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Diameters of the Liquid–Liquid Coexistence Curves of Aqueous Solutions of Tetrahydrofuran[1]

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The diameters of the coexistence curves of aqueous solutions of tetrahydrofuran and two quasibinary, isotopically related mixtures near their lower consolute points are analyzed in terms of different composition variables including mole, mass, and volume fractions, using various possible definitions of the reduced temperature. A $(1-\alpha)$ anomaly is observed for all choices of the temperature and concentration variables. In terms of mole fraction the diameters are free from a regular contribution as well as from a spurious 2β contribution arising from the inappropriate choice of the order parameter. The mass and volume fractions lead to an apparent symmetrization of the coexistence curve, but cause significant 2β contributions to the diameter that could mask the $1-\alpha$ anomaly. A reduced temperature that accounts for the presence of both upper and lower critical consolute points is found to be preferable, although the second critical point is 80 K away.

KEY WORDS: aqueous solutions; coexistence curve diameter; critical point; tetrahydrofuran.

1. INTRODUCTION

The universality of critical behavior among fluids and certain lattice models is well established, but there are problems regarding the lack of symmetry in real fluids. In ferromagnets the magnetization of the coexisting phases is symmetric around zero. Lattice models with "hole-particle" symmetry [1] obey the law of the "rectilinear diameter" for the order parameter P of the coexisting phases 1 and 2; $P_d \equiv (P_1 + P_2)/2 = P_c + A\tau$, where index c refers

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to the value at the critical point and τ is the temperature distance from the critical temperature T_c. Analytical equations of state predict such a linear temperature dependence of the diameter as well.

Liquid-vapor and liquid-liquid coexistence curves lack this symmetry. Lattice and continuum models without hole-particle symmetry predict P_d to show a $\tau^{1-\alpha}$ singularity due to "field mixing" that occurs when the intermolecular potential is a function of thermodynamical variables [2]. α is the exponent of the heat capacity. Experimentally, this $(1-\alpha)$ anomaly is observed for one-component fluids [3], where the density ρ provides a measure for P. In two-component mixtures, decisive results are obscured by problems regarding the choice of P [3, 4]. Criteria for a "good" choice make use of symmetry arguments, such as a critical concentration close to 0.5, a symmetrical coexistence curve, or a $(1-\alpha)$ anomaly of the diameter. Moreover, the diameter should be free from a spurious $\tau^{2\beta}$ term that arises from a "wrong" choice of P [4, 5] (β is the critical exponent of the coexistence curve). Thus, a proper description of the diameter anomaly has often been used as a means for assessing the choice of P [5]. However, usually the various requirements cannot be satisfied simultaneously [6, 7]. In the present study we examine these aspects by considering data near the lower critical solution temperature of tetrahydrofuran (THF)—water mixtures.

2. RESULTS

2.1. Experimental Data

We analyze the diameters of three isotopically related aqueous solutions of tetrahydrofuran (THF) [8] near their lower consolute temperatures (LCT); solutions of THF in normal water possess a closed-loop phase diagram limited by upper (UCT) and lower (LCT) critical solution temperatures at 344 and 410 K, respectively, at a critical mole fraction $X = 0.2255$ of THF. Deuteration of water results in an extension of the miscibility gap in the binary THF + D_2O mixture by about 20 K. Progressive substitution of THF by its fully deuterated homologue THF_d leads to a shrinkage of the miscibility gap, which eventually disappears for 75% deuteration. This results in a quasibinary THF + THF_d + D_2O mixture with UCT and LCT close to those of the normal THF + H_2O mixture. Comparison of results for these isotopically related mixtures can be used to single out nonuniversal, substance-specific contributions that occur further away from the critical point [8].

Coexistence curve data measured by the minimum beam deviation method are reported elsewhere [8, 9]. The refractive index data were converted to mole, weight, and volume fractions using excess volumes and thermal expansion coefficients [9]. Large excess volumes result in substantial changes of the location and shape of the coexistence curves in terms of different concentration variables. A detailed analysis [8, 9] of the coexistence curves indicated that not only the magnitude of the critical amplitudes, but also the sign of the corrections to scaling, depend on the choice of the order parameter.

As a further problem, there is the need for a redefinition of τ for reentrant phase transitions, because then τ depends on the location of the second critical point [10]. In fact, some binary ionic systems studied recently near the UCT [6] later proved to be closed loops with the LCT hidden by crystallization [11]. It was therefore of interest to us, to what extent a second critical point affects the data analysis, if the latter is typically 80 K and more away.

2.2. Variables and Fitting Equations

We compare here reduced temperatures defined as usual by $\tau = (T-T_c)/T_c$ and also by $\tau' = (T-T_c)/T$ [12, 3], where T_c refers to the LCT. Moreover, we also used $\tau_{\mathrm{UL}} = \tau(T_U - T)/T_U$ and $\tau'_{\mathrm{UL}} = \tau'(T_U - T)/T$ [10], where T_U is the UCT. The mole fraction X and weight fraction w of THF in the coexisting phases were evaluated in Ref. 9. The volume fraction φ was estimated by assuming that the volume reduction results from a change in the specific volume of only water [9].

Because in the experiments the composition of both coexisting phases P_1 and P_2 were probed, the order parameter $\Delta P = (P_1 - P_2)/2$ and diameter $P_d = (P_1 + P_2)/2$ of the coexistence curves can be analyzed independently. We use a modified Wegner expansion [13]:

$$P_d = P_c + A_{1-\alpha}\tau^{1-\alpha}(1 + A_\Delta \tau^\Delta + A_{2\Delta}\tau^{2\Delta} + \cdots) + A_1\tau \cdots A_{2\beta}\tau^{2\beta} \quad (1)$$

with the Ising critical exponents $\alpha = 0.109$, $\beta = 0.3258$, and $\Delta = 0.504$ [14]; A_i's are the nonuniversal amplitudes. For comparison, we used the crossover equation for the diameter proposed by Nicoll and Albright [15] in the form of a Wegner expansion with 2 correction terms [5b]

$$P_d = P_c + d_1\tau + d_2\tau(y^{-\alpha/\Delta} - 1) + d_3\tau(t^{1-\alpha/\Delta} - 1) \quad (2)$$

where $y^{-1} = 1 + d_0(\tau^{-\Delta} - 1)$; the d_i are substance-specific amplitudes. Third, exploiting the similarity between the diameter and specific heat anomalies, we also tested our data against the extended equation available for the heat capacity, by relating the amplitude of the first Wegner correction-to-scaling

A_Δ for heat capacity to the amplitude of the leading singular term and critical linear term of the diameter expansion [16]. Then, Eq. (1) can be rewritten as

$$P_d = P_c + A_{1-\alpha}\tau^{1-\alpha}(1 + A'_\Delta\tau^\Delta + A_{2\Delta}\tau^{2\Delta}) - A_{1-\alpha}B_1\tau + B_{\text{reg}}\tau \tag{3a}$$

with

$$A'_\Delta = \frac{1-\alpha}{1-\alpha+\Delta}\left(\frac{R_B^- B_1}{1-\alpha}\right)^{\Delta/\alpha} \tag{3b}$$

where $R_B^- = 1.334$ [16] is the universal amplitude ratio for the ordered state of the system, and $B_{\text{reg}}\tau$ is the regular, noncritical contribution.

Initially, we fitted the experimental data to Eq. (1) with various order parameters. The best choice (here the mole fraction) was also fitted to Eqs. (2) and (3). The quality of the fits was assessed using the χ^2-criterion with 0.0007 and 0.001 assumed as standard deviations of the mole and weight (volume) fractions, respectively [9].

2.3. Results

The diameters of the THF + D_2O mixture are shown in Fig. 1 for different composition variables. Similar features were observed for the THF + H_2O and THF + THF_d + D_2O mixtures. Figure 1 shows that (i) the weight fraction w provides the most symmetric coexistence curves; (ii) far from the critical point the slope of the "rectilinear diameter" has a different sign for different variables; and (iii) the critical anomaly, i.e., the bend of the diameter near T_c for mole fraction X, is opposite to that for the two other variables.

The fits to Eq. (1) in Tables I and II, however, do not reflect these qualitative observations; the amplitude $A_{1-\alpha}$ of the leading critical contribution is found to be positive for all composition variables in all mixtures. The linear term, which includes both critical and noncritical effects, appears to be negligible in all cases. The most important conclusion is, however, absence of the 2β contribution for diameters on the mole fraction scale (cf. Table I). In contrast, this spurious contribution is significant for weight and volume fractions (cf. Table II), causing the apparent negative amplitudes of the bend seen in Fig. 1. Moreover, from the comparison of the fits in Table II, it becomes obvious that relative importance of the 2β term compared to the $1-\alpha$ term is larger for volume fractions than for weight fractions. The 2β contribution to the diameters in the weight and volume fraction scales possesses similar magnitudes.

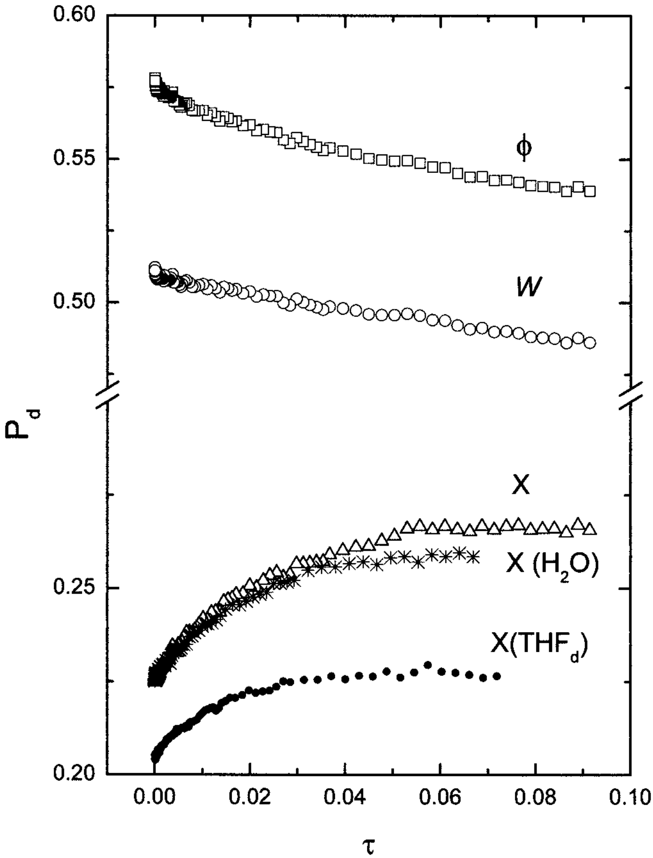

Fig. 1. Diameter of $THF + D_2O$ mixture for different composition variables: mole fraction x (△), weight fraction w (○), and volume fraction φ (□). For mixtures $THF + H_2O$ (∗) and $THF + THF_d + D_2O$ (●), the diameter is shown on the mole fraction scale.

We have also tried to achieve a symmetrization of the coexistence curves by applying the generalized transformation [7],

$$P_1 = \frac{mX_1}{mX_1 + 1 - X_1} \tag{4}$$

which reduces to the weight fraction if m is the ratio of the molar masses of the components, to the volume fraction if m is the ratio of molar masses normalized their densities, or to the effective molar concentration if the

Table I. Parameters of the Fits of the Diameter to Eq. (1) in Terms of X, Mole Fraction of THF, versus Reduced Temperature τ. (The Absence of the 2β-Contribution As Well As the Linear Term Is Evident. For the THF + D_2O Mixture the Fitting Data Set Was Reduced on 11 Points in Order to Get Similar Temperature Intervals in Terms of τ: $\tau < 0.07$. The Best Fit for Each Mixture Is Marked with an Asterisk. The Uncertainties Denote 1 Standard Deviation)

Mixture	N	X_c	$A_{1-\alpha}$	A_Δ	$A_{2\Delta}$	$A_{2\beta}$	A_1	χ^2
THF + H_2O	1*	0.2255	1.124 ± 0.012	−2.68 ± 0.02	(0)	(0)	(0)	0.65
THF + H_2O	2	0.2255	1.131 ± 0.036	−2.74 ± 0.25	0.19 ± 0.88	(0)	(0)	0.66
THF + H_2O	3	0.2239	−0.527 ± 0.04	(0)	(0)	0.494 ± 0.017	(0)	2.39
THF + H_2O	4	0.2255	1.142 ± 0.10	−2.67 ± 0.08	(0)	−0.006 ± 0.031	(0)	0.66
THF + H_2O	5	0.2255	1.108 ± 0.25	−2.74 ± 0.94	(0)	(0)	0.029 ± 0.45	0.66
THF + D_2O	6	0.2255	1.178 ± 0.015	−2.47 ± 0.03	(0)	(0)	(0)	1.18
THF + D_2O	7*	0.2250	1.449 ± 0.039	−4.02 ± 0.17	5.25 ± 0.58	(0)	(0)	0.78
THF + D_2O	8	0.2245	0.486 ± 0.11	−3.58 ± 0.43	(0)	0.218 ± 0.035	(0)	0.87
THF + D_2O	9	0.2251	1.604 ± 0.35	−4.00 ± 0.15	5.40 ± 0.61	0.037 ± 0.083	(0)	0.79
THF + D_2O	10	0.2249	3.027 ± 0.27	−0.07 ± 0.14	(0)	(0)	−3.38 ± 0.49	0.81
THF + D_2O	11	0.2248	2.62 ± 0.87	−0.71 ± 1.4	0.93 ± 1.8	(0)	−2.47 ± 1.8	0.81
THF + THF_d + D_2O	12	0.2047	0.929 ± 0.012	−2.95 ± 0.02	(0)	(0)	(0)	0.78
THF + THF_d + D_2O	13*	0.2044	1.12 ± 0.03	−4.32 ± 0.15	4.88 ± 0.54	(0)	(0)	0.53
THF + THF_d + D_2O	14	0.2043	0.644 ± 0.087	−3.50 ± 0.24	(0)	0.089 ± 0.027	(0)	0.63
THF + THF_d + D_2O	15	0.2044	1.156 ± 0.26	−4.30 ± 0.19	4.93 ± 0.64	−0.008 ± 0.060	(0)	0.54
THF + THF_d + D_2O	16	0.2044	1.14 ± 0.64	−4.18 ± 4.17	4.73 ± 5.0	(0)	−0.042 ± 1.3	0.54

Table II. Parameters of the Fits of the Diameter to Eq. (1) in Terms of Volume and Weight Fractions of THF Versus Reduced Temperature τ. (The Importance of the 2β-Contribution Is Demonstrated. For the THF + D_2O Mixture the Fitting Data Set was Reduced on 11 Points in Order to Get Similar Temperature Intervals in Terms of τ: $\tau < 0.07$. The Best Fit for each Variable Is Marked with an Asterisk. The Uncertainties Denote 1 Standard Deviation)

Mixture	N	P	P_c	$A_{1-\alpha}$	A_Δ	$A_{2\Delta}$	$A_{2\beta}$	A_1	χ^2
THF + H_2O	1	φ	0.5773	-6.11 ± 1.0	2.22 ± 0.23	-2.38 ± 0.43	(0)	11.2 ± 2.2	0.56
THF + H_2O	2*	φ	0.5787	1.36 ± 0.42	-3.00 ± 0.39	4.38 ± 1.2	-0.52 ± 0.10	(0)	0.55
THF + H_2O	3	w	0.5378	-0.552 ± 1.1	2.41 ± 0.22	-2.53 ± 0.45	(0)	10.5 ± 2.2	0.57
THF + H_2O	4*	w	0.5382	1.44 ± 0.42	-3.10 ± 0.35	4.16 ± 1.2	-0.48 ± 0.10	(0)	0.56
THF + D_2O	5	φ	0.5868	-5.72 ± 1.0	2.25 ± 0.23	-2.25 ± 0.23	(0)	10.2 ± 2.2	0.55
THF + D_2O	6*	φ	0.5874	1.45 ± 0.41	-3.97 ± 0.20	7.56 ± 0.65	-0.56 ± 0.10	(0)	0.53
THF + D_2O	7	w	0.5128	-5.10 ± 1.1	2.86 ± 0.16	-3.60 ± 0.32	(0)	10.0 ± 2.2	0.58
THF + D_2O	8*	w	0.5132	1.71 ± 0.42	-3.94 ± 0.18	6.87 ± 0.56	-0.50 ± 0.10	(0)	0.56
THF + THF_d + D_2O	9	φ	0.5570	-5.52 ± 0.85	2.24 ± 0.19	-2.66 ± 0.31	(0)	9.85 ± 1.8	0.48
THF + THF_d + D_2O	10*	φ	0.5570	1.11 ± 0.34	-3.88 ± 0.22	6.98 ± 0.68	-0.47 ± 0.08	(0)	0.46
THF + THF_d + D_2O	11	w	0.4867	-4.17 ± 0.86	2.67 ± 0.18	-3.12 ± 0.35	(0)	7.93 ± 1.8	0.48
THF + THF_d + D_2O	12*	w	0.4871	1.32 ± 0.35	-3.95 ± 0.19	6.35 ± 0.52	-0.41 ± 0.08	(0)	0.46

second component is assumed to be associated with m molecules in each cluster [17].

Figure 2 shows the diameters for THF + D_2O for several values of m. Evidently, both, a symmetric coexistence curve centered around a critical composition of 0.5 and a minimized curvature of the diameter, cannot be achieved simultaneously. The value $m = 3.45$ provides the critical concentration 0.5, while $m = 2.6$ reduces the overall temperature change of the diameter down to the lowest value (1.5%). The most important fact, however, is the monotonic increase of the 2β contribution with m, observed for all mixtures. The ratio of the amplitude $A_{2\beta}$ of the "spurious" 2β term

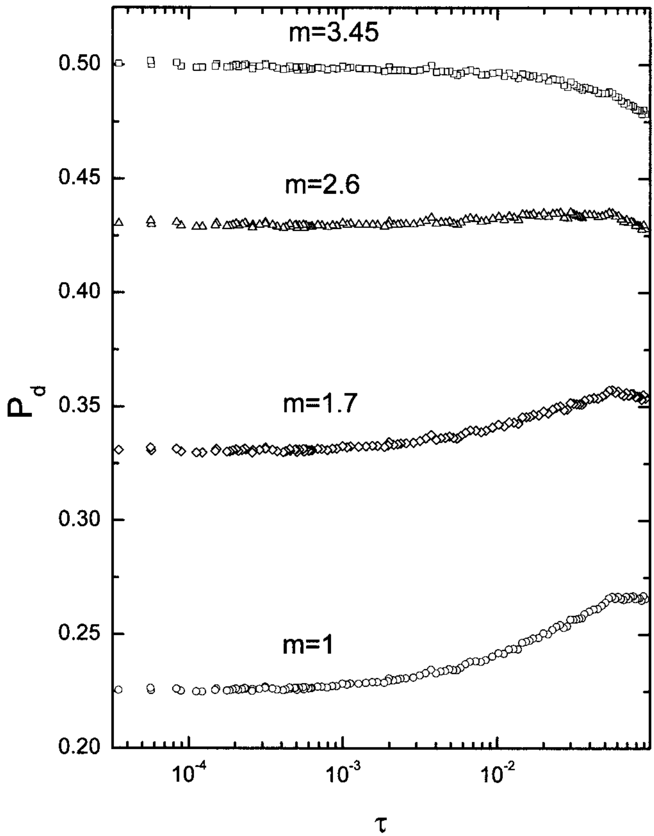

Fig. 2. Behavior of the diameter in THF + D_2O mixture as a function of temperature for several choices of the composition variable defined by Eq. (5): $m = 1$ (○), $m = 2.6$ (△), $m = 1.7$ (◇), $m = 3.45$ (□).

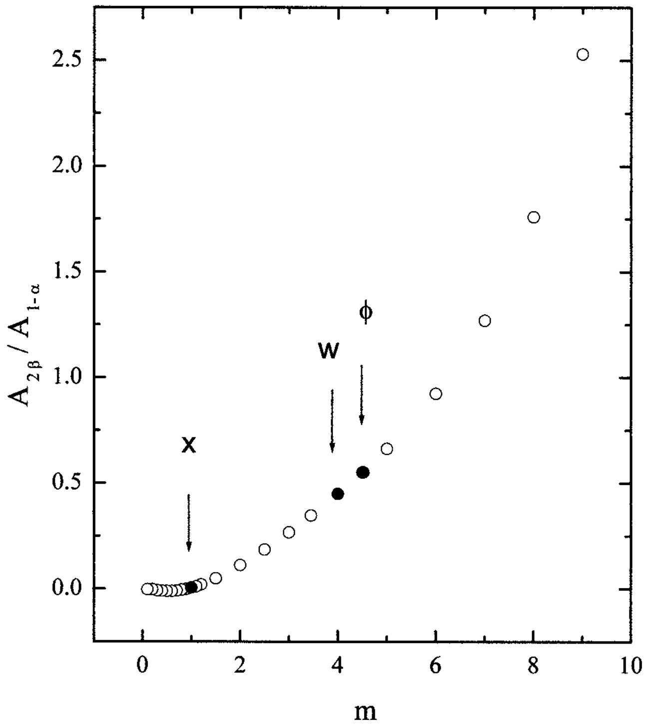

Fig. 3. Ratio of the amplitudes $A_{2\beta}/A_{1-\alpha}$ obtained from the fits of the diameter of THF + H_2O to Eq. (2) assuming $A_{2\Delta} = 0$ as a function of parameter m for a variety of choices of the composition variable defined by Eq. (5). The fits corresponded to mole, weight and volume fractions are indicated by arrows.

to the amplitude of the critical anomaly $A_{1-\alpha}$ for the various order parameters is shown in Fig. 3 for THF + H_2O. Below $m = 1.2$ the 2β contribution to the diameter is always negligible. Because the physical meaning of P is doubtful for $m < 1$, we conclude that the mole fraction X, corresponding to $m = 1$, is the preferable composition variable in the cases considered here.

In Ref. 9 we have shown that modified reduced temperatures τ', and especially, τ_{UL} and τ'_{UL}, that account for the presence of the UCT, are preferable for describing the shape of the coexistence curve over a wide temperature range. We obtained no noticeable difference when τ is replaced by τ' for all composition variables. Results of the fits to Eq. (1) using the reduced temperature τ_{UL} are given in Table III. Again, the 2β contribution is only negligible in the mole fraction scale. Satisfactory fits for w and φ are, however, obtained with only one correction term to scaling. Recalling

Table III. Parameters of the Fits to Eq. (1) of the Diameter in Terms of Different Composition Variables Using the Reduced Temperature τ_{UL}. (For the THF + D_2O Mixture the Fitting Data Set Was Reduced by Excluding 20 Points in Order to Get Similar Intervals in Terms of τ_{UL}: $\tau_{UL} < 0.007$ for all Mixtures.) The Uncertainties Denote 1 Standard Deviation

N	P	P_c	$A_{1-\alpha}$	A_Δ	$A_{2\Delta}$	$A_{2\beta}$	χ^2
				THF + H_2O			
1	X	0.2254	6.06 ± 0.09	−6.68 ± 0.11	(0)	(0)	0.78
1a	X	0.2256	4.86 ± 0.05	(0)	−68.2 ± 1.6	(0)	0.65
2	φ	0.5781	6.18 ± 0.98	−5.87 ± 0.17	(0)	−1.62 ± 0.18	0.55
3	w	0.5382	7.07 ± 0.99	−6.21 ± 0.18	(0)	−1.58 ± 0.18	0.56
				THF + D_2O			
4	X	0.2251	5.68 ± 0.10	−6.18 ± 0.14	(0)	(0)	0.69
5	φ	0.5873	4.10 ± 1.10	−6.18 ± 0.32	(0)	−1.36 ± 0.20	0.53
6	w	0.5131	5.01 ± 1.12	−6.15 ± 0.27	(0)	−1.15 ± 0.20	0.55
				THF + THF_d + D_2O			
7	X	0.2044	5.51 ± 0.07	−8.26 ± 0.07	(0)	(0)	0.55
8	φ	0.5573	4.40 ± 0.86	−7.71 ± 0.49	(0)	−1.40 ± 0.16	0.46
9	w	0.4870	5.61 ± 0.86	−7.73 ± 0.39	(0)	−1.24 ± 0.16	0.47

that two correction terms are necessary when the ordinary reduced temperature is used (see Table II), the reduced temperatures τ_{UL} and τ'_{UL} are preferable.

Figure 4 shows that the relative importance of the 2β contribution for the diameter in terms of volume fractions is indeed significantly reduced, if the reduced temperature τ_{UL} is used. Moreover, for τ_{UL} (see Table III) the amplitudes of the first corrections to scaling are independent of the composition variable, and the amplitude of the 2β contribution for w and φ is the same for each mixture. The amplitudes $A_{1-\alpha}$ for the leading singular term for w and φ coincide with the same amplitudes for X, if the uncertainty of fitting parameters are taken into account. The amplitudes A_Δ are more precisely obtained from the fits than the leading singularities, as seen from Tables II and III. A_Δ is found to be negative for all temperature and composition variables. The absolute value of the first corrections $|A_\Delta|$ do not depend on the composition variable, but on the choice of the reduced temperature. The amplitude A_Δ in the THF + THF_d + D_2O mixture is always more negative than in the THF + H_2O mixture. A similar trend is observed for the amplitude of the first Wegner correction for the order parameter [9].

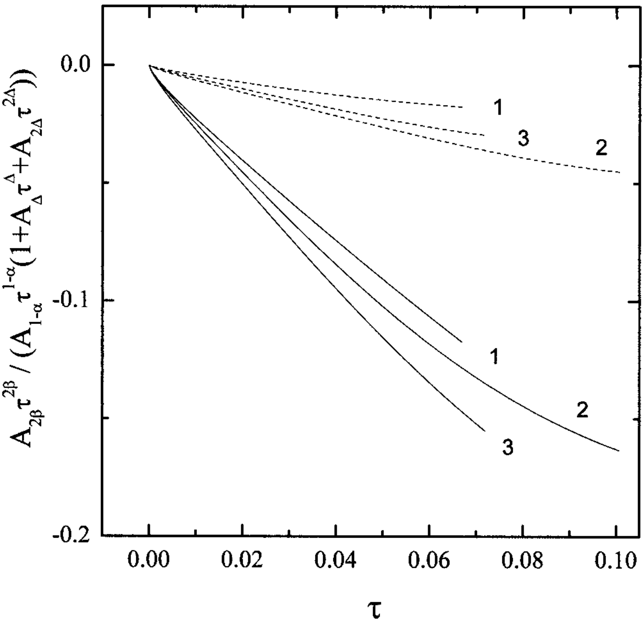

Fig. 4. Relative importance of 2β-contribution in the diameter in volume fraction as a function of reduced temperature τ for two definitions of the reduced temperature : $\tau = (T - T_c)/T_c$ (—) and $\tau_{UL} = \tau(T - T_U)/T_U$ (---). The amplitudes A_i are taken from fits 2 (Tables II and III) for $THF + H_2O$ (curves 1), fits 6 (Table II) and 5 (Table III) for $THF + D_2O$ (curves 2), and fits 10 (Table II) and 8 (Table III) for $THF + THF_d + D_2O$ (curves 3).

Summarizing the results at this stage, we observe that (i) for all mixtures the diameter in weight and volume fractions has a 2β contribution, while this contribution is negligible for the mole fraction. (ii) The linear contribution is insignificant for all concentration and temperature variables. (iii) The reduced temperatures τ_{UL} and τ'_{UL} are more appropriate than τ and τ', although the second critical point is comparatively far away.

Finally, we analyze briefly our experimental data by fits based on Eqs. (2) and (3). In both cases a 2β term is not required. For simplicity we consider here only results for the mole fraction representation. Equation (2) provides the best fits when the ordinary reduced temperature τ is used (cf. Table IV). Because the fitting parameters in Eq. (2) have no clear connections with the parameters in Eq. (1), we are not able to make any physical conclusion based on these fits.

In Eq. (3) the linear contribution to the diameter is represented by a superposition of the critical linear contribution $A_{1-\alpha}B_1\tau$ and the regular

Table IV. Results of the Fits to Eq. (2) of the Diameter in Terms of Mole Fraction using the Reduced Temperature τ. For the THF+D_2O Mixture the Fitting Data Set Was Reduced By Excluding 11 Points in Order to Get the Same Interval in Terms of τ: $\tau < 0.07$. The Uncertainties Denote 1 Standard Deviation.

Mixture	X_c	d_0	d_1	d_2	d_3	χ^2
THF+H_2O	0.2256	0.40 ± 0.27	-1.09 ± 0.44	0.197 ± 1.5	-3.43 ± 0.89	0.66
THF+D_2O	0.2251	0.13 ± 0.17	-0.255 ± 0.08	0.194 ± 5.7	-4.08 ± 3.4	0.78
THF+THF_d+D_2O	0.2045	0.13 ± 0.06	-0.488 ± 0.07	-0.95 ± 4.0	-4.00 ± 2.3	0.54

contribution $B_{reg}\tau$. The critical linear term in field theory is connected with the first correction to scaling and thus does not lead to a new free fitting parameter. The fits improve in the series τ, τ', τ_{UL}, and τ'_{UL} , i.e., τ'_{UL} provides the best fits shown in Table V. Significant contributions from the second correction to scaling are observed, because, owing to its interrelation to the critical linear term, the first correction is bound to positive values. In spite of more adjustable parameters than in Eq. (1), Eq. (3) is, however, unable to improve the fits, even if the regular noncritical contribution $B_{reg}\tau$ is included (c.f. Table V). This bound of the amplitudes in Eq. (3) results thus in the large uncertainties. However, no significant

Table V. Results of the Fits to Eqs. (1) and (3) of the Diameter in Terms of Mole Fraction Using the Reduced Temperature τ'_{UL}. (For the THF+D_2O Mixture the Fitting Data Set Was Reduced by Excluding 20 Points in Order to Get the Same Interval in Terms of τ'_{UL}: $\tau'_{UL} < 0.007$ for All Mixtures. The Uncertainties Denote 1 Standard Deviation)

N	Eq.	X_c	$A_{1-\alpha}$	A_Δ / A^*_Δ	$A_{2\Delta}$	B_{reg}	χ^2
				THF+H_2O			
1	(1)	0.2253	4.25 ± 0.09	(0)	-56.0 ± 1.4	–	0.67
2	(3)	0.2256	6.59 ± 0.17	4.98 ± 0.35	-60.6 ± 11	(0)	0.66
3	(3)	0.2255	10.3 ± 5.9	6.73 ± 0.35	-52.9 ± 11	-5.3 ± 8.5	0.66
				THF+D_2O			
4	(1)	0.2251	4.69 ± 0.08	-5.30 ± 0.14	(0)	–	0.68
5	(3)	0.2252	5.67 ± 6.3	0.69 ± 2.2	-29.4 ± 13	(0)	0.73
6	(3)	0.2249	9.39 ± 6.4	1.48 ± 0.89	-13.7 ± 18	-4.5 ± 5.9	0.71
				THF+THF_d+D_2O			
7	(1)	0.2045	4.39 ± 0.22	-4.98 ± 1.4	-27.5 ± 14	–	0.56
8	(3)	0.2255	5.43 ± 4.3	0.74 ± 1.6	-49.7 ± 1.3	(0)	0.57
9	(3)	0.2253	9.80 ± 5.2	3.27 ± 0.22	-34.3 ± 7.1	-5.1 ± 6.8	0.56

differences are observed between amplitudes $A_{1-\alpha}$ and B_{reg} in the three mixtures, while it is not so for the corrections to scaling. The largest value of A_Δ is found in THF + H_2O compare to deuterated mixtures.

3. CONCLUSIONS

All three isotopically related H_2O-THF mixtures show a critical $(1-\alpha)$ anomaly in the diameter which is independent of the choice of reduced temperature or composition variable. A significant 2β contribution is found for the weight and volume fractions, which masks the true critical anomaly, while the mole fraction is free of the 2β contribution. No linear terms were observed for all choices of concentration and reduced temperature. In agreement with previous results for the coexistence curves, reduced temperatures that account for the presence of both upper and lower critical solution points were found to be most appropriate for data reduction, although the second critical point is about 80 K away.

By analogy with the lattice-gas model, the density is a good, albeit not perfect, order parameter for one-component systems (a more appropriate choice is based on the linear combination $\rho - bs$, where s is the entropy, and b is a mixing coefficient, but from practical purposes such an analysis is usually not feasible). In contrast, it is usually stated that there is some ambiguity in the order parameter for mixtures, because, on thermodynamic or experimental grounds, many choices exist. If one accepts, however, the principle of isomorphism between one- and two-component systems, one expects that, among all variables of practical relevance, the volume fraction is the best choice [18]. The mole fraction X is expected to be suitable, when the molar volumes of the components are of similar size. In the present case, we found however the mole fraction to be most suitable, in clear contrast to these expectations.

Second, the correction amplitudes in the Wegner series are not independent, but related to A_Δ through $A_{2\Delta} \propto A_\Delta^2$, $A_{3\Delta} \propto A_\Delta^3$, etc. with $A_\Delta > 0$ as an important condition for a converging series [19]. In practice, it is however difficult to implement these restrictions in data evaluation, and Eq. (1) is usually treated as an expansion with freely adjustable coefficients. It is seen that such an expansion does not provide the expected regularities concerning the relative magnitudes of the correction terms and the sign of these terms. A negative value of A_Δ may reflect some additional non-asymptotic effects irrelevant to the Wegner expansion. This additional contribution might originate from fifth- and higher-order terms in the Landau–Ginzburg Hamiltonian [20] or from regular non-critical terms. The latest contribution is expected to be negative and dominates in the range $\tau > 10^{-2}$ [18]. Our analysis of the order parameter [9] and diameter indicates that this negative regular contribution could be significantly reduced by proper choice of the reduced temperature: τ_{UL} and τ'_{UL}. The results of fits to the restricted Eqs. (3) given in Table V show the values of the first Wegner correction, assuming that non-Wegner terms contribute to the amplitudes $A_{2\Delta}$ and B_{reg}. The largest value of A_{Δ} for the THF+H_2O mixture indicates the strongest trend to mean-field criticality compared to deuterated mixtures. This tendency is also present, at a reduced level, for other composition and temperature variables.

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