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Liquid−Liquid Equilibrium Phase Diagram and Density of Three Water + Nonionic Surfactant C_iE_j Binary Systems

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Liquid−liquid equilibrium and density data for three binary systems, water + C_6E_2, water + C_6E_3, and water + C_7E_3, ranging from their lower critical consolute solution temperature to 70 °C at atmospheric pressure are presented in this paper. (C_iE_j is the abbreviation of nonionic surfactant $CH_3(CH_2)_{i-1}(OCH_2CH_2)_j$-OH.) The experimental results were correlated with the UNIQUAC model by fitting the UNIQUAC interaction parameters as a function of temperature. Agreement between the calculated and experimental data was excellent for all three systems. The lower critical consolute solution temperature, critical weight fraction, and critical density were estimated by fitting the experimental data to the critical scaling law.

Introduction

Although the homologous series of nonionic surfactant poly(oxyethylene) alcohol $CH_3(CH_2)_{i-1}(OCH_2CH_2)_jOH$, abbreviated by C_iE_j hereafter, is extensively used, both in industrial and in fundamental research applications, there is little reliable information on its phase behavior, especially for short-chain ($i < 10$) C_iE_js. The liquid−liquid equilibrium phase diagram and density of three binary mixtures, water + C_6E_2, water + C_6E_3, and water + C_7E_3, ranging from their lower critical consolute solution temperature to 70 °C at atmospheric pressure are reported in this paper. The phase diagrams of these systems are important for the design of experiments and interpretation of data on wetting transition (Chen et al., 1994), phase diagram of ternary systems water + oil + C_iE_j (Kahlweit and Strey, 1985), and phase conductivity (Kahlweit et al., 1993) studies. Although the phase diagram of the system water + C_6E_2 has been performed by using the phase volume method (Lim et al., 1993), the liquid−liquid equilibrium measurements of this system were redone to cross-check the validity and accuracy of the Karl Fischer titration method, which was applied in this study. On the other hand, there are, to the best of our knowledge, neither liquid−liquid equilibrium nor density measurements for the systems water + C_6E_3 and water + C_7E_3 available in the literature.

Experimental Section

The surfactant C_6E_2 was purchased from Aldrich Chemical Co. with a nominal purity of 99%, while surfactants C_6E_3 and C_7E_3 were provided by Bachem Feinchemikalien AG with a nominal purity of 98%. Both the Karl Fischer reagents hydranal-coulomat A and hydranal-coulomat C were purchased from Riedel-deHaën AG. All the chemicals were used as received without any further purification. Water was purified in a Barnstead NANOpure II system with the resistivity better than 17.8 MΩ·cm.

The mixtures of water + C_6E_2 were prepared in a 1 cm diameter test tube and placed in a computer-controlled water thermostat, whose temperature stability was better than ±0.004 °C. These samples were kept in the thermostat for at least 3 h and sometimes up to 2 days, to allow the system to reach equilibrium. Before and during the equilibration process, the samples were shaken vigorously several times to ensure thorough mixing. After equilibrium was reached, both liquid phases were transparent with a sharp, mirrorlike interface; except for some system temperatures close to the lower consolute solution temperature, both liquid phases became slightly milky, which is known as critical opalescence. Following equilibration, both liquid phases were carefully sampled by syringe for further experiments on the determinations of composition and density for each liquid phase.

Table 1. Experimental Mass Fraction of Water and Density of Equilibrium Liquid Phases for the Binary System Water + C_6E_2 at Various Temperatures

t/°C	W_l	W_u	$\rho_l/(g\cdot cm^{-3})$	$\rho_u/(g\cdot cm^{-3})$
11.00	0.942	0.822	0.998 34	0.993 30
12.00	0.951	0.752	0.999 07	0.990 87
13.00	0.957	0.709	0.999 26	0.989 14
14.00	0.961	0.675	0.999 17	0.987 17
15.00	0.964	0.657	0.999 11	0.985 95
16.00	0.966	0.634	0.998 99	0.984 51
18.00	0.975	0.601	0.998 68	0.981 74
20.00	0.976	0.566	0.998 20	0.978 81
22.00	0.975	0.531	0.997 88	0.976 08
24.00	0.979	0.515	0.997 35	0.972 69
25.00	0.982	0.494	0.997 04	0.971 99
26.00	0.979	0.481	0.996 83	0.970 48
28.00	0.979	0.456	0.996 23	0.967 70
30.00	0.980	0.429	0.995 69	0.964 86
32.00	0.979	0.400	0.995 01	0.962 20
35.00	0.981	0.384	0.993 92	0.958 27
40.00	0.981	0.341	0.992 06	0.951 47
44.00	0.982	0.309	0.990 53	0.945 58
50.00	0.984	0.284	0.987 93	0.939 19
55.00	0.986	0.255	0.985 56	0.932 95
65.00	0.986	0.229	0.980 56	0.921 67

The water content of each liquid phase was analyzed by a coulometric Karl Fischer moisture titrator (MKC-210, Kyoto Electronics Co.). At least six measurements of water content were performed for each liquid phase at a given temperature. The estimated experimental error was less than 1.0 wt %.

Densities were measured with a vibrating tube density meter (DMA-58, Anton-Paar) equipped with a built-in

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Table 2. Experimental Mass Fraction of Water and Density of Equilibrium Liquid Phases for the Binary System Water + C_6E_3 at Various Temperatures

t/°C	W_l	W_u	ρ_l/(g·cm^{-3})	ρ_u/(g·cm^{-3})
44.30	0.923	0.784	0.989 93	0.986 34
44.50	0.943	0.770	0.990 40	0.986 00
45.00	0.959	0.728	0.990 33	0.984 67
46.00	0.969	0.675	0.990 06	0.982 62
48.00	0.972	0.614	0.989 31	0.979 05
50.00	0.977	0.574	0.988 14	0.976 09
55.00	0.986	0.487	0.985 92	0.969 3[a]
60.00	0.988	0.411	0.983 54	0.962 9[a]
65.00	0.988	0.347	0.981 09	0.955 9[a]
70.00	0.989	0.290	0.978 45	0.949 4[a]

[a] The estimated experimental uncertainty was less than ±0.0001 g·cm^{-3}.

Table 3. Experimental Mass Fraction of Water and Density of Equilibrium Liquid Phases for the Binary System Water + C_7E_3 at Various Temperatures

t/°C	W_l	W_u	ρ_l/(g·cm^{-3})	ρ_u/(g·cm^{-3})
22.30	0.951	0.883	0.997 57	0.996 31
22.50	0.955	0.857	0.997 63	0.995 85
23.00	0.963	0.823	0.997 55	0.994 94
24.00	0.968	0.781	0.997 33	0.993 47
26.00	0.977	0.726	0.996 95	0.991 29
28.00	0.979	0.682	0.996 47	0.988 96
30.00	0.979	0.650	0.995 95	0.986 78
32.00	0.979	0.619	0.995 33	0.984 60
35.00	0.980	0.577	0.994 27	0.981 48
40.00	0.980	0.508	0.992 35	0.975 58
44.00	0.982	0.449	0.990 80	0.970 55
50.00	0.984	0.386	0.988 53	0.962 73
55.00	0.986	0.335	0.986 28	0.956 43
60.00	0.988	0.295	0.983 79	0.950 17
70.00	0.991	0.225	0.978 57	0.938 07

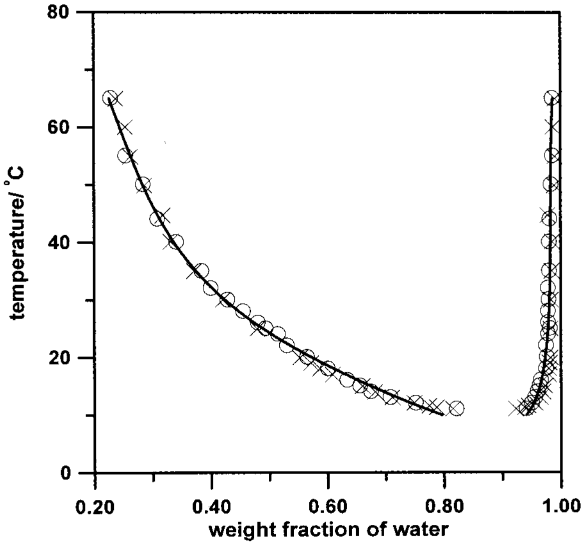

Figure 1. Coexistence curve for the binary system water + C_6E_2: experimental results of this study (○) and of Lim et al. (1993) (×) and calculated results by the UNIQUAC model (solid line).

thermostat with a temperature stability of ±0.01 K. The calibration of the density meter was carried out with water (purified by the Barnstead NANOpure II system mentioned above) and dry air. The accuracy of the density measurements was ±0.00001 g·cm^{-3}. At least five measurements of density were performed for each liquid phase at a given temperature. The estimated experimental uncertainty was less than ±0.00005 g·cm^{-3}.

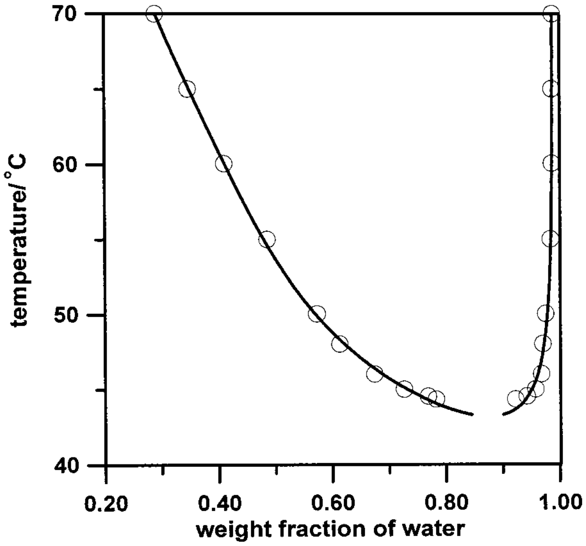

Figure 2. Coexistence curve for the binary system water + C_6E_3: experimental results (○) and calculated results by the UNIQUAC model (solid line).

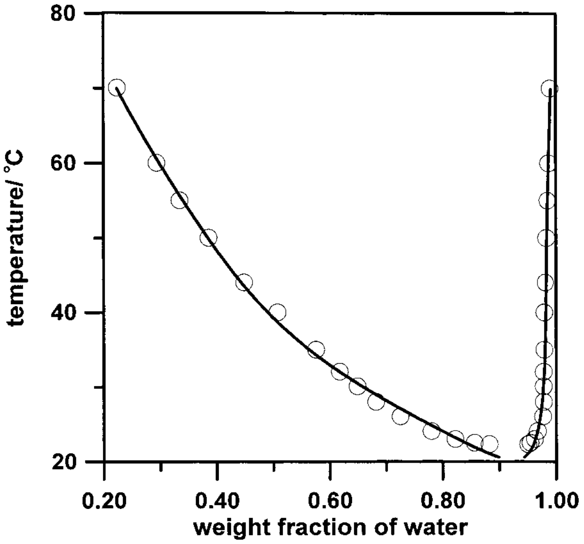

Figure 3. Coexistence curve for the binary system water + C_7E_3: experimental results (○) and calculated results by the UNIQUAC model (solid line).

Results and Discussion

The experimental compositions and densities of the equilibrium phases obtained for the systems water + C_6E_2, water + C_6E_3, and water + C_7E_3 under investigation at atmospheric pressure are reported in Tables 1−3, respectively. The data are expressed in units of weight fraction. The subscripts u and l stand for the upper and lower phases, respectively. Our experimental data for the system water + C_6E_2 have an excellent agreement with that of Lim et al. (1993), as shown in Figure 1.

The UNIQUAC model of Abrams and Prausnitz (1975) was used to correlate experimental data. The relative van der Waals volume, r, and van der Waals surface area, q, of the UNIQUAC model were calculated from the UNIFAC group contribution table of Hansen et al. (1992) and are listed for each component in Table 4. The effective binary interaction parameters a_{12} and a_{21} were exactly solved for each temperature by numerical methods and then were correlated with temperature by the following polynomial equations:

Table 4. Relative van der Waals Volume *r* and van der Waals Surface Area *q*

compd	*r*	*q*	compd	*r*	*q*
C_6E_2	7.9884	6.772	C_7E_3	10.2555	8.632
C_6E_3	9.5811	8.092	H_2O	0.9200	1.400

Table 5. Estimated UNIQUAC Parameters for Three Water + C_iE_j Systems

param	water + C_6E_2	water + C_6E_3	water + C_7E_3
$a_{12}°$	621.995	729.886	955.218
$b_{12}°$	−0.051 372 6	−10.3509	−15.9616
$c_{12}°$	−0.160 264	0.345 009	0.201 700
$d_{12}°$	0.001 573 62	−0.003 615 92	−0.001 416 28
$a_{21}°$	−344.574	−1329.17	−570.014
$b_{21}°$	2.146 67	51.8544	13.3854
$c_{21}°$	0.035 968 3	−0.939 729	−0.235 891
$d_{21}°$	−0.000 349 155	0.006 072 43	0.001 871 03

Table 6. Critical Properties of Three Water + C_iE_j Systems

	water + C_6E_2	water + C_6E_3	water + C_7E_3
T_c/K	283.94	317.24	295.39
W_c	0.888	0.859	0.916
$\rho_c/(g\cdot cm^{-3})$	0.99614	0.98883	0.99704

$$a_{12} = a_{12}° + b_{12}°T + c_{12}°T^2 + d_{12}°T^3 \tag{1}$$

$$a_{21} = a_{21}° + b_{21}°T + c_{21}°T^2 + d_{21}°T^3 \tag{2}$$

The coefficients $a_{12}°$, $b_{12}°$, $c_{12}°$, $d_{12}°$, $a_{21}°$, $b_{21}°$, $c_{21}°$, and $d_{21}°$ were estimated by regression of the effective binary interaction parameters a_{ij}s over the whole experimental temperature range and are given in Table 5. The effective binary interaction parameter a_{ij} is defined by

$$a_{ij} = \frac{U_{ij} - U_{ji}}{R} \tag{3}$$

where R is the gas constant and u_{ij} is the UNIQUAC interaction parameter between molecules i and j. Figures 1−3 show a comparison between the experimental results and the calculated phase boundaries obtained from the UNIQUAC model with the correlated parameters given by eqs 1 and 2. The calculated phase behavior describes the experimental data very well.

When a system is very close to its critical temperature, T_c, according to the renormalization theory, the phase boundary points W_l and W_u should behave as a power law (Rowlinson and Widom, 1982) of the form

$$(W_l - W_u) \sim \epsilon^{\beta} \tag{4a}$$

$$\left(\frac{W_l + W_u}{2} - W_c\right) \sim \epsilon^{1-\alpha} \tag{4b}$$

where ϵ is the reduced temperature defined as $\epsilon \equiv (T - T_c)/T_c$, W_c is the critical weight fraction, and α and β are the critical exponents with the universal values of 0.11 and 0.325, respectively. The experimental results of the coexistence curve were used to fit the scaling law, eqs 4a,b, the estimates for the lower critical consolute solution temperature T_c, and the critical weight fraction W_c were obtained and are given in Table 6. Instead of using the weight fraction in eq 4, the density can be used to replace the weight fraction that was applied to determine the critical density, ρ_c. The critical densities of three binary systems are also listed in Table 6.

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