Liquid−Liquid Coexistence Curves of Dimethyl Carbonate + Hexadecane and Dimethyl Carbonate + Octadecane in the Critical Region[†]

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The liquid−liquid coexistences of temperature vs refractive index ($T-n$), temperature vs mole fraction ($T-x$), and temperature vs volume fraction ($T-\phi$) for dimethyl carbonate + hexadecane and dimethyl carbonate + octadecane have been determined within 10 K from the critical temperatures. The critical amplitudes B and the critical exponents β have been deduced from the coexistence curves. The results have also been analyzed to determine Wegner correction terms and to examine the asymmetric behavior of the diameters of the coexistence curves. Experimental values of β are consistent with the 3D Ising value in the whole temperature range investigated for ($T-n$) and ($T-\phi$), while the tendency of crossover to the mean field value was detected for ($T-x$). The data of coexistence curves ($T-x$) were fitted with the crossover equation proposed by Anisimov and Sengers to obtain the crossover parameters. It was found that the contribution of the regular term was significant as the temperature was far away from the critical point and the value of effective critical exponent increased with the distance from the critical point, exhibiting the monotonic crossover from the Ising to the mean-field critical behaviors.

Introduction

It is well-known that the character of critical behavior depends on the long-range nature of the order parameters. Approaching the critical point, the correlation length of critical fluctuations becomes so large that the microscopic details of the system such as the interaction potential, or even the existence of mesoscopic structures, became irrelevant. Therefore, fluids and fluid mixtures exhibit similar critical behavior that belongs to the 3D-Ising-like universality class. However, as the distance from the critical points increases, a crossover from the 3D-Ising to the classical mean-field should be expected. Recently, researchers have paid much attention to the study of the critical crossover behavior.[1−10]

Sufficiently close to the critical point, various thermodynamic properties of chemically different systems, such as the difference of the general density variable of two coexisting phases $\Delta\rho$, the correlation length ξ, and osmotic compressibility χ, can be described by universal power−law equations depending on the reduced temperature τ ($\tau = |(T - T_c)/T_c|$, T_c is the critical temperature)

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

$$\chi \propto \tau^{-\gamma} = \chi_0\tau^{-\gamma} \quad (2)$$

$$\xi \propto \tau^{-\nu} = \xi_0\tau^{-\nu} \quad (3)$$

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, χ_0, and ξ_0 are the critical amplitudes. The values of critical exponents β, γ, and ν are 0.326, 1.239, and 0.630 for 3D-Ising universality class, while they are 0.5, 1, and 0.5 from the classical mean-field theory.

Dimethyl carbonate is a green solvent widely used in the dope and pharmaceutical industry and a raw material for the synthesis of gasoline additive and polycarbonate. The physical properties of dimethyl carbonate + alkanes mixtures are important in establishing dimethyl carbonate as a potential fuel additive. As one of the polar + nonpolar mixtures, thermodynamic properties of dimethyl carbonate + alkane mixtures provide information about the interactions between polar and nonpolar molecules.[11] These systems also have appropriate critical temperatures to be easily experimentally approached, thus the critical phenomena corresponding to the coexistence curve may be precisely examined.

In this paper, we report the experimental results of the coexistence curves of dimethyl carbonate + hexadecane and dimethyl carbonate + octadecane. The results are analyzed to obtain the critical exponents and critical amplitudes. The experimental results of the coexistence curves have also been analyzed to examine the Wegner correction terms and the asymmetric behavior of the diameters of the coexistence curves. Furthermore, in terms of the crossover theory proposed by Anisimov and Sengers,[12] the crossover parameters are obtained, and the crossover behavior is discussed.

Experimental Section

Dimethyl carbonate (0.99 mass fraction), hexadecane (0.99 mass fraction), and octadecane (0.99 mass fraction) were obtained from ABCR GmbH & Co. KG. They were all dried and stored over 0.4 nm molecular sieves.

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.

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Table 1. Critical Compositions and Critical Temperatures for Dimethyl Carbonate + Alkanes

	T_c/K		x_c	
alkane	this study	ref 15	this study	ref 15
hexadecane	316.5 ± 0.1	316.21	0.804 ± 0.001	0.8137
octadecane	324.4 ± 0.1		0.829 ± 0.001	

Mixtures of (dimethyl carbonate + hexadecane) and (dimethyl carbonate + octadecane) 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.[13] The volume ratio of the upper and lower phases was so sensitive to the composition of the prepared solution that the critical mole fraction x_c was able to be determined within ± 0.001 just by visual observations of the height ratio of the two phases.

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 and taken as the critical temperature. It was observed that the mixtures nominally of the same composition had different critical temperatures, differing by as much as 0.1 K. This might have been a result of uncontrollable moisture or other impurities introduced into 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 parameters. The uncertainty in measurement of ($T_c - T$) was ± 0.003 K.

The refractive indexes were measured according to the method of minimum deviation.[14] A He−Ne laser with $\lambda = 632.8$ 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) hexadecane} and {x dimethyl carbonate + (1 − x) octadecane} were determined and are listed in Table 1, where x and x_c are the mole fraction of dimethyl carbonate and its critical value, respectively. The values reported in ref 15 for {x dimethyl carbonate + (1 − x) hexadecane} are also listed in Table 1 for comparison. The differences are as large as 0.3 K for the critical temperature and 0.01 for the critical mole fraction, respectively. It is not surprising because the values reported in ref 15 were obtained from the fits of the visually determined phase-separation points, each of the points corresponding to a prepared mixture. The standard deviation in temperature for the fit was reported to be 0.4 K, and the corresponding uncertainty in determination of x_c could be much larger than 0.01.

The refractive indexes n were measured for each coexisting phase at various temperatures at wavelength $\lambda = 632.8$ nm. The results are listed in columns 2 and 3 of Table 2 for {x dimethyl carbonate + (1 − x) hexadecane} and in columns 2 and 3 of Table 3 for {x dimethyl carbonate + (1 − x) octadecane}. 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 2. 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*) Hexadecane}[a]

T/K	n_1	n_2	x_1	x_2	ϕ_1	ϕ_2
316.451	1.3842	1.3815	0.788	0.815	0.518	0.560
316.447	1.3847	1.3809	0.782	0.821	0.509	0.570
316.444	1.3849	1.3808	0.780	0.822	0.506	0.572
316.439	1.3852	1.3805	0.777	0.825	0.502	0.577
316.426	1.3858	1.3799	0.770	0.831	0.492	0.587
316.415	1.3861	1.3796	0.767	0.834	0.487	0.592
316.403	1.3863	1.3793	0.765	0.836	0.485	0.596
316.387	1.3865	1.3791	0.763	0.838	0.482	0.599
316.364	1.3871	1.3786	0.756	0.843	0.472	0.608
316.344	1.3874	1.3783	0.753	0.846	0.468	0.613
316.320	1.3877	1.3781	0.749	0.848	0.463	0.617
316.293	1.3879	1.3778	0.747	0.850	0.460	0.621
316.260	1.3883	1.3775	0.743	0.853	0.455	0.626
316.219	1.3887	1.3773	0.738	0.855	0.449	0.630
316.173	1.3890	1.3769	0.735	0.859	0.445	0.638
316.115	1.3896	1.3765	0.728	0.863	0.436	0.645
316.049	1.3900	1.3762	0.723	0.865	0.430	0.649
315.977	1.3904	1.3759	0.719	0.868	0.425	0.655
315.892	1.3908	1.3755	0.714	0.872	0.419	0.663
315.775	1.3914	1.3752	0.707	0.875	0.411	0.669
315.625	1.3921	1.3747	0.699	0.880	0.401	0.679
315.462	1.3927	1.3742	0.692	0.884	0.394	0.688
315.254	1.3934	1.3738	0.684	0.888	0.385	0.696
314.953	1.3943	1.3732	0.673	0.894	0.373	0.709
314.546	1.3955	1.3728	0.659	0.899	0.358	0.720
313.970	1.3969	1.3720	0.642	0.907	0.341	0.738
313.341	1.3982	1.3715	0.627	0.913	0.327	0.752
312.557	1.3996	1.3710	0.610	0.920	0.311	0.769
311.549	1.4012	1.3706	0.592	0.926	0.295	0.783
310.451	1.4029	1.3702	0.571	0.933	0.278	0.801
309.257	1.4048	1.3700	0.547	0.938	0.259	0.814
307.849	1.4063	1.3698	0.531	0.944	0.246	0.830
306.840	1.4075	1.3698	0.517	0.947	0.236	0.838

[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[16]

$$n(T, x) = n(T^0, x) + R(x)(T - T^0) \tag{4a}$$

$$R(x) = xR_1 + (1 - x)R_2 \tag{4b}$$

where $R(x)$ is the derivative of n with respect to T for a particular composition x; and R_1 and R_2 are the values of $R(x)$ for $x = 1$ and $x = 0$, respectively. Equations 4a and 4b have been tested in earlier papers.[14,16,17] It allowed us to obtain (T, x) as a function of T and x simply from measurements of $R(x)$ for two pure components and of the refractive indexes for mixtures with various known compositions at a fixed temperature. As a further test, the refractive indexes of a series of mixtures of {x dimethyl carbonate + (1 − x) hexadecane} with known compositions were measured at various temperatures in the one-phase region. The results are listed in Table 4.

Fitting eqs 4a and 4b to the values listed in Table 4 gives $R_1 = -0.000476\ \mathrm{K}^{-1}$ and $R_2 = -0.000414\ \mathrm{K}^{-1}$ for dimethyl carbonate and hexadecane, respectively. The results for $n(T, x)$ at each composition were fitted with eqs 4a and 4b to obtain $n(T^0, x)$ with standard deviation of ± 0.0001 in n. The value of T^0 was chosen as 311.646 K, which is the middle temperature of the coexistence curve determined in this work. The small standard deviation indicates that eqs 4a and 4b are valid. A

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) Octadecane}[a]

T/K	n_1	n_2	x_1	x_2	ϕ_1	ϕ_2
324.369	1.3821	1.3779	0.808	0.844	0.521	0.583
324.365	1.3824	1.3776	0.805	0.847	0.516	0.588
324.353	1.3830	1.3770	0.800	0.851	0.508	0.596
324.344	1.3832	1.3767	0.798	0.854	0.505	0.602
324.317	1.3840	1.3760	0.790	0.859	0.493	0.611
324.303	1.3842	1.3758	0.789	0.861	0.491	0.615
324.278	1.3846	1.3753	0.785	0.865	0.485	0.623
324.250	1.3851	1.3749	0.780	0.868	0.478	0.629
324.223	1.3854	1.3747	0.777	0.870	0.474	0.633
324.195	1.3857	1.3744	0.774	0.872	0.469	0.637
324.164	1.3860	1.3741	0.771	0.874	0.465	0.642
324.131	1.3864	1.3737	0.768	0.877	0.461	0.648
324.089	1.3867	1.3736	0.765	0.878	0.457	0.650
324.043	1.3871	1.3733	0.761	0.881	0.451	0.656
323.984	1.3874	1.3730	0.758	0.883	0.447	0.661
323.906	1.3880	1.3725	0.752	0.887	0.439	0.670
323.819	1.3884	1.3722	0.748	0.889	0.434	0.674
323.716	1.3890	1.3718	0.742	0.892	0.426	0.681
323.566	1.3896	1.3713	0.736	0.896	0.418	0.690
323.389	1.3904	1.3708	0.728	0.900	0.409	0.699
323.184	1.3912	1.3704	0.720	0.904	0.399	0.709
322.882	1.3921	1.3697	0.711	0.909	0.388	0.721
322.517	1.3932	1.3691	0.699	0.914	0.375	0.733
321.957	1.3946	1.3685	0.685	0.920	0.360	0.748
321.253	1.3962	1.3678	0.668	0.927	0.342	0.766
320.401	1.3978	1.3672	0.652	0.933	0.326	0.782
319.405	1.3995	1.3667	0.634	0.939	0.309	0.799
318.192	1.4015	1.3663	0.613	0.945	0.290	0.816
316.784	1.4034	1.3661	0.593	0.950	0.273	0.831
315.210	1.4055	1.3660	0.570	0.955	0.255	0.846

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

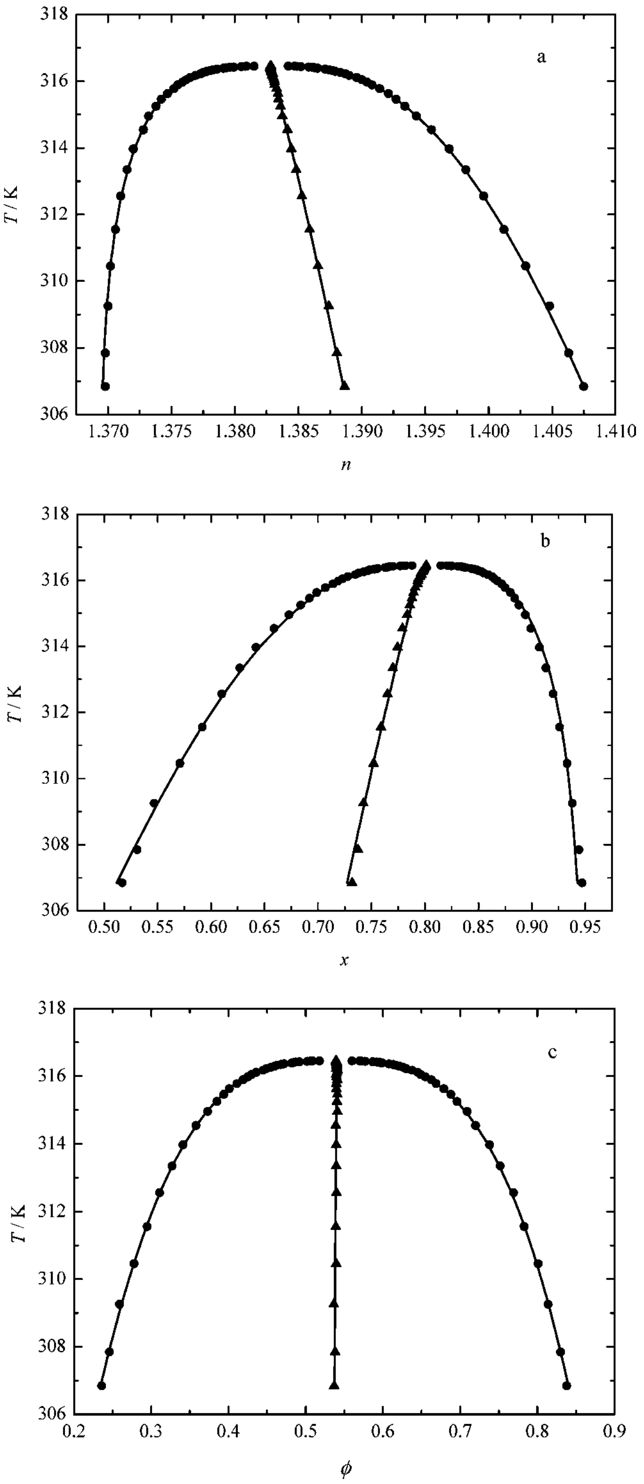

Figure 1. Coexistence curves of (a) temperature against refractive index (T, n), (b) temperature against mole fraction (T, x), and (c) temperature against volume fraction (T, ϕ) for {x dimethyl carbonate + (1 − x) hexadecane}. ▲, experimental values of diameter ρ_d of the coexisting phases; ●, experimental 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 a combination of eq 10 to eq 11 with coefficients listed in Tables 8 and 9.

polynomial form of $n(T^0, x)$ for various compositions at T^0 was obtained as follows

$$n(T^0 = 311.646\ \text{K}, x) = 1.4255 - 0.0310x - 0.0031x^2 - 0.0366x^3 + 0.0470x^4 - 0.0427x^5 \quad (5a)$$

with a standard deviation of less than ± 0.0001.

Fitting eqs 4a and 4b to the values listed in Table 5 gives $R_1 = -0.000485\ \text{K}^{-1}$ and $R_2 = -0.000407\ \text{K}^{-1}$ for dimethyl carbonate and octadecane, respectively. Due to the validity of eqs 4a and 4b, we only measured the values of n for various compositions at the fixed temperature 327.67 K for {x dimethyl carbonate + (1 − x) octadecane}. The results are listed in Table 6 and were used to obtain the polynomial form of $n(T^0, x)$ for various compositions at $T^0 = 319.790$ K

$$n(T^0 = 319.790\ \text{K}, x) = 1.4263 - 0.0256x - 0.0184x^2 - 0.0275x^3 + 0.0613x^4 - 0.0609x^5 \quad (5b)$$

with a standard deviation 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 4a, 4b, and 5a for {x dimethyl carbonate + (1 − x) hexadecane} or eqs 4a, 4b, and 5b for {x dimethyl carbonate + (1 − x) octadecane} with the Newton iteration method.

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

$$1/\phi = (1 - K) + K/x \quad (6a)$$

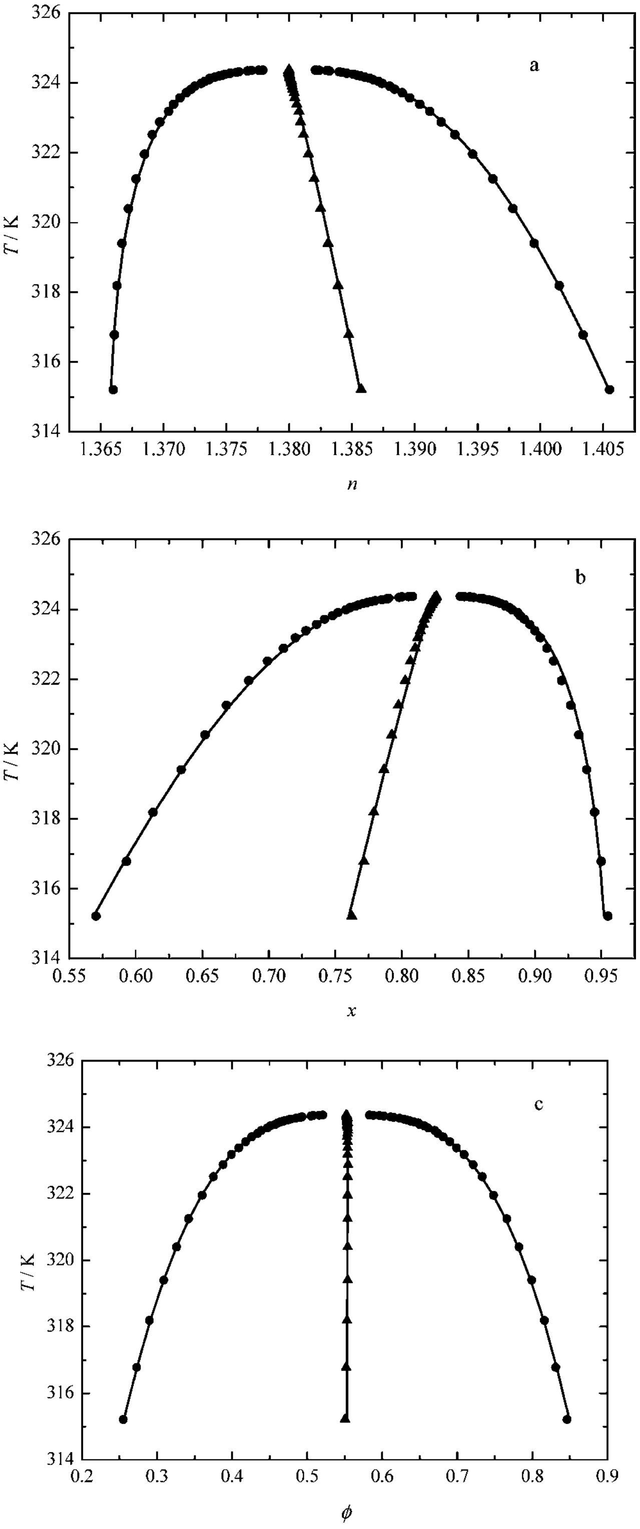

Figure 2. Coexistence curves of (a) temperature against refractive index (T, n), (b) temperature against mole fraction (T, x), and (c) temperature against volume fraction (T, ϕ) for {x dimethyl carbonate + (1 − x) octadecane}. ▲, experimental values of diameter ρ_d of the coexisting phases; ●, experimental 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 a combination of eq 10 to eq 11 with coefficients listed in Tables 8 and 9.

$$K = (d_1 M_2 / d_2 M_1) \tag{6b}$$

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 Chemistry.[18] The values of x and ϕ of coexisting phases at various temperatures are listed in columns 4 to 7 of Tables 2 and 3 and are shown in b and c of Figures 1 and 2.

Table 4. Refractive Indexes n at Wavelength $\lambda = 632.8$ nm for {x Dimethyl Carbonate + (1 − x) Hexadecane} at Various Temperatures

x	T/K	n	T/K	n	T/K	n	T/K	n
0	308.208	1.4270	311.240	1.4256	314.442	1.4244	317.556	1.4231
	309.244	1.4265	312.302	1.4252	315.535	1.4239	318.613	1.4226
	310.207	1.4261	313.342	1.4248	316.549	1.4235		
0.132	308.192	1.4228	311.386	1.4214	314.548	1.4201	317.665	1.4188
	309.248	1.4224	312.433	1.4210	315.575	1.4197	318.743	1.4183
	310.327	1.4219	313.513	1.4206	316.645	1.4192		
0.219	308.350	1.4197	311.090	1.4185	313.947	1.4173	317.082	1.4160
	309.657	1.4191	312.535	1.4179	315.587	1.4166	318.501	1.4154
0.291	308.398	1.4170	312.086	1.4153	315.922	1.4136		
	309.538	1.4164	313.335	1.4147	317.198	1.4131		
	310.826	1.4158	314.630	1.4142	318.492	1.4125		
0.397	308.286	1.4128	311.417	1.4113	314.616	1.4100	317.807	1.4085
	309.322	1.4123	312.464	1.4108	315.707	1.4094	318.895	1.4080
	310.377	1.4118	313.528	1.4104	316.731	1.4090		
0.517	312.202	1.4052	314.256	1.4043	316.417	1.4033		
	313.159	1.4048	315.336	1.4038	317.506	1.4028		
0.600	312.176	1.4005	314.442	1.3994	316.559	1.3984		
	313.320	1.3999	315.501	1.3989	317.673	1.3979		
0.689	316.188	1.3925	317.890	1.3917	319.741	1.3909		
	317.024	1.3921	318.844	1.3913				
0.804	316.452	1.3827	318.056	1.3819	319.787	1.3810		
	317.248	1.3823	318.911	1.3815	320.642	1.3806		
0.872	316.858	1.3751	318.552	1.3743	320.277	1.3735		
	317.737	1.3747	319.400	1.3739				
1.000	308.249	1.3607	311.364	1.3592	314.534	1.3577	317.666	1.3562
	309.260	1.3602	312.438	1.3587	315.560	1.3572	318.717	1.3557
	310.321	1.3597	313.486	1.3582	316.664	1.3567		

Table 5. Refractive Indexes n at Wavelength $\lambda = 632.8$ nm for Pure Dimethyl Carbonate and Octadecane at Various Temperatures T

T/K	n	T/K	n	T/K	n
		Dimethyl Carbonate			
318.588	1.3556	321.745	1.3540	324.847	1.3525
319.657	1.3551	322.774	1.3536	325.851	1.3521
320.706	1.3545	323.837	1.3530	326.851	1.3516
		Octadecane			
318.640	1.4269	321.748	1.4256	324.965	1.4243
319.663	1.4265	322.811	1.4252	325.992	1.4239
320.683	1.4261	323.897	1.4248	327.068	1.4235

Table 6. Refractive Indexes n at Wavelength $\lambda = 632.8$ nm for {x Dimethyl Carbonate + (1 − x) Octadecane} at the Temperatures 327.67 K

x	n	x	n	x	n	x	n
0.000	1.4231	0.299	1.4132	0.601	1.3979	0.902	1.3685
0.099	1.4203	0.399	1.4089	0.701	1.3907	1.000	1.3514
0.202	1.4169	0.509	1.4034	0.807	1.3806		

In the region sufficiently close to the critical temperature, the coexistence curve can be represented by

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

where τ, ρ, the subscripts 1 and 2, B, and β are the same as those described above. The differences of ($\rho_2 - \rho_1$) of general density variables n, x, ϕ of coexisting phases obtained in this work were fitted to eq 7, 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 for the order parameters n and ϕ in the whole temperature range we investigated. However, for the order parameter x, only in the temperature range ($T - T_c$) < 1 K, the

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) Hexadecane} and {x Dimethyl Carbonate + (1 − x) Octadecane} in Equation 7

order parameter	$T_c - T < 1$ K		$T_c - T < 10$ K	
	B	β	B	β
	x Dimethyl Carbonate + (1 − *x*) Hexadecane			
n	0.120 ± 0.002	0.326 ± 0.002	0.119 ± 0.001	0.324 ± 0.001
x	1.27 ± 0.03	0.329 ± 0.003	1.35 ± 0.02	0.337 ± 0.002
ϕ	1.92 ± 0.05	0.326 ± 0.003	1.90 ± 0.02	0.324 ± 0.002
	x Dimethyl Carbonate + (1 − *x*) Octadecane			
n	0.129 ± 0.001	0.325 ± 0.001	0.127 ± 0.001	0.323 ± 0.001
x	1.15 ± 0.01	0.329 ± 0.002	1.24 ± 0.01	0.338 ± 0.002
ϕ	1.92 ± 0.02	0.326 ± 0.001	1.90 ± 0.01	0.325 ± 0.001

Table 8. Fitting Parameters of Equation 8 for Coexistence Curves of (T, n), (T, x), and (T, ϕ) for {x Dimethyl Carbonate + (1 − x) Hexadecane} and {x Dimethyl Carbonate + (1 − x) Octadecane}

order parameter	*x* dimethyl carbonate + (1 − *x*) hexadecane		*x* dimethyl carbonate + (1 − *x*) octadecane	
	B	B_1	B	B_1
n	0.1196 ± 0.0002		0.1284 ± 0.0002	
	0.1217 ± 0.0003	−0.019 ± 0.002	0.1308 ± 0.0002	−0.024 ± 0.002
x	1.298 ± 0.007		1.176 ± 0.007	
	1.215 ± 0.004	0.75 ± 0.03	1.098 ± 0.002	0.77 ± 0.02
ϕ	1.908 ± 0.003		1.913 ± 0.003	
	1.936 ± 0.005	−0.25 ± 0.05	1.935 ± 0.004	−0.22 ± 0.03

3D-Ising value was obtained; as the temperature range increased to 10 K, the values of exponent β significantly increased.

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

$$|\rho_2 - \rho_1| = B\tau^{\beta} + B_1\tau^{\beta+\Delta} + ... \qquad (8)$$

to obtain the parameters B and B_1. The results are summarized in Table 8. The larger value of B_1 for x is consistent with the larger value of exponent β in a larger temperature range discussed above and indicates that the crossover from the 3D-Ising value to the mean-field one should be taken into account for the order parameter x.

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,[19] while the presence of the term $\tau^{2\beta}$ was attributed to a wrong choice for the order parameters in the past.[20,21] 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

$$\rho_d = \rho_c + D\tau^{Z} \qquad (9)$$

with an apparent exponent Z being fixed at the values 1, (1 − α) = 0.89, and $2\beta = 0.652$ 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 of x_c and ϕ_c were determined by the technique "equal volume" and calculated by using eqs 6a and 6b.

Table 9. Fitting Parameters of Equation 9 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) Hexadecane} and {x Dimethyl Carbonate + (1 − x) Octadecane}[a]

	(T, n)	(T, x)	(T, ϕ)
	x Dimethyl Carbonate + (1 − *x*) Hexadecane		
$\rho_{c,expt}$	1.3829 ± 0.0001	0.804 ± 0.001	0.542 ± 0.001
	$Z = 1$		
ρ_c	1.3828 ± 0.00001	0.789 ± 0.0006	0.540 ± 0.0002
D	0.196 ± 0.001	−2.39 ± 0.06	−0.09 ± 0.02
χ^2/N	0.374	8.842	0.567
	$Z = 2\beta = 0.652$		
ρ_c	1.3825 ± 0.0001	0.803 ± 0.0002	0.540 ± 0.0002
D	0.055 ± 0.002	−0.68 ± 0.01	−0.02 ± 0.005
χ^2/N	6.402	0.755	0.678
	$Z = 1 - \alpha = 0.89$		
ρ_c	1.3827 ± 0.00001	0.799 ± 0.0004	0.540 ± 0.0002
D	0.131 ± 0.001	−1.61 ± 0.03	−0.06 ± 0.01
χ^2/N	0.341	5.618	0.593
	x Dimethyl Carbonate + (1 − *x*) Octadecane		
$\rho_{c,expt}$	1.3799 ± 0.0001	0.829 ± 0.001	0.556 ± 0.002
	$Z = 1$		
ρ_c	1.3800 ± 0.00001	0.823 ± 0.0005	0.554 ± 0.0002
D	0.206 ± 0.001	−2.31 ± 0.06	−0.05 ± 0.02
χ^2/N	0.128	5.236	0.204
	$Z = 2\beta = 0.652$		
ρ_c	1.3796 ± 0.00007	0.828 ± 0.0002	0.554 ± 0.0002
D	0.056 ± 0.002	−0.65 ± 0.01	−0.008 ± 0.007
χ^2/N	6.781	0.769	0.224
	$Z = 1 - \alpha = 0.89$		
ρ_c	1.3799 ± 0.00002	0.825 ± 0.0003	0.554 ± 0.0002
D	0.137 ± 0.001	−1.55 ± 0.02	−0.03 ± 0.02
χ^2/N	0.495	2.060	0.210

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

The goodness of fit to eq 9 may be indicated by the reduced chi-squared value χ^2/N (N is the number of degrees of freedom of the fitting),[22] 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 − α, the fit with 2β is worse than that with 1 − α, and the 2β term has a smaller contribution to the diameter of the coexistence curve. Thus, the difference between the χ^2/N values of the fits with 1 − α and 2β for a particular order parameter may indicate the goodness of the parameter, the smaller the difference, the better the parameter is.

For both (x dimethyl carbonate + (1 − x) hexadecane) and (x dimethyl carbonate + (1 − x) octadecane), we found that the fits for order parameter ϕ have the similar reduced chi-squared value for all three terms, while for the order parameter x, the value of fits with 1 − α was significantly larger than that with 2β, which indicates that the $\tau^{2\beta}$ term has a larger contribution to order parameter x than to ϕ. Moreover, the values of coefficient D are significantly 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 more symmetric than that of (T, n) and

(T, x).Therefore, ϕ is the best order parameter among the three order parameters we chose. 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 the 2β term could not be neglected compared with the other two terms, which is consistent with the consequence of complete scaling.

Combination of eqs 8 and 9 yields

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

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

fixing Z, β, and Δ as 0.89, 0.326, and 0.5, respectively, for both {x dimethyl carbonate + $(1 - x)$ hexadecane} and {x dimethyl carbonate + $(1 - x)$ octadecane}, 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 10 and 11, which are shown as lines in Figures 1 and 2. The values from calculation are in good agreement with experimental results.

As pointed out above, our experimental results detected the existence of crossover for the order parameter x; therefore, we reanalyzed the coexistence curves in terms of the crossover theory proposed by Anisimov and Sengers.[12] According to this theory, the difference of the general density variable Δx of the two coexisting phases can be expressed as

$$\Delta x/(2x_c) = B_0(\tau Y^{(2\beta-1)/\Delta s})^{1/2} + a\tau \qquad (12)$$

where B_0 is critical amplitude, and a is a coefficient, which reflects a regular dependence of Δx on temperature along the coexistence curve. Y is the crossover function determined from

$$1 - (1 - \bar{u})Y = \bar{u}\left[1 + \left(\frac{\Lambda}{k}\right)^2\right]Y^{\nu/\Delta s} \qquad (13)$$

where $\bar{u}$ and Λ are the crossover parameters; $\nu = 0.630$ and $\Delta s = 0.50$ are the Ising critical exponents; $k^2 = c_t\tau Y^{(2\nu-1)/\Delta s}$ with c_t being the scaling amplitude. The first term of the right side of eq 12 is called the singular term, and the second term is called the regular term. The critical behavior is determined by the singular term.

In principle, the values of $\bar{u}$, $c_t^{0.5}/\Lambda$, B_0, and a could be obtained by fitting the experimental data to eq 12; however, the strong coupling between the parameters made the fit quite difficult. Since the value of $\bar{u}$ is of the order of unity for simple fluid systems, we set $\bar{u}$ at the values between 0.5 and 2.5 with an increment of 0.001 separately, and for each of the setting values we fitted the measured data of the coexistence curves to the crossover eq 12 with $c_t^{0.5}/\Lambda$, B_0, and a as adjustable parameters. We accepted the value of $\bar{u}$ and the corresponding values of the other parameters with the smallest standard deviation of the fit as the optimal ones.

The values of $\bar{u}$, B_0, a, and $c_t^{0.5}/\Lambda$ for (x dimethyl carbonate + $(1 - x)$ hexadecane) and (x dimethyl carbonate + $(1 - x)$ octadecane) are listed in Table 10. These $\bar{u}$ values are satisfactory as crossover theory establishes that $\bar{u}$ takes values smaller than 1 for the simple mixtures and greater than 1 for complex mixtures such as polymer solutions, ionic solutions, etc.[23,24] Figure 3 shows the comparison of the experimental density variable Δx with the values calculated by eq 12 for (x dimethyl carbonate + $(1 - x)$ hexadecane) and (x dimethyl carbonate + $(1 - x)$ octadecane), respectively. The experimental values are in good agreement with the calculated ones which indicate that the crossover theory proposed by Anisimov and Sengers can well describe the coexistence curve of dimethyl carbonate + alkane.

Table 10. Crossover Parameters of Coexistence Curve Data for {x Dimethyl Carbonate + $(1 - x)$ Hexadecane} and {x Dimethyl Carbonate + $(1 - x)$ Octadecane}

order parameters	$\bar{u}$	B_0	a	$c_t^{0.5}/\Lambda$
x Dimethyl Carbonate + $(1 - x)$ Hexadecane				
x	0.608	1.375	−0.370	3.386
x Dimethyl Carbonate + $(1 - x)$ Octadecane				
x	0.722	1.071	0.212	2.798

The effective critical exponent of the mole fraction is defined as $\beta_{\text{eff}}^{x} = \mathrm{d}\ln\Delta x/\mathrm{d}\ln\tau$. The effective critical exponents were calculated by the numerical derivatives of eq 12 and the singular term only of eq 12 for (x dimethyl carbonate + $(1 - x)$ hexadecane) and (x dimethyl carbonate + $(1 - x)$ octadecane), respectively, which are shown in Figure 4. It can be seen in Figure 4 that as the temperature is close to the critical point the values of $\beta_{\text{eff}}^{\text{sig}}$ are consistent with those calculated by crossover eq 12, while they significantly depart from them as the temperature gets further away from the critical point. It is evidence that the contribution of the regular term is important when the system is far away from the critical point. It is also clearly shown in Figure 4 that the effective critical exponents

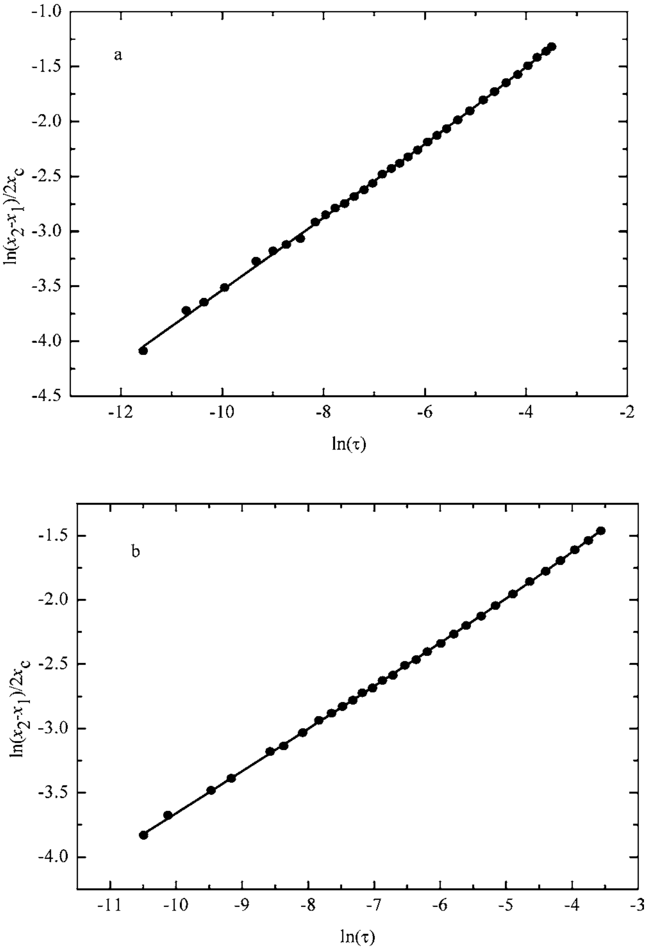

Figure 3. Plots of $\ln(\Delta x/2x_c)$ vs $\ln(\tau)$ for (a) {x dimethyl carbonate + $(1 - x)$ hexadecane} and (b) {x dimethyl carbonate + $(1 - x)$ octadecane}. The solid line is calculated by eq 12, and the points are from experimental values.

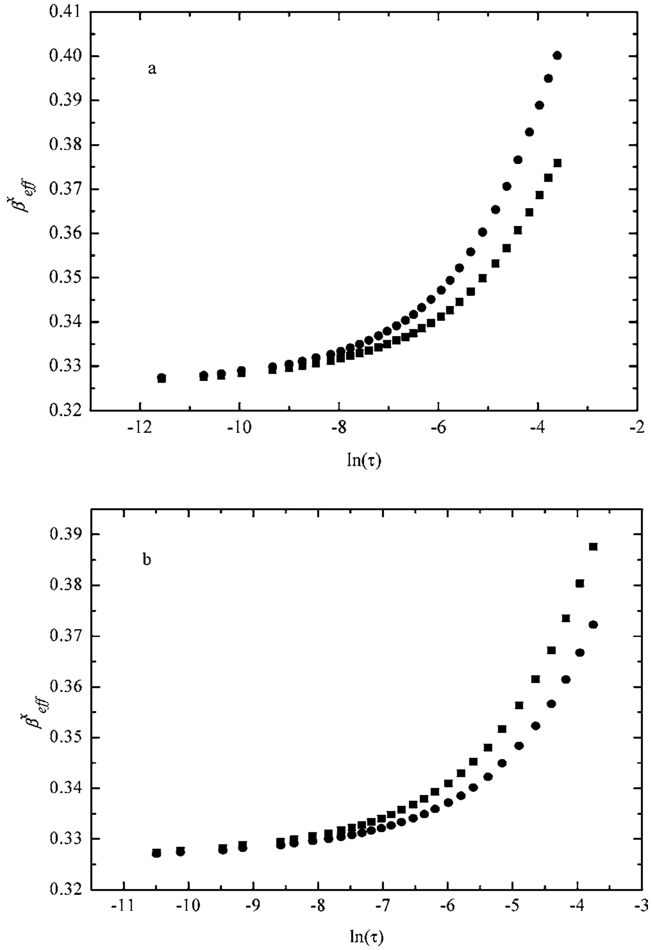

Figure 4. Plots of effective exponent β^x_{eff} of mole fraction vs ln(τ) for (a) {x dimethyl carbonate + (1 − x) hexadecane} and (b) {x dimethyl carbonate + (1 − x) octadecane}. ●, the numerical derivative of the singular term of eq 12; ■, the numerical derivative of the critical crossover eq 12.

exhibit monotonic crossovers from the Ising to the mean-field critical behaviors.

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