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Experimental study of the approach to a double critical point in the poly(styrene) plus acetone system: Test of fluctuation-isomorphism theory

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The phase-separation temperature has been measured as a function of pressure and composition for the poly(styrene) plus acetone system. From the experimental data, the coexistence curves at different pressures have been interpolated. The analysis of the curves in terms of simple scaling equations leads to values of the critical exponent β which, near the double critical point, seem to be larger than twice the single-critical-point value 0.325. Contrary to what was expected from previous work [F. Monroy *et al.*, Phys. Rev. B **47**, 630 (1993)], the use of the thermodynamic field suggested by Malomuzh and Veytsman [N. P. Malomuzh and B. A. Veytsman, Phys. Lett. A **136**, 239 (1989)] and simple scaling did not describe the data with a constant $\beta=0.325$ for all the isobars. However, the use of an effective β_{eff} given by a theory that assumes a fluctuation-isomorphism hypothesis describes very accurately the crossover from single- to double-critical-point behavior, with a universal $\beta=0.325$ critical exponent. The theory predicts that the region in which simple scaling is valid shrinks, even beyond the experimentally accessible range of this work, in the proximity of the double critical point.

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I. INTRODUCTION

It has been well established that near-critical-point (CP) fluids present a universal behavior described by a set of critical exponents characteristic of what is called a universality class [1]. Binary mixtures near a liquid-liquid equilibrium critical point belong to the three-dimensional (3D) Ising class [2], together with ferromagnets and pure fluids near a liquid-gas critical point.

According to the renormalization group, the order parameter $\Delta\lambda$ near a CP is described by [3]

$$\Delta\lambda\equiv\lambda_R-\lambda_L=B_0\epsilon^{\beta}+B_1\epsilon^{\beta+\Delta}+B_2\epsilon^{\beta+2\Delta}+\cdots\ , \tag{1}$$

where the critical exponents take the universal values $\beta=0.325$ and $\Delta=0.5$ in the Ising class, and ϵ is the thermodynamic field that describes the distance to the CP, and is usually expressed as $\epsilon=|(T-T_c)/T_c|$, with T_c being the critical temperature. The B_i's are called the critical amplitudes, and the order parameter $\Delta\lambda$ is defined, for the case of mixtures, as a difference of concentrations of the coexisting phases, R and L referring to the right and left branches of the coexistence curve, respectively. The CP is located in the phase diagram at (T_c,λ_c).

The application of an external field such as the pressure p is not expected to drive the system outside the 3D Ising class since it does not affect the symmetry of its Hamiltonian [4]. Therefore p should not have any effect upon the critical exponents, although it will, in general, affect the critical amplitudes [5] and the location of the critical point, which will describe a trajectory called the critical line (CL), $(T_c(p),\lambda_c(p))$, in the coexistence surface.

Even though there is a correspondence between each universality class and the values of the critical exponents, they also depend on the curvature of the CL. In most fluid mixtures both T_c and λ_c vs p are almost straight lines [6]; however, for reentrant phase transitions [7] there are regions of the phase diagram in which this is no longer true and therefore one must expect some change in the critical exponents with p. This situation occurs as one approaches the double critical points [8] (DCP's). Griffiths and Wheeler [9] have discussed this issue using a geometrical picture of the approach to the CP and concluded that if the curvature of the CL is described by an exponent n the critical exponents renormalize in such a way that, asymptotically close to the DCP, they take the value $n\beta_{\text{SCP}}$, the subscript SCP referring to the typical Ising-like single CP. The conclusions of the geometrical approach have been later confirmed by other theoretical treatments such as the decorated lattice model [10] or a model based on the catastrophe theory [11].

During the past few years there has been strong activity in order to confirm that on approaching a DCP the CL was quadratic [12] and that the critical exponents double near the DCP [13]. However, less work has been devoted to study how the critical exponents change from the value near a SCP to a DCP [14]. A general observation from these studies is that the renormalization process starts far from the DCP and thus the critical exponents take values significantly different from the SCP values.

We have recently carried out an experimental study of the renormalization of the exponent β for the lower critical solution point transition (LCST) of the 2-butanol plus water system as the DCP is approached by changing p [15]. Our results are in reasonable agreement with those of Prafulla, Narayanan, and Kumar [14], from resistivity measurements, and seem to indicate that instead of ϵ, a new thermodynamic field $\epsilon_{\text{TU}}=|(T-T_U)(T-T_L)/$

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$T_U T_L|$ should be used in Eq. (1). T_u and T_l refer to the upper critical solution point transition (UCST) and LCST of the reentrant phase transition, respectively. Notice that near the DCP, $|T_U - T_L| \to 0$ and $\epsilon_{TU} \to \epsilon^2$, which is equivalent to say that in Eq. (1) $\beta_{DCP} \to 2\beta_{SCP}$. A recent description of the behavior of systems near DCP given by Malomuzh and Veytsman [16] leads to ϵ_{TU} as the natural field for describing the approach to a DCP. Kumar and co-workers [14] have also found that constant Ising-like exponents are suitable when ϵ_{TU} is used.

Malomuzh and Veytsman's theory [16] assumes that the algebra of strongly fluctuating variables is isomorphic to the algebra of the variables describing l-g (liquid-gas) isolated CP of the phase transition in the Ising model and describes the renormalization of the critical exponent β by

$$\frac{\beta_{\text{eff}}}{\beta_{\text{SCP}}} = \Psi_0(\epsilon,\epsilon_0) + g\Psi_1(\epsilon,\epsilon_0) + O(g^2) , \qquad (2)$$

where

$$\Psi_0 = 1 + \frac{\ln|\epsilon_0+\epsilon|}{\ln|\epsilon|} , \quad \Psi_1 = 2\frac{3\epsilon_0^2 + 3\epsilon_0\epsilon + \epsilon^2}{(\epsilon_0+\epsilon)\ln|\epsilon|} ,$$

$$g = \frac{l_2}{l_1^2} T_{\text{DCP}} , \quad \epsilon_0 = \frac{T_u - T_l}{2T_{\text{DCP}}} . \qquad (3)$$

The l_i's are the coefficients of the equation that describes the CL [15]:

$$T_{c,p} - T_{\text{DCP}} = l_1(p - p_{\text{DCP}})^{1/2} + l_2(p - p_{\text{DCP}}) , \qquad (4)$$

with $l_2 \ll l_1$ in most cases, thus ensuring the parabolic behavior in the neighborhood of the DCP. In Eq. (2), the subscript eff refers to the value of the critical exponent that one would obtain by fitting experimental data corresponding to given values of ϵ_0 to a simple scaling equation, i.e., Eq. (1) with $B_i = 0$, $i > 0$. Equations (2)–(4) indicate that the renormalization of β will depend on the distance to the DCP measured by two variables ϵ_0 and ϵ and on the shape of the CL measured by l_1 and l_2.

In our previous work [15] we assumed the validity of simple scaling as in most of the previous work dealing with the study of the renormalization of critical exponents as the DCP is approached [12,13]. However, Eqs. (2) and (3) introduce some doubts on such an assumption as it can be easily seen for the data of the 2-butanol plus water system [15]. A given value of ϵ_0 corresponds to each isobar, i.e., the coexistence curve at a given pressure; such a value is calculated according to Eq. (2) using the CL reported in Ref. [15]. The arrows in Fig. 1(a) show in the ϵ axis the values of ϵ_0 that correspond to the isobars of 101.5 bar (very close to the pressure of the DCP) and 170 bar.

For each of the values of ϵ_0, Fig. 1 shows the curves $\beta_{\text{eff}}/\beta_{\text{SCP}}$ calculated according to Eqs. (2)–(4). It can be observed that $\beta_{\text{eff}}/\beta_{\text{SCP}}$ cannot be considered as constant except perhaps extremely close to the CP of each isobar ($\epsilon \to 0$). More specifically it appears that for the range $10^{-3} \le \epsilon \le 10^{-2}$, for which simple scaling is usually valid for binary mixtures [2], $\beta_{\text{eff}}/\beta_{\text{SCP}}$ shows a non-negligible ϵ dependence which seems to be larger for the $p = 101.5$ bar isobar, i.e., closer to the DCP ($p_{\text{DCP}} = 100.7 \pm 0.1$ bar for 2-butanol plus water [15]).

The behavior predicted by the Malomuzh-Veytsman theory [16] introduces therefore a further complexity in the analysis of thermophysical properties near CP as the DCP approaches, and the use of a value β_{eff} independent of ϵ in many of the work published so far suggests that a work aiming to clarify this point is worthwhile and will be the object of this paper, focusing our attention on the exponent β.

The 2-butanol plus water system was studied near the LCST [15] and the mass fraction was found to be suitable for relatively symmetrical coexistence curves. The use of more unsymmetrical curves might enhance the above-mentioned effect, therefore polymer-solvent systems might be good candidates for testing the predictions of the Malomuzh-Veytsman theory [16]. Zeman and Patterson [17] have studied the effect of molecular weight and pressure upon the phase diagram of a poly(styrene) plus acetone (PS+AC) system; their results indicate that for a polymer of molecular weight $M_w \simeq 20\,000$, the system might have a DCP at relatively low pressure and approximately 340 K. We have studied the coexistence curve of this system near the UCST.

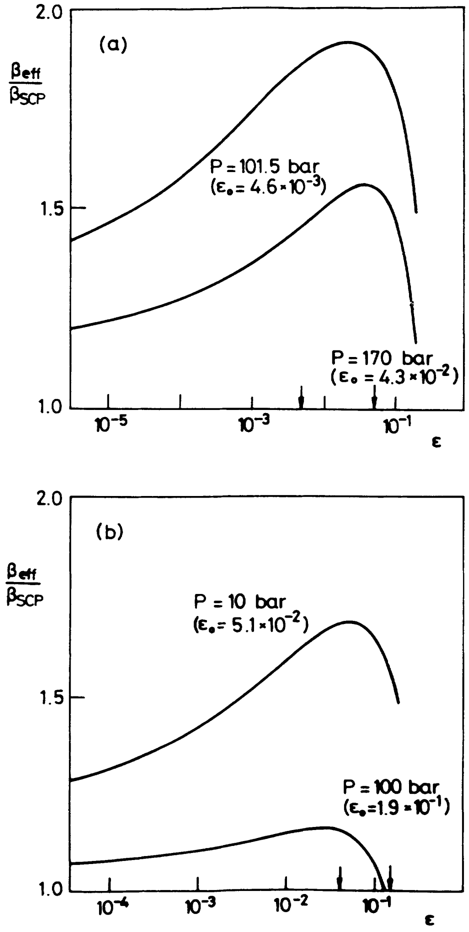

FIG. 1. Dependence of the ratio $\beta_{\text{eff}}/\beta_{\text{SCP}}$ on ϵ $[=|(T-T_c)/T_c|]$, given by Eqs. (2) and (3), for the binary systems (a) 2-butanol plus water and (b) polystyrene plus acetone. The arrows indicate the value of ϵ_0 for each isobar.

The rest of this paper is organized as follows. Section II gives some details of the experimental procedure and the results are presented in Sec. III. Section IV discusses the behavior of the critical exponent β and the adequacy of the Malomuzh-Veytsman theory [16] to describe our results. Finally, Sec. V summarizes the conclusions.

II. EXPERIMENT

The acetone used in the experiments was Carlo Erba RPE with an initial purity greater than 99% and was kept over molecular sieves (3 Å). The poly(styrene) supplied by Polysciencies is a standard of molecular weight $M_w \simeq 20\,000$ and very low polydispersity $M_w/M_n = 1.03$, where M_w and M_n are the molecular and number average molecular weights, respectively.

The experimental setup is similar to that used by Sassen *et al.* [18]. The sample was contained in a glass cell, trapped with mercury, and magnetically stirred. The whole cell was contained in a stainless-steel autoclave. Water was used as pressure transmission fluid. The sample was illuminated from outside and observed through sapphire windows. The autoclave was placed inside a water thermostat whose temperature stability, ±1 mK over 20-h periods, was obtained with a Tronac PTC-41 controller and a Tronac TCP-25-S probe. The temperature was measured with a quartz thermometer Hewlett-Packard HP-2804-A, frequently calibrated against a gallium melting point standard YSF-17402. The temperature scale agrees with the ITS-90 to within ±0.01 K. The pressure was generated and measured as in a previous work [15], but using a Maywood P-102 transducer. The precision in p was ±0.1 bar for the range of the measurements reported in this work.

TABLE I. Experimental isopleths of polystyrene plus acetone system. w stands for the weight fraction of polystyrene.

P (bar)	T (°C)	P (bar)	T (°C)	P (bar)	T (°C)	P (bar)	T (°C)	P (bar)	T (°C)	P (bar)	T (°C)
$w=0.1015$		$w=0.1136$		$w=0.1250$		36.1	42.334	24.2	47.127	27.7	44.045
112.6	21.651	131.0	20.071	137.1	20.020	31.2	44.337	19.1	49.633	22.9	45.992
92.5	25.025	100.2	25.006	104.7	25.010	26.5	46.338	14.7	52.117	18.7	48.040
67.3	30.087	74.0	30.077	77.8	30.020	22.3	48.342	11.1	54.604	14.9	50.014
45.0	35.123	52.2	35.064	56.3	35.020	18.5	50.375	7.9	57.116	11.3	52.031
29.3	40.044	35.8	40.017	39.5	40.070	15.5	52.332	5.3	59.608	8.1	54.005
23.8	42.015	30.0	42.053	33.7	42.010	12.6	54.305	3.4	61.635	5.3	56.048
18.8	44.005	24.5	44.067	28.3	44.000	9.9	56.303				
13.8	46.034	19.5	46.044	23.5	46.040	7.7	58.39				
9.3	48.016	15.8	48.034	19.1	48.030						
5.8	50.069	11.6	50.051	15.9	50.030	$w=0.1985$		$w=0.2021$		$w=0.2075$	
2.8	52.023	8.8	52.019	12.5	52.040	140.2	20.025	139.1	20.026	137.1	20.080
		5.9	54.027	9.5	54.020	106.2	25.022	105.3	25.039	103.9	25.021
						79.2	30.005	78.3	30.046	77.4	30.053
$w=0.1325$		$w=0.1415$		$w=0.1517$		57.2	35.048	56.3	35.095	55.3	35.075
107.5	25.010	104.3	25.890	146.1	19.660	47.5	37.65	39.0	40.023	38.2	40.014
80.5	30.011	82.3	29.868	111.5	24.661	39.8	40.038	33.0	42.026	32.2	42.019
58.5	35.005	60.0	34.938	83.9	29.632	33.8	42.044	27.6	44.041	26.8	44.028
40.9	40.014	43.0	39.840	61.8	34.664	28.5	44.042	22.9	46.017	21.8	46.056
35.1	42.014	37.0	41.859	43.8	39.711	23.6	45.999	18.6	48.044	17.6	48.030
30.2	44.008	32.0	43.846	37.9	41.643	19.3	48.043	14.8	50.007	13.7	50.016
25.1	46.006	27.1	45.859	32.5	43.664	15.5	50.026	11.4	52.029	10.3	52.047
20.9	48.032	22.9	47.871	27.6	45.682	11.9	52.012	8.3	54.075	7.2	54.023
17.8	50.021	18.9	49.866	23.5	47.671	8.9	54.013	5.7	56.039	4.8	56.077
14.9	52.040	15.8	51.885	20.0	49.682	6.4	56.028				
11.5	54.007	12.8	53.886	16.5	51.643	3.9	58.053				
8.7	56.007	10.1	55.895	13.5	53.671						
6.2	58.011	7.8	57.888	11.0	55.690	$w=0.2197$		$w=0.2275$		$w=0.2392$	
4.2	60.055	5.8	59.902	9.0	57.660	132.7	20.026	93.5	25.392	122.7	20.037
3.0	62.016	4.4	61.874			99.9	25.023	69.9	30.061	91.1	25.065
		2.8	63.880			73.4	29.997	48.9	35.024	65.9	30.066
						51.9	35.009	32.9	40.017	45.7	35.026
						34.8	40.055	25.9	42.535	29.6	40.067
$w=0.1616$		$w=0.1743$		$w=0.1912$		29.1	42.023	20.1	45.004	24.1	42.050
156.0	18.317	143.6	19.898	141.5	20.014	23.9	44.037	15.2	47.281	19.2	43.994
120.0	23.369	104.6	25.775	106.9	25.046	19.3	45.998	10.1	50.034	14.8	46.060
90.9	28.358	83.7	29.610	79.4	30.009	15.1	48.036	6.2	52.510	10.9	48.029
66.8	33.342	61.7	34.636	56.9	35.061	11.4	50.025	3.0	55.002	7.3	50.043
47.9	38.340	43.9	39.679	39.1	40.060	8.1	52.010			4.5	52.027
41.4	40.326	30.3	44.467	33.2	42.040	5.0	54.052				

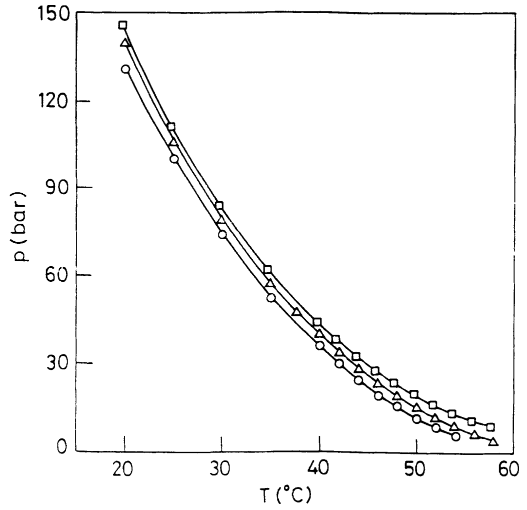

FIG. 2. Some experimental isopleths of the polystyrene plus acetone system near its double critical point. The composition w of each of them is 0.1136 (△), 0.1415 (□), and 0.2197 (○).

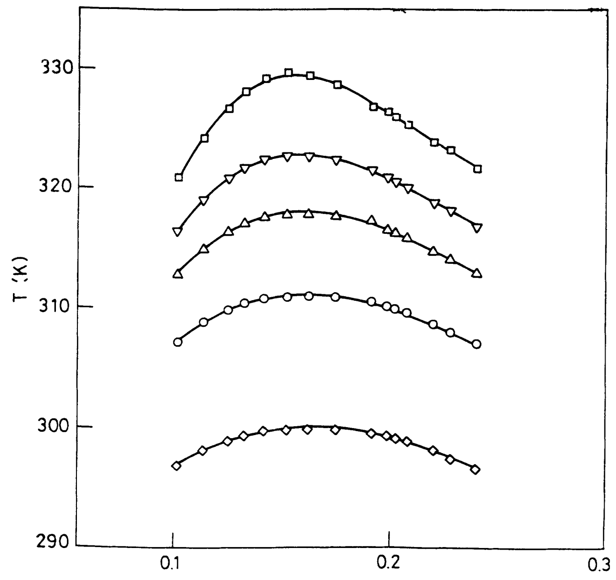

FIG. 3. Coexistence curves of the polystyrene plus acetone system at different pressures [10.0 bar (□), 20.0 bar (▽), 30.0 bar (△), 50.0 bar (○), and 100.0 bar (◇)]. The composition variable w is the weight fraction of polystyrene.

As previously [6,15], 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, rending p-T curves or isopleths. The mixtures were prepared by weight just before use, with a precision of ±0.01 mg, thus the uncertainty in the weight fraction was less than ±0.0001. All the samples were thoroughly degassed.

III. RESULTS

Table I shows the experimental data. In general the isopleths are almost straight lines, except in the low-pressure region where, as it can be observed in Fig. 2, there is a marked curvature as expected in the proximity of a DCP [20]. It is unfortunate that due to experimental difficulties it was not possible to measure the high-temperature branch of the isopleths. For those mixtures far from that of the DCP the extrapolation of the isopleths to $p=0.1$ MPa leads to values in good agreement with the previous measurements at low pressure [17].

For each composition the data were fitted to

$$P\ (\text{MPa})=a+bs+cs^2+ds^3\ , \tag{5}$$

where $s=[T\ (\text{K})]-273.15$. The constants a-d were obtained using a method based in the maximum-likelihood principle, and are collected in Table II together with the mean standard deviation of the variables. By interpolating in Eq. (5), the coexistence curves at constant pressure can be easily obtained. Figure 3 shows several isobars; it can be observed that, as expected, there

TABLE II. Parameters of fittings of the experimental isopleths of the polystyrene plus acetone system in terms of a cubic polynomial [Eq. (5)]. The standard deviations on pressure and temperature are estimated from these fittings.

w	a	b	$10c$	10^4d	$\sigma(p)$ (bar)	$\sigma(T)$ (K)
0.1015	305.52	−11.82	1.48	−6.27	0.3	0.003
0.1136	317.23	−12.04	1.50	−6.30	0.2	0.002
0.1250	337.15	−13.23	1.79	−8.59	0.2	0.001
0.1325	346.66	−13.65	1.86	−8.91	0.3	0.001
0.1415	347.71	−13.57	1.83	−8.62	0.2	0.001
0.1517	352.44	−13.90	1.90	−9.15	0.2	0.002
0.1616	352.58	−13.93	1.92	−9.37	0.1	0.001
0.1743	347.46	−13.56	1.84	−8.81	0.2	0.002
0.1912	355.12	−14.26	1.99	−10.00	0.1	0.001
0.1985	346.80	−13.72	1.87	−9.15	0.2	0.002
0.2021	345.39	−13.70	1.88	−9.17	0.1	0.002
0.2075	339.07	−13.32	1.79	−8.51	0.2	0.002
0.2197	337.03	−13.62	1.89	−9.46	0.1	0.001
0.2275	320.09	−12.80	1.74	−8.37	0.1	0.001
0.2392	318.48	−13.07	1.83	−9.20	0.1	0.001

is a clear change in the shape of the coexistence curve, which passes from nearly parabolic at low pressures to almost cubic at higher pressures as shown by the β values; this change will be discussed below.

IV. DISCUSSION

The experimental data have been analyzed taken $\lambda \equiv w$, the weight fraction of PS, to define the order parameter. As in our previous work [15], the analysis of the coexistence curve was carried out using

$$\lambda = \lambda_c \pm (B/2)\epsilon^{\beta} + A_0\epsilon \ , \tag{6}$$

where λ_c stands for the critical composition and A_0 is the amplitude of the diameter of the coexistence curve. Table III collects the parameters characteristic of the different isobars.

The couples $(T_{c,p}, p)$, together with Eq. (4) lead to $T_{\mathrm{DCP}} = 343.01 \pm 0.07$ K, $P_{\mathrm{DCP}} = 3.33 \pm 0.05$ bar, $l_1 = -5.39 \pm 0.01$, and $l_2 = 0.1013 \pm 0.0007$, which are not very different from those of the 2-butanol plus water system [15]. Figure 4 shows the β values, from Table III, versus $\Delta T \equiv |T_U - T_L|$, confirming the previous results in the sense that $\beta > \beta_{\mathrm{SCP}}$ even for large values of ΔT. However, for the PS+AC system it can be seen that $\beta > 2\beta_{\mathrm{SCP}}$ for small ΔT's, i.e., close to the DCP, which introduces some doubts on the validity of the previous analysis, which is otherwise quite standard in the literature.

According to the Malomuzh-Veytsman model [16], the order parameter should behave, close enough to the CL, as

$$\Delta\lambda \alpha \epsilon_{\mathrm{TU}}^{\beta} \ , \tag{7}$$

with $\beta = 0.325$. We have analyzed our isobars with the field ϵ_{TU} instead of ϵ and leaving β as a fitting parameter. The results obtained for β are shown in Fig. 4, where it can be observed that instead of a constant value, β increases as ΔT is decreased, while at ΔT large enough β takes values smaller than β_{SCP}. The apparent failure of Eq. (7) contrasts with its ability to describe the data of 2-butanol plus water and light scattering results of Prafulla, Narayanan, and Kumar [14] on the system of 3-methylpyridine, water, and heavy water Eqs. (2) and (3) suggest that the value of β in Eq. (7) should depend upon the value of ϵ in addition to ϵ_0; therefore we have used Eq. (7) with β given by Eqs. (2)–(4) and found that it is possible to describe the experimental data with values of $\chi^2 < 0.1$ (notice that β is not fitted). Figure 1(b) shows the ratio $\beta_{\mathrm{eff}}/\beta_{\mathrm{SCP}}$ for two isobars of PS+AC according to Eqs. (2)–(4), confirming the strong dependence on ϵ within the experimental range of the present study.

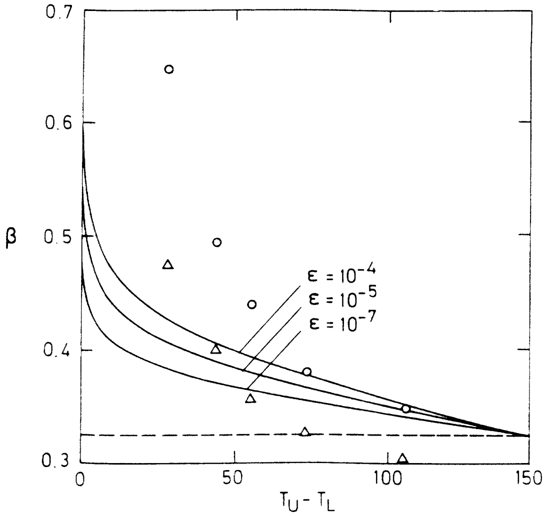

FIG. 4. Loop size dependence $\Delta T = (T_U - T_L)$ of β for different values of ϵ $[= |(T - T_c)/T_c|]$. The (○) are the values given by the fit with Eq. (6) and the (△) the fit with Eq. (7).

These results indicate that the influence of a DCP on the critical behavior must be taken into account not only on the change of the critical exponents but also on the range of validity of simple scaling law, which might decrease below the experimentally accessible range for small ϵ_0. Figure 4 shows the calculated values of β_{eff} as a function of ϵ_0 for different values of ϵ; it can be observed that even for $\epsilon < 10^{-4}$, which is not usually attainable in most of the experimental work described in the literature, it seems that the $\epsilon \rightarrow 0$ limit, i.e., simple scaling, has not been reached for the PS+AC system even for the smaller $|T - T_c|$ experimental values.

We have carried out the same analysis with the 2-butanol plus water system [15], with similar conclusions, although in this case the use of Eq. (7) with $\beta = 0.325$ leads to reasonably good results.

Similar results have been obtained using an extended scaling description for the order parameter

$$\Delta\lambda = B_0\epsilon_{\mathrm{TU}}^{\beta} + B_1\epsilon_{\mathrm{TU}}^{(\beta+\Delta)} \ , \tag{8}$$

TABLE III. Analysis of the interpolated isobars of the polystyrene plus acetone system in terms of Eq. (6). These fittings have been performed assuming the uncertainties $\sigma(T) = \pm 0.02$ K and $\sigma(w) = \pm 0.002$.

p (bar)	T_c (K)	w_c	$B/2$	A_0	β	χ^2
10.0	329.76±0.03	0.1526±0.0005	1.50±0.10	0.77±0.04	0.649±0.016	0.05
20.0	322.688±0.011	0.1567±0.0006	0.98±0.06	0.78±0.06	0.495±0.014	0.09
30.0	317.876±0.010	0.1584±0.0009	0.83±0.08	0.78±0.11	0.44±0.02	0.21
50.0	319.912±0.002	0.1601±0.0009	0.71±0.06	0.79±0.14	0.380±0.017	0.18
100.0	299.801±0.003	0.161±0.003	0.66±0.07	0.9±0.2	0.348±0.018	0.27

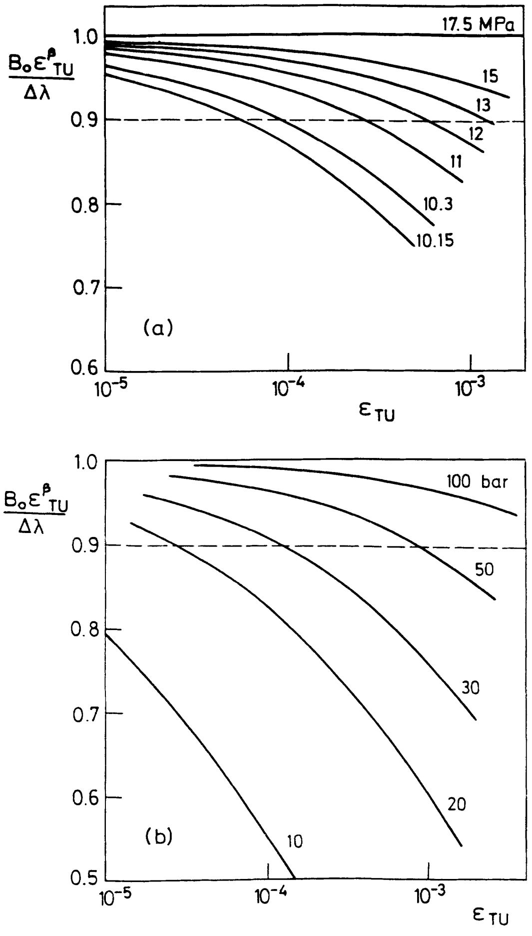

FIG. 5. Relative weight of the simple scaling term in Eq. (8) for (a) 2-butanol plus water and (b) polystyrene plus acetone.

with $\beta=0.325$ and $\Delta=0.5$. In all the cases it has been possible to obtain variances $\chi^2<1$ showing that Eq. (8) is able to describe the results with a random distribution of the residuals. Equation (7) has been recently used by Prafulla, Narayanan, and Kumar [19] in the analysis of their light scattering data for 3-methylpyridine plus water doped with NaCl. Figure 5 shows the relative weight of the simple-scaling term in Eq. (8) both for 2-butanol plus water and for poly(styrene) plus acetone. It can be observed that while for the first system simple scaling accounts for 80% of $\Delta\lambda$ even for the isobar which is closest to the DCP, the situation is rather different for the polymer system even if ϵ_{TU} has been used. This stresses the need of using Eqs. (2)–(4) in analyzing the critical data near a DCP.

The use of volume fraction instead of weight fraction to define the order parameter does not lead to any qualitative difference in the above discussion.

V. CONCLUSIONS

The coexistence curves of the PS+AC system have been obtained as a function of the distance of the DCP. Even though the CPL shows a parabolic curvature in the proximity of the DCP, the values of the critical exponent β obtained when the usual simple scaling equation and the field ϵ are used are larger than the single critical point value $\beta=0.325$ for very large values of ϵ_0 and even larger than twice that value for low ϵ_0's. The use of simple scaling and the field ϵ_{TU} does not lead to a constant value of $\beta=0.325$, but to a critical exponent that increases as the DCP is approached and seems to take values $\beta<0.325$ for large ϵ_0. The use of an effective β_{eff} given by the theory of Malomuzh and Veytsman describes very accurately the crossover from single- to double-critical-point behavior, with a universal $\beta=0.325$ critical exponent. The theory predicts that the region in which simple scaling is valid shrinks as the DCP is approached.

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