Liquid–liquid critical phenomena. The influence of pressure on the coexistence curve of the methanol + cyclohexane system

Arturo G. Aizpiri, Ramón G. Rubio, and Mateo Díaz Peña
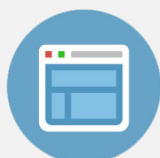
Liquid–liquid critical phenomena. The influence of pressure on the coexistence curve of the methanol + cyclohexane system

Arturo G. Aizpiri, Ramón G. Rubio,[a] and Mateo Díaz Peña

Departamento de Química Física, Facultad de Químicas, Universidad Complutense, 28040-Madrid, Spain

The liquid–liquid coexistence curve of methanol + cyclohexane has been measured in the range $0.1 \leqslant P/\text{MPa} \leqslant 13.0$. The difference in mole fraction between both branches of the coexistence curve has been found to be a more convenient order parameter than the volume fraction difference. The diameter of the coexistence curve has been found to show no anomaly within the experimental uncertainty. The pressure dependence of the correction to simple scaling terms are mostly masked by their estimated uncertainties. Reliable values for x_c and T_c have been determined, being x_c invariant with pressure within the experimental uncertainty. The data have been found to be compatible with the two-scale-factor universality hypothesis.

I. INTRODUCTION

The concept of critical point universality states that all the systems with the same spatial dimensionality and the same dimensionality of the order parameter should be in the same universality class, and should have the same critical exponents which describe the behavior of thermodynamic properties as the critical temperature T_c is approached.[1] Thus the Ising model, pure fluids at gas–liquid critical points, and binary liquid mixtures at liquid–liquid critical points all belong to the same class.[2] Binary liquid mixtures have been found to be very convenient for the study of these critical exponents. Simple scaling is valid in pure fluids for $t \leqslant 10^{-4}$, where $t = (T_c - T)/T_c$,[3] while in binary mixtures that range extends to $t \simeq 0.01$.[2,4] In addition, some of the experimental difficulties that arise in the studies of pure fluids, like gravitation induced gradients, can be almost eliminated in binary mixtures by choosing the two components in such a way that both phases in equilibrium are isopycnic.[4] Furthermore, in many cases the liquid–liquid critical temperature is not far from room temperature, and the experimental variables can be best measured and controlled.

Over a wide temperature range the shape of the coexistence curve can be described by[5]

$$\Delta \lambda = Bt^{\beta} + B_1 t^{\beta + \Delta} + B_2 t^{\beta + 2\Delta} + \cdots, \qquad (1)$$

where $\beta = 0.325$ and $\Delta = 0.50$ are critical exponents; B, B_1, and B_2 critical amplitudes; and $\Delta \lambda$ is the difference in order parameter between coexisting phases.

The renormalization group approach predicts[6] that the diameter of the coexistence curve should behave as

$$(\lambda_R + \lambda_L)/2 = \lambda_c + A_1 t + A_2 t^{1-\alpha}$$
$$+ A_3 t^{1-\alpha+\Delta} + \cdots, \qquad (2)$$

where $\alpha = 0.110$ is[2] the critical exponent that describes the divergence of the specific heat at the critical point, λ_R and λ_L refer to the composition variable in the right and left branches of the coexistence curve and λ_c is the critical composition.

The analysis of the experimental results is complicated

by the fact that there is no clear evidence of which is the best order parameter for binary mixtures, thus mole fraction, volume fraction, and mass fraction have been frequently used.[2,4,6] In addition, contradictory conclusions have been arrived at concerning the existence of an anomaly in the linear behavior of the diameter.[2,6] For the system methanol + cyclohexane such at anomaly was found by Hartley et al.[7] when the coexistence curve was studied measuring the refractive indices of the two phases in equilibrium. The same authors, in a later study, did not find such an anomaly.[8] It is known that the hole–particle asymmetry, which causes the diameter anomaly, also implies that the difference in the intensity of the light scattered from the two coexisting phases diverges as $t^{\beta-1}$.[9] This was experimentally proved for this system by Wong et al.[10] However, Jacobs et al.[8] did not consider the anomalous behavior of the thermal expansion coefficient of methanol + cyclohexane when analyzing the diameter from refractive index data, and the Lorentz–Lorenz relation that they used has been shown to be accurate to within 0.5% only when the critical behavior of the density is taken into account.[11] Even though some precise excess volume data in the critical region have been referred to for this system,[12] they have not been published yet, thus a reanalysis of the refractive index data should be postponed.

Mixtures of methanol and cyclohexane are peculiar because they show striking wetting properties,[13] and also because the densities of both liquid phases are matched to 1 part in 1000,[14] which reduces to $t < 10^{-6}$ the temperature range in which gravity induces noticeable composition gradients in the mixture.[2] Furthermore, the possibility of getting an even closer density match by using mixtures of cyclohexane and deuterated cyclohexane has made it a most proper system to study the dynamic aspects of phase separation[15,16] and to get microgravity environments.[16]

The methanol + cyclohexane system shows a large specific heat anomaly,[2] which makes it suitable to test the two-scale-factor universality hypothesis.[17] An accurate knowledge of the critical composition x_c is necessary to test such a hypothesis, and to study weakly divergent properties. In recent experiments,[8,11,16] x_c was calculated from an extrapolation of the diameter of the coexistence curve obtained from refractive index data, assuming no anomaly in the di-

---

[a] To whom correspondence should be addressed.

ameter. Thus, a further study of the coexistence curve seems to be convenient for this system.

Even though there are some indications that pressure must have an effect on the diameter of the coexistence curve,[2] not much is known yet. Thus, in this paper we have measured the coexistence curve for the methanol + cyclohexane system in the range $0.1 < P/\text{MPa} < 13.0$, being our attention focused on the near critical region. An analysis of its shape and diameter is carried out in terms of Eqs. (1) and (2). The pressure dependence of the critical temperature has also been studied and combined with correlation length data to test the compatibility of our results with the two-scale-factor universality hypothesis.

II. EXPERIMENTAL SECTION

Although small amounts of impurities have no noticeable effect upon the critical exponents, they change T_c and the critical amplitudes appreciably.[18] In particular, water has been shown to have dramatic effects in this mixture,[18] thus, extreme care has been taken to remove it, which is especially difficult in the case of methanol. The drying procedure has been described in detail by Ewing et al.[19] The cyclohexane used was Merck, with a purity of 99.5%, while two different kinds of methanol were used in order to check the reproducibility of the purification method, Fluka puriss., with an initial water content of less than 0.05% and Carlo Erba RS-ACS, with purity > 99.9%. No organic impurities were detected by vapor-phase chromatography. The liquids were kept under dry nitrogen, and over adequate molecular sieves (3 Å for methanol and 4 Å for cyclohexane), and were introduced in the measuring tube by means of hypodermic syringes.

The experimental set up is similar to that described by De Loos et al.,[20] the cell consisting in a thick walled glass tube of 2 mm I.D. and 10 mm O.D. in which the mixture is trapped with bidistilled mercury, that also acts as pressure transmitter. The amount of each component in the mixture is known by weighing with an analytical balance Mettler H10W, precise to 0.1 mg. In order to prevent gravity effects, care was taken to keep the sample height below 2 cm, except for the mixtures with $x_M < 0.25$, of which a larger sample was used to make easier the visual determination of the phase separation. Even though the effect of dissolved nitrogen on the phase separation temperature seemed to be smaller that reported recently,[21] the samples were degassed and the mixtures were prepared and trapped with mercury using a vacuum line. The pressure was measured using a Maywood P102 pressure transducer calibrated against a Desgranges et Huot dead weight balance. Pressure was thus known to within ± 0.01 MPa through the whole range of our study. The temperature stability in the water bath, obtained with a Tronac PTC-41 controller and a Tronac TCP-25-S probe, was of ± 1 mK over 20 h periods, and was measured with a quartz thermometer Hewlett–Packard model HP2804A, frequently calibrated against a gallium melting point standard, YSI model 17402 and compared with a platinum resistance thermometer Leeds and Northrup model 8930 calibrated at the N.M.L. Thus, the temperature scale agrees with the IPTS-68 to within 0.003 K. The quartz

probe, HP 18111A, was placed in close contact with the glass bulb, in order to minimize any temperature gradient. The pressure line, including the pressure transducer, was set inside a dry box in which temperature was kept constant to within ± 0.01 K.

The method followed to obtain the coexistence curve is a point-by-point determination in which the phase separation temperature is measured as a function of pressure for each composition. As time required for equilibrium is much longer in the two-phase region than in the one-phase region, data under orthobaric pressure were always taken while cooling the samples. A glass-coated iron bar was used as a stirrer in order to prevent the formation of any gradient near T_c or supercooling far from the critical point. Once one point was taken at the lowest pressure, the temperature was increased and equilibrium in a homogeneous phase was reached while mildly stirring. The stirrer was then stopped and the pressure increased until a turbidity appeared. The stirrer was activated again to prevent the formation of any metastable state. The pressure was increased until the turbidity was permanent. The procedure was repeated until the phase separation pressure for given temperature and composition keeps constant for three to five readings. Near the critical composition the thermal diffusivity approaches zero, thus longer relaxation times were allowed for the liquids to attain equilibrium after each temperature change. Each isopleth (constant composition curve) consists on two sets of points: one measured for rising temperatures and one for falling ones, no difference being noticed between them. The advantages and disadvantages of this point-by-point method compared to the one sample method have been discussed in detail by Nagarajan et al.[22] One of the isopleths was reproduced after a three week period, and no differences were found between both sets of data, thus any possible effect of mercury may be discarded.

III. RESULTS

Table I shows the experimental isopleths obtained. Each one has been fitted to a polynomial of the form

$$T(°C) = a + b(P/\text{MPa}) + c(P/\text{MPa})^2. \qquad (3)$$

The parameters, a, b, and c have been obtained using a regression method based on the maximum likelihood principle, frequently used in the analysis of fluid phase equilibria data.[23,24] In opposition to the more usual least-squares methods no distinction is made between dependent and independent variables. The relative weight of each variable is chosen according to its experimental uncertainty. However, when the last significant digit in P and T were used as standard deviations, the value of χ^2 was found to be larger than 5, indicating that the residuals do not present a Gaussian distribution centered in zero. For all isopleths it was enough to consider $\sigma(T) = 5$ mK and $\sigma(P) = 0.01$ MPa to get $\chi^2 < 1$. This value of $\sigma(T)$ is similar to that reported by Nagarajan et al.[22] Furthermore, as will be seen below, this value leads to consistent results for the fittings of the coexistence curves and of the diameters.

With this method, we have not obtained the composition of the two phases in equilibrium at a given P and T,

TABLE I. Isopleths for the system methanol + cyclohexane, and characteristics of their fittings to Eq. (3).

$T(K)$	$P(MPa)$	$T(K)$	$P(MPa)$	$T(K)$	$P(MPa)$
$x = 0.1630$		$x = 0.2041$		$x = 0.2468$	
306.720	1.01	310.521	1.13	313.479	0.78
307.218	2.64	310.984	2.72	313.971	2.28
307.781	4.49	311.516	4.49	314.385	3.56
308.300	6.28	311.990	6.23	314.810	4.87
308.808	8.09	312.463	7.79	315.247	6.25
309.321	9.80	312.874	9.15	315.481	6.99
309.863	11.69	313.284	10.62	315.872	8.28
310.246	13.05	313.646	11.95	316.363	9.87
$a = 33.270 \pm 0.015$		313.943	13.03	316.685	10.94
$b = 0.304 \pm 0.004$		$a = 37.028 \pm 0.022$		316.951	11.81
$c = (- 0.84 \pm 0.26) \times 10^{-3}$		$b = 0.300 \pm 0.005$		317.299	12.97
$\sigma(T/K) = 8.0 \times 10^{-3}$		$c = (- 0.77 \pm 0.37) \times 10^{-3}$		$a = 40.070 \pm 0.005$	
$\sigma(P/MPa) = 1.8 \times 10^{-4}$		$\sigma(T/K) = 1.2 \times 10^{-2}$		$b = 0.333 \pm 0.001$	
		$\sigma(P/MPa) = 5.2 \times 10^{-7}$		$c = (- 1.44 \pm 0.08) \times 10^{-3}$	
				$\sigma(T/K) = 3.1 \times 10^{-3}$	
				$\sigma(P/MPa) = 2.5 \times 10^{-4}$	
$x = 0.2611$		$x = 0.2991$		$x = 0.3538$	
314.425	1.15	315.922	0.88	317.286	0.40
314.764	2.01	316.389	2.18	317.620	1.41
315.495	4.51	316.778	3.31	317.898	2.24
316.205	6.86	317.361	4.99	318.162	3.04
316.728	8.35	317.843	6.43	318.463	3.96
317.277	10.29	318.156	7.36	318.797	4.97
317.700	11.82	318.562	8.60	319.199	6.18
$a = 40.926 \pm 0.059$		318.981	9.87	319.535	7.24
$b = 0.326 \pm 0.019$		319.351	11.01	319.881	8.32
$c = (- 1.49 \pm 1.46) \times 10^{-3}$		319.674	12.02	320.258	9.48
$\sigma(T/K) = 2.5 \times 10^{-2}$		320.059	13.22	320.772	11.07
$\sigma(P/MPa) = 8.0 \times 10^{-6}$		$a = 42.464 \pm 0.005$		321.141	12.24
		$b = 0.357 \pm 0.001$		321.376	12.99
		$c = (- 1.59 \pm 0.09) \times 10^{-3}$		$a = 44.001 \pm 0.003$	
		$\sigma(T/K) = 3.1 \times 10^{-3}$		$b = 0.335 \pm 0.001$	
		$\sigma(P/MPa) = 7.0 \times 10^{-7}$		$c = (- 0.72 \pm 0.06) \times 10^{-3}$	
				$\sigma(T/K) = 2.8 \times 10^{-3}$	
				$\sigma(P/MPa) = 8.2 \times 10^{-5}$	
$x = 0.3791$		$x = 0.3997$		$x = 0.4199$	
317.853	0.50	318.156	0.68	318.376	0.66
318.198	1.47	318.493	1.68	318.800	1.92
318.673	2.91	318.826	2.69	319.084	2.82
319.031	4.01	319.241	3.97	319.428	3.86
319.411	5.20	319.677	5.31	319.513	4.14
319.863	6.54	320.107	6.64	319.949	5.52
320.272	7.82	320.515	7.93	320.480	7.11
320.718	9.23	320.894	9.13	320.842	8.24
321.179	10.73	321.293	10.42	321.167	9.28
321.524	11.86	321.659	11.61	321.613	10.71
321.867	13.03	321.963	12.61	321.976	11.89
$a = 44.535 \pm 0.008$		322.048	12.88	322.268	12.86
$b = 0.345 \pm 0.002$		$a = 44.779 \pm 0.002$		$a = 45.002 \pm 0.005$	
$c = (- 1.83 \pm 0.14) \times 10^{-3}$		$b = 0.336 \pm 0.001$		$b = 0.336 \pm 0.002$	
$\sigma(T/K) = 4.7 \times 10^{-3}$		$c = (- 1.29 \pm 0.04) \times 10^{-3}$		$c = (- 1.22 \pm 0.12) \times 10^{-3}$	
$\sigma(P/MPa) = 1.0 \times 10^{-7}$		$\sigma(T/K) = 1.6 \pm 10^{-3}$		$\sigma(T/K) = 3.6 \times 10^{-3}$	
		$\sigma(P/MPa) = 1.1 \pm 10^{-4}$		$\sigma(P/MPa) = 4.7 \times 10^{-4}$	
$x = 0.4409$		$x = 0.4489$		$x = 0.4809$	
318.552	0.85	318.664	0.96	318.471	0.92
318.855	1.74	319.032	2.04	319.069	1.73
319.301	3.13	319.398	3.14	319.486	2.97
319.656	4.22	319.851	4.53	319.831	4.05
320.041	5.39	320.232	5.69	320.283	5.41
320.509	6.79	320.644	6.97	320.624	6.47
320.870	8.00	320.961	7.97	320.964	7.50
321.228	9.07	321.366	9.27	321.366	9.27
321.619	10.28	321.788	10.62	321.788	10.62
321.932	11.31	322.120	11.71	322.120	11.71
322.398	12.89	322.478	12.88	322.478	12.60
$a = 45.126 \pm 0.011$		$a = 45.191 \pm 0.003$		$a = 45.342 \pm 0.007$	
$b = 0.330 \pm 0.004$		$b = 0.341 \pm 0.001$		$b = 0.338 \pm 0.002$	

TABLE I. (*continued*).

$T(K)$	$P(MPa)$	$T(K)$	$P(MPa)$	$T(K)$	$P(MPa)$
$c = (-0.59 \pm 0.41) \times 10^{-3}$		$c = (-1.54 \pm 0.05) \times 10^{-3}$		$c = (-1.38 \pm 0.21) \times 10^{-3}$	
$\sigma(T/K) = 5.0 \times 10^{-3}$		$\sigma(T/K) = 1.8 \times 10^{-3}$		$\sigma(T/K) = 3.8 \times 10^{-3}$	
$\sigma(P/MPa) = 3.0 \times 10^{-7}$		$\sigma(P/MPa) = 3.0 \times 10^{-7}$		$\sigma(P/MPa) = 5.0 \times 10^{-6}$	
$x = 0.5151$		$x = 0.5446$		$x = 0.5685$	
318.638	0.57	318.569	0.70	318.412	0.62
318.790	1.01	319.034	2.06	318.820	1.82
319.081	1.81	319.418	3.23	319.197	2.96
319.464	2.95	319.819	4.43	319.603	4.22
319.777	3.90	320.211	5.61	320.031	5.54
320.164	5.09	320.599	6.79	320.399	6.67
320.584	6.39	320.994	8.04	320.778	7.87
320.978	7.60	321.383	9.23	321.155	9.06
321.440	9.07	321.791	10.54	321.498	10.14
321.774	10.18	322.156	11.74	321.852	11.28
322.114	11.28	322.541	12.99	322.306	12.77
322.522	12.61	$a = 45.177 \pm 0.006$		$a = 45.058 \pm 0.004$	
$a = 45.292 \pm 0.006$		$b = 0.345 \pm 0.001$		$b = 0.336 \pm 0.001$	
$b = 0.349 \pm 0.002$		$c = (-1.55 \pm 0.11) \times 10^{-3}$		$c = (-1.17 \pm 0.08) \times 10^{-3}$	
$c = (-2.12 \pm 0.13) \times 10^{-3}$		$\sigma(T/K) = 3.9 \times 10^{-3}$		$\sigma(T/K) = 2.9 \times 10^{-3}$	
$\sigma(T/K) = 4.8 \times 10^{-3}$		$\sigma(P/MPa) = 1.0 \times 10^{-7}$		$\sigma(P/MPa) = 8.0 \times 10^{-5}$	
$\sigma(P/MPa) = 9.8 \times 10^{-4}$					
$x = 0.5822$		$x = 0.6003$		$x = 0.6283$	
318.404	1.02	318.011	0.44	317.597	0.69
318.800	2.17	318.346	1.45	318.004	1.92
319.204	3.42	318.713	2.56	318.394	3.05
319.642	4.75	319.089	3.70	318.848	4.44
320.073	6.06	319.417	4.72	319.215	5.59
320.509	7.45	319.743	5.73	319.614	6.79
320.938	8.79	320.183	7.08	320.018	8.01
321.378	10.23	320.608	8.43	320.404	9.25
321.752	11.42	320.899	9.36	320.793	10.43
322.159	12.72	321.326	10.74	321.289	12.02
$a = 44.915 \pm 0.008$		321.674	11.87	321.594	12.99
$b = 0.339 \pm 0.002$		321.966	12.83	$a = 44.213 \pm 0.008$	
$c = (-1.34 \pm 0.14) \times 10^{-3}$		$a = 44.712 \pm 0.003$		$b = 0.338 \pm 0.002$	
$\sigma(T/K) = 4.3 \times 10^{-3}$		$b = 0.336 \pm 0.001$		$c = (-0.97 \pm 0.14) \times 10^{-3}$	
$\sigma(P/MPa) = 5.0 \times 10^{-5}$		$c = (-1.26 \pm 0.05) \times 10^{-3}$		$\sigma(T/K) = 5.3 \times 10^{-3}$	
		$\sigma(T/K) = 2.1 \times 10^{-3}$		$\sigma(P/MPa) = 5.0 \times 10^{-6}$	
		$\sigma(P/MPa) = 1.0 \times 10^{-4}$			
$x = 0.6577$		$x = 0.6882$		$x = 0.7091$	
316.913	0.52	316.116	0.38	315.037	0.96
317.291	1.61	316.510	1.45	315.425	2.11
317.636	2.62	317.010	2.87	316.020	4.15
318.081	3.97	317.433	3.92	316.605	6.02
318.498	5.21	317.973	5.41	317.115	7.58
318.794	6.12	318.640	7.58	317.607	8.94
319.227	7.45	319.150	9.02	318.033	10.24
319.342	7.82	319.823	11.05	318.175	10.63
319.827	9.36	320.290	12.35	318.666	12.10
320.184	10.50	321.035	14.36	318.902	12.84
320.655	12.01	$a = 42.832 \pm 0.035$		319.173	13.73
321.076	13.42	$b = 0.369 \pm 0.010$		$a = 41.586 \pm 0.019$	
$a = 43.586 \pm 0.003$		$c = (-1.89 \pm 0.84) \times 10^{-3}$		$b = 0.322 \pm 0.006$	
$b = 0.347 \pm 0.001$		$\sigma(T/K) = 2.5 \times 10^{-2}$		$c = (-0.13 \pm 0.44) \times 10^{-3}$	
$c = (-1.74 \pm 0.06) \times 10^{-3}$		$\sigma(P/MPa) = 3.6 \times 10^{-4}$		$\sigma(T/K) = 1.0 \times 10^{-2}$	
$\sigma(T/K) = 2.7 \times 10^{-3}$				$\sigma(P/MPa) = 1.9 \times 10^{-4}$	
$\sigma(P/MPa) = 8.0 \times 10^{-7}$					
$x = 0.7296$		$x = 0.7685$		$x = 0.8151$	
313.591	0.62	309.502	1.37	299.930	0.65
313.910	1.60	310.035	2.85	300.542	2.59
314.298	2.80	310.366	4.03	301.230	4.73
314.749	4.21	310.875	5.85	301.589	5.89
315.178	5.58	311.456	8.03	302.168	7.62
315.519	6.66	311.956	9.39	302.718	9.59
315.852	7.76	312.465	11.11	303.022	10.61
316.124	8.63	313.086	12.96	$a = 26.554 \pm 0.021$	

TABLE I. (*continued*).

$T(K)$	$P(MPa)$		$T(K)$	$P(MPa)$		$T(K)$	$P(MPa)$
316.467	9.74		$a = 35.972 \pm 0.063$			$b = 0.333 \pm 0.009$	
316.723	10.56		$b = 0.309 \pm 0.019$			$c = (-1.85 \pm 0.80) \times 10^{-3}$	
317.060	11.65		$c = (-0.77 \pm 1.48) \times 10^{-3}$			$\sigma(T/K) = 1.5 \times 10^{-2}$	
317.372	12.68		$\sigma(T/K) = 2.2 \times 10^{-2}$			$\sigma(P/MPa) = 5.8 \times 10^{-7}$	
$a = 40.246 \pm 0.005$			$\sigma(P/MPa) = 0.0$				
$b = 0.327 \pm 0.001$							
$c = (-0.81 \pm 0.11) \times 10^{-3}$							
$\sigma(T/K) = 3.9 \times 10^{-3}$							
$\sigma(P/MPa) = 8.0 \times 10^{-7}$							

which are necessary to analyze the coexistence curve and its diameter. Thus, each branch of the isobars considered [obtained from interpolation in Eq. (3)] has been fitted to the following function[25]:

$$\lambda = A_0 + A_1 t + A_2 t^{1-\alpha} + Bt^\beta, \qquad (4)$$

where λ is the composition variable, which has been taken to be the mole fraction of methanol x or the volume fraction ϕ. A similar procedure has been followed by Beysens.[26] Table II shows the characteristics of the fitting for different isobars. In order to obtain $\chi^2 \leqslant 1$ the following uncertainties have been considered: $\sigma(T) = \pm 5$ mK and $\sigma(\lambda) = \pm 3 \cdot 10^{-3}$. The exponents $\alpha = 0.110$ and $\beta = 0.325$ take their renormalization group values, and the value of T_c for each pressure, also included in Table II, has been chosen to get the best possible fit. Though, the definitive value of T_c for each pressure will be obtained below. It can be observed that the standard deviations of the fittings are compatible with the assumed values of $\sigma(T)$ and $\sigma(\lambda)$, however, the parameters A_2 and B are highly correlated, being possible to obtain different sets of parameters which lead to equivalent fittings. We will not discuss this point any further since Eq. (2) is used only for interpolation purposes, and the shape of

the coexistence curves, their diameters, and the values of T_c will be studied in Sec. IV.

The Appendix gives the compositions in equilibrium as a function of temperature for the different isobars.

IV. THE SHAPE OF THE COEXISTENCE CURVES AND THEIR DIAMETERS

The data shown in the Appendix have been analyzed with Eq. (1) using the difference in both mole fractions and volume fractions as the order parameter. Estimated standard deviations have been taken to be $\sigma(\Delta\lambda) = \pm 3 \cdot 10^{-3}$ and $\sigma(T) = \pm 5$ mK, according to the results of Table II. For all the isobars, the fitted value of T_c was lower than the separation temperature found for the two points located at the maximum of the coexistence curve ($x = 0.4809$ and $x = 0.5151$, marked with asterisks in the Appendix). These two points were thus discarded to eliminate the strong systematic errors introduced by them in the fittings. Table III shows the parameters of Eq. (1) in each case, and Fig. 1 shows the shape of three of the isobars.

Singh and Van Hook[21] have summarized most of the values of T_c reported at $P \simeq 0.1$ MPa for this system. Our

TABLE II. Parameters of Eq. (4), their estimated uncertainties, and standard deviations of the fittings of the two branches of some selected isobars.

$P(MPa)$	$T_c(K)$	Branch	A_0	A_1	A_2	B	$\sigma(\lambda) \times 10^3$	$\sigma(T/K) \times 10^3$
				$\lambda = x$ (mole fraction)				
0.1	318.50	R	0.4469 ± 0.0037	-1.7249 ± 0.4260	-0.1216 ± 0.3810	1.2013 ± 0.0304	3.1	0.001
		L	0.5286 ± 0.0031	9.2991 ± 0.215	-7.2027 ± 0.232	-0.9434 ± 0.0284	14.1	4.2
1.0	318.84	R	0.4412 ± 0.0057	-1.7540 ± 0.587	-0.2435 ± 0.577	1.2392 ± 0.0527	3.1	1.3
		L	0.5400 ± 0.0044	2.6141 ± 0.290	-1.8506 ± 0.269	-1.0883 ± 0.0364	2.8	1.8
2.5	319.34	R	0.4439 ± 0.0060	-1.1297 ± 0.364	-0.6545 ± 0.400	1.2277 ± 0.0515	3.3	3.1
		L	0.5228 ± 0.0057	11.6510 ± 0.605	-9.273 ± 0.445	-0.8625 ± 0.0514	3.4	2.4
5.0	320.17	R	0.4371 ± 0.0065	-0.9009 ± 0.756	-1.0019 ± 0.509	1.2770 ± 0.0428	3.7	0.8
		L	0.5602 ± 0.0042	-0.6634 ± 0.288	1.2535 ± 0.311	-1.2743 ± 0.0371	2.2	2.2
10.0	321.75	R	0.4556 ± 0.0043	-4.2172 ± 0.317	2.0780 ± 0.285	1.1030 ± 0.0339	2.1	6.0
		L	0.5313 ± 0.0061	8.8360 ± 0.445	-6.8620 ± 0.309	-0.9563 ± 0.0516	3.2	2.7
13.0	322.66	R	0.4487 ± 0.0055	-0.3789 ± 0.531	-1.1743 ± 0.501	1.2081 ± 0.0479	2.4	1.3
		L	0.5354 ± 0.0062	9.2602 ± 0.497	-6.8408 ± 0.550	-1.0049 ± 0.0519	2.6	1.8
				$\lambda = \phi$ (volume fraction)				
0.1	318.42	R	0.2206 ± 0.0050	-4.4439 ± 0.843	3.0794 ± 0.621	1.0509 ± 0.0394	3.4	7.5
		L	0.2931 ± 0.0021	2.3880 ± 0.600	-1.1108 ± 0.417	-0.7381 ± 0.0187	1.3	4.3
10.0	321.67	R	0.2389 ± 0.0053	-4.6095 ± 1.01	3.5169 ± 0.811	0.9341 ± 0.0464	3.4	8.5
		L	0.2763 ± 0.0045	1.6751 ± 0.890	-0.7774 ± 0.608	-0.6654 ± 0.0381	2.8	7.4

TABLE III. Analysis of the shape of the coexistence curves in terms of extended scaling. Parameters of Eq. (1) and critical temperature.

P(MPa)	B	B_1	B_2	T_c (°C)	$\sigma(\Delta\lambda) \times 10^3$	$\sigma(T/K) \times 10^3$
			$\lambda = x$ (mole fraction)			
0.1	1.534 ± 0.013	4.228 ± 0.149	-13.987 ± 0.461	45.272 ± 0.005	2	1
1.0	1.553 ± 0.016	3.913 ± 0.178	-12.731 ± 0.532	45.578 ± 0.006	3	1
2.5	1.498 ± 0.012	4.648 ± 0.147	-15.106 ± 0.504	46.095 ± 0.006	3	1
5.0	1.540 ± 0.019	4.612 ± 0.224	-15.313 ± 0.654	46.899 ± 0.008	4	2
10.0	1.504 ± 0.026	4.548 ± 0.305	-14.562 ± 0.778	48.516 ± 0.010	4	1
13.0	1.537 ± 0.016	4.303 ± 0.218	-14.896 ± 0.822	49.426 ± 0.006	3	2

$(T_c/°C) = (45.266 \pm 0.024) + (0.321\,45 \pm 0.002\,47) \times (P/\text{MPa})$ $\sigma(T/K) = 0.025$ $\sigma(P/\text{MPa}) = 0.1 \times 10^{-5}$

$(T_c/°C) = (45.240 \pm 0.009) + (0.342\,41 \pm 0.003\,70) \times (P/\text{MPa}) - (1.5673 \pm 0.270) \times 10^{-4} \times (P/\text{MPa})^2$; $\sigma(T/K) = 0.0076$; $\sigma(P/\text{MPa}) = 0.0$

			$\lambda = \phi$ (volume fraction)			
0.1	1.229 ± 0.015	3.588 ± 0.163	-11.226 ± 0.423	45.268 ± 0.006	2	1
10.0	1.274 ± 0.010	2.786 ± 0.147	-8.705 ± 0.601	48.481 ± 0.004	2	1

value (45.272 ± 0.005) °C is in the low range of the interval of T_c reported, indicating that the water content of our mixtures is very small; the agreement with the value of Ewing et al.[19] is satisfactory, showing that with their purification procedures one can expect quite reproducible results for T_c.

According to the results of Ahlers[27] and Sivaranam et al.[28] we have considered no pressure dependence of the critical exponents. This is confirmed by the fact that the residuals of the fittings show no significant change with increasing pressure. It can be observed that there is no clear advantage in using the volume fraction instead of the mole fraction as λ. However, as will be seen below, the discussion of the diameters show that the mole fraction is preferrable. Figure 2(a) shows that within their estimated uncertainties the critical amplitudes do not exhibit any clear pressure dependence. More experimental data at $(T_c - T) \leqslant 5$ K would be necessary to give a better statistical significance to the amplitudes of the correction to simple scaling terms, in order to discuss their pressure dependence, as well as the pressure influence upon the range of t for which each correction term is important. Nevertheless, T_c does depend strongly on pressure, as can be observed in Fig. 2(b). T_c has been fitted to a straight line and to a second order polynomial, assuming for each T_c

the standard deviation shown in Table III, and for the pressure $\sigma(P) = \pm 0.01$ MPa. The results are also shown in Table III. It can be observed that the linear fit leads to standard deviations well above the uncertainties of the T_c's, while the
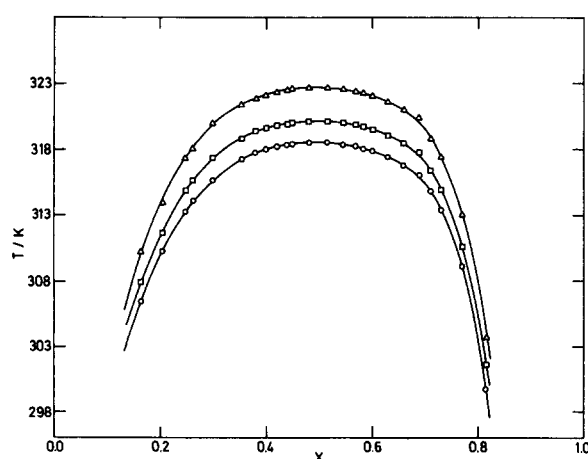

FIG. 1. Isobars for the system methanol + cyclohexane, given by Eq. (4) with coefficients from Table II, for P/MPa: O, 0.1; □, 5.0; Δ, 13.0.
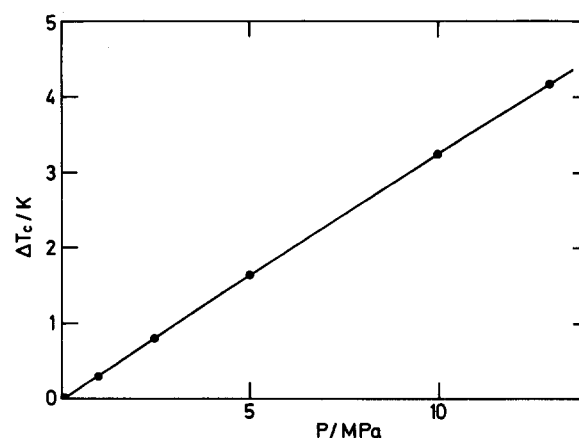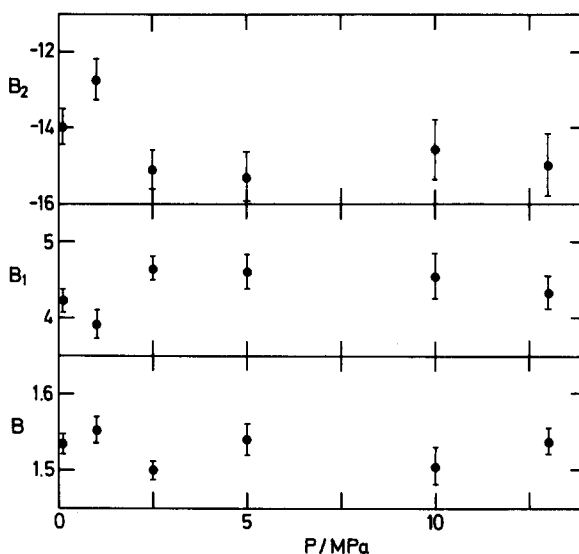

FIG. 2. (a) Critical amplitudes, given by Eq. (1), as a function of pressure (see Table III). (b) Pressure dependence of $T_c (P/\text{MPa}) - T_c (0.1$ MPa$)$ from results shown in Table III. The curve corresponds to the fit to a second order polynomial, from which the value (dT_c/dP) has been determined.

quadratic fit leads to a value of $\chi^2 \simeq 1$. So the result $(dT_c/dP) = (34.2 \pm 0.4)$ mK/bar of this fitting will be used in the calculations that follow. The value $(dT_c/dP) = (32.1 \pm 0.2)$ mK/bar given by the linear fit agrees strikingly well with that of (31.7 ± 0.1) mK/bar reported by Singh and Van Hook[29] for the same system, and is slightly larger than the value 22 mK/bar reported by Sivaraman *et al.*[28] for methanol + *n*-heptane, using also a linear fit.

The two-scale-factor universality hypothesis states that the ratio[30]

$$R_\xi = \xi_0 \left(\frac{T_c A}{K_B (dT_c/dP)} \right)^{1/3} \qquad (5)$$

is universal and takes the value $R_\xi = 0.270 \pm 0.001$, ξ_0 being the amplitude of divergence of the correlation length and A the amplitude of the thermal expansion coefficient $(1/V)(\partial V/\partial T)_P$. Several values have been reported for ξ_0 for methanol + cyclohexane, the most recent one being that of Jacobs[17] $\xi_0 = (3.24 \pm 0.06)$ Å, while Sorenson *et al.*[31] gave 2.38 Å, Hartley *et al.*[7] gave 4.7 Å, Yosida[32] gave (4.1 ± 0.5) Å, and Kipelman *et al.*[33] gave (3.87 ± 0.97) Å. Using $\xi_0 = 3.24$ Å, the value $T_c = (318.422 \pm 0.005)$ K obtained in this work for $P = 0.1$ MPa, and $(dT_c/dP) = 34.2$ mK/bar, we have calculated $A = (8.6 \pm 0.7)10^{-6}$ K^{-1}. If the value $\xi_0 = 2.38$ Å is used it results to be $A = 2.2 \times 10^{-5}$ K^{-1}, which gives a better agreement to the value $A = 2.5 \times 10^{-5}$ K^{-1} reported by Scheibner *et al.*[34] It has been shown that the amplitudes of the thermal expansion coefficient A and of the specific heat C are related through[35]

$$C = \frac{A T_c}{(dT_c/dP)} . \qquad (6)$$

Using the value $A = 8.6 \times 10^{-6}$ K^{-1} calculated above for $\xi_0 = 3.4$ Å we obtain $C = (8.0 \pm 0.7) \ 10^{-3}$ J cm^{-3} K^{-1}, which compares favorably with the value $C = (7.3 \pm 0.5)$ 10^{-3} J cm^{-3} K^{-1} reported by Klein and Woermann[36] from C_p data of Anisomov *et al.*[37] The use of other values of ξ_0
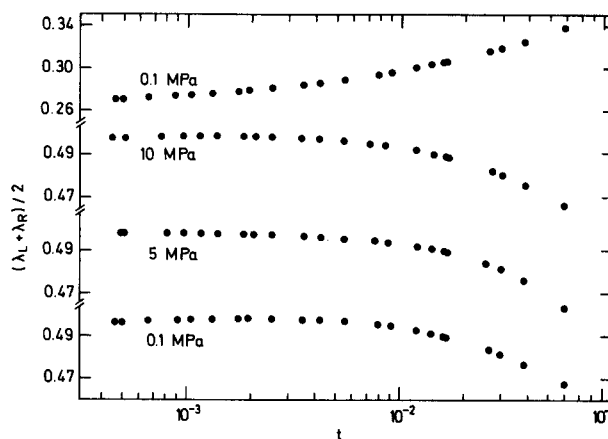

FIG. 3. The diameter $(\lambda_R + \lambda_L)/2$ of the coexistence curves as a function of t for several pressures, considering different concentration variables. Top curve corresponds to $\lambda = \phi$ (volume fraction), the other curves to $\lambda = x$ (mole fraction). The points represent the data listed in the Appendix. Notice that the scales for $\lambda = x$ and for $\lambda = \phi$ are different.

lead to calculated values of C which are further away from that of Klein and Woermann. For instance, $\xi_0 = 2.38$ Å[31] leads to $C = 20.2 \times 10^{-3}$ J cm^{-3} K^{-1}, while $\xi_0 = 4.1$ Å[32] leads to $C = 3.9 \times 10^{-3}$ J cm^{-3} K^{-1}, discrepancies which are far beyond the combined uncertainties of the two sets of data. The use of the value of (dT_c/dP) given by Singh and Van Hook[29] does not change the conclusions. In addition Scheibner *et al.*[34] have suggested that there is a possibility of their mixture to be slightly off critical, which would have noticeable effects upon the value of their critical amplitude. Nevertheless, we have found no clear reason to prefer one value of ξ_0 over the others, thus we may only conclude that our present data are compatible with the two-scale-factor universality hypothesis within the experimental uncertainties (the main contribution to the error coming from ξ_0). The lack of data prevents the test of such a hypothesis at higher pressures.

Table IV shows the results of the analysis of the diame-

TABLE IV. Analysis of the diameter of the coexistence curves in terms of extended scaling. Parameters of Eq. (2) and critical composition.

| P(MPa)	λ_c	A_1	A_2	$\sigma(\lambda) \times 10^3$	$\sigma(T/K) \times 10^5$
		$\lambda = x$ (mole fraction)			
0.1	$0.498\,20 \pm 0.000\,28$	-0.5386 ± 0.0154		1	1
	$0.497\,89 \pm 0.000\,32$	-0.7777 ± 0.1970	0.1703 ± 0.132	1	1
1.0	$0.498\,52 \pm 0.000\,38$	-0.5887 ± 0.0204		1	1
	$0.496\,86 \pm 0.000\,16$	-1.8659 ± 0.0652	0.8938 ± 0.046	0.5	0.5
2.5	$0.498\,87 \pm 0.000\,40$	-0.5672 ± 0.0214		1	0.8
	$0.498\,32 \pm 0.000\,44$	-1.0180 ± 0.1540	0.3143 ± 0.108	1	1
5.0	$0.498\,80 \pm 0.000\,05$	-0.6005 ± 0.0027		0.2	0.0
	$0.498\,56 \pm 0.000\,00$	-0.7986 ± 0.0008	0.1386 ± 0.0005	0.6	0.0
10.0	$0.498\,81 \pm 0.000\,17$	-0.5795 ± 0.0090		0.6	0.6
	$0.499\,14 \pm 0.000\,19$	-0.2709 ± 0.1000	-0.2007 ± 0.0692	0.5	0.6
13.0	$0.498\,39 \pm 0.000\,37$	-0.5205 ± 0.0201		1	0.0
	$0.499\,28 \pm 0.000\,30$	0.3106 ± 0.0917	-0.5769 ± 0.0620	0.9	0.0
		$\lambda = \phi$ (volume fraction)			
0.1	$0.279\,27 \pm 0.001\,7$	1.2226 ± 0.0981		6	0.6
	$0.271\,15 \pm 0.000\,4$	-5.3480 ± 0.154	4.6026 ± 0.108	1	0.2
10.0	$0.276\,01 \pm 0.001\,9$	1.2468 ± 0.102		6	0.5
	$0.268\,21 \pm 0.000\,4$	-5.5579 ± 0.252	4.7452 ± 0.174	1	0.4
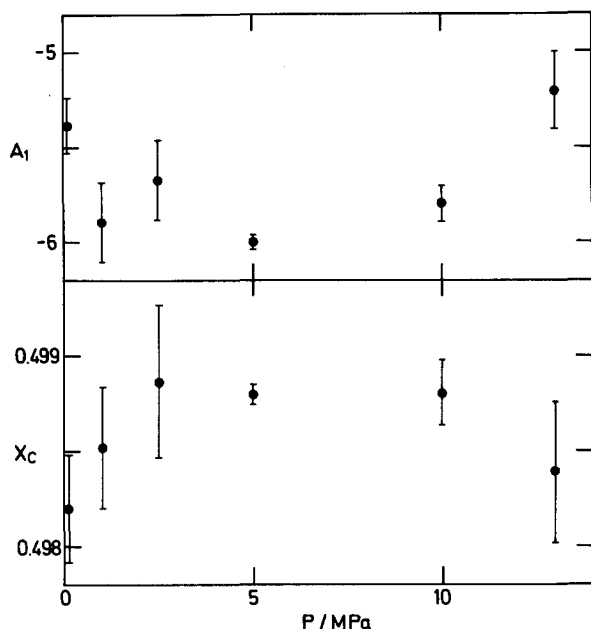
FIG. 4. Critical mole fraction x_c and critical amplitude A_1 of Eq. (2) for different pressures. A linear behavior has been considered for the diameter of the coexistence curve, with coefficients from Table IV.

ter of the coexistence curve in terms of Eq. (2). It is noticeable that the scattering of the data is smaller than in the case of the order parameter. When the standard deviations in x and t deduced from Table III are used, a value χ^2 below 10^{-2} is obtained. The values 2×10^{-3} and 1×10^{-3}, respectively, lead to $\chi^2 \simeq 1$. Figure 3 shows the diameter for several pressures when both mole fraction x, and volume fraction ϕ are used. As it can be observed in Table IV, when $\lambda = x$ there is no statistical reason for assuming a $(1 - \alpha)$ (or a 2β) anomaly in the diameter within the experimental uncertainty, however, such an anomaly is necessary when $\lambda = \phi$, which makes x preferable as the order parameter, a result consistent with the conclusions of Jacobs et al.[8]

Again, it is not possible to discuss the pressure dependence of x_c and A_1 since, as shown in Fig. 4, it is masked by

their uncertainties, and a much higher precision in x, as well as more experimental data, would be necessary. An average value of $x_c = 0.4986 \pm 0.0005$ can be selected, which is slightly lower than other values reported in the literature, shown in Table V. However, the flat shape of the top of the coexistence curve makes it difficult the determination of x_c, and the disagreement among values from different works is quite large, ranging from $x = 0.561$[16] to $x = 0.505$[39], which is well above that between Ewing et al.'s[12] and ours. A clear example of how difficult it is to obtain a value of x_c due to the flatness of the coexistence curve has been given recently by Vani et al.[4] Our result is closest to that of Ewing et al.[12] which confirms what has been said above about T_c. Furthermore, when Ewing et al.'s $x_c = 0.5055$ is used to solve Eq. (2) with the parameters listed in Table III, the result $T = 318.420$ K differs from our $T_c = 318.422$ less than the uncertainty ± 0.005 K, hence, according to our calculation procedure, both values of x_c are equivalent.

V. SUMMARY

The phase separation temperatures of the methanol + cyclohexane system as a function of pressure and composition have been measured by means of a visual technique. Using renormalization group values of the critical exponents the data are compatible with the extended scaling expression for the coexistence curve, while the diameter shows no significant anomaly when the difference in mole fraction is used as the order parameter. The data at $P = 0.1$ MPa and the value obtained for (dT_c/dP) are compatible with the two-scale-factor universality hypothesis. The uncertainties in the critical amplitudes prevent any discussion of their pressure dependence, especially with reference to the amplitudes of the correction to scaling terms. A much larger number of experimental isopleths with $|T_c - T| > 4$ K could reduce such uncertainties, making possible to study the influence of the pressure in the t ranges in which each correction term would be important. Finally, no clear pressure dependence has been found for x_c (and neither for A_1), and an average value has been selected.

TABLE V. Critical mole fraction of methanol in the methanol + cyclohexane system according to different authors.

x	Authors	Year	Reference
0.505	Jones and Amstell	1930	38
0.511	Eckfeldt and Lucasse	1943	38
0.517	Huang and Webb	1969	40
0.533	Hartley, Jacobs, Mockler, and O'Sullivan	1974	7
0.516	Jacobs, Anthony, Mockler, and O'Sullivan	1977	8
0.511	Scheibner, Sorensen, Jacobs, Mockler, and O'Sullivan	1978	34
0.511	Yosida and Ikushima	1978	32
0.525	Cohn and Jacobs	1984	41
0.561 0.534[a]	Houessou, Guenoun, Gastand, Perrot, and Beysens	1985	16
0.516	Singh and Van Hook	1986	21
0.508	Singh and Van Hook	1986	29
0.5232	Jacobs	1986	17
0.521	Schmidt	1986	13
0.5055	Ewing, Jonhson, and McGlashan	1986	12
0.4986	This work	1988	

[a] After correcting Lorentz–Lorenz relation by volume aditivity.

APPENDIX: TABLE VI. Compositions in equilibrium for the isobars.

$T(K)$	$x(R)$	$x(L)$	$T(K)$	$x(R)$	$x(L)$	$T(K)$	$x(R)$	$x(L)$
	$P = 0.1$ MPa			$P = 1.0$ MPa			$P = 2.5$ MPa	
299.748	0.8141	0.1212	300.040	0.8120	0.1115	300.521	0.8138	0.1196
306.443	0.7896	0.1641	306.719	0.7894	0.1626	307.174	0.7896	0.1623
309.154	0.7728	0.1900	309.426	0.7732	0.1903	309.878	0.7731	0.1885
310.225	0.7643	0.2023	310.486	0.7651	0.2029	310.922	0.7650	0.2007
313.263	0.7318	0.2468	313.551	0.7328	0.2840	314.043	0.7321	0.2470
313.409	0.7298	0.2495	313.719	0.7305	0.2510	314.200	0.7299	0.2499
314.072	0.7199	0.2621	314.370	0.7208	0.2633	314.860	0.7202	0.2627
314.726	0.7087	0.2762	315.020	0.7096	0.2769	315.509	0.7092	0.2768
315.639	0.6898	0.2990	315.969	0.6898	0.3001	316.496	0.6887	0.3018
316.025	0.6802	0.3102	316.344	0.6804	0.3108	316.874	0.6792	0.3130
316.774	0.6575	0.3359	317.081	0.6578	0.3356	317.593	0.6573	0.3379
317.186	0.6414	0.3533	317.485	0.6419	0.3523	317.984	0.6421	0.3543
317.398	0.6316	0.3637	317.702	0.6318	0.3628	318.205	0.6319	0.3650
317.719	0.6137	0.3822	318.028	0.6134	0.3814	318.536	0.6134	0.3837
317.898	0.6012	0.3946	318.197	0.6016	0.3931	318.695	0.6024	0.3945
317.962	0.5961	0.3996	318.264	0.5962	0.3983	318.762	0.5972	0.3995
318.099	0.5836	0.4118	318.402	0.5836	0.4106	318.875	0.5872	0.4089
318.186	0.5740	0.4208	318.486	0.5745	0.4193	318.984	0.5758	0.4193
318.231	0.5684	0.4261	318.542	0.5675	0.4260	319.041	0.5688	0.4256
318.309	0.5569	0.4367	318.605	0.5584	0.4345	319.097	0.5609	0.4325
318.361	0.5474	0.4452	318.670	0.5470	0.4452	319.179	0.5466	0.4448
318.375	0.5445	0.4478	318.680	0.5449	0.4470	319.184	0.5456	0.4456
*318.476	0.5135	0.4747	*318.789	0.5132	0.4761	*319.303	0.5081	0.4759
*318.498	0.5002	0.4859	*318.817	0.4969	0.4908	*319.329	0.4873	0.4917
	$P = 5.0$ MPa			$P = 10.0$ MPa			$P = 13.0$ MPa	
301.311	0.8122	0.1143	302.841	0.8136	0.1191	303.728	0.8130	0.1306
307.922	0.7899	0.1623	309.381	0.7903	0.1618	310.232	0.7886	0.1663
310.632	0.7740	0.1886	312.141	0.7734	0.1880	313.046	0.7716	0.1904
312.098	0.7626	0.2055	313.110	0.7659	0.1990	313.933	0.7650	0.1997
314.848	0.7332	0.2454	316.402	0.7311	0.2465	317.304	0.7308	0.2454
314.994	0.7312	0.2479	316.551	0.7290	0.2491	317.468	0.7286	0.2483
315.657	0.7214	0.2601	317.182	0.7197	0.2611	318.052	0.7203	0.2590
316.325	0.7101	0.2739	317.956	0.7065	0.2775	318.934	0.7058	0.2773
317.359	0.6884	0.2994	319.022	0.6839	0.3047	319.986	0.6838	0.3041
317.751	0.6783	0.3110	319.441	0.6725	0.3171	320.501	0.6702	0.3201
318.427	0.6571	0.3346	320.024	0.6548	0.3380	320.952	0.6559	0.3365
318.807	0.6421	0.3510	320.426	0.6393	0.3551	321.381	0.6393	0.3552
319.033	0.6315	0.3623	320.651	0.6291	0.3662	321.597	0.6293	0.3662
319.365	0.6125	0.3825	320.954	0.6125	0.3837	321.863	0.6145	0.3820
319.511	0.6022	0.3933	321.100	0.6029	0.3937	322.019	0.6041	0.3929
319.578	0.5969	0.3988	321.165	0.5981	0.3986	322.083	0.5993	0.3979
319.723	0.5837	0.4124	321.315	0.5855	0.4114	322.238	0.5858	0.4116
319.800	0.5754	0.4210	321.390	0.5780	0.4189	322.315	0.5777	0.4196
319.859	0.5681	0.4285	321.451	0.5711	0.4257	322.378	0.5702	0.4271
319.911	0.5608	0.4359	321.517	0.5625	0.4341	322.467	0.5572	0.4397
320.008	0.5439	0.4531	321.597	0.5495	0.4466	322.514	0.5486	0.4478
320.011	0.5432	0.4538	321.619	0.5452	0.4507	322.546	0.5417	0.4543
*320.137	0.5013	0.4960	*321.726	0.5120	0.4815	*322.628	0.5152	0.4785
*320.148	0.4935	0.5039	*321.736	0.5060	0.4869	*322.655	0.4976	0.4939

$T(K)$	$\phi(R)$	$\phi(L)$	$T(K)$	$\phi(R)$	$\phi(L)$
	$P = 0.1$ MPa			$P = 10.0$ MPa	
299.748	0.6252	0.0503	302.841	0.6217	0.0476
306.443	0.5823	0.0684	309.381	0.5784	0.0675
309.154	0.5574	0.0805	312.141	0.5534	0.0800
310.225	0.5458	0.0865	313.110	0.5431	0.0853
313.253	0.5041	0.1091	316.402	0.4993	0.1089
313.428	0.5012	0.1108	316.551	0.4969	0.1102
314.072	0.4896	0.1174	317.182	0.4860	0.1163
314.726	0.4764	0.1251	317.956	0.4710	0.1249
315.650	0.4546	0.1380	319.022	0.4462	0.1394
316.025	0.4442	0.1443	319.441	0.4346	0.1464
316.771	0.4198	0.1594	320.024	0.4155	0.1580
317.184	0.4030	0.1700	320.426	0.3995	0.1679
317.398	0.3928	0.1765	320.651	0.3890	0.1745
317.719	0.3746	0.1882	320.954	0.3720	0.1854
317.896	0.3624	0.1961	321.100	0.3621	0.1918
317.963	0.3572	0.1996	321.165	0.3571	0.1950

TABLE VI (*continued*).

$T(K)$	$\phi(R)$	$\phi(L)$	$T(K)$	$\phi(R)$	$\phi(L)$
318.099	0.3451	0.2076	321.315	0.3438	0.2038
318.186	0.3359	0.2137	321.390	0.3356	0.2092
318.241	0.3292	0.2182	321.451	0.3279	0.2144
318.309	0.3196	0.2246	321.517	0.3176	0.2213
318.361	0.3108	0.2306	321.597	0.2998	0.2335
318.375	0.3081	0.2324	321.619	0.2925	0.2385
*318.476	0.2213	0.2927	*321.726	0.2397	0.2760
*318.498	0.2217	0.2925	*321.736	0.2398	0.2759

ACKNOWLEDGMENTS

[1] S. K. Ma, *Modern Theory of Critical Phenomena* (Benjamin Cummings, Reading, 1976).

[2] A. Kumar, H. R. Krisnamurthy, and E. S. R. Gopal, Phys. Rep. **98**, 57 (1983).

[3] J. M. H. Levelt Sengers and J. V. Sengers, in *Studies in Statistical Mechanics*, edited by E. W. Montroll and J. L. Lebowitz (North-Holland, Amsterdam, 1981), Vol. IX.

[4] V. Vani, S. Guha, and E. S. R. Gopal, J. Chem. Phys. **84**, 3999 (1986).

[5] M. Ley Koo and M. S. Green, Phys. Rev. A **16**, 2483 (1977).

[6] S. C. Greer, B. K. Das, A. Kumar, and E. S. R. Gopal, J. Chem. Phys. **79**, 4545 (1983).

[7] C. L. Hartley, D. T. Jacobs, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. **33**, 1129 (1974).

[8] D. T. Jacobs, D. J. Anthony, R. C. Mockler, and W. J. O'Sullivan, Chem. Phys. **20**, 219 (1977).

[9] N. D. Mermin, Phys. Rev. Lett. **26**, 957 (1971).

[10] N. C. Wong and J. S. Huang, Phys. Rev. Lett. **35**, 42 (1975).

[11] W. V. Andrew, T. B. K. Khoo, and D. T. Jacobs, J. Chem. Phys. **85**, 3985 (1986).

[12] M. B. Ewing, K. A. Johnson, and M. L. McGlashan, J. Chem. Thermodyn. **18**, 979 (1986).

[13] J. W. Schmidt, J. Chem. Phys. **85**, 3631 (1986).

[14] H. Chaar, M. R. Moldover, and J. W. Schmidt, J. Chem. Phys. **85**, 418 (1986).

[15] G. M. Schneider, M. Dittmann, U. Metz, and J. Wenzel, Pure Appl. Chem. **59**, 79 (1986).

[16] C. Houessou, P. Guenoun, R. Gastand, F. Perrot, and D. Beysens, Phys. Rev. A **32**, 1818 (1985).

[17] D. T. Jacobs, Phys. Rev. A **33**, 2605 (1986).

[18] J. L. Tveekrem and D. T. Jacobs, Phys. Rev. A **27**, 2773 (1983).

[19] M. B. Ewing, K. A. Johnson, and M. L. McGlashan, J. Chem. Thermodyn. **17**, 513 (1985).

[20] Th. W. De Loos, H. J. van der Kooi, W. Poot, and P. L. Ott, Delft Prog. Rep. **8**, 200 (1983).

[21] R. R. Singh and W. A. Van Hook, J. Chem. Thermodyn. **18**, 1021 (1986).

[22] N. Nagarajan, A. Kumar, E. S. R. Gopal, and S. C. Greer, J. Phys. Chem. **84**, 2883 (1980).

[23] A. E. Bryson and Y. B. Ho, *Applied Optimal Control, Optimization, Estimation and Control* (Blaisdel, Waltham, MA, 1969).

[24] T. F. Anderson, D. S. Abrams, and E. A. Grens, Am. Inst. Chem. Eng. J. **24**, 20 (1978).

[25] S. Jüngst, B. Knuth, and F. Hensel, Phys. Rev. Lett. **55**, 2160 (1985).

[26] D. Beysens, J. Chem. Phys. **71**, 2557 (1979).

[27] G. Ahlers, in *Physics of Liquid and Solid Helium, Part I*, edited by K. H. Bennemann and J. B. Ketterson (Wiley, New York, 1976).

[28] A. Sivaranam, M. K. Tiwari, S. Jyothi, and E. S. R. Gopal, Ber. Bunsenges. Phys. Chem. **84**, 196 (1980).

[29] R. R. Singh and W. A. Van Hook, 9th IUPAC Conference on Chemical Thermodynamics, Paper 1.15 (IUPAC, Lisbon, July 1986).

[30] E. A. Clerke, Ph. D. thesis, University of Maryland, 1982.

[31] C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. A **16**, 365 (1977).

[32] Y. Yosida and A. Ikushima, J. Phys. Soc. Jpn. **45**, 1949 (1978).

[33] R. B. Kopelman, R. W. Gammon, and M. R. Moldover, Phys. Rev. A **29**, 2048 (1984).

[34] B. A. Scheibner, C. M. Sorenson, D. T. Jacobs, R. C. Mockler, and W. J. O'Sullivan, Chem. Phys. **31**, 209 (1978).

[35] H. Klein and D. Woermann, J. Chem. Phys. **65**, 1599 (1976).

[36] H. Klein and D. Woermann, Ber. Bunsenges. Phys. Chem. **82**, 1084 (1978).

[37] M. A. Anisomov, A. V. Voronel, and T. B. Ododova, Sov. Phys. JEPT **34**, 583 (1972).

[38] E. L. Eckfeldt and W. W. Lucasse, J. Phys. Chem. **47**, 164 (1943).

[39] D. C. Jones and S. Amstell, J. Chem. Soc. **1930**, 1316.

[40] J. Huang and W. W. Webb, J. Chem. Phys. **50**, 3677 (1969).

[41] R. H. Cohn and D. T. Jacobs, J. Chem. Phys. **80**, 856 (1984).