J. Chem. Eng. Data **2001,** *46,* 967−973

Fits of Scaling and UNIQUAC Equations to Liquid−Liquid Equilibrium (LLE) Phase Compositions of the Binary Amphiphile 2-Butoxyethanol (1) + Water (2) Measured by the Phase Volume Method

Ki Young Kim and Kyung-Hee Lim*

Department of Chemical Engineering, Chung-Ang University, Seoul 156-756, Korea

The liquid−liquid coexistence curve of the binary nonionic amphiphile 2-butoxyethanol (1) + water (2) was determined around the lower consolute solution temperature, T_c, by phase volume measurements. The phase volume method uses the linear relationship between the phase volume and the component concentration according to the lever rule. The method is much more convenient to use for low-pressure phase studies than other methods. Moreover, the results show that this method yields equilibrium compositions as accurate and precise as other methods. The coexistence curve of the binary system is fitted to (critical-)scaling equations. The scaling equations have a valid region that is limited near the critical point. This region is extended from $\Delta T = |T - T_c| = 8$ K to $\Delta T = 20$ K by defining a new order parameter and incorporating this parameter into the equations. These new equations yield excellent fits to the liquid−liquid equilibrium data of the binary system. When compared to UNIQUAC, the scaling equations with a new order parameter are slightly better than UNIQUAC. In addition, they give correct information on the critical points, which are usually predicted erroneously by UNIQUAC.

Introduction

Although the liquid−liquid equilibrium (LLE) for the binary system of 2-butoxyethanol (C_4E_1) + water was already reported in the literature,[1] measurements of the LLE data for this system were redone, but with the phase volume method. One of the objectives of this work was to compare liquid−liquid equilibria by the phase volume method to those by other methods. In the phase volume method samples are prepared along a tie line, and phase boundary points or equilibrium phase compositions are determined by a regression to the linear relationship between the phase volume and the component concentration according to the lever rule. The reason for employing this method in this work is that it has several advantages over other conventional methods. First, it is much more convenient to use for the study of low-pressure phase equilibria. A thermostat bath with viewing windows and graduated cylinders may be the major components of the apparatus. Second, it is noninvasive and nondestructive, because, unlike the analytical method, the phase volume method does not require either sampling or chemical analysis. Also, as opposed to the cloud point method, it is a true equilibrium method. Third, although the equilibrium phase compositions are obtained as the components' mass fractions from linear regressions of measured data, density measurements are not needed. Rather, either of the phase densities can be obtained from the slope of the regression; see eq 1 in the subsequent section. Fourth and most importantly, the accuracy and the precision of the results can be greatly improved by preparation of more samples inside the two-phase region and particularly samples near the phase boundary points.

The LLE phase compositions for this binary system were fitted by scaling equations, and the results are compared to those by UNIQUAC.

LLE data are often fitted by UNIQUAC, because it provides a satisfactory description for many typical mixtures and because it is relatively simple with its only two adjustable parameters. Its wide range of applicability is also one of the advantages. However, UNIQUAC cannot always represent high-quality data with high accuracy, because the number of adjustable parameters is only two. Furthermore, it cannot provide accurate information on the critical point.

In contrast to UNIQUAC, critical-scaling (or scaling) equations not only yield excellent fits to LLE data but also give accurate information on the critical point. Moreover, they are virtually the same for the fluid systems, except that only the coefficients (or amplitudes) of the terms can take different values from system to system. This is due to the universality of the scaling exponents.[2] However, the range of validity of the scaling equations is limited to the region close to the critical point. How close is close may be disputable, but in general, the scaling equations are valid for $\epsilon = |T - T_c|/T_c < O(10^{-2})$ with T_c being the critical temperature.[3] For the binary system of 2-(2-hexyloxyethoxy)ethanol (C_6E_2 in short) and water, where the amphiphile C_6E_2 is the second smallest in the homologue series of polyethylglycol ethers (denoted as C_iE_j) of which the smallest is 2-butoxyethanol (C_4E_1) studied in this article, the range of validity was where $\epsilon < 0.03$, which amounts to $\Delta T = |T - T_c| = 8$ K.

Usually for LLE studies, the temperature range was extended to ϵ values 10 times larger than that for which the scaling equations were normally valid. In this work, the range of validity of the scaling equations was extended to $\Delta T = 20$ K by defining a new order parameter similar

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* To whom correspondence should be addressed. E-mail: khlim@cau.ac.kr.

10.1021/je000306l CCC: $20.00

to the one previously used for the scaling equations of excess enthalpy and incorporating this order parameter into the scaling equations.[4] These new equations yielded excellent fits to the LLE data of the binary 2-butoxyethanol (C_4E_1) + water. The fitting results by these equations are no worse than those by UNIQUAC. Moreover, the scaling equations give accurate values for the critical temperature and critical composition of the system, which are usually predicted erroneously by UNIQUAC.

Experimental Section

Materials. The amphiphile 2-butoxyethanol, $C_4H_9(OCH_2CH_2)OH$, was from Aldrich. It is usually denoted as C_4E_1, where C_4 and E_1 indicate the number of carbons in the hydrophobic chain and the number of ethoxylate groups (OCH_2CH_2) in the hydrophilic part, respectively. The amphiphile had a stated purity of 99%, which was confirmed by gas chromatography. The amphiphile was used as received. The water was distilled and deionized.

Phase Volume Measurements. For determination of liquid–liquid equilibrium phase compositions, a series of binary mixtures of samples of various component mass fractions were weighed, put into 25-mL graduated cylinders, and placed in a microprocessor-controlled constant-temperature bath with viewing windows (Tamson Model 45, Neslab Instruments Inc., Newington, New Hampshire) for at least 1 day. The weighing balance and the temperature of the bath were regulated within ±0.5 mg and ±0.005 K, respectively. After phase separation was complete, the volumes of each phase were recorded through the viewing windows and volume fractions were calculated.

In the two-phase region the volume fraction of a phase is proportional to the amphiphile mass fraction according to the lever rule. The linear relationship between the amphiphile mass fraction, w, and the phase volume fraction, v, is expressed by

$$v = \left(\frac{w - w_-}{w_+ - w_-}\right)\frac{\bar{d}}{d_+} \tag{1}$$

or

$$1 - v = \left(\frac{w - w_+}{w_- - w_+}\right)\frac{\bar{d}}{d_-} \tag{2}$$

where w_- and w_+ are the amphiphile mass fractions of two equilibrium conjugate phases with phase densities d_- and d_+, respectively, and $\bar{d}$ is the overall average density of the two phases. Equations 1 and 2 are obtained from the total and component mass balances; details for the derivation of these equations may be found elsewhere.[5]

Equations 1 and 2 imply that the amphiphile concentrations at the phase volume fractions of zero and one correspond to those of the conjugate phase boundary points; w_- and w_+ are obtained at $v = 0$ and $v = 1$ from eq 1, as illustrated in Figure 1, and the other way around from eq 2. Hence, w_- and w_+ are determined by simply making a linear regression of v to w and extrapolating v to zero and one at each temperature. In this method, therefore, there is no need for knowing the phase densities d_- and d_+. Rather, these phase densities can be obtained from the slopes ($\bar{d}/d_+$ and $\bar{d}/d_-$) of the regressions, because $\bar{d}$ is recorded when samples are prepared.

The precision of the measurements of the phase volume fractions was 0.005, and the correlation coefficients of the linear regressions were better than 0.999. Since w_- and w_+ were determined from the regressions via eq 1, their final precisions were thought to be better than 0.005, and therefore w_- and w_+ were presented in three significant digits or a total of four digits.

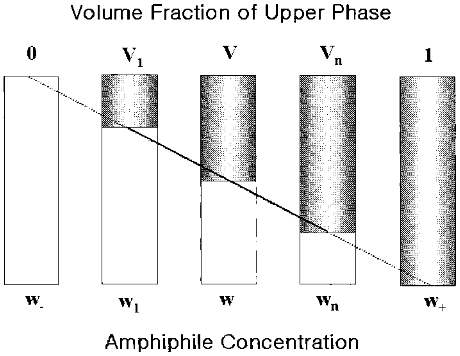

Figure 1. Schematic of relative amounts of equilibrium phase volumes v at different mass fractions w of the amphiphile 2-butoxyethanol (C_4E_1) in the two-phase region. The linear relationship between v and w is observed according to the lever rule. The quantities w_- and w_+ are the phase boundary points between the single- and two-phase regions.

Equations for the Fits to LLE Data

UNIQUAC Equations. For the equilibria between two liquid phases I and II, the following condition should be satisfied:

$$w_i^{\mathrm{I}}\,\gamma_i^{\mathrm{I}} = w_i^{\mathrm{II}}\,\gamma_i^{\mathrm{II}} \tag{3}$$

To obtain the equilibrium compositions w_i^{I} and w_i^{II}, the activity coefficients γ_i at each phase should be calculated. These calculations were done by using the UNIQUAC (universal quasi-chemical) model, which was developed by Abrams and Prausnitz (1975)[6] on the basis of statistical mechanical theory. This model yields γ_i as

$$\ln \gamma_k = \ln \gamma_k^{\mathrm{comb}} + \ln \gamma_k^{\mathrm{res}} \tag{4}$$

where γ_k^{comb} and γ_k^{res} are the combinatorial and residual contributions, respectively, to the activity coefficients, which are given by

$$\ln \gamma_k^{\mathrm{comb}} = \ln \frac{\Phi_k}{x_k} + 1 - \frac{\Phi_k}{x_k} - 5q_k\left[\ln \frac{\Phi_k}{\theta_k} + 1 - \frac{\Phi_k}{\theta_k}\right] \tag{5}$$

$$\ln \gamma_k^{\mathrm{res}} = q_k\left[1 - \ln\left(\sum_i \theta_i \tau_{ik}\right) - \sum_j \frac{\theta_j \tau_{kj}}{\sum_i \theta_i \tau_{ij}}\right] \tag{6}$$

Here x_i, Φ_i, and θ_i are the mole fraction, molecular volume fraction, and surface fraction of component i, respectively. Φ_i and θ_i are calculated from the molecular size parameter r_j and the shape parameter q_j, of which values may be found from various sources.[7] The quantity τ_{ij} is the energy parameter and related to the binary interaction parameter a_{ij} by the equation

$$\tau_{ij} = \exp(-a_{ij}/T) \tag{7}$$

With γ_i described by eqs 3–5 and the material balances ($\sum w_i^{\mathrm{I}} = 1$ and $\sum w_i^{\mathrm{II}} = 1$) the equilibrium compositions w_i^{I} and w_i^{II} can be obtained from eq 5. When UNIQUAC is applied to a binary LLE, the number of the fitting parameters is two and they are τ_{12} and τ_{21} (or a_{12} and a_{21}).[8]

Critical-Scaling (or Scaling) Equations. According to renormalization group theory, the phase boundary points w_- and w_+ should behave as

$$w_\pm = w_c \pm B\epsilon^\beta \pm C\epsilon^{\beta+\Delta} + D\epsilon^{1-\alpha} \qquad (8)$$

where w_c is the critical concentration, B, C, and D are parameters (or amplitudes) that depend on the chemical system, and β, α, and Δ are universal scaling exponents whose values are 0.324,[9−14] 0.112,[11−14] and 0.5,[9,10,14] respectively. The quantity ϵ is the reduced temperature, defined as $\epsilon \equiv |T - T_c|/T_c$.

From eq 8 one obtains

$$w_+ - w_- = 2B\epsilon^\beta + 2C\epsilon^{\beta+\Delta} \qquad (9)$$

$$\frac{w_+ + w_-}{2} \equiv w_{avg} = w_c + D\epsilon^{1-\alpha} \qquad (10)$$

On the right-hand side of eq 9 the first term predominates in the vicinity of the critical point, while the second term is more significant away from the critical point because of the larger exponent value ($\beta + \Delta = 0.824$ versus $\beta = 0.324$). Hence, on the right-hand side of eq 9, only the first term was retained for the fit. Without the second term on the right-hand side, eq 9 is rewritten as

$$(w_+ - w_-)^{1/\beta} = B'|T - T_c| \qquad (11)$$

where $B' = (2B)^{1/\beta}/T_c$.

In the terminology of critical phenomena, the chemical potential approximates the ordering field, and a fractional concentration such as the mole fraction approximates the order parameter. This critical behavior is basically symmetric in the order parameter. However, liquid−liquid equilibria in real fluids usually display asymmetries in the common fractional concentrations, and these asymmetries limit the applicability of eqs 7−9 to the region close to the critical point. Hence a successful incorporation of the asymmetries, which real fluids exhibit, into the scaling theory will make the theory accurate for liquid−liquid equilibria at considerable distances from the critical point. One of the ways to incorporate the asymmetries is to define a new order parameter OP. Then, the new order parameter OP should have the temperature dependence like eq 8, that is,[2,4]

$$\mathrm{OP}_\pm = \mathrm{OP}_c \pm \tilde{B}\epsilon^\beta \pm \tilde{C}\epsilon^{\beta+\Delta} + \tilde{D}\epsilon^{1-\alpha} \qquad (12)$$

where OP_c is the OP value at the critical point.

It is still a matter of some controversy whether the mass fraction or the mole fraction or the volume fraction is the correct order parameter for binary mixtures.[15] However, the literature seems to support a fractional concentration as the likely order parameter. Furthermore, a fractional order parameter is also consistent with a fractional activity being the ordering field, which has also been used in the literature.[4,16]

Consider the transformation from, for example, mass fraction w to volume fraction v:

$$v = \frac{V_1}{V_1 + V_2} = \frac{w_1/d_1}{w_1/d_1 + w_2/d_2} = \frac{fw}{1 + (f-1)w} \qquad (13)$$

where $f = d_2/d_1$ with d_i and V_i being the density and volume of species i, respectively. Because the a priori preference for one type of fractional order parameter over another is not justified at present, it is appealing to work with a fractional order parameter where the transformation factor f is a fitting parameter. Fractional densities similar to this are used in the Flory−Huggins theory of polymer solutions and have been used in critical scaling fits to liquid−liquid equilibria in polymer solutions.[17−20] For these reasons a new order parameter is chosen to have the form

$$\mathrm{OP}_\pm = \frac{fw_\pm}{1 + (f-1)w_\pm} \qquad (14)$$

where f is a fitting parameter to make the best fit of the data to the inherently symmetric critical scaling equations.

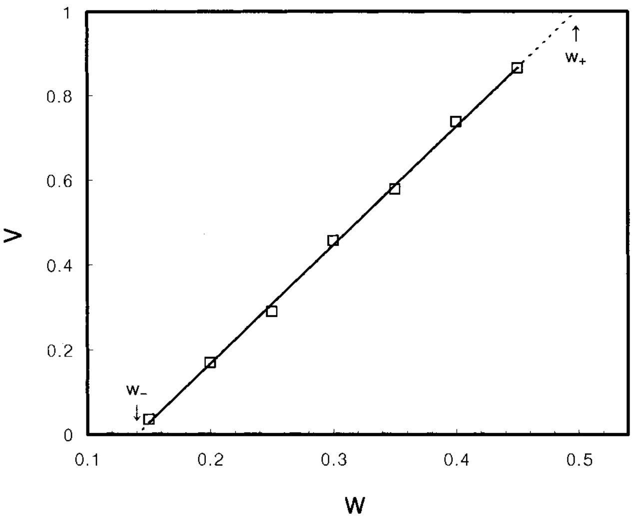

Figure 2. Volume fraction of the upper phase versus mass fraction of C_4E_1 in the 2-butoxyethanol (C_4E_1)/water system at 327.14 K.

Results and Discussion

Liquid−Liquid Coexistence Curve. The liquid−liquid coexistence curve for the binary C_4E_1 + water was determined by phase volume measurements at 15 temperatures from 323.18 K to 342.94 K. At each temperature, volume fractions of the upper phase (amphiphilic phase) were measured at several C_4E_1 concentrations. Figure 2 shows a typical example of upper phase volume fraction, v, versus C_4E_1 mass fraction, w. The linear relationship between these quantities is a replica of the trend of the gray portions at different w's in Figure 1. The correlation is excellent; the correlation coefficient is 0.9993. The phase boundary points w_- and w_+, where the volume fractions v are zero and one, respectively, are found from the plot. The points w_- and w_+ thus determined are tabulated in Table 1 and also plotted in Figure 3 along with data from the literature. The phase boundary points on the aqueous side are in excellent agreement with one another, irrespective of the methods employed. On the amphiphilic side, however, there exist substantive differences among the different methods.

The coexistence curve is more symmetric in mass (or volume) fraction than in mole fraction. Since enhanced symmetry provides more accurate fitting results,[4,21] the equilibrium compositions are expressed in terms of mass fractions of the components, as represented in Figure 2. Poorer symmetry in mole fraction is due to the large disparity between the components' molecular weights (118.18 vs 18.016).

Table 2 shows the overall densities, d, from the masses and the volumes of the liquids inside the glass cylinders in the thermostat. Estimated changes in $\bar{d}/d_-$ and $\bar{d}/d_+$ inside the two-phase region were in the range 0.985 and

Table 1. Liquid−Liquid Phase Boundary Points for the 2-Butoxyethanol/Water System[a]

T/K (t/°C)	w_- (aqueous)	w_+ (amphiphilic)
323.18 (50.03)	0.1826	0.4211
324.19 (51.04)	0.1667	0.4484
324.92 (51.77)	0.1529	0.4694
326.12 (52.97)	0.1469	0.4752
327.14 (53.99)	0.1400	0.5977
328.07 (54.92)	0.1360	0.5140
329.17 (56.02)	0.1340	0.5155
330.13 (56.98)	0.1236	0.5452
331.14 (57.99)	0.1176	0.5525
333.10 (59.95)	0.1188	0.5533
325.17 (62.02)	0.1152	0.5630
337.01 (63.86)	0.1086	0.5834
338.99 (65.84)	0.1094	0.5896
341.00 (67.85)	0.1048	0.5958
342.94 (69.79)	0.1071	0.6121

[a] The quantities w_- and w_+ are the mass fractions of the amphiphile 2-butoxyethanol for the aqueous and amphiphilic phases, respectively.

1.014. As mentioned previously, the phase densities d_- and d_+ can be determined from the slopes of the regressions to eqs 1 and 2. The phase densities from the phase volume method and densitometry will be compared, and the results will be reported in a separate article.

Fit by UNIQUAC Equations. The molecular size parameter r and the shape parameter q were found for the two components r_{water} and q_{water} for water from the list and $r_{C_4E_1} = 5.517$ and $q_{C_4E_1} = 4.988$ calculated for 2-butoxyethanol. Using these r_j and q_j values, molecular volume fraction Φ_j and the surface fraction θ_j were obtained and then γ_i was obtained from eqs 3 to 5. Then the binary interaction parameters a_{12} and a_{21} were determined at each temperature by solving eq 3 with the measured w_- and w_+. Figure 4 shows the temperature dependence of a_{12} and a_{21} thus determined. The parameter a_{12} increases with temperature but remains negative over the temperature range examined. On the other hand, a_{21} decreases with temperature and remains positive. Over the temperature range examined, the extent of change in a_{12} and a_{21} is almost identical; it is around 80 in absolute value.

The binary interaction parameter a_{ij} is then fitted to the third order polynomial of temperature, as was done previously:[22]

$$a_{ij} = b_0 + b_1T + b_2T^2 + b_3T^3 \tag{15}$$

Here the coefficients b_k for a_{12} and a_{21} are found as shown in Table 3.

With the a_{12} and a_{21} described by eq 15, the phase boundary points w_- and w_+ at a temperature of interest were calculated from eq 3. Figure 5 shows the results of the fit by UNIQUAC. It shows that the values calculated by UNIQUAC follow very closely the measured data; the sum of squares for the 30 data points is 6.5525×10^{-3}.

Fit by Scaling Equations. The values of T_c and w_c are first determined from eqs 9 and 10 and the LLE data of Table 1. A linear regression of $(w_+ - w_-)^{1/\beta}$ to T yields T_c from the x-axis intercept of the fit (eq 11). Figure 6 shows a $(w_+ - w_-)^{1/\beta}$ versus T plot. Close to the lower critical solution temperature T_c, the data increase linearly with temperature up to 331.15 K, above which the increase in rate is reduced. Hence, the first nine data points are used for the regression to determine T_c; T_c is found to be 321.7 ± 0.3 K with the correlation coefficient of 0.9875.

Equation 11 is valid only close to the critical point. Since how close is close is arguable, this issue may be examined in two ways. One is to make linear fits to eq 11 but by adding datum by datum, and the other is to make nonlinear fits to eq 9. For linear fits with more data included, larger fitting errors were obtained; with the first 10 points, the root-mean-square error (0.06) of the fit increased by 50%, and with the first 11 points, it (0.08) increased by 100%, compared to that (0.04) with the first 9 points. This trend continued, and with the first 15 points the error (0.11) was three times larger. For nonlinear fits to eq 9, the T_c value obtained was almost the same as that from the linear regression with the first 9 points but the fitting error was 10% larger. When more data points were included for the fits, a trend similar to that with the linear fits was observed. All these results may imply that an accurate T_c can be obtained with the linear fits to eq 11.

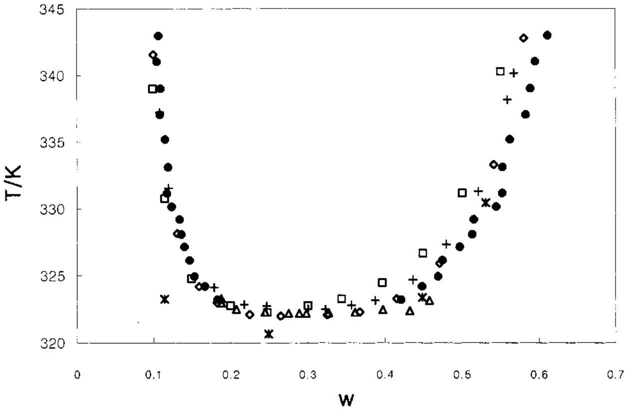

Figure 3. Phase boundary points for the binary 2-butoxyethanol (C_4E_1) and water: ◇, Ellis (1967);[28] □, Cox and Cretcher (1926);[32] △, Elizalde et al. (1988);[29] +, Ito et al. (1983);[34] ∗, Poppe (1935);[24] ●, this study.

After T_c is determined, ϵ is calculated, and the linear regression of w_{avg} to $\epsilon^{1-\alpha}$ is done to determine w_c. Similar behavior is observed for this plot, that is, eq 10 is valid for the first 9 data points. This may point to the fact that the critical scaling equations are valid for ϵ up to 0.0294 for this binary system when the mass fraction is used as the order parameter. From the regression, $w_c = 0.294 \pm 0.002$ is obtained. These values of T_c and w_c are comparable to those determined by a different method as presented in Table 4.

As seen in Figure 6, the validity of the critical scaling equations is restricted to the region of $\epsilon \le 0.0294$. Hence, to extend their region of validity, the order parameter defined by eq 14 is used in place of mass fraction and eq 12 is used for the fit of the phase boundary points. The fitting results are presented in Figure 4. The figure reveals that the curve representing the values calculated by eq 12 is in excellent agreement with the measured LLE data; for these fits $f = 1.6312$, $\tilde{B} = 0.859\,81$, $\tilde{C} = 0.720\,50$, $\tilde{D} = 0.400\,53$, and the sum of squares is 8.1490×10^{-4}.

The fits give residuals with no systematic pattern as shown in Figure 7. This may indicate that there are few systematic errors in the measurements of phase compositions and in the fits of eq 15 to the compositions.

The sums of squares for the fits by UNIQUAC and the scaling equations are 6.5525×10^{-3} and 8.1490×10^{-4}, respectively. Comparison of the sums of squares by UNIQUAC and by the scaling equations tells that the scaling equations give better fits to the data. However, the larger sum of squares for the fit by UNIQUAC is mainly due to large error at the critical point, which is one of the problems UNIQUAC has inherently. Except at the critical point, the fits by UNIQUAC are as good as those by the

Table 2. Overall Densities (d/g·cm^{-3}) at Different Volume Fractions (v) and Temperatures

324.92 K		326.12 K		330.13 K		333.10 K		325.17 K		337.01 K		338.99 K		341.00 K		342.94 K	
v	*d*	*v*	*d*	*v*	*d*	*v*	*d*	*v*	*d*	*v*	*d*	*v*	*d*	*v*	*d*	*v*	*d*
0.118	0.971	0.167	0.971	0.175	0.962	0.051	0.967	0.066	0.962	0.073	0.967	0.068	0.967	0.078	0.962	0.082	0.957
0.282	0.961	0.286	0.965	0.295	0.956	0.165	0.962	0.170	0.962	0.179	0.957	0.179	0.957	0.183	0.953	0.183	0.953
0.378	0.965	0.371	0.960	0.381	0.960	0.302	0.947	0.295	0.956	0.307	0.947	0.295	0.956	0.305	0.943	0.290	0.956
0.442	0.959	0.442	0.959	0.435	0.955	0.377	0.951	0.377	0.951	0.373	0.951	0.368	0.951	0.371	0.947	0.366	0.947
0.528	0.952	0.519	0.952	0.491	0.952	0.425	0.941	0.419	0.946	0.415	0.941	0.412	0.946	0.408	0.937	0.406	0.941
0.754	0.953	0.747	0.949	0.686	0.949	0.479	0.947	0.474	0.947	0.472	0.943	0.467	0.943	0.458	0.943	0.458	0.943
0.896	0.944	0.868	0.944	0.804	0.935	0.652	0.944	0.643	0.944	0.636	0.940	0.628	0.940	0.621	0.936	0.612	0.936
						0.759	0.926	0.748	0.935	0.742	0.922	0.728	0.939	0.719	0.922	0.708	0.926
						0.867	0.918	0.848	0.931	0.832	0.918	0.820	0.931				

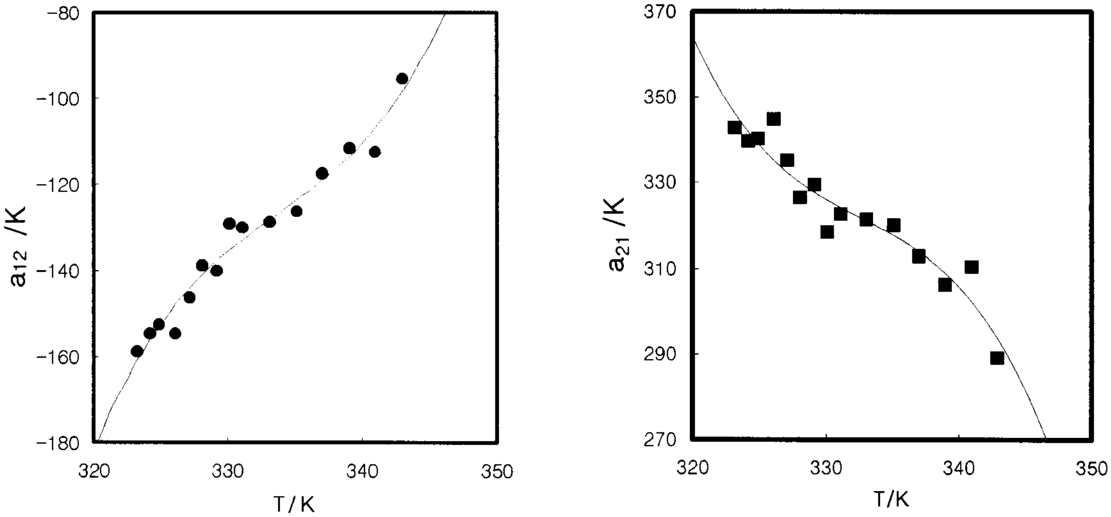

Figure 4. UNIQUAC parameters a_{12} and a_{21} as a function of temperature.

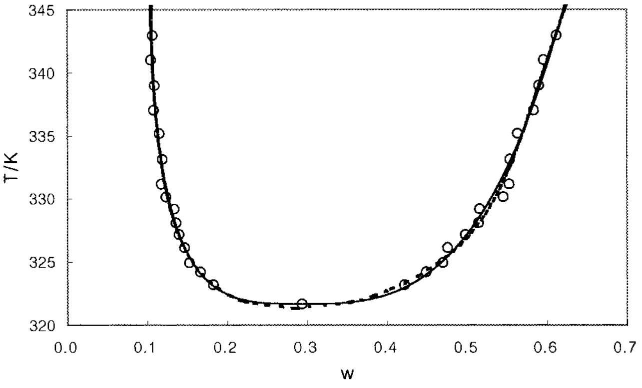

Figure 5. Liquid−liquid coexistence curve for the binary 2-butoxyethanol and water, and the fits by the critical-scaling equations with a new order parameter (solid line) and by UNIQUAC (broken line).

Table 3. UNIQUAC Parameters a_{12} and a_{21} for the Binary 2-Butoxyethanol + Water System ($a_{ij} + b_0 + b_1T + b_2T^2 + b_3T^3$)

	b_0	b_1	b_2	b_3
a_{12}/K	-3.6405×10^5	3.2684×10^3	-9.7910	9.7834×10^3
a_{21}/K	4.1101×10^5	-3.7003×10^3	11.118	-1.1139×10^2

critical scaling equations, which is manifested by the residuals shown in Figure 7. In fact, better fits by UNIQUAC can be made, for example, using higher-order polynomials of temperature for a_{ij} as in eq 15. Although this can be achieved, it may be insignificant. UNIQUAC still can predict the critical point incorrectly. It is because eq 15 is not theory-based,

Compared to UNIQUAC, the scaling equations yield the correct critical point, and although their use is limited to the region close to the critical point, they fit excellently the LLE data. Farther away from the critical point the scaling equations with a new order parameter were used. The new order parameter worked well for the liquid−liquid coexistence curve for the binary system examined in this work. This order parameter is reminiscent of volume of site fraction in the Flory−Huggins model for polymer solu-

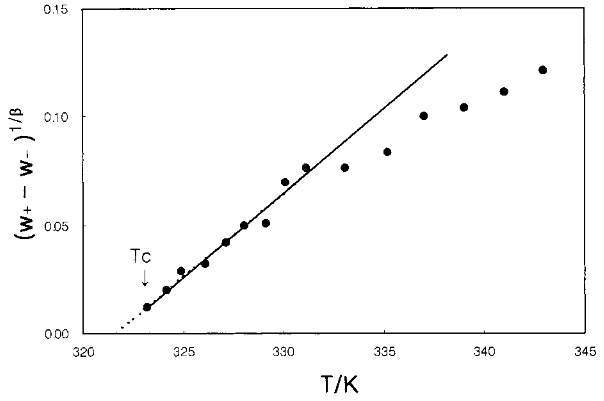

Figure 6. Plot of $(w_+ - w_-)^{1/\beta}$ versus temperature, T.

Table 4. Lower Critical Solution Temperature (T_c) and the C_4E_1 Mole Fraction (x_c) at T_c for the Binary Amphiphile 2-Butoxyethanol (C_4E_1) and Water

t_c/°C	x_c	ref	t_c/°C	x_c	ref
44.5	0.053	23	49.0	0.058	29
47.5	0.048	24	49.0	0.059	30
48.0	0.048	25	49.0	0.059	31
48.2	0.061	26	49.1	0.048	32
48.3	0.052	1	49.2		33
48.5	0.059 (w_c = 0.294)	this study	49.4	0.07	34
48.7	0.059	27	49.8	0.051	35
48.8	0.054	28			

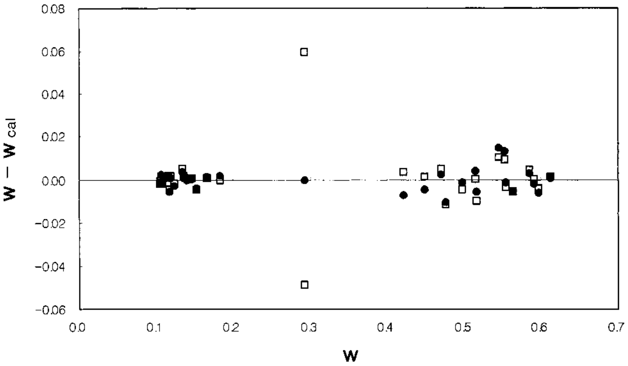

Figure 7. Residuals, $w_{+} - w_{\mathrm{cal}}$, of the fits versus C_4E_1 mass concentration: □, UNIQUAC; ●, critical-scaling equations.

tions,[36] and order parameters similar to OP defined in eq 14 are found in various mixtures.[4,16−20,37] In the new order parameter OP, the value of the factor f should be well examined. If f were around 1.13, which is the density ratio d_2/d_1 (=0.9858/0.8744, for example, at 328.15 K), OP would be the volume fraction v, as represented by eq 16. However, f for the best fit is 1.6338 and is 80% larger than d_2/d_1. This indicates that scaling equations with a simple fractional concentration (volume-, mass-, or mole-fraction) as the order parameter may be inadequate to describe liquid−liquid coexistence curves correctly and that f may be represented by quantities other than component densities. In fact, f may be equal to the ratio of the activity coefficients of the two components for binary systems.[4] Hence, the near-constancy of f over a wide range of temperature and compositions implies a kind of very extended "Henry's law" behavior for the highly polar 2-butoxyethanol/water system.

Conclusions

The liquid−liquid coexistence curve of the binary nonionic amphiphile 2-butoxyethanol (1) + water (2) was determined around the lower consolute solution temperature, T_c, by phase volume measurements, and the fits of data to UNIQUAC and scaling equations were made and compared.

The phase boundary points determined by the phase volume method are in excellent agreement on the aqueous side with literature values determined by other methods. On the amphiphilic side this method also, like other methods, yields the phase boundary points which agree less well with literature values. These results imply that the phase volume method is as effective as other methods for the determination of liquid−liquid equilibrium (LLE) phase compositions. Taking account for its advantages over other methods, such as its being convenient to use, noninvasive and nondestructive, capable of determining phase densities, and capable of improving greatly the accuracy and the precision by preparation of more samples inside the two-phase region and particularly samples near the phase boundary points, the phase volume method may be one of the powerful methods for low-pressure phase studies.

The LLE phase compositions were fitted to UNIQUAC and scaling equations with a new order parameter. These equations followed very closely the measured data over the experimental temperature range of 20 K, and the scaling equation gave slightly better fits than UNIQUAC. The incorporation of the new order parameter into the scaling equations made the range of validity of the scaling equations extended from 8 K to 20 K. Although the scaling equations have more fitting parameters than UNIQUAC (5 vs 2), they may be considered as being more useful, because they are based on the rigorous theory and more importantly they yield also the correct critical point through a linear regression to eq 11.

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Received for review September 13, 2000. Accepted April 30, 2001.

JE000306L