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Critical Behavior of a Microemulsion with an Ionic Liquid

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The critical concentrations and the critical temperatures for the microemulsion systems of {water + 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) + sodium di(2-ethyl-1-hexyl)sulfosuccinate (AOT) + decane} with various compositions of [bmim][BF_4] have been measured. The coexistence curves for the quaternary microemulsion with the molar ratio of water to AOT being 40.8 and the mass fraction of [bmim][BF_4] being $1.1 \cdot 10^{-4}$ have been determined by measuring the refractive index at constant pressure in the critical region. The critical exponent β has been deduced from the coexistence curves. The value of β is very close to the 3D-Ising exponent in the critical region. It was found that the addition of [bmim][BF_4] significantly reduced the lower critical temperature, which was contrary to the {water + KCl + AOT + decane} system, while the critical composition was almost kept unchanged. It may be attributed to the unique role of the ionic liquid which is capable of modifying the physicochemical properties of microemulsions.

Introduction

The universality class of criticality of complex fluids such as polymers, amphiphiles, and electrolyte solutions has been actively investigated by experimentalists and theorists for the past few decades. The criticality in these systems has been found to be affected by nonuniversal features such as the details of intermolecular interactions.[1] There are some controversies about whether microemulsion systems and micelle solutions near the critical points belong to the 3D-Ising universality class.[2] It has been pointed out by Fisher that the critical exponents of a binary solution become renormalized when a third component as an impurity is added into it, and the coexistence curve should be characterized by an exponent $\beta^* = \beta/(1 - \alpha) = 0.367$ with $\alpha = 0.11$ and $\beta = 0.3265$.[3] Most of the experiments involved measurements of critical exponents ν, γ, and α, which characterize the divergence of the correlation length and osmotic compressibility and the specific heat at constant pressure and critical concentration.[4] A few experimental studies have been carried out to determine the critical exponent β, which characterizes the shape of the coexistence curve, but the results were not precise enough to support unambiguously the Ising value or the Fisher renormalization value.[5,6]

Three-component mixtures of water, sodium di(2-ethyl-1-hexyl)sulfosuccinate (AOT), and *n*-alkane can form water-in-oil microemulsions of well-defined droplet size determined by fixing the molar ratio ω of water to AOT.[7,8] For these mixtures, the lower critical points were observed. Above the lower critical temperatures T_c, the mixtures separated into two microemulsion phases of different compositions of the droplet but with the same ratio ω.[2,8] Therefore, such a microemulsion system can be regarded as a pseudobinary mixture.[2] The recent researches have shown that the ternary microemulsion system of {AOT + water + alkane} and the quaternary microemulsion system of {water + KCl + AOT + decane} can be regarded as the pseudobinary mixtures with one component being the (AOT + water) or (AOT + water + KCl) droplet (or known as the water pool) and the other being the alkane at certain conditions, and their critical behaviors belong to the 3D-Ising class in a region sufficiently close to the critical temperature.[2,9–11] With an assumption of the droplet in microemulsion being a pseudocomponent and the two coexisting phases having different concentrations of the same droplets, a coexistence curve of temperature against a density variable of the droplet, such as the mole fraction or volume fraction, can be drawn in the same way as done for a real binary solution.[2,11]

It is well-known that addition of an inorganic salt to a microemulsion or a micelle system can modify the size, the shape of the droplets, and the interaction between the droplets, thus modifying the phase behavior of the system.[9] Our previous study showed that the addition of KCl significantly reduced the region of validity of simple scaling and remarkably increased critical temperature.[9] Room-temperature ionic liquids (RTILs) are attracting much interest in many fields of chemistry and industry due to their unique physical and chemical properties.[12,13] The critical behaviors of the binary solutions with one component being the RTIL have been studied recently.[14,15] To the best of our knowledge, the critical phenomena of pseudobinary microemulsion systems containing an ionic liquid (IL) have not yet been reported. It is the aim of this paper to study the critical behaviors of coexistence curves of quaternary microemulsions consisting of water, [bmim][BF_4], AOT, and decane, to investigate whether these four component microemulsions can be regarded as pseudobinary mixtures at certain conditions, and to examine the effects of IL on the critical behaviors of the microemulsions.

Experimental Section

Materials and Sample Preparations. AOT was obtained from Fluka, and decane and [bmim][BF_4] were supplied from Merck.

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The three chemicals with not less than 99 % mass fraction of the purities were used without further treatments. The water was twice distilled from deionized water in our laboratory.

Aqueous solutions with required various concentrations of [bmim][BF_4] were prepared by weighing proper amounts of [bmim][BF4] and deionized water. The resulting aqueous solution, AOT, and decane were then used to prepare the {water (1) + [bmim][BF_4] (2) + AOT (3) + decane (4)} microemulsions. The amount of each of the components was obtained by careful weighing. Taking the assumption that the volume of the droplet is the sum of volumes of water and AOT (neglecting the contribution of [bmim][BF_4] to the volume of the droplets and the excess volume), the volume fractions (Φ) of the droplet for the pseudobinary mixtures were calculated by the masses and the densities of water, AOT, and decane.

Determination of Critical Composition and Critical Temperature. The experimental principle has been described in the previous works.[16–18] The critical volume fraction Φ_c was approached by fixing the molar ratio ω of water to AOT at 40.8 and adjusting the amount of decane to achieve equal volumes of the two phases near the critical temperature.[2] A sample with the critical composition was prepared in a rectangular fluorometer cell with a Teflon plug. The phase-separation temperature of the sample was then carefully measured and taken as the critical temperature T_c. It was observed that samples nominally of the same composition had different values of the critical temperature, and the difference was as much as 1 K, which probably resulted from the uncontrollable hydrolysis of AOT. However, it did not affect the final results because only one sample was used throughout the measurements of the whole coexistence curve, and only the temperature difference ($T - T_c$), where T represent the experimental temperature, was important in data reductions to obtain the critical parameters.

Measurements of Refractive Indices. Refractive indices n of each coexistence phase for the sample with the critical composition were measured at constant pressure and various temperatures by using the standard method of "minimum of deviation". The apparatus used in this work was described previously.[18] During refractive index measurements, the temperature was constant to $\pm\ 1\cdot10^{-3}$ K. The uncertainty of measurements was about $\pm\ 1\cdot10^{-2}$ K for temperature and $\pm\ 1\cdot10^{-4}$ for the refractive index. Continuous downward-slow shifts of the phase-separation temperature near the critical point were observed. The rate of shifts was determined to be about 0.001 $K\cdot h^{-1}$ by repeating measurements of the critical temperature. The reason for such a shift is not clearly understood, and it may be due to the slow hydrolysis of AOT. A correction was made to each observed temperature by subtraction of the shift value. Several measurements with these corrections in both heating and cooling modes were consistent within experimental uncertainties. This is evidence that the shift of the critical temperature does not affect the shape of the coexistence curve. The uncertainty in measurement of temperature difference ($T - T_c$) was about $\pm\ 3\cdot10^{-3}$ K.

Results and Discussion

As it was expected, the lower critical points were observed for these microemulsion systems. The critical volume fractions Φ_c of the droplet and the critical temperatures T_c for {Φ(water + [bmim][BF_4] + AOT) + (1 − Φ)decane} microemulsion systems with a fixed molar ratio of water to AOT being 40.8 and various mass fractions of [bmim][BF_4] (w_2) in the microemulsion system were determined, and the results were listed in Table 1. As shown in Table 1 and Figure 1, the critical volume fraction Φ_c almost keeps constant, while the critical temperature increases significantly with IL concentration.

Table 1. Critical Volume Fractions Φ_c and the Critical Temperature T_c of {Φ(Water (1) + [bmim][BF_4] (2) + AOT (3)) + (1 − Φ)Decane (4)} Microemulsion Systems for Various Concentrations of the Ionic Liquid [bmim][BF_4]

mass fraction of [bmim][BF_4]	Φ_c	T_c/K
$1.1\cdot10^{-4}$	0.095 ± 0.001	298.687 ± 0.003
$2.1\cdot10^{-4}$	0.095 ± 0.001	299.960 ± 0.003
$4.6\cdot10^{-4}$	0.096 ± 0.001	303.982 ± 0.003

Interestingly enough, for the microemulsion system of {water (1) + [bmim][BF_4] (2) + AOT (3) + decane (4)}, the critical temperature of 298.7 K is significantly lower than the values of (310.8 and 323.5) K of ternary microemulsions of {water + AOT + decane}[2] and of {water + KCl + AOT + decane},[9] respectively. Contrary to the KCl, addition of [bmim][BF_4] to the {water + AOT + decane} system drastically decreases the lower critical temperature, which indicates the increase of the interaction between the droplets or decrease of the interaction between the droplets and the chain oil molecules. It might be attributed to the complexation between the cation of [bmim][BF_4] ($bmim^+$) and the anionic surfactant headgroup possibly formed, and the ionic liquid [bmim][BF_4] possibly behaved as a cosurfactant.[19] This unique role of the ionic liquid can be used to modify the physicochemical properties of microemulsions.

The refractive indices n of coexisting phases of the microemulsion with w_2 being $1.1\cdot10^{-4}$ and ω being 40.8 were measured at wavelength $\lambda = 632.8$ nm and various temperatures. The results are listed in columns 2 and 3 of Table 2, and the coexistence curve of T against n, denoted by (T, n), is shown in Figure 2a. In Table 2, the subscripts 1 and 2 represent the upper phase and lower phase, respectively.

To obtain the coexistence curve of temperature against volume fraction denoted by (T, Φ), a series of quaternary mixtures of {water (1) + [bmim][BF_4] (2) + AOT (3) + decane (4)} with known volume fractions of the droplet were prepared, where w_2 and ω were fixed at $1.1\cdot10^{-4}$ and 40.8, respectively. The refractive indices of these mixtures were measured in the one-phase region at various temperatures. The results are listed in Table 3.

The refractive index of the microemulsion may be expressed as a linear function of temperature in a certain temperature range

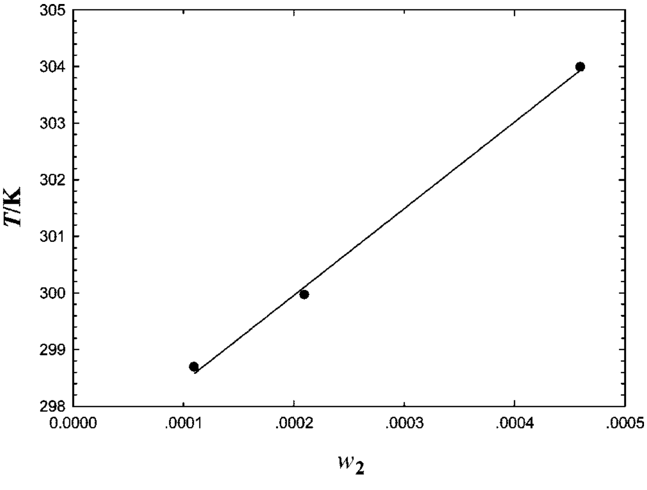

Figure 1. Critical temperature increasing with the mass fraction of [bmim][BF_4] w_2.

$$n(\Phi, T) = n(\Phi, T^0) + (\partial n/\partial T)(T - T^0) \qquad (1)$$

$$(\partial n/\partial T) = \Phi(\partial n_A/\partial T) + (1 - \Phi)(\partial n_B/\partial T) \qquad (2)$$

T^0 is chosen as 300.43 K (about the middle temperature of the coexistence curve determined in this work); $(\partial n/\partial T)$ is the derivative of n with respect to T; and $(\partial n_A/\partial T)$ and $(\partial n_B/\partial T)$ represent the values of $(\partial n/\partial T)$ for $\Phi = 1$ and 0, respectively. From the temperature dependence of refractive indices of pure decane, the value of $(\partial n_B/\partial T)$ was calculated to be $-4.4 \cdot 10^{-4}$ K^{-1}. Rearrangement of eqs 1 and 2 yields

$$n(\Phi, T) = n(\Phi, T^0) + [\Phi(\partial n_A/\partial T) + (1 - \Phi)(\partial n_B/\partial T)](T - T^0) \qquad (3)$$

The values of $n(\Phi, T)$ listed in Table 3 were fitted to eq 3 to obtain $(\partial n_A/\partial T)$, which is $-4.3 \cdot 10^{-4}$ K^{-1}. The small standard deviation of 0.0001 in refractive index indicates that eq 3 is valid. This allowed us to simplify the procedure of determination of the dependence of n on Φ just by calculating $n(\Phi, T^0)$ through eq 3 and fitting a polynomial form to $n(\Phi, T^0)$ for various Φ at T^0. We obtained the expression

$$n(\Phi, T^0) = 1.4070 - 0.0270\Phi - 0.0110\Phi^2 + 0.0157\Phi^3 \qquad (4)$$

with a standard deviation < 0.0001 in the refractive index. All of our experimental data used in fitting eq 4 are in the range of $\Phi = (0 \text{ to } 0.268)$; therefore, extrapolation of eq 4 to the range of $\Phi > 0.268$ is unreliable. The values of the refractive index then were converted to volume fractions by calculating $n(\Phi,$

Table 2. Coexistence Curves of (T, n), (T, Φ), and (T, Ψ) for {Water (1) + [bmim][BF$_4$] (2) + AOT (3) + Decane (4)} Microemulsion with $w_2 = 1.1 \cdot 10^{-4}$ and $\omega = 40.8$[a]

$(T - T_c)$/K	n_1	n_2	Φ_1	Φ_2	Ψ_1	Ψ_2
0.014	1.4056	1.4043	0.079	0.122	0.450	0.569
0.020	1.4057	1.4042	0.075	0.127	0.435	0.581
0.033	1.4059	1.4041	0.066	0.129	0.402	0.584
0.048	1.4061	1.4041	0.062	0.130	0.384	0.586
0.066	1.4061	1.4039	0.061	0.136	0.381	0.599
0.087	1.4061	1.4038	0.059	0.140	0.374	0.608
0.105	1.4061	1.4037	0.058	0.144	0.369	0.614
0.138	1.4063	1.4035	0.053	0.148	0.347	0.622
0.190	1.4064	1.4034	0.047	0.150	0.318	0.627
0.241	1.4064	1.4032	0.045	0.157	0.308	0.639
0.303	1.4065	1.4030	0.041	0.164	0.290	0.650
0.381	1.4066	1.4028	0.038	0.169	0.274	0.659
0.480	1.4066	1.4025	0.035	0.177	0.256	0.672
0.608	1.4067	1.4023	0.030	0.182	0.227	0.679
0.771	1.4068	1.4020	0.025	0.189	0.197	0.689
0.948	1.4068	1.4017	0.022	0.198	0.178	0.702
1.428	1.4067	1.4010	0.016	0.216	0.132	0.723
1.871	1.4067	1.4005	0.010	0.225	0.086	0.734
2.376	1.4065	1.3999	0.007	0.237	0.059	0.747
3.483	1.4061	1.3988	0.004	0.259	0.035	0.768

[a] Subscripts 1 and 2 represent the upper and lower phase; w_2, T, n, Φ, and Ψ are the mass fraction of [bmim][BF$_4$] in the microemulsion, the experimental temperature, the refractive index, the volume fraction of the droplet, and the effective volume fraction of the droplet, respectively; $T_c = 298.687$ K. The uncertainties in measurements of n, Φ, and Ψ are ± 0.0001, ± 0.004, and ± 0.015, respectively.

Table 3. Refractive Indices n at a Wavelength $\lambda = 632.8$ nm for Microemulsion of {Water (1) + [bmim][BF$_4$] (2) + AOT (3) + Decane (4)} with $w_2 = 1.1 \cdot 10^{-4}$ and $\omega = 40.8$ for Various Temperatures T and Volume Fractions Φ of the Droplet

Φ	T/K	n	T/K	n	T/K	n
0.000	293.859	1.4100	294.785	1.4096	295.751	1.4091
	296.700	1.4087	297.599	1.4083	298.533	1.4079
	299.406	1.4075	300.260	1.4071		
0.052	292.778	1.4088	293.759	1.4083	294.715	1.4079
	295.618	1.4075	296.588	1.4071	297.495	1.4066
	298.495	1.4062				
0.095	293.987	1.4071	295.112	1.4066	296.158	1.4061
	297.116	1.4057	297.911	1.4054	298.650	1.4051
0.153	294.552	1.4054	295.454	1.4050	296.316	1.4046
	297.226	1.4042	298.095	1.4038	298.948	1.4034
	299.833	1.4030	300.712	1.4027		
0.219	294.863	1.4028	295.775	1.4024	296.643	1.4021
	297.536	1.4017	298.394	1.4014	299.260	1.4011
	300.180	1.4007	301.075	1.4003		
0.268	296.539	1.4010	297.526	1.4005	298.553	1.4001
	299.509	1.3997	300.486	1.3993	301.457	1.3989
	302.418	1.3985	303.327	1.3981		

Table 4. Parameters in Equations 6 and 7 for Coexistence Curves (T, n), (T, Φ), and (T, Ψ) for the Microemulsion of {Water (1) + [bmim][BF$_4$] (2) + AOT (3) + Decane (4)} with $w_2 = 1.1 \cdot 10^{-4}$ and $\omega = 40.8$

order parameters	B	B_1	$\lvert B_1/B \rvert$
n	0.0307 ± 0.0002		
	0.0345 ± 0.0002	−0.028 ± 0.003	0.81
Φ	1.140 ± 0.007		
	1.203 ± 0.008	−0.973 ± 0.108	0.81
Ψ	3.360 ± 0.026		
	3.553 ± 0.038	−2.983 ± 0.531	0.84

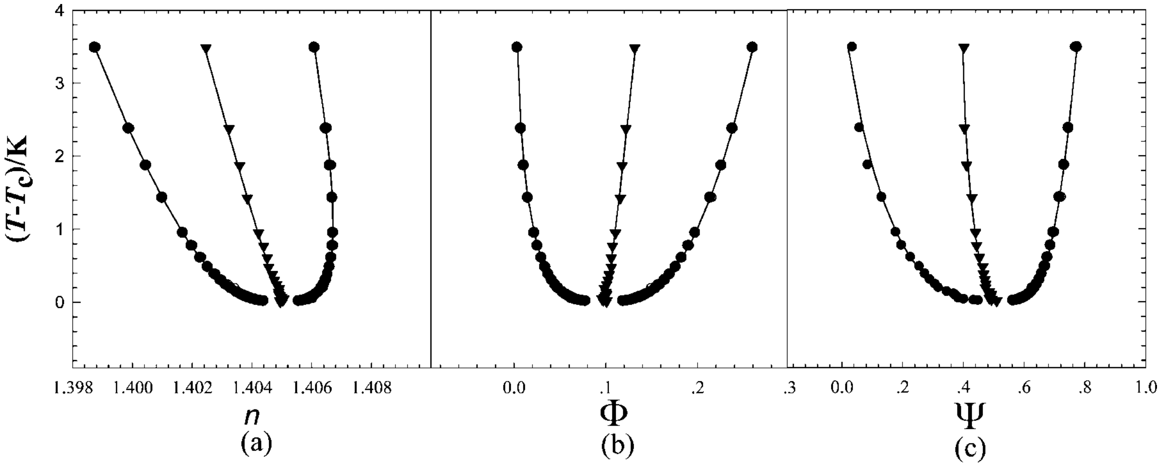

Figure 2. Coexistence curves of (T, n), (T, Φ), and (T, Ψ) for microemulsion of {Φ(water (1) + [bmim][BF$_4$] (2) + AOT (3)) + (1 − Φ) decane (4)} with $w_2 = 1.1 \cdot 10^{-4}$ and $\omega = 40.8$: (a) T vs n; (b) T vs Φ; (c) T vs Ψ; •, experimental values of concentration variables (ρ) of coexisting phases; ▼, experimental values of diameter (ρ_d) of the coexisting phases; the lines, concentration variables (ρ_{calcd}) and diameter (ρ_{dcalcd}) calculated from eqs 9, 10, and 11 with coefficients listed in Tables 4 and 5. n, Φ, and Ψ are the refractive indices, volume fraction, and effective volume fraction, respectively.

Table 5. Parameters of Equations 8 and 9 and Standard Deviations *S* in ρ for Diameters of Coexistence Curves of (T, n), (T, Φ), and (T, Ψ) for {Water (1) + [bmim][BF$_4$] (2) + AOT (3) + Decane (4)} with $w_2 = 1.1 \cdot 10^{-4}$ and $\omega = 40.8$[a]

	(T, n)	(T, Φ)	(T, Ψ)
$\rho_{c,exptl}$	1.4050 ± 0.0001	0.095 ± 0.001	0.500 ± 0.001
	$\rho_d = \rho_c + A_0\tau + A_1\tau^{1-\alpha}$		
ρ_c	1.4050 ± 0.0001	0.098 ± 0.001	0.503 ± 0.002
A_0	-0.032 ± 0.062	-2.48 ± 2.19	69.2 ± 7.1
A_1	-0.12 ± 0.04	3.3 ± 1.3	-47.9 ± 4.3
S	$4.4 \cdot 10^{-5}$	$1.5 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$
	$\rho_d = \rho_c + A_0\tau + C\tau^{2\beta}$		
ρ_c	1.4050 ± 0.0002	0.098 ± 0.001	0.509 ± 0.002
A_0	-0.171 ± 0.018	1.48 ± 0.65	12.9 ± 2.0
C	-0.011 ± 0.004	0.31 ± 0.14	-4.8 ± 0.4
S	$4.5 \cdot 10^{-5}$	$1.6 \cdot 10^{-3}$	$4.9 \cdot 10^{-3}$

[a] Where $\rho_{c,exptl}$ is the experimental critical value of the order parameter.

T^0) through eq 3 and iteratively solving eq 4. The results are listed in columns 4 and 5 in Table 2 and shown in Figure 2b.

The choice of the concentration variable may affect the symmetry and the size of the asymptotic region of a coexistence curve. One of the choices is to define an effective volume fraction Ψ[20]

$$\Psi = \Phi/[\Phi + \Phi_c \cdot (1 - \Phi)/(1 - \Phi_c)] \tag{5}$$

We used eq 5 to convert (T, Φ) to (T, Ψ) which denotes the coexistence curve of temperature against effective volume fraction. The results are listed in columns 6 and 7 of Table 2 and shown in Figure 2c.

The difference of concentration variables $|\rho_2 - \rho_1|$ may be expressed by the Wegner expression[21]

$$|\rho_2 - \rho_1| = B\tau^{\beta} + B_1\tau^{\beta+\Delta} + \cdots \tag{6}$$

where $\tau = (T - T_c)/T_c$, β, and $\Delta = 0.5$[22,23] are critical exponents; B_1 is the amplitude of the first Wegner correction term; ρ is the concentration variable; and ρ_1 and ρ_2 are the values of ρ in the upper and lower coexisting phases, respectively. When the region of temperature is sufficiently close to the critical temperature, the simple scaling is valid

$$|\rho_2 - \rho_1| = B\tau^{\beta} \tag{7}$$

It is well-known that the region of validity of eq 7 is affected by the choices of the variables. A wrong choice of the variable may cause a significant reduction of the region of validity of eq 7. The values of β in different τ regions for n, Φ, and Ψ were estimated by fitting the experimental data to eq 7. Figure 3 shows the dependence of the value of β on the temperature range for the three choices of the order parameters, where the temperature range is represented by the cutoff value of maximum ($T - T_c$) denoted by $(T - T_c)_{max}$. When all the experimental data were used to fit eq 7, the values of β were obtained to be 0.317 ± 0.003, 0.317 ± 0.003, and 0.326 ± 0.005 for n, Φ, and Ψ, respectively. When ($T - T_c$) < 1 K, the values of β are 0.321 ± 0.004, 0.321 ± 0.004, and 0.335 ± 0.006 for n, Φ, and Ψ, respectively. The critical exponents are very close to the 3D-Ising value of 0.327 and obviously inconsistent with the Fisher renormalized value of 0.367.[3] It is evidence that this quaternary microemulsion may also be taken as pseudobinary mixture. This could result from the fact that the fourth component ionic liquid is only dissolved in the water droplets in the microemulsions. Thus, the droplets in microemulsion consist of water, [bmim][BF$_4$], and AOT, and their spherical structure and size are related with the molar ratio (ω) of water to AOT and the concentration (w_2) of [bmim][BF$_4$]. As ω and w_2 stay constant, the droplets of microemulsion can be considered as a pseudocomponent.

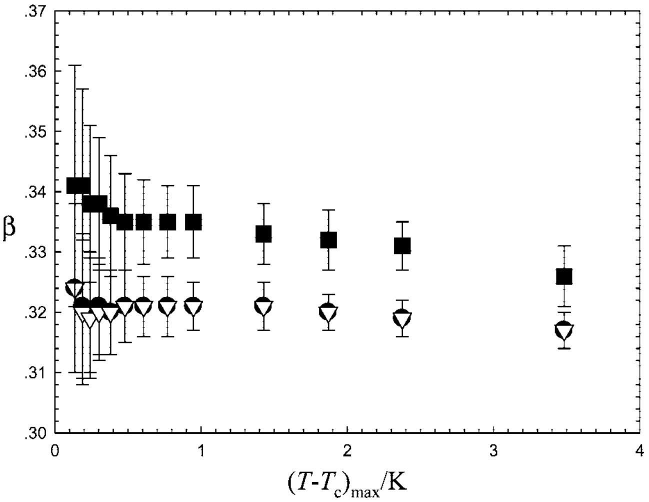

Figure 3. Plot of the critical exponent in the different temperature range of $(T - T_c)_{max}$ for n, Φ, and Ψ obtained by fitting the experimental data to eq 7 for {Φ(water (1) + [bmim][BF$_4$] (2) + AOT (3)) + (1 − Φ)decane (4)} with $w_2 = 1.1 \cdot 10^{-4}$ and $\omega = 40.8$. ▽, refractive index n; •, volume fraction Φ; □, effective volume fraction Ψ.

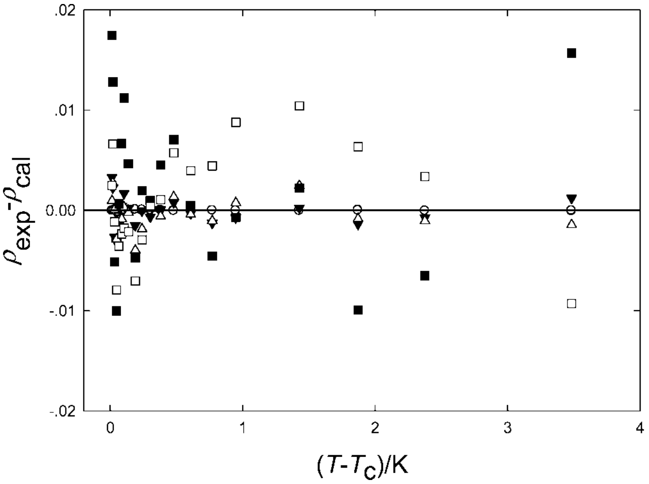

Figure 4. Plot of the residuals ($\rho_{exptl} - \rho_{calcd}$) as a function of the temperature difference ($T - T_c$) for coexistence curves of {Φ(water (1) + [bmim][BF$_4$] (2) + AOT (3)) + (1 − Φ)decane (4)} with $w_2 = 1.1 \cdot 10^{-4}$ and $\omega = 40.8$, where ρ_{exptl} is the experimental value, ρ_{calcd} is calculated by eqs 10 and 11, and subscripts 1 and 2 represent upper and lower phases, respectively. •, n_1; ○, n_2; ▼, Φ_1; △, Φ_2; □, Ψ_1; ■, Ψ_2.

The goodness of variables used to construct the order parameters can also be tested by fitting the experimental data to eq 6 with fixed values of $\beta = 0.3265$ and $\Delta = 0.5$ and by comparing the significance of the first Wegner correction. The critical amplitudes are listed in Table 4. The significance of the first Wegner correction term may be qualitatively indicated by the ratio of $|B_1/B|$. As shown in Table 4, the smaller values of $|B_1/B|$ for order parameters n and Φ indicate that they possibly are better choices than Ψ in this microemulsion system; however, the uncertainties in $|B_1/B|$ are so large that the priority is not unambiguous. It is well-known that when a good variable is used to construct an order parameter, the diameter of the coexistence curve may be expressed as

$$\rho_d = (\rho_1 + \rho_2)/2 = \rho_c + A_0\tau + A_1\tau^{1-\alpha} + \cdots \qquad (8)$$

Otherwise, the diameter shows a 2β anomaly

$$\rho_d = (\rho_1 + \rho_2)/2 = \rho_c + A_0\tau + C\tau^{2\beta} + \cdots \qquad (9)$$

The experimental data in the range of $(T - T_c) < 3.5$ K were fitted by eqs 8 and 9 in separate fitting procedures with $\alpha = 0.11$ and $\beta = 0.3265$, and ρ_c, A_0, A_1, and C were obtained. The characteristics of the fits are summarized in Table 5, where $\rho_{c,exptl}$ is the experimental critical value of the order parameter. The experimental value of n_c was obtained by extrapolating refractive index against temperature in the one-phase region to the critical temperature.[18] The value of $\Phi_{c,exptl}$ was determined by the technique of equal volume, and the value of $\Psi_{c,exptl}$ was calculated from Φ with eq 5. The standard deviation S in fitting eq 9 for variables n and Φ is lager than that in fitting eq 8, which indicates that the $(1 - \alpha)$ anomaly is more significant than that of 2β. However, the 2β anomaly is more preferred to variable Ψ than $(1 - \alpha)$. It confirms once again that n and Φ possibly are better variables than Ψ.

Combination of eqs 6 and 9 yields

$$\rho_1 = \rho_c + A_0\tau + C\tau^{2\beta} - (1/2)B\tau^{\beta} - (1/2)B_1\tau^{\beta+\Delta}\cdots \qquad (10)$$

$$\rho_2 = \rho_c + A_0\tau + C\tau^{2\beta} + (1/2)B\tau^{\beta} + (1/2)B_1\tau^{\beta+\Delta}\cdots \qquad (11)$$

when α, β, Δ, and T_c/K were fixed at 0.11, 0.3265, 0.5, and 298.687, and the values of B, B_1, A_0, and C were taken from Tables 4 and 5, and the values of ρ_1, ρ_2, and ρ_d were calculated from eqs 9, 10, and 11, respectively. The results are shown as lines in Figure 2. The residuals as a function of the temperature deference, which denotes the distance from the critical point, are shown in Figure 4. The values from calculation are in good agreement with experimental results.

Conclusions

We have determined the coexistence curves of quarternary microemulsion of {water (1) + [bmim][BF$_4$] (2) + AOT (3) + decane (4)} by measuring refractive indices in the critical region, and the critical exponent β was deduced from the coexistence curves. It has been found that this system may reasonably be taken as a pseudobinary solution due to the factor that the ionic liquid [bmim][BF$_4$] is dissolved only in the water pool of the quaternary microemulsion. Our results show that the critical exponent β approached the 3D-Ising value in the critical region. Contrary to the {water + KCl + AOT + decane} system, the critical temperature was significantly decreased with the concentration of the ionic liquid, while the critical volume fraction Φ_c almost stayed constant. It may be attributed to the unique role of the ionic liquid which is capable of significantly modifying the physicochemical properties of microemulsions.

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