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Critical Behavior of Binary Mixtures of Dimethyl Carbonate + Nonane and Dimethyl Carbonate + Dodecane: Measurements of the Coexistence Curves

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ABSTRACT: The liquid−liquid coexistence for dimethyl carbonate + nonane and dimethyl carbonate + dodecane have been measured. The critical amplitudes and the critical exponents are obtained from the measured experimental data. The critical exponents corresponding to the coexistence curve β are consistent with the 3D-Ising values. The liquid−liquid coexistence results have also been analyzed to determine Wegner-correction terms when β and Δ are fixed at their theoretical values and to examine the diameters and the asymmetry of the coexistence curves.

INTRODUCTION

The most attractive character of critical behavior is the universality which indicates that sufficiently close to the critical point, systems of different physical natures may exhibit similar critical behavior due to the large critical fluctuations and can be grouped into several universal classes. Fluids and fluid mixtures belong to the 3D-Ising universality class, thus the difference of the general density variable of two coexisting phases $\Delta\rho$ can be described by universal power-law of the reduced temperature τ near the critical point ($\tau = |(T - T_c)/T_c|$, T_c is the critical temperature)

$$\Delta\rho = |\rho_2 - \rho_1| = B\tau^{\beta} \qquad (1)$$

where ρ is the general density variable, such as refractive index, mole fraction and volume fraction, the subscripts 1 and 2 represent upper and lower phases, and B is the critical amplitude. The value of critical exponent β is 0.326 for 3D-Ising universality class; while it is 0.5 from the classical mean-field theory.

The asymmetric criticality of the coexistence curve has been paid much attention by researches recently. A few years ago, Fisher and co-workers[1,2] proposed a general formulation of complete scaling for one-component fluids, which showed that the three scaling fields should be the linear mix of all physical fields: not only the chemical potential and the temperature but also the pressure. It was concluded that the strong singularity of the diameter of the coexistence densities was a consequence of the complete scaling. Recently, Anisimov et al.[3−5] have extended the complete scaling to binary mixtures for both incompressible and weakly compressible liquid mixtures and tested the complete scaling by analyzing experimental coexisting-curve data for a series of binary liquid mixtures.

As a part of our continuous studies on the critical behavior of the binary mixtures of dimethyl carbonate + alkanes,[6,7] in this paper, we report the measurements of the liquid−liquid coexistence of dimethyl carbonate + nonane and dimethyl carbonate + dodecane. The results are analyzed to obtain the critical exponents and critical amplitudes, and to examine the Wegner correction terms. Further more, the diameter and the asymmetry of the coexistence curve are also discussed according to the complete scaling theory proposed by Anisimov et al.[3−5]

EXPERIMENTAL SECTION

Chemicals. Dimethyl carbonate (0.99 mass fraction) was purchased from ABCR GmbH & Co. KG. Nonane (0.99 mass fraction) and dodecane (0.99 mass fraction) were purchased from Alfa Aesar. They were all dried and stored over 0.4 nm molecular sieves. The purities after drying were reconfirmed by gas chromatography: the mass fractions were 99.4 %, 99.3 %, and 99.0 % for dimethyl carbonate, nonane, and dodecane, respectively. The refractive index of the pure components at 298.15 K and their comparison with literatures[8,9] are listed in Table 1.

Apparatus and Experimental Procedure. The apparatus and the experimental procedure for measurements of refractive index, and the techniques for determination of the critical composition x_c and critical temperature T_c have been described in details previously.[6,7,10,11] The temperature of the water bath which was used for determination of the critical compositions, the critical temperatures and the coexistence curves was controlled to within ± 0.002 K. The temperature in the bath was measured with a platinum resistance thermometer and a Keithley 2700 digital multimeter with an uncertainty of ± 0.001 K.

Mixtures of (dimethyl carbonate + nonane) and (dimethyl carbonate + dodecane) were prepared in glass tubes provided with Ace-thread connections, and the tubes were placed into the water bath. The critical composition was approached by adjusting the proportion of the two components to achieve "equal volume" of the two phases at the phase-separation point.[10] The uncertainty in determination of x_c was about ± 0.001.

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Table 1. Comparison of Refractive Index n at Wavelength λ = 589.3 nm with Literature Data for Pure Components at 298.15 K

	n	
components	this study	ref
dimethyl carbonate	1.3663	1.3665[8]
nonane	1.4035	1.4032[9]
dodecane	1.4195	1.4196[8]

Table 2. Critical Compositions and Critical Temperatures for $\{x$ Dimethyl Carbonate + $(1 - x)$ Nonane$\}$ and $\{x$ Dimethyl Carbonate + $(1 - x)$ Dodecane$\}$

	T_c/K		x_c	
system	this study	ref	this study	ref
nonane	281.08 ± 0.1	281.670[12] 297.82[8]	0.663 ± 0.001	
dodecane	298.07 ± 0.1	298.62 ± 0.01[13]	0.739 ± 0.001	0.7379[8]

A mixture with the critical composition was prepared in a rectangular fluorimeter cell provided also with an Ace-thread connection and was placed in the water bath for measurements of the refractive indexes of two coexisting phases. The phase-separation temperature was carefully determined with an uncertainty of ± 0.002 K and taken as the critical temperature. It was observed that the mixtures nominally of the same composition had different critical temperatures, differing by a few hundred mK. This might have been a result of uncontrollable moisture or other impurities introduced during the preparation of the mixtures. However, it did not affect the final results, because only one sample was used throughout the determination of the whole coexistence curve and only temperature difference $(T_c - T)$ was important to obtain the critical properties. The uncertainty in measurement of $(T_c - T)$ was about ± 0.003 K.

The refractive indexes were measured according to the method of minimum deviation.[11] A He−Ne laser with λ = 632.8 nm was used as the light source. The uncertainty in measurement of refractive index in each coexisting phase was ± 0.0001.

■ RESULTS AND DISCUSSION

The critical mole fractions and the critical temperatures for $\{x$ dimethyl carbonate + $(1 - x)$ nonane$\}$ and $\{x$ dimethyl carbonate + $(1 - x)$ dodecane$\}$ were determined and are listed in Table 2, where x and x_c are the mole fraction of dimethyl carbonate and its critical value, respectively. The values of critical mole fractions and the critical temperatures reported in the reference[8,12,13] are also listed in Table 2 for comparison. The differences are as large as 0.59 K for the critical temperature, and 0.001 for the critical mole fraction, respectively. It is not surprising because it was frequently observed that the critical temperatures differed by as much as a few hundred mK, while the critical composition kept almost unchanged for the solutions prepared by the chemicals from the different sources.

The refractive indexes n were measured for each coexisting phase at various temperatures at wavelength λ = 632.8 nm. The results are listed in columns 2 and 3 of Table 3 for $\{x$ dimethyl carbonate + $(1 - x)$ nonane$\}$, and in columns 2 and 3 of Table 4 for $\{x$ dimethyl carbonate + $(1 - x)$ dodecane$\}$. They are also shown in Figures 1a and 2a, as the plots of temperature against refractive index, and denoted as the (T, n) coexistence curve.

Table 3. Refractive Indexes n, Mole Fraction of Dimethyl Carbonate x and Volume Fraction of Dimethyl Carbonate ϕ of the Coexisting Phases at Various Temperatures T for $\{x$ Dimethyl Carbonate + $(1 - x)$ Nonane$\}$[a]

T/K	n_1	n_2	x_1	x_2	ϕ_1	ϕ_2
281.071	1.3895	1.3874	0.631	0.685	0.447	0.507
281.068	1.3896	1.3873	0.629	0.688	0.445	0.511
281.063	1.3898	1.3871	0.623	0.693	0.439	0.516
281.059	1.3898	1.3870	0.623	0.695	0.439	0.519
281.050	1.3901	1.3868	0.615	0.700	0.431	0.525
281.039	1.3903	1.3867	0.610	0.703	0.425	0.528
281.026	1.3904	1.3865	0.608	0.708	0.423	0.534
281.010	1.3906	1.3863	0.602	0.713	0.417	0.540
280.989	1.3909	1.3860	0.594	0.721	0.409	0.550
280.965	1.3911	1.3859	0.589	0.723	0.404	0.553
280.937	1.3912	1.3858	0.587	0.726	0.402	0.556
280.902	1.3915	1.3856	0.579	0.731	0.394	0.563
280.859	1.3917	1.3853	0.574	0.739	0.389	0.573
280.810	1.3920	1.3852	0.566	0.742	0.382	0.576
280.753	1.3922	1.3850	0.561	0.747	0.377	0.583
280.683	1.3925	1.3848	0.553	0.752	0.369	0.589
280.597	1.3929	1.3846	0.543	0.758	0.360	0.597
280.512	1.3931	1.3844	0.538	0.763	0.355	0.604
280.413	1.3934	1.3842	0.530	0.769	0.348	0.612
280.259	1.3938	1.3839	0.521	0.778	0.340	0.624
280.094	1.3941	1.3838	0.514	0.782	0.334	0.629
279.897	1.3946	1.3835	0.502	0.790	0.323	0.640
279.541	1.3953	1.3832	0.485	0.801	0.308	0.656
279.095	1.3961	1.3830	0.467	0.810	0.293	0.669
278.545	1.3969	1.3827	0.450	0.822	0.279	0.686
277.915	1.3978	1.3826	0.431	0.831	0.264	0.699
277.239	1.3986	1.3825	0.416	0.840	0.252	0.713
276.305	1.3997	1.3824	0.394	0.851	0.235	0.730

[a] Subscripts 1 and 2 relate to upper and lower phases.

It has been shown that the refractive index of the binary mixtures of polar solvent + alkane may be expressed as a linear function of temperature in a certain temperature range by using the equations[14]

$$n(T, x) = n(T^0, x) + R(x)(T - T^0) \tag{2a}$$

$$R(x) = x \cdot R_1 + (1 - x)R_2 \tag{2b}$$

where $R(x)$ is the derivative of n with respect to T for a particular composition x, R_1 and R_2 are the values of $R(x)$ for x = 1 and 0, respectively. The values of n for pure dimethyl carbonate, nonane and dodecane at different temperatures, and for binary mixtures $\{x$ dimethyl carbonate + $(1 - x)$ nonane$\}$ at 281.69 K and $\{x$ dimethyl carbonate + $(1 - x)$ dodecane$\}$ at 299.73 K with various compositions were measured and are listed in Tables 5 and 6, respectively. Fitting eq 2a to the values listed in Table 5 gives $R_1 = -0.00047\ \mathrm{K}^{-1}$ for dimethyl carbonate; $R_2 = -0.00048\ \mathrm{K}^{-1}$ for nonane, and $R_2 = -0.00043\ \mathrm{K}^{-1}$ for dodecane. Then $R(x)$ and $n(T^0, x)$ for $\{x$ dimethyl carbonate + $(1 - x)$ nonane$\}$ and $\{x$ dimethyl carbonate + $(1 - x)$ dodecane$\}$ at various compositions

Table 4. Refractive Indexes n, Mole Fraction of Dimethyl Carbonate x and Volume Fraction of Dimethyl Carbonate ϕ of the Coexisting Phases at Various Temperatures T for $\{x$ Dimethyl Carbonate $+ (1 - x)$ Dodecane$\}$[a]

T/K	n_1	n_2	x_1	x_2	ϕ_1	ϕ_2
298.064	1.3883	1.3857	0.713	0.754	0.480	0.533
298.061	1.3886	1.3855	0.709	0.757	0.475	0.537
298.057	1.3888	1.3852	0.705	0.761	0.471	0.542
298.049	1.3891	1.3850	0.700	0.764	0.465	0.546
298.042	1.3893	1.3847	0.697	0.769	0.461	0.553
298.035	1.3896	1.3845	0.692	0.772	0.455	0.557
298.022	1.3898	1.3842	0.689	0.776	0.452	0.563
298.007	1.3900	1.3840	0.686	0.779	0.448	0.567
297.985	1.3904	1.3837	0.679	0.784	0.440	0.574
297.959	1.3907	1.3834	0.674	0.788	0.435	0.580
297.934	1.3910	1.3832	0.669	0.791	0.429	0.585
297.906	1.3913	1.3830	0.664	0.794	0.424	0.589
297.874	1.3916	1.3827	0.659	0.799	0.418	0.597
297.834	1.3919	1.3825	0.654	0.802	0.413	0.601
297.783	1.3922	1.3822	0.650	0.806	0.409	0.607
297.723	1.3926	1.3819	0.643	0.811	0.401	0.615
297.663	1.3929	1.3816	0.638	0.815	0.396	0.621
297.592	1.3932	1.3814	0.633	0.818	0.391	0.626
297.509	1.3936	1.3811	0.626	0.823	0.384	0.634
297.416	1.3940	1.3808	0.620	0.827	0.378	0.640
297.262	1.3945	1.3805	0.612	0.832	0.370	0.648
297.081	1.3951	1.3801	0.602	0.839	0.360	0.660
296.879	1.3957	1.3798	0.592	0.844	0.350	0.668
296.579	1.3964	1.3793	0.581	0.852	0.340	0.682
296.152	1.3974	1.3789	0.565	0.859	0.326	0.694
295.605	1.3986	1.3784	0.546	0.869	0.309	0.712
294.958	1.3997	1.3780	0.529	0.877	0.295	0.726
294.173	1.4009	1.3778	0.511	0.884	0.280	0.739
293.288	1.4022	1.3775	0.491	0.893	0.264	0.756
292.263	1.4035	1.3773	0.472	0.901	0.250	0.772
291.141	1.4049	1.3772	0.451	0.908	0.234	0.786
289.791	1.4064	1.3771	0.430	0.916	0.219	0.802
288.245	1.4080	1.3772	0.408	0.923	0.204	0.817

[a] Subscripts 1 and 2 relate to upper and lower phases.

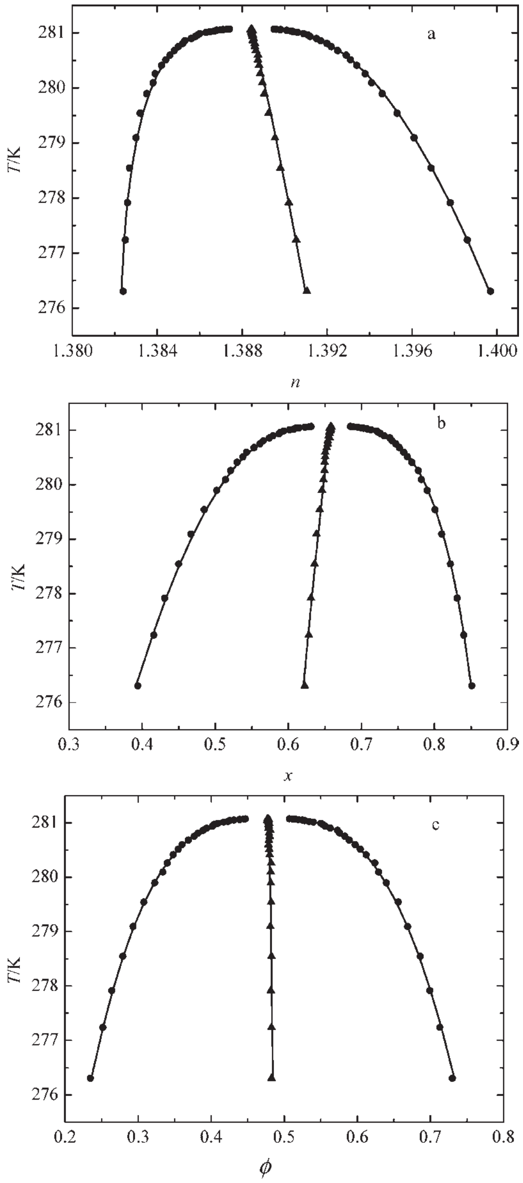

Figure 1. Coexistence curves of (a) temperature against refractive index (T, n), (b) temperature against mole fraction (T, x) and (c) temperature against volume fraction (T, ϕ) for $\{x$ dimethyl carbonate $+ (1 - x)$ nonane$\}$. ▲, experimental values of diameter ρ_d of the coexisting phases; ●, experimental values of general density variables ρ of the coexisting phases; —, general density variables ρ(calc.) and diameters ρ_d(calc.) of the coexisting phases calculated from eqs 7 and 8 with coefficients listed in Tables 8 and 9.

and at their middle temperatures $T^0 = (278.692$ and $293.157)$ K of the coexistence curves were calculated from the data listed in Table 6 by using eqs 2a and 2b; finally $n(T^0, x)$ were fitted into the polynomial form to obtain

$$n(T^0 = 278.692K, x) = 1.4109 - 0.0311x - 0.0121x^2 + 0.0624x^3 - 0.1010x^4 + 0.0451x^5 \tag{3a}$$

for $\{x$ dimethyl carbonate $+ (1 - x)$ nonane$\}$ and

$$n(T^0 = 293.157K, x) = 1.4202 - 0.0315x - 0.0068x^2 - 0.0002x^3 - 0.0141x^4 \tag{3b}$$

for $\{x$ dimethyl carbonate $+ (1 - x)$ dodecane$\}$ with standard deviations of less than ±0.0001. The refractive indexes measured for the coexisting phases at various temperatures were converted to the mole fractions by simultaneously solving eqs 2a, 2b, and 3a for $\{x$ dimethyl carbonate $+ (1 - x)$ nonane$\}$ or eqs 2a, 2b, and 3b for $\{x$ dimethyl carbonate $+ (1 - x)$ dodecane$\}$ with the Newton's iteration method.

In order to convert the (T, x) curve to the coexistence curve of temperature against volume fraction (T, ϕ), the volume fraction ϕ of dimethyl carbonate was calculated from the mole fraction by

$$1/\phi = (1 - K) + K/x \tag{4a}$$

$$K = (d_1M_2/d_2M_1) \tag{4b}$$

where d is mass density, M is the molar mass and subscripts 1 and 2 relate to dimethyl carbonate and alkane, respectively. The values of d_1 and d_2 were obtained from Lange's Handbook of

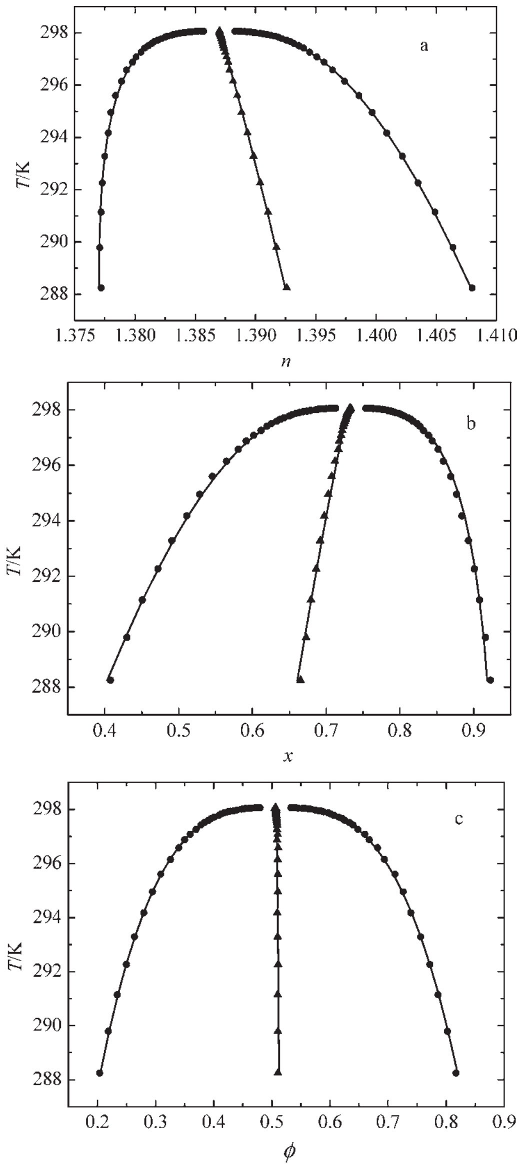

Figure 2. Coexistence curves of (a) temperature against refractive index (T, n), (b) temperature against mole fraction (T, x) and (c) temperature against volume fraction (T, ϕ) for $\{x$ dimethyl carbonate + $(1 - x)$ dodecane$\}$. ▲, experimental values of diameter ρ_d of the coexisting phases; ●, experimental values of general density variables ρ of the coexisting phases; —, general density variables ρ(calc.) and diameters ρ_d(calc.) of the coexisting phases calculated from eqs 7 and 8 with coefficients listed in Tables 8 and 9.

Table 5. Refractive Indexes n at Wavelength λ = 632.8 nm for Pure Dimethyl Carbonate, Nonane, and Dodecane at Various Temperatures T

T/K	n	T/K	n	T/K	n	T/K	n
			Dimethyl Carbonate				
277.784	1.3747	280.250	1.3735	294.274	1.3671	297.376	1.3656
278.133	1.3745	280.744	1.3733	295.295	1.3666	298.398	1.3651
279.182	1.3740	293.189	1.3676	296.338	1.3661	299.476	1.3647
			Nonane				
277.149	1.4116	279.204	1.4106	280.280	1.4101		
278.188	1.4111	279.711	1.4104				
			Dodecane				
293.278	1.4203	295.373	1.4194	297.583	1.4184	299.724	1.4175
294.331	1.4198	296.539	1.4189	298.651	1.4180		

Table 6. Refractive Indexes n at Wavelength λ = 632.8 nm for $\{x$ Dimethyl Carbonate + $(1 - x)$ Nonane$\}$ and $\{x$ Dimethyl Carbonate + $(1 - x)$ Dodecane$\}$ at the Temperatures (281.69 and 299.73) K, Respectively

x	n	x	n	x	n
		x Dimethyl Carbonate + $(1 - x)$ Nonane			
0.000	1.4095	0.405	1.3968	0.800	1.3822
0.105	1.4061	0.505	1.3936	0.888	1.3781
0.201	1.4031	0.596	1.3905	1.000	1.3728
0.305	1.3999	0.706	1.3863		
		x Dimethyl Carbonate + $(1 - x)$ Dodecane			
0.103	1.4140	0.409	1.4028	0.713	1.3875
0.204	1.4106	0.512	1.3983	0.791	1.3823
0.299	1.4071	0.611	1.3934	0.899	1.3739

Chemistry.[15] The values of x and ϕ of coexisting phases at various temperatures are listed in columns 4 to 7 of Tables 3 and 4, and are shown in b and c of Figures 1 and 2.

In the region sufficiently close to the critical temperature, the coexistence curve can be represented by eq 1. The differences of $(\rho_2 - \rho_1)$ of general density variables n, x, and ϕ of coexisting phases obtained in this work were fitted to eq 1, with all points equally weighted to obtain β and B. The results are listed in Table 7. The values of β are in very good agreement with that of other (polar liquid + alkane) systems we reported previously, and the theoretical prediction of 0.326.

With the critical exponents β and Δ to be fixed at the theoretical values (β = 0.326, Δ = 0.5), a least-squares program was used to fit the Wegner equation[16]

$$|\rho_2 - \rho_1| = B\tau^{\beta} + B_1 \cdot \tau^{\beta + \Delta} + ... \qquad (5)$$

to obtain the parameters B and B_1. The results are summarized in Table 8, which indicates that the contributions of the first term $B\tau^{\beta}$ in eq 5 are larger than 95 %.

It was known that the diameter ρ_d of a coexistence curve at least is the sum of the three terms proportional to $\tau^{1-\alpha}$, $\tau^{2\beta}$, and τ, where α characterizes the divergence of the heat capacity at constant volume for pure fluids as the critical point is approached. These terms were thought as a direct consequence of complete scaling,[3] while the presence of the term $\tau^{2\beta}$ was attributed to a wrong choice for the order parameters in the past.[17,18] It is almost impossible to simultaneously obtain the coefficients of the above three terms by fitting the experimental data of the coexistence curves to a corresponding equation, however the diameter ρ_d may be fitted to the form

$$\rho_d = \rho_c + D\tau^{z} \qquad (6)$$

with an apparent exponent Z being fixed at the values 1, $1 - \alpha = 0.89$, and 2β = 0.652 in separate fitting procedures. The results are compared in Table 9.

In Table 9, the experimental values of n_c were obtained by extrapolating refractive indexes against temperatures in the one-phase region to the critical temperature. The experimental values

Table 7. Values of Critical Amplitude B and Critical Exponent β for Coexistence Curves of (T, n), (T, x), and (T, ϕ) for $\{x$ Dimethyl Carbonate $+ (1 - x)$ Nonane$\}$ and $\{x$ Dimethyl Carbonate $+ (1 - x)$ Dodecane$\}$ in eq 1

	$T_c - T < 1$ K		$T_c - T < 10$ K	
order parameter	B	β	B	β
	x Dimethyl Carbonate $+ (1 - x)$ Nonane			
n	0.066 ± 0.001	0.327 ± 0.002	0.066 ± 0.001	0.326 ± 0.001
x	1.73 ± 0.03	0.328 ± 0.002	1.75 ± 0.02	0.330 ± 0.002
ϕ	1.89 ± 0.04	0.327 ± 0.002	1.89 ± 0.02	0.327 ± 0.001
	x Dimethyl Carbonate $+ (1 - x)$ Dodecane			
n	0.098 ± 0.001	0.329 ± 0.002	0.095 ± 0.001	0.325 ± 0.001
x	1.56 ± 0.02	0.331 ± 0.002	1.58 ± 0.01	0.332 ± 0.001
ϕ	1.95 ± 0.03	0.328 ± 0.002	1.89 ± 0.01	0.324 ± 0.001

Table 8. Fitting Parameters of eq 5 for Coexistence Curves of (T, n), (T, x), and (T, ϕ) for $\{x$ Dimethyl Carbonate $+ (1 - x)$ Nonane$\}$ and $\{x$ Dimethyl Carbonate $+ (1 - x)$ Dodecane$\}$

	x dimethyl carbonate $+ (1 - x)$ nonane		x dimethyl carbonate $+ (1 - x)$ dodecane	
order parameter	B	B_1	B	B_1
n	0.0657 ± 0.0001		0.0953 ± 0.0002	
	0.0660 ± 0.0002	-0.004 ± 0.003	0.0974 ± 0.0002	-0.02 ± 0.002
x	1.716 ± 0.003		1.541 ± 0.004	
	1.693 ± 0.006	0.29 ± 0.07	1.501 ± 0.003	0.36 ± 0.02
ϕ	1.881 ± 0.003		1.897 ± 0.004	
	1.889 ± 0.008	-0.10 ± 0.09	1.943 ± 0.004	-0.41 ± 0.03

of x_c and ϕ_c were determined by the technique "equal volume" and calculated by using eqs 4a and 4b.

The goodness of fit to eq 6 may be indicated by the reduced chi-squared value χ^2/N (N is the number of degree of freedom of the fitting),[19] which are also listed in Table 9. The uncertainties of optimal parameters reported in Table 9 include no systematic uncertainties contributed by converting n to x and x to ϕ. Such uncertainties in x and ϕ were estimated to be about ± 0.001 and ± 0.002, respectively. These uncertainties together with the uncertainty of ± 0.0001 in measurements of refractive index were used to estimate χ^2/N. The smaller the value of χ^2/N, the more significant the contribution of the term is. For a particular order parameter, if the value of χ^2/N for a fit with 2β is larger than that for a fit with $1 - \alpha$, the fit with 2β is worse than that with $1 - \alpha$, and the 2β term does less contribution to the diameter of coexistence curve. Thus the difference between the χ^2/N values of the fits with $1 - \alpha$ and 2β for a particular order parameter may indicate the so-called goodness of the parameter, the smaller the difference, the better the parameter is.

For both (x dimethyl carbonate $+ (1 - x)$ nonane) and (x dimethyl carbonate $+ (1 - x)$ dodecane), we found that the fits for order parameter ϕ have the similar reduced chi-squared value for all the three terms, while for the order parameter x, the value of fits with $1\text{-}\alpha$ was significantly larger than that with 2β, which indicates that the $\tau^{2\beta}$ term does more contribution to order parameter x than to ϕ. Moreover, the values of coefficient D are significant smaller for ϕ than that for the other two parameters, which is consistent with what the symmetry of coexistence curves show: the (T, ϕ) coexistence curves are significantly symmetric than that of (T, n) and (T, x). However, the significance of the three terms for the order parameter ϕ is comparable, which indicates that even for a "good order parameter", the contribution of 2β term could not be neglected comparing with the other two terms, which is consistent with the consequence of complete scaling.

Combination of eqs 5 and 6 yields

$$\rho_1 = \rho_c + D\tau^z - (1/2)B\tau^\beta - (1/2)B_1\tau^{\beta + \Delta} \tag{7}$$

$$\rho_2 = \rho_c + D\tau^z + (1/2)B\tau^\beta + (1/2)B_1\tau^{\beta + \Delta} \tag{8}$$

fixing Z, β, and Δ as 0.89, 0.326, and 0.5, respectively, for both $\{x$ dimethyl carbonate $+ (1 - x)$ nonane$\}$ and $\{x$ dimethyl carbonate $+ (1 - x)$ dodecane$\}$, and taking the values of D, ρ_c, B, and B_1 from Tables 8 and 9, the values of ρ_1, ρ_2, and ρ_d were calculated from eqs 7 and 8, which are shown as lines in Figures 1 and 2. The values from calculation are in good agreement with experimental results.

In terms of the theory proposed by Perez-Sanchez and coworkers recently[5] for the weakly compressible liquid mixtures, the diameter of the coexistence curve may be expressed by

$$\Delta x_d \equiv \frac{x_1 + x_2}{2} \approx x_c + \hat{D}_2^x|\tau|^{2\beta} + \hat{D}_1^x\left(\frac{\hat{A}_0^-}{1 - \alpha}|\tau|^{1-\alpha} + \hat{B}_{cr}|\tau|\right) \tag{9}$$

$$\Delta x_{cxc} \equiv \frac{|x_1 - x_2|}{2} \approx \hat{B}_0^x|\tau|^\beta(1 + \hat{B}_1^x|\tau|^\Delta + \hat{B}_2^x|\tau|^{2\beta}) \tag{10}$$

Table 9. Fitting Parameters of eq 6 and the Reduced Chi-squared Value χ^2/N in ρ_d for Diameters of Coexistence Curves of (T, n), (T, x), and (T, ϕ) for $\{x$ Dimethyl Carbonate + $(1 - x)$ Nonane$\}$ and $\{x$ Dimethyl Carbonate + $(1 - x)$ Dodecane$\}$[a]

	(T, n)	(T, x)	(T, ϕ)
	x Dimethyl Carbonate + (1 − *x*) Nonane		
$\rho_{c,expt}$	1.3884 ± 0.0001	0.663 ± 0.001	0.482 ± 0.002
	$Z = 1$		
ρ_c	1.3884 ± 0.0001	0.659 ± 0.001	0.479 ± 0.001
D	0.155 ± 0.001	−2.21 ± 0.07	0.30 ± 0.05
χ^2/N	0.070	0.283	0.148
	$Z = 2\beta = 0.652$		
ρ_c	1.3882 ± 0.0001	0.660 ± 0.001	0.478 ± 0.001
D	0.035 ± 0.001	−0.52 ± 0.01	0.08 ± 0.01
χ^2/N	1.786	0.077	0.108
	$Z = 1 - \alpha = 0.89$		
ρ_c	1.3884 ± 0.0001	0.658 ± 0.001	0.479 ± 0.001
D	0.097 ± 0.001	−1.40 ± 0.03	0.20 ± 0.03
χ^2/N	0.226	0.147	0.136
	x Dimethyl Carbonate + (1 − *x*) Dodecane		
$\rho_{c,expt}$	1.3869 ± 0.0001	0.739 ± 0.001	0.513 ± 0.002
	$Z = 1$		
ρ_c	1.3870 ± 0.0001	0.730 ± 0.001	0.508 ± 0.001
D	0.172 ± 0.001	−2.16 ± 0.06	0.13 ± 0.02
χ^2/N	0.148	2.066	0.089
	$Z = 2\beta = 0.652$		
ρ_c	1.3867 ± 0.0001	0.735 ± 0.001	0.507 ± 0.001
D	0.049 ± 0.001	−0.63 ± 0.01	0.04 ± 0.01
χ^2/N	6.010	0.131	0.063
	$Z = 1 - \alpha = 0.89$		
ρ_c	1.3869 ± 0.0001	0.731 ± 0.001	0.508 ± 0.001
D	0.116 ± 0.001	−1.46 ± 0.03	0.09 ± 0.02
χ^2/N	0.324	0.936	0.081

[a] $\rho_{c,expt}$ is the critical value of the order parameter determined by the techniques described in the text.

Table 10. Critical Mole Fractions, the Molecular Volume Ratios V_1^0/V_2^0 of Dimethyl Carbonate and Alkane, Parameters $\hat{D}_2^x$ and $\hat{B}_0^x$ in eqs 9 and 10, and the Asymmetric Coefficient a_1 Calculated from eq 11 for Systems of Dimethyl Carbonate + Alkanes

system	x_c	V_1^0/V_2^0	$\hat{D}_2^x$	$\hat{B}_0^x$	a_1
nonane	0.663	0.471	−0.607 ± 0.018	0.858 ± 0.002	0.533
decane[6]	0.691	0.432	−0.632 ± 0.010	0.830 ± 0.001	0.561
dodecane	0.739	0.370	−0.704 ± 0.015	0.771 ± 0.002	0.632
tetradecane[6]	0.775	0.324	−0.674 ± 0.004	0.706 ± 0.003	0.660
hexadecane[7]	0.804	0.288	−0.700 ± 0.005	0.649 ± 0.003	0.711
octadecane[7]	0.829	0.259	−0.663 ± 0.005	0.588 ± 0.004	0.740

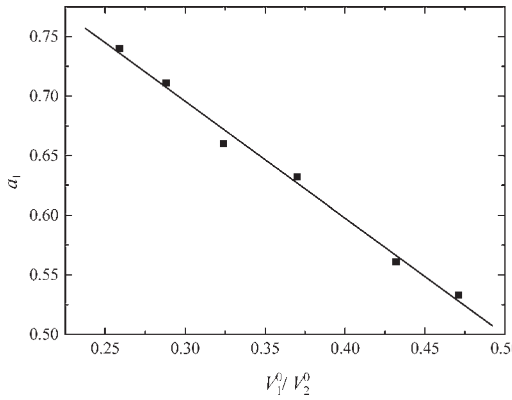

Figure 3. Asymmetric coefficient a_1 as a function of the molecular volume ratio V_1^0/V_2^0 of two components for the dimethyl carbonate + alkane mixtures.

where x is the mole fraction of dimethyl carbonate, the subscripts 1 and 2 relate to upper and lower phases; $\hat{D}_2^x$, $\hat{D}_1^x$, $\hat{B}_0^x$, $\hat{B}_1^x$, and $\hat{B}_2^x$ are the system dependent amplitudes, $\hat{B}_{cr}$ is the critical background of the heat capacity, $\hat{A}_0^-$ is the critical amplitude corresponding to the heat capacity in two-phase region. As discussed above the contribution of the τ^β term in eq 10 is dominant, therefore we neglected the terms of $|\tau|^\Delta$ and $|\tau|^{2\beta}$. Perez-Sanchez and co-workers[5] pointed that the contributions of $|\tau|^{1-\alpha}$ and $|\tau|$ in eq 9 have opposite sign and the net effect of the contributions appears to be minor significance to Δx_d. Following their fitting procedure, we set the parameter $\hat{D}_1^x$ equal to zero and fitted the experimental data of (T, x) coexistence curves within $T_c - T < 10$ K with β being fixed at the theoretical value 0.326 and x_c at their experimental values for six systems of dimethyl carbonate + nonane, + decane,[6] + dodecane, + tetradecane,[6] + hexadecane,[7] and + octadecane.[7] We obtained the system dependent amplitudes $\hat{D}_2^x$ and $\hat{B}_0^x$, which are listed in Table 10.

The asymmetric criticality of the coexistence curve was related to the ratio of $\hat{D}_2^x$ and $(\hat{B}_0^x)^2$ by Perez-Sanchez and co-workers[5] according to the complete scaling theory through eq 11:

$$\hat{D}_2^x/(\hat{B}_0^x)^2 = -\frac{a_1}{1 - a_1 x_c} \tag{11}$$

where a_1 is the asymmetric coefficient of the coexistence curve. With the known critical mole fraction x_c and the obtained values of $\hat{D}_2^x$ and $\hat{B}_0^x$ listed in Table 10 for the six binary solutions of dimethyl carbonate + alkane, the asymmetric coefficients a_1 were calculated by eq 11, which are also summarized in Table 10.

It was found that the asymmetry of the coexistence curve is related the difference of sizes between the two individual components in the binary solutions.[5,20,21] In a nearly incompressible limit of a binary solution in which the volume of mixing may be negligible, it has been shown[5] that the asymmetric coefficient a_1 is dependent on the molecular volume ratio V_1^0/V_2^0 of two components

$$a_1 \approx 1 - V_1^0/V_2^0 \tag{12}$$

where V_1^0 and V_2^0 are the molecular volumes of dimethyl carbonate and alkane, respectively. As shown in Figure 3, a plot of a_1 against V_1^0/V_2^0 yields a good straight line with the slope and the intercept being −0.98 ± 0.04 and 0.99 ± 0.02, respectively, indicating eq 12 being valid. It is well-known that V_2^0 increases with the length of the alkane molecule, thus the significance of the asymmetry of the coexistence curve accordingly increases with the carbon number of the alkane, which is in consistence with the experimental observations of the asymmetry for the coexistence curves of the binary solutions of dimethyl carbonate + alkane. It is also consistent with the conclusion of the dependence of the asymmetry on the difference of size between the two individual components from analyzing the binary systems of nitrobenzene + alkane,[3,4] although the formulation $a_1/(1 - a_1x_c) \propto 1 - V_1^0/V_2^0$ instead of $a_1 \approx 1 - V_1^0/V_2^0$ was used in the analysis,[3,4] which is questionable.

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REFERENCES

(1) Fisher, M. E.; Orkoulas, G. The Yang-Yang Anomaly in Fluid Criticality: Experiment and Scaling Theory. *Phys. Rev. Lett.* **2000**, *85*, 696–699.

(2) Kim, Y. C.; Fisher, M. E.; Orkoulas, G. Asymmetric Fluid Criticality. II. Finite-Size Scaling for Simulations. *Phys. Rev. E* **2003**, *67*, 061506.

(3) Cerdeiriña, C. A.; Anisimov, M. A.; Sengers, J. V. The Nature of Singular Coexistence-Curve Diameters of Liquid-Liquid Phase Equilibria. *Chem. Phys. Lett.* **2006**, *424*, 414–419.

(4) Wang, J. T.; Cerdeiriña, C. A.; Anisimov, M. A.; Sengers, J. V. Principle of Isomorphism and Complete Scaling for Binary-fluid Criticality. *Phys. Rev. E* **2008**, *77*, 031127.

(5) Perez-Sanchez, G.; Losada-Perez, P.; Cerdeirina, C. A.; Sengers, J. V.; Anisimov, M. A. Asymmetric Criticality in Weakly Compressible Liquid Mixtures. *J. Chem. Phys.* **2010**, *132*, 154502.

(6) Huang, M. J.; Xiang, Y. S.; Chen, Z. Y.; Cai, L.; An, X. Q.; Shen, W. G. Liquid-Liquid Coexistence Curves of Dimethyl Carbonate + *n*-Decane and Dimethyl Carbonate + *n*-Tetradecane in the Critical Region. *J. Chem. Eng. Data* **2009**, *54*, 1477–1482.

(7) Huang, M. J.; Chen, Z. Y.; Yin, T. X.; Bai, Y. L.; An, X. Q.; Shen, W. G. Liquid-Liquid Coexistence Curves of Dimethyl Carbonate + Hexadecane and Dimethyl Carbonate + Octadecane in the Critical Region. *J. Chem. Eng. Data* **2010**, *55*, 4378–4384.

(8) Gonzalez, J. A.; Garcia, I.; Cobos, J. C.; Casanova, C. Thermodynamics of Binary Mixtures Containing Organic Carbonates. 4. Liquid-Liquid Equilibria of Dimethyl Carbonate + Selected n-Alkanes. *J. Chem. Eng. Data* **1991**, *36*, 162–164.

(9) Real, J. N.; Iglesias, T. P.; Pereira, S. M.; Rivas, M. A. Analysis of Temperature Dependence of Some Physical Properties of (*n*-Nonane + Tetraethylene Glycol Dimethyl Ether). *J. Chem. Thermodyn.* **2002**, *34*, 1029–1043.

(10) Shen, W. G.; Smith, G. R.; Knobler, C. M.; Scott, R. L. Turbidity Measurements of Binary Polystyrene Solutions Near Critical Solution Points. *J. Phys. Chem.* **1991**, *95*, 3376–3379.

(11) An, X. Q.; Shen, W. G.; Wang, H. J.; Zheng, G. K. The (Liquid + Liquid) Critical Phenomena of (a Polar Liquid + an n-Alkane) I. Coexistence Curves of (N, N-Dimethylacetamide + Hexane). *J. Chem. Thermodyn.* **1993**, *25*, 1373–1383.

(12) Souto-Caride, M.; Troncoso, J.; Peleteiro, J.; Carballo, E.; Romani, L. Influence of Chemical Structure on Critical Parameters for Dimethyl Carbonate + Alkane Systems. *J. Thermal Anal. Calorim.* **2007**, *89*, 125–129.

(13) Souto-Caride, M.; Troncoso, J.; Peleteiro, J.; Carballo, E.; Romani, L. Determination of the Critical Anomaly in the Viscosity for the Dimethyl Carbonate + (Undecane or Dodecane) Systems. *Fluid Phase Equilib.* **2006**, *249*, 42–48.

(14) An, X. Q.; Zhao, H. H.; Jiang, F. G.; Mao, C. F.; Shen, W. G. The Coexistence Curves of $\{xC_6H_5NO_2 + (1 - x)CH_3(CH_2)_{12}CH_3\}$ in the Critical Region. *J. Chem. Thermodyn.* **1997**, *29*, 1047–1054.

(15) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed; McGraw-Hill: New York, 1998.

(16) Wenger, F. J. Corrections to Scaling Laws. *Phys. Rev. B* **1972**, *5*, 4529–4536.

(17) Greer, S. C.; Moldover, M. R. Thermodynamic Anomalies at Critical Points of Fluids. *Annu. Rev. Phys. Chem.* **1981**, *32*, 233–265.

(18) Oleinikova, A.; Weingärtner, H. Isotope Effect on the Coexistence Curve and Crossover Behavior of Water + Tetrahydrofuran. *Chem. Phys. Lett.* **2000**, *319*, 119–124.

(19) Bevington, P. R. *Data Reduction and Error Analysis for Physical Sciences*; McGraw-Hill: New York, 1969.

(20) Hildebrand, J. H.; Scott, R. L. *The solubility of Nonelectrolytes*; Reinhold: New York, 1950.

(21) Pierre, D.; Francoise, L. Asymmetry of the Coexistence Curve in Binary Systems. Size Effect. *J. Chem. Phys.* **1991**, *95*, 590–599.