameter. The range of validity of simple scaling has been determined, and found to be dependent upon the thermodynamic field used only when the correct order parameter is chosen. In this case the use of $t' = (T - T_c)/T$ instead of $t = (T - T_c)/T_c$ increases the range of simple scaling. The strong correlation among the amplitudes of the correction-to-scaling terms in the order parameter expansion discourages the frequent practice of fitting them simultaneously to the whole set of data. Instead, the amplitude of the leading term should be determined from data in the simple scaling region, and fixing it, the subsequent amplitudes may be determined.

The diameter of the coexistence curve shows a significant anomaly which corresponds to a $(1-\alpha)$ exponent when volume fraction is chosen for the composition variable, and to a 2β exponent in the case of mole fraction. An analysis in terms of the crossover formulation of Albright and Nicoll[49] is difficult due to the nonlinear character of the equation corresponding to the diameter, and the strong dependence of the fitting parameters upon their initial guesses.

Finally, the pressure dependence of the critical temperature has been measured up to 13 MPa. The result obtained, together with values of the leading amplitude for C_p taken from the literature, have allowed us to calculate the amplitude of the isobaric expansion coefficient assuming the two-scale-factor universality hypothesis. The result is comparable to the values reported for the methanol+cyclohexane system.

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