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Three-Liquid-Phase Equilibria for the Quaternary System Water + *tert*-Butanol + *n*-Decane + *n*-Undecane in the Tricritical Region

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The three-liquid-phase equilibria data of the quaternary system water (1) + *tert*-butanol (2) + *n*-decane (3) + *n*-undecane (4) in the tricritical region are reported. It has been found that the mass fraction of *n*-decane in (*n*-decane + *n*-undecane) controls the size of the three-phase region and the approach to the tricritical point. The experimental data have been analyzed to obtain the tricritical temperature and the tricritical composition.

Introduction

In a multicomponent liquid mixture, a tricritical point is defined as a point at which three coexistence phases become simultaneous identical.[1] According to the phase rule, at least three components are required for the existence of an isolated point in four-dimensional $T-P-$composition space. The tricritical phenomena of three-component mixtures with one being low molecular mass hydrocarbon solvent, the others being two higher molar mass hydrocarbons, such as methane + 2,2-dimethyl butane + 2,3-dimethylbutane and ethane + *n*-heptadecane + *n*-octadecne, have been extensively studied.[2−7] The experimental results demonstrated that the two higher molecular mass hydrocarbons in the ternary mixtures could be treated as a single component. The tricritical phenomena have also been studied in the quaternary mixtures, such as water + *n*-decane + *n*-dodecane + *tert*-butanol,[8] either at the equilibrium vapor pressure or at constant pressure, where two similar components were treated as a quasi "pure" component. The relative amounts of two similar components in above quasi-binary and quasi-ternary mixtures successfully controlled the approach to the tricritical points.

When two *n*-alkanes are used to construct a quasi-pure component, the closer the carbon number of the two *n*-alkanes is, the more similar to the pure one the behavior of quasi-pure component is. Therefore, recently we studied the three-liquid-phase coexistences of the quasi-ternary mixtures of water + *tert*-butanol + *n*-decane + *n*-undecane in the tricriticl region by measurements of the refractive index of each coexisting phase for various temperatures and various overall compositions.[9] The experimental results were used to discuss the non-classical behavior of tricritical amplitude ratios through Scott's extended theory[10] and found that the refractive index was a good order parameter. However, the coexistence curves of temperature versus refractive index are unable to be converted into that of temperature versus the compositions for the mixtures with three or more components. We also determined the compositions of three coexisting phases for the quaternary system water + formamide + cyclohexane + diethylene glycol monobutyl ether near the trictitical point by measurements of volumes of each of coexisting phase for various temperatures and various overall compositions.[11] In this paper, we report equilibrium data for the system water (1) + *tert*-butanol (2) + *n*-decane (3) + *n*-undecane (4) in the tricritical region, where a binary mixture of *n*-decane and *n*-undecane was considered to be a quasi pure component (abbreviated as A). The mass fraction (denoted as w) of *n*-decane in the quasi pure component determines the property of this component and thereby determines the temperature range and the composition range of the three coexisting phases of the system and controls the approach to the tricritical point.

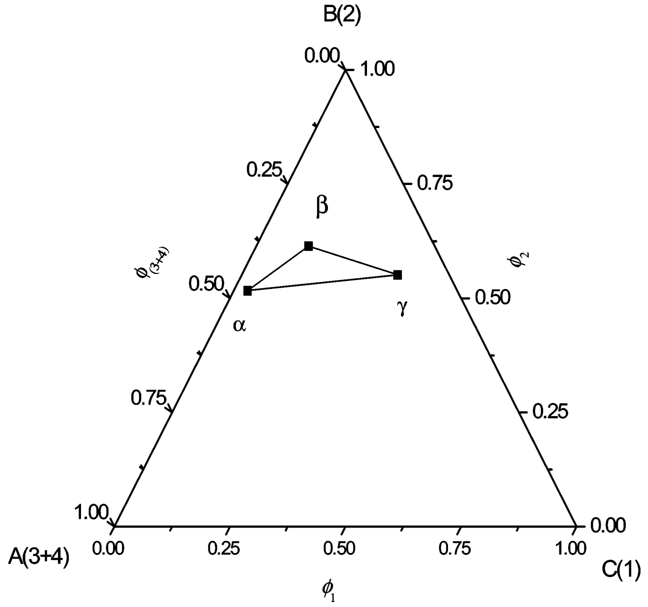

Figure 1. Isothermal quasi-ternary-phase diagram for the system water (1) + *tert*-butanol (2) + *n*-decane (3) + *n*-undecane (4) at t = 53.844 °C and w = 0.092. The mixture of *n*-decane and *n*-undecane is taken as pure component A.

Experimental Section

Principle. The experimental principle has been described by Knobler and Scott[12] and in our previous works.[11,13] A point in the triangle ABC shown in Figure 1 represents the composition

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Table 1. Experimental Values of the Density of Pure Components at 20 °C

liquid	ρ/g·cm^{-3} this work	ρ/g·cm^{-3} literature
water (1)	0.9520	0.9520[a]
tert-butanol (2)	0.7858	0.7856[b]
decane (3)	0.7298	0.7301[c]
undecane (4)	0.7404	0.7402[c]

[a] Ref 16. [b] Ref 17. [c] Ref 18.

of a ternary mixture at a certain temperature. Any mixture with a total composition in triangle $\alpha\beta\gamma$ separates into three phases, the concentrations of which are specified by the three vertices of the triangle. If the cross-sectional area of the sample cell is uniform, the total height H_i of a fluid component i in the cell may be expressed as

$$H_i = h^{\alpha}(1 + a)\varphi_i^{\alpha} + h^{\beta}(1 + b)\varphi_i^{\beta} + h^{\gamma}(1 + c)\varphi_i^{\gamma} \qquad (1)$$

where h^{α}, h^{β}, and h^{γ} denote the heights of α, β, and γ phases; φ_i^{α}, φ_i^{β}, and φ_i^{γ} are the volume fractions of component i in the α, β, and γ phases; a, b, and c are the contributions from the excess volumes in the α, β, and γ phases, which were estimated from the excess heights of three phases.[11,13] $H_i = m_i/(\rho_i S)$ with ρ_i, S, and m_i being the density, cross-sectional area of the sample cell, and mass of the sample weighed into the cell. Subscript i denotes water, *tert*-butanol, or A (the mixed oils).

The values of h^{α}, h^{β}, and h^{γ} may be measured with a cathetometer, and H_i may be calculated from the mass of each component and its corresponding density. If a series of samples with different overall compositions were made over the three-phase regions, we may obtain a series of simultaneous equations. The values of the volume fractions in eq 1 may be obtained by fitting the experimental values of h^{α}, h^{β}, and h^{γ} to the equation. The sum of the volume fractions in each phase should equal 1, which is a criterion of good experimental data.

Materials. The *n*-decane (> 99 %) and *n*-undecane (> 99 %) were obtained from Merck-Schucardt Co. *tert*-Butanol (> 99 %) was supplied by Tianjin Chemical Co. The water was distilled and deionized, and its electrolytic conductivity was about 1.8×10^{-7} s·cm^{-1}. The densities of these materials were measured over a temperature range of (35 to 57) °C with an Anton Paar DMA60 DMA602 vibrating-tube densimeter, and the dependences of density ρ on temperature t are expressed below with an uncertainty of better than 0.0001 g·cm^{-3}:

$$\rho_1/\text{g·cm}^{-3} = 1.0020 - 1.25 \times 10^{-4}(t/°\text{C}) \qquad (2\text{-}1)$$

$$\rho_2/\text{g·cm}^{-3} = 0.8066 - 1.038 \times 10^{-3}(t/°\text{C}) \qquad (2\text{-}2)$$

$$\rho_3/\text{g·cm}^{-3} = 0.7442 - 7.218 \times 10^{-4}(t/°\text{C}) \qquad (2\text{-}3)$$

$$\rho_4/\text{g·cm}^{-3} = 0.7554 - 7.494 \times 10^{-4}(t/°\text{C}) \qquad (2\text{-}4)$$

where ρ_1, ρ_2, ρ_3, and ρ_4 are the densities of water, *tert*-butanol, decane, and undecane, respectively. For the quasi-pure component (A), the dependence of density $\rho_A/(\text{g·cm}^{-3})$ on ρ_3 and ρ_4 with fixed w can be expressed as $\rho_A = \rho_3\rho_4/[w\rho_3 + (1 - w)\rho_4]$.

Table 1 shows the densities of the four materials measured in this work at 20 °C together with those reported in the literature for comparison. The density data were used to calculate H_i in eq 1.

Procedure. The experimental procedure was described in detail in our previous paper.[11] The sample cells with Teflon screw plugs were purchased from Ace Glass Inc. and were calibrated by measuring the heights of the cyclohexane weighed into each cell. The volume of the cell was about 3.5 cm^3. The uniform cross-section area was then obtained for each sample cell with an uncertainty of 0.001 cm^2, which was used to calculate H_i in eq 1. The quasi-pure component was prepared by mixing the proper amounts of *n*-decane and *n*-undecane in a flask to form a binary solution (quasi-pure component A) with the desired mass fraction w. A series of samples with various overall compositions of water, *tert*-butanol, and quasi-pure A were prepared by weighing water, *tert*-butanol, and A into the sample cells. The heights of the three coexisting phases for each of samples were measured by a cathetometer with a precision of ± 0.001 cm after phase equilibrium was reached at various temperatures. The total height of three phases was about 4 cm. The precision of the temperature measurement and the temperature stability in the water bath were about ± 0.002 K. The phase heights measured for (10 to 20) samples with various overall compositions at constant w were fitted to eq 1 to obtain φ_i^{α}, φ_i^{β}, and φ_i^{γ} for each temperature. The uncertainty in the determination of the volume fraction for each phase was estimated to be about ± 0.005.

Results and Discussion

With the value of w being fixed at 0.000, 0.092, 0.185, 0.281, 0.379, 0.416, and 0.477, seven quasi-pure components were made separately. Various quasi-ternary solutions of water + *tert*-butanol + A with different compositions for each of quasi-pure components were prepared. The heights of three coexisting phases were measured in the three-phase regions. The volume fractions for various temperatures then were obtained by fitting the heights to eq 1. Most of the sums of three volume fractions in each of the three phases were 1.000 ± 0.001; however, the differences from 1 for a few sums in α and γ phases were found to be ± 0.005 to ± 0.012, which supports the estimated precision of ± 0.005 for the volume fraction determined in this work. The volume fractions of *n*-decane and *n*-undecane then were calculated from the values of volume fraction φ_A of A and w under the assumption of the quasi-ternary system. The results are listed in Table 2.

To test the hypothesis of the quasi-ternary solutions, eq 1 was used to fit part of the experimental data for components *n*-decane and *n*-undecane separately to obtain the volume fractions of *n*-decane and *n*-undecane in each phase at certain temperatures. It has been found that the ratios of these two volume fractions and therefore the ratios of the mass fractions of *n*-decane and *n*-undecane in the three phases at each of the temperatures are identical within the experimental uncertainties. This is evidence that the hypothesis of the quasi-ternary solutions is valid.

The volume fractions listed in Table 2 may be converted to the mole fractions of components for the coexisting phases by the following equations:

$$x_1 = \frac{M_A M_2 \rho_1 \varphi_1}{M_1 M_2 \rho_A \varphi_A + M_A M_2 \rho_1 \varphi_1 + M_1 M_A \rho_2 \varphi_2} \qquad (3\text{-}1)$$

$$x_2 = \frac{M_1 M_A \rho_2 \varphi_2}{M_1 M_2 \rho_A \varphi_A + M_A M_2 \rho_1 \varphi_1 + M_1 M_A \rho_2 \varphi_2} \qquad (3\text{-}2)$$

$$x_A = \frac{M_1 M_2 \rho_A \varphi_A}{M_1 M_2 \rho_A \varphi_A + M_A M_2 \rho_1 \varphi_1 + M_1 M_A \rho_2 \varphi_2} \qquad (3\text{-}3)$$

Table 2. Volume Fractions of the Coexisting Three Phases at Different Temperatures with Different Values of *w* for the System Water (1) + *tert*-Butanol (2) + Decane (3) + Undecane(4)

t	α (upper phase)					β (middle phase)					γ (lower phase)				
°C	ϕ_1	ϕ_2	ϕ_3	ϕ_4	$\Sigma\phi_{i\alpha}$	ϕ_1	ϕ_2	ϕ_3	ϕ_4	$\Sigma\phi_{i\beta}$	ϕ_1	ϕ_2	ϕ_3	ϕ_4	$\Sigma\phi_{i\gamma}$
								w = 0.000							
54.888	0.126	0.510	0.000	0.364	1.000	0.303	0.613	0.000	0.084	1.000	0.418	0.550	0.000	0.032	1.000
54.966	0.104	0.527	0.000	0.369	1.000	0.319	0.605	0.000	0.076	1.000	0.440	0.546	0.000	0.013	0.999
55.042	0.117	0.522	0.000	0.360	0.999	0.286	0.618	0.000	0.097	1.001	0.457	0.535	0.000	0.007	0.999
55.126	0.124	0.526	0.000	0.349	0.999	0.283	0.617	0.000	0.100	1.000	0.463	0.533	0.000	0.004	1.000
55.210	0.118	0.537	0.000	0.345	1.000	0.265	0.621	0.000	0.114	1.000	0.480	0.515	0.000	0.004	0.999
55.283	0.111	0.545	0.000	0.343	0.999	0.266	0.620	0.000	0.114	1.000	0.449	0.540	0.000	0.011	1.000
55.366	0.117	0.540	0.000	0.335	0.992	0.248	0.621	0.000	0.130	0.999	0.495	0.513	0.000	0.000	1.008
55.440	0.116	0.552	0.000	0.327	0.995	0.243	0.623	0.000	0.133	0.999	0.507	0.499	0.000	0.000	1.006
55.517	0.132	0.551	0.000	0.308	0.991	0.228	0.618	0.000	0.152	0.998	0.506	0.506	0.000	0.000	1.012
								w = 0.092							
53.606	0.106	0.539	0.033	0.323	1.001	0.321	0.595	0.008	0.076	1.000	0.405	0.546	0.005	0.044	1.000
53.661	0.107	0.541	0.033	0.318	0.999	0.305	0.603	0.009	0.083	1.000	0.423	0.538	0.004	0.035	1.000
53.717	0.105	0.545	0.033	0.316	0.999	0.292	0.608	0.009	0.091	1.000	0.44	0.528	0.003	0.030	1.001
53.786	0.119	0.542	0.032	0.307	1.000	0.284	0.613	0.010	0.093	1.000	0.434	0.530	0.003	0.032	0.999
53.844	0.112	0.551	0.031	0.307	1.001	0.273	0.614	0.011	0.102	1.000	0.454	0.517	0.003	0.027	1.001
53.902	0.115	0.553	0.031	0.302	1.001	0.262	0.616	0.011	0.112	1.001	0.462	0.511	0.003	0.024	1.000
53.970	0.116	0.56	0.030	0.294	1.000	0.254	0.617	0.012	0.116	0.999	0.472	0.504	0.002	0.022	1.000
54.026	0.118	0.562	0.030	0.290	1.000	0.249	0.618	0.012	0.121	1.000	0.474	0.502	0.002	0.021	0.999
54.141	0.129	0.569	0.028	0.274	1.000	0.233	0.618	0.014	0.135	1.000	0.482	0.497	0.002	0.019	1.000
54.201	0.141	0.580	0.026	0.254	1.001	0.23	0.620	0.014	0.136	1.000	0.498	0.488	0.001	0.012	0.999
54.260	0.146	0.590	0.025	0.240	1.001	0.216	0.620	0.015	0.150	1.001	0.511	0.477	0.001	0.011	1.000
								w = 0.185							
52.815	0.170	0.594	0.044	0.192	1.000	0.216	0.617	0.031	0.136	1.000	0.452	0.490	0.011	0.047	1.000
52.736	0.149	0.582	0.050	0.219	1.000	0.228	0.618	0.029	0.125	1.000	0.465	0.501	0.006	0.028	1.000
52.669	0.136	0.573	0.054	0.237	1.000	0.240	0.618	0.027	0.115	1.000	0.458	0.511	0.006	0.025	1.000
52.596	0.168	0.540	0.056	0.245	1.009	0.251	0.618	0.025	0.106	1.000	0.419	0.542	0.007	0.032	1.000
52.526	0.132	0.559	0.058	0.251	1.000	0.264	0.616	0.022	0.098	1.000	0.439	0.525	0.007	0.029	1.000
52.452	0.136	0.554	0.058	0.253	1.001	0.276	0.613	0.021	0.089	0.999	0.423	0.533	0.008	0.036	1.000
52.387	0.124	0.551	0.061	0.2650	1.001	0.293	0.609	0.018	0.080	1.000	0.419	0.541	0.007	0.032	0.999
52.315	0.126	0.547	0.061	0.266	1.000	0.307	0.603	0.017	0.073	1.000	0.397	0.552	0.010	0.041	1.000
								w = 0.281							
51.022	0.106	0.569	0.092	0.233	1.000	0.314	0.595	0.026	0.064	0.999	0.402	0.551	0.014	0.034	1.001
51.070	0.125	0.561	0.089	0.225	1.000	0.285	0.607	0.030	0.077	0.999	0.421	0.545	0.011	0.027	1.003
51.124	0.125	0.564	0.088	0.223	1.000	0.275	0.610	0.033	0.082	1.000	0.427	0.539	0.010	0.024	1.000
51.175	0.134	0.563	0.086	0.216	0.999	0.262	0.613	0.035	0.090	1.000	0.426	0.538	0.010	0.025	0.999
51.230	0.140	0.568	0.083	0.208	0.999	0.252	0.615	0.038	0.100	1.001	0.437	0.530	0.010	0.023	0.999
51.292	0.147	0.574	0.079	0.200	1.000	0.237	0.616	0.042	0.105	1.000	0.447	0.523	0.009	0.021	1.000
51.337	0.140	0.576	0.081	0.203	1.000	0.234	0.616	0.043	0.108	1.001	0.458	0.522	0.006	0.015	1.001
51.397	0.153	0.582	0.075	0.189	0.999	0.22	0.615	0.047	0.118	1.000	0.456	0.516	0.008	0.021	1.001
								w = 0.379							
49.666	0.124	0.574	0.115	0.185	0.998	0.284	0.607	0.042	0.067	1.000	0.408	0.550	0.017	0.027	1.002
49.695	0.132	0.572	0.112	0.182	0.998	0.278	0.609	0.044	0.070	1.001	0.405	0.552	0.018	0.028	1.003
49.719	0.134	0.574	0.110	0.179	0.997	0.270	0.610	0.046	0.074	1.000	0.416	0.543	0.016	0.027	1.002
49.742	0.137	0.576	0.109	0.176	0.998	0.264	0.612	0.048	0.077	1.001	0.425	0.536	0.015	0.025	1.001
49.767	0.140	0.577	0.108	0.175	1.000	0.253	0.614	0.051	0.082	1.000	0.424	0.534	0.016	0.025	0.999
49.797	0.144	0.577	0.107	0.172	1.000	0.247	0.614	0.053	0.086	1.000	0.426	0.535	0.016	0.026	1.003
49.819	0.145	0.579	0.106	0.171	1.000	0.241	0.614	0.055	0.089	0.999	0.428	0.536	0.015	0.023	1.002
49.848	0.146	0.581	0.104	0.168	0.999	0.234	0.615	0.057	0.092	0.998	0.430	0.538	0.013	0.022	1.003
49.867	0.150	0.587	0.101	0.162	1.000	0.226	0.613	0.061	0.099	0.999	0.432	0.534	0.014	0.022	1.002
49.896	0.160	0.588	0.095	0.154	0.997	0.221	0.613	0.063	0.102	0.999	0.431	0.533	0.014	0.022	1.000
								w = 0.416							
49.119	0.129	0.572	0.125	0.174	1.000	0.294	0.602	0.043	0.060	0.999	0.377	0.561	0.026	0.036	1.000
49.142	0.137	0.569	0.123	0.171	1.000	0.291	0.604	0.044	0.061	1.000	0.374	0.564	0.026	0.036	1.000
49.187	0.151	0.571	0.117	0.161	1.000	0.274	0.607	0.050	0.069	1.000	0.381	0.560	0.025	0.034	1.000
49.214	0.151	0.573	0.116	0.161	1.001	0.270	0.61	0.050	0.070	1.000	0.385	0.553	0.026	0.035	0.999
49.238	0.160	0.576	0.111	0.153	1.000	0.258	0.611	0.055	0.076	1.000	0.383	0.552	0.027	0.037	0.999
49.264	0.141	0.599	0.109	0.150	0.999	0.261	0.61	0.055	0.075	1.001	0.392	0.540	0.029	0.039	1.000
49.290	0.171	0.584	0.103	0.142	0.999	0.263	0.604	0.056	0.078	1.001	0.381	0.549	0.029	0.041	1.000
49.338	0.174	0.588	0.096	0.132	0.990	0.246	0.612	0.060	0.082	1.000	0.381	0.543	0.032	0.044	1.000
49.362	0.181	0.597	0.093	0.128	0.999	0.242	0.611	0.062	0.086	1.001	0.385	0.534	0.034	0.048	1.001
49.387	0.223	0.563	0.090	0.124	1.000	0.247	0.61	0.064	0.089	1.010	0.342	0.576	0.035	0.048	1.001
								w = 0.477							
48.157	0.142	0.566	0.132	0.160	1.000	0.294	0.606	0.046	0.057	1.003	0.376	0.572	0.025	0.030	1.003
48.178	0.141	0.580	0.126	0.154	1.001	0.280	0.607	0.051	0.062	1.000	0.384	0.566	0.023	0.028	1.001
48.202	0.149	0.581	0.122	0.148	1.000	0.269	0.610	0.055	0.066	1.000	0.384	0.562	0.025	0.030	1.001
48.230	0.154	0.581	0.119	0.146	1.000	0.260	0.612	0.058	0.070	1.000	0.380	0.562	0.026	0.032	1.000
48.251	0.164	0.585	0.113	0.138	1.000	0.251	0.613	0.061	0.075	1.000	0.381	0.555	0.029	0.036	1.001
48.272	0.157	0.590	0.114	0.139	1.000	0.247	0.614	0.063	0.076	1.000	0.392	0.548	0.027	0.034	1.001
48.299	0.158	0.596	0.111	0.135	1.000	0.240	0.614	0.066	0.080	1.000	0.398	0.540	0.028	0.034	1.000

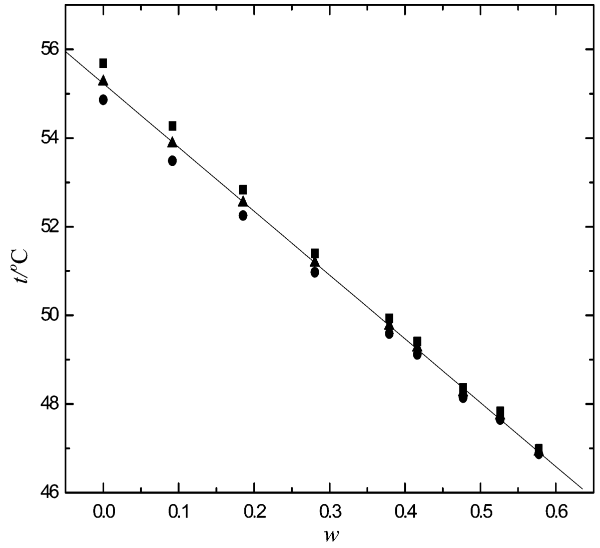

Figure 2. Plots of the upper critical end temperature t_u (■), lower critical end temperature t_l (●), and middle temperature t_m (▲) vs w for the system water (1) + *tert*-butanol (2) + *n*-decane (3) + *n*-undecane (4). The straight line is the least-squares fit of t_m.

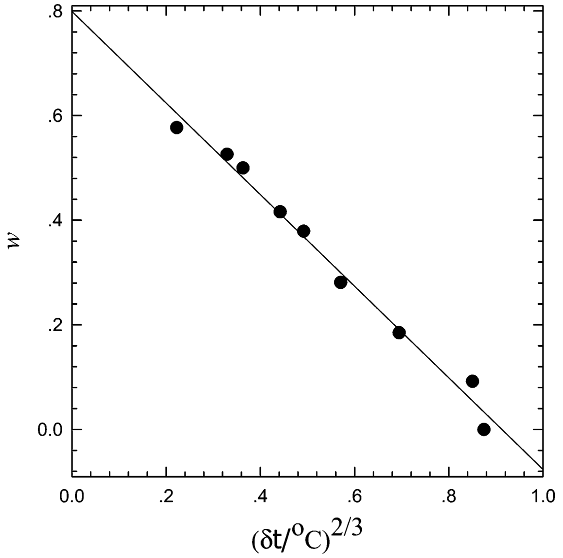

Figure 3. Plot of w vs $(\delta t\ /°C)^{2/3}$ for the system water (1) + *tert*-butanol (2) + *n*-decane (3) + *n*-undecane (4). The straight line is the least-squares fit.

where M_1, M_2, and M_A are the molar masses of water, *tert*-butanol, and quasi-pure component A, respectively. The mole fractions of *n*-decane and *n*-undecane (x_3 and x_4) were then calculated from the values of x_A and w.

The three-phase equilibria may be illustrated by an "S"-type curve in a plot of temperature against volume fraction. However, only for a sample with a proper overall composition does an entire S-type curve appear, thereby allowing the upper critical end temperature t_u and lower critical end temperature t_l to be obtained by changing the temperature.

We carefully searched for the proper composition using the method described by Shen et al.[14] and determined the t_u, t_l, mean temperature t_m $\{t_m = (t_u + t_l)/2\}$, and critical compositions at the critical end-points for each value of w. Figure 2 shows a plot of t_u, t_l, and t_m against w. The three temperatures approached to one point called the tricritical point, at which the difference δt of the upper critical temperature and the lower critical temperature approaches to zero, the interfaces between the upper

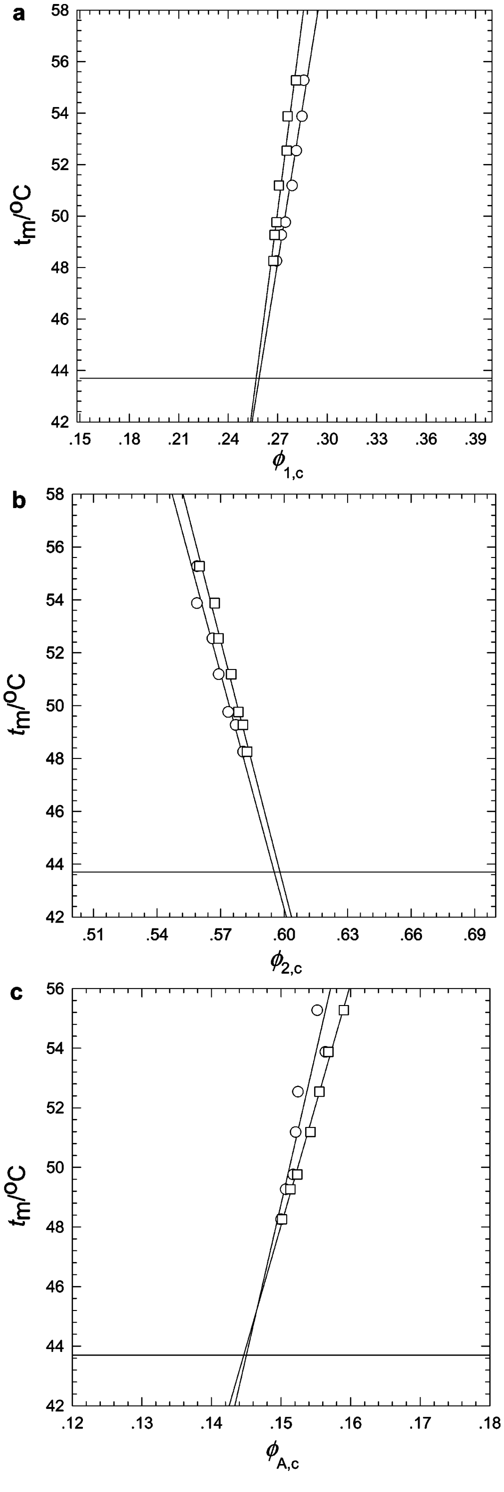

Figure 4. (a) Temperature dependences of the volume fractions $\varphi_{1,c}$ of the centroids of the critical end-point tie lines for the system water (1) + *tert*-butanol (2) + *n*-decane (3) + *n*-undecane (4): ○, centroids of the lower critical end-point tie lines; □, centroids of the upper critical end-point tie lines. The straight lines are the least-squares fits. (b) Temperature dependence of the volume fraction $\varphi_{2,c}$ of the centroids of the critical end-point tie lines for the system water (1) + *tert*-butanol (2) + *n*-decane (3) + *n*-undecane (4): ○, centroids of the lower critical end-point tie lines; □, centroids of the upper critical end-point tie lines; the straight lines are the least-squares fits. (c) Temperature dependences of the volume fractions $\varphi_{A,c}$ of the centroids of the critical end-point tie lines for the system water (1) + *tert*-butanol (2) + *n*-decane (3) + *n*-undecane (4): ○, centroids of the lower critical end-point tie lines; □, centroids of the upper critical end-point tielines. The straight lines are the least-squares fits. The mixture of *n*-decane and *n*-undecane is taken as "pure" component A. The straight lines are the least-squares fits.

and middle phases and the middle and lower phases disappear simultaneously, and the three phases become identical.

A plot of t_m against w yielded a straight line shown in Figure 2, which demonstrates that w is a good variable for controlling the approach to the tricritical point. According to the classical tricritical theory, $(\delta t)^{2/3}$ is proportional to t_m; therefore, plotting $(\delta t)^{2/3}$ against w should also yield a straight line. Figure 3 shows such a plot, which indicates that the classical tricritical theory is valid for our systems. From Figure 3, we obtained the tricritical value of w at $\delta t = 0$, which is 0.80 ± 0.02. The value of the tricritcal temperature was then obtained by extrapolating the straight line in Figure 2 to the tricritical value 0.80 of w, which is (43.7 ± 0.3) °C.

According to Bocko's definition of the centroid compositions of the critical end-point tie lines,[15] we defined the centroid volume fraction as

$$\phi_{i,\mathrm{c}} = \left(\frac{2}{3}\right)\phi_{i,\mathrm{ce}} + \left(\frac{1}{3}\right)\phi_{i,\mathrm{sp}} \tag{4}$$

with $\phi_{i,\mathrm{ce}}$ and $\phi_{i,\mathrm{sp}}$ being the volume fractions of the ith component in the critical phase and in the spectator phase of the critical end-point tie lines, respectively. The values of $\phi_{i,\mathrm{ce}}$ were obtained by extrapolating the average volume fractions of two coexisting phases close to the critical end-points, whereas the values of $\phi_{i,\mathrm{sp}}$ were obtained by extrapolating the volume fractions of spectator phases to the lower or upper critical temperatures. The plots of mean temperature t_m against $\phi_{i,\mathrm{c}}$ for $i = 1$ (water), 2 (*tert*-butanol) and A (quasi-pure component) are shown in Figure 4a−c, from which it can be clearly seen that the values of $\phi_{i,\mathrm{c}}$ and t_m have linear dependences. The two lines in each panel represent that the centroids of the upper critical end-point and lower critical end-point tie lines should intersect at the tricritical temperature of 43.7 °C. At this temperature, the volume fractions from the two lines for all three components are consistent within 0.003. The averages of these volume fractions are taken as the tricritical values which were 0.146 ± 0.004, 0.259 ± 0.007, and 0.597 ± 0.008 for A, water, and *tert*-butanol, respectively. The sum of these three values of tricritical volume fractions was 1.002, which was consistent with the value of 1 within the experimental uncertainties. With the tricritical values of $w = 0.80$ at $t_c = 43.7$ °C, the tricritical volume fractions for *n*-decane and *n*-undecane were calculated to be 0.117 ± 0.004 and 0.029 ± 0.003, respectively.

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