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Liquid−Liquid Coexistence Curves of Dimethyl Carbonate + *n*-Decane and Dimethyl Carbonate + *n*-Tetradecane in the Critical Region[†]

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The liquid−liquid coexistence of dimethyl carbonate + *n*-decane and dimethyl carbonate + *n*-tetradecane has been determined within 10 K from the critical temperature by measurements of refractive index *n*. The critical amplitude *B* and the critical exponent β have been deduced from the coexistence curves. Experimental values of β are consistent with theoretical prediction. The results have also been analyzed to determine Wegner-correction terms when β and Δ are fixed at the theoretical values and to examine the asymmetric behavior of the diameters of the coexistence curves.

Introduction

Recently the complete scaling has been extended to binary fluid mixtures to match asymmetric fluid-phase behavior with the symmetric Ising model.[1] Some experimental data of liquid−liquid coexistence of binary mixtures in the critical region were analyzed to test the validity of the complete scaling in binary liquid mixtures.[1,2] However, the accurate data as experimental evidence for complete scaling are very scarce. Binary mixtures of dimethyl carbonate + *n*-alkane are good systems for study of the principle of critical isomorphism and complete scaling because they show very asymmetric coexisting-phase behavior with respect to mole fraction. Thermodynamic properties such as excess molar volumes,[3] speed of sound,[4] heat capacity,[4,5] density at various pressures,[6] and viscosity[7] have been widely studied for the binary mixtures of dimethyl carbonate + *n*-alkane. Although some coexistence temperatures as a function of mole fraction for these systems have also been reported,[8] their accuracies were not good enough for the studies of the critical phenomena, mainly due to the larger uncertainties in determination of the phase-separation temperatures, which were generally required to be less than a few milliKelvin for deducing the precise critical exponents and amplitudes corresponding to the liquid−liquid coexistence curves.

In this paper, we reported the coexistence curves of (dimethyl carbonate + *n*-decane) and (dimethyl carbonate + *n*-tetradecane) determined by measurements of the refractive index *n*. The experimental results are analyzed to determine the critical exponent β and the critical amplitude *B* and to examine the asymmetric behavior of the diameters ρ_d of the coexistence curves over a temperature range of about 10 K from the critical temperature.

Experimental Section

Dimethyl carbonate (99 mass percent), *n*-decane (99 mass percent), and *n*-tetradecane (99 mass percent) were obtained from ABCR GmbH & Co. KG. They were all dried and stored over 0.4 nm molecular sieves.

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

	T_c/K		X_c	
n-alkane	this study	ref 8	this study	ref 8
n-decane	287.1 ± 0.1	286.62	0.691 ± 0.001	0.6864
n-tetradecane	307.8 ± 0.1	307.61	0.775 ± 0.001	0.7825

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 + *n*-decane) and (dimethyl carbonate + *n*-tetradecane) were prepared in glass tubes provided with Ace-thread connections, and the tubes were placed in the water bath. The heights of two phases for each mixture were measured near the phase-separation point. 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.[9] The uncertainty in determination of the critical mole fraction x_c is about ± 0.001.

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 the 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.[10,11] A He−Ne laser with $\lambda =$

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Table 2. Coexistence Curves of (T, n), (T, x), and (T, ϕ) for {x Dimethyl Carbonate + $(1-x)$ n-Decane}[a]

T/K	n_1	n_2	x_1	x_2	ϕ_1	ϕ_2
287.096	1.3895	1.3871	0.662	0.713	0.459	0.519
287.088	1.3897	1.3868	0.658	0.719	0.455	0.526
287.076	1.3901	1.3865	0.649	0.725	0.445	0.534
287.066	1.3904	1.3862	0.642	0.731	0.438	0.541
287.054	1.3906	1.3860	0.638	0.735	0.433	0.546
287.037	1.3908	1.3859	0.634	0.737	0.429	0.549
287.015	1.3911	1.3856	0.627	0.743	0.422	0.556
286.992	1.3913	1.3854	0.623	0.748	0.418	0.563
286.969	1.3915	1.3852	0.619	0.752	0.414	0.568
286.941	1.3917	1.3850	0.614	0.756	0.408	0.574
286.909	1.3920	1.3848	0.608	0.760	0.402	0.579
286.867	1.3922	1.3847	0.603	0.762	0.397	0.582
286.824	1.3925	1.3844	0.597	0.768	0.391	0.590
286.776	1.3927	1.3843	0.593	0.771	0.387	0.594
286.719	1.3930	1.3841	0.586	0.775	0.381	0.599
286.654	1.3933	1.3839	0.580	0.779	0.375	0.605
286.581	1.3936	1.3836	0.573	0.786	0.368	0.614
;286.501	1.3938	1.3835	0.569	0.788	0.364	0.617
286.415	1.3942	1.3833	0.560	0.792	0.356	0.623
286.322	1.3944	1.3831	0.557	0.797	0.353	0.630
286.217	1.3947	1.3829	0.550	0.801	0.347	0.636
286.108	1.3949	1.3827	0.547	0.806	0.344	0.643
285.921	1.3954	1.3825	0.536	0.811	0.334	0.651
285.636	1.3960	1.3822	0.524	0.819	0.323	0.663
285.233	1.3968	1.3819	0.508	0.827	0.309	0.675
284.655	1.3978	1.3815	0.489	0.839	0.293	0.693
284.007	1.3989	1.3813	0.468	0.848	0.276	0.708
283.308	1.3999	1.3811	0.449	0.856	0.261	0.721
282.444	1.4009	1.3809	0.432	0.866	0.248	0.737
281.436	1.4021	1.3809	0.411	0.874	0.232	0.750
280.775	1.4029	1.3809	0.397	0.879	0.222	0.759
279.174	1.4045	1.3809	0.371	0.891	0.204	0.780
277.610	1.4060	1.3811	0.348	0.899	0.188	0.794

[a] Refractive indexes n were measured at wavelength $\lambda = 632.8$ nm and $T_c = 287.102$ K. x and ϕ are mole fraction and volume fraction of dimethyl carbonate. Subscripts 1 and 2 relate to upper and lower phases.

Table 3. Coexistence Curves of (T, n), (T, x), and (T, ϕ) for {x Dimethyl Carbonate + $(1-x)$ n-Tetradecane}[a]

T/K	n_1	n_2	x_1	x_2	ϕ_1	ϕ_2
307.751	1.3863	1.3836	0.757	0.790	0.503	0.550
307.741	1.3870	1.3829	0.748	0.799	0.491	0.564
307.737	1.3872	1.3828	0.746	0.800	0.488	0.565
307.731	1.3874	1.3825	0.743	0.803	0.485	0.570
307.722	1.3877	1.3823	0.739	0.806	0.479	0.575
307.711	1.3880	1.3820	0.735	0.809	0.474	0.579
307.697	1.3882	1.3818	0.732	0.812	0.470	0.584
307.680	1.3887	1.3814	0.726	0.816	0.463	0.590
307.661	1.3889	1.3811	0.723	0.820	0.459	0.597
307.639	1.3892	1.3809	0.719	0.822	0.454	0.600
307.613	1.3896	1.3806	0.714	0.825	0.448	0.605
307.585	1.3898	1.3803	0.711	0.829	0.444	0.612
307.554	1.3901	1.3801	0.707	0.831	0.440	0.615
307.514	1.3904	1.3798	0.703	0.835	0.435	0.622
307.468	1.3907	1.3795	0.699	0.838	0.430	0.627
307.411	1.3911	1.3791	0.694	0.843	0.424	0.636
307.347	1.3915	1.3789	0.688	0.845	0.418	0.639
307.271	1.3920	1.3785	0.681	0.849	0.410	0.646
307.188	1.3923	1.3782	0.678	0.853	0.406	0.654
307.075	1.3928	1.3779	0.671	0.857	0.399	0.661
306.924	1.3934	1.3775	0.663	0.861	0.390	0.668
306.765	1.3941	1.3771	0.653	0.866	0.380	0.678
306.559	1.3947	1.3767	0.645	0.871	0.371	0.687
306.259	1.3956	1.3762	0.632	0.877	0.358	0.699
305.857	1.3966	1.3756	0.619	0.885	0.346	0.714
305.256	1.3979	1.3751	0.601	0.892	0.329	0.729
304.602	1.3992	1.3746	0.584	0.900	0.313	0.745
303.811	1.4005	1.3742	0.566	0.907	0.298	0.760
302.799	1.4021	1.3739	0.545	0.914	0.280	0.776
301.595	1.4038	1.3735	0.522	0.922	0.262	0.794
300.390	1.4053	1.3734	0.503	0.928	0.248	0.807
299.162	1.4068	1.3733	0.483	0.934	0.233	0.821
297.965	1.4081	1.3734	0.467	0.938	0.222	0.831

[a] Refractive indexes n were measured at wavelength $\lambda = 632.8$ nm and $T_c = 307.754$ K. x and ϕ are mole fraction and volume fraction of dimethyl carbonate. Subscripts 1 and 2 relate to upper and lower phases.

632.8 nm was used as the light source. The uncertainty in measurement of the refractive index in each coexisting phase was ± 0.0001.

Results and Discussion

The critical mole fractions and the critical temperatures for {x dimethyl carbonate + $(1-x)$ n-decane} and for {x dimethyl carbonate + $(1-x)$ n-tetradecane} 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 the reference[8] are also listed in Table 1 for comparison. The differences are as large as 0.5 K for the critical temperature and 0.008 for the critical mole fraction, respectively. It is not surprising because the values reported in the reference[8] were obtained from the fits of the visually determined phase-separation points, each of the points corresponding to a prepared mixture, and the standard deviation of the fit was as large as 0.4 K.

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 + $(1-x)$ n-decane} and in columns 2 and 3 of Table 3 for {x dimethyl carbonate + $(1-x)$ n-tetradecane}. 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.

To convert the refractive index n to the mole fraction x to obtain the coexistence curves of temperature against mole fraction (T, x), the refractive indexes n of pure dimethyl carbonate, n-decane, and n-tetradecane at various temperatures and their binary mixtures with known compositions at fixed temperatures of $T = 287.95$ K for {x dimethyl carbonate + $(1-x)$ n-decane} and $T = 308.14$ K for {x dimethyl carbonate + $(1-x)$ n-tetradecane} in the one-phase region were measured and are listed in Table 4 and Table 5.

It has been shown that the refractive index of the binary mixtures of polar solvent + n-alkane may be expressed as a linear function of temperature in a certain temperature range by using the equations[12]

$$n(T, x) = n(T^0, x) + R(x) \cdot (T - T^0) \qquad (1a)$$

$$R(x) = x \cdot R_1 + (1 - x) \cdot R_2 \qquad (1b)$$

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. Fitting eq 1a to the values listed in Table 4 gives $R_1 = -0.00045\ \mathrm{K}^{-1}$ (from (277.336 to 286.927) K) and $R_1 = -0.00047\ \mathrm{K}^{-1}$ (from (299.638 to 308.136) K), respectively, for dimethyl carbonate. Fitting eq 1a to the values listed in Table 4 gives $R_2 = -0.00044\ \mathrm{K}^{-1}$ for n-decane and $R_2 = -0.00042\ \mathrm{K}^{-1}$ for n-tetradecane. $R(x)$ and $n(T, x)$ at given x may then be calculated by eq 1a and eq 1b. The values of n for various compositions at the temperatures (287.95 and 308.14) K are listed in Table 5 and were used to obtain the polynomial

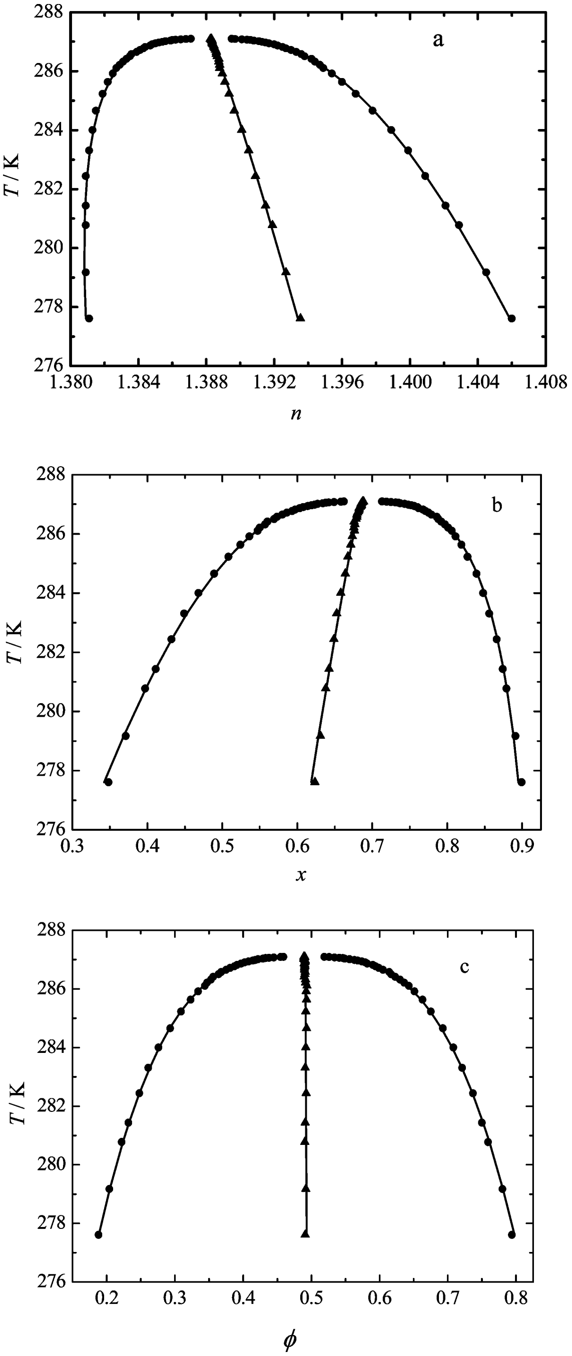

Figure 1. Coexistence curves of (a) temperature against refractive index (T, n), (b) temperature against mole fraction (T, x), and (c) temperature against volume fraction (T, ϕ) for {x dimethyl carbonate + $(1-x)$ n-decane}. ▲, experimental values of diameter ρ_d of the coexisting phases; ●, experimental values of general density variables ρ of the coexisting phases; −, general density variables ρ(calcd) and diameters ρ_d(calcd) of the coexisting phases calculated from a combination of eq 5 to eq 6 with coefficients listed in Tables 7 and 8.

forms 2a and 2b for {x dimethyl carbonate + $(1-x)$ n-decane} and {x dimethyl carbonate + $(1-x)$ n-tetradecane} at their middle temperatures T^0 being (282.355 and 302.858) K of the coexistence curves, respectively

$$n(T^0 = 282.355\ \mathrm{K}, x) = 1.4154 - 0.0345x + 0.0113x^2 - 0.0212x^3 + 0.0013x^4 \quad (2a)$$

$$n(T^0 = 302.858\ \mathrm{K}, x) = 1.4235 - 0.0316x - 0.0094x^2 - 0.0031x^3 - 0.0034x^4 - 0.0128x^5 \quad (2b)$$

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 eq 1a, eq 1b, and eq 2a for {x dimethyl carbonate + $(1-x)$ n-decane} or eq 1a, eq 1b, and eq 2b for {x dimethyl carbonate + $(1-x)$ n-tetradecane} by the Newton iteration method.

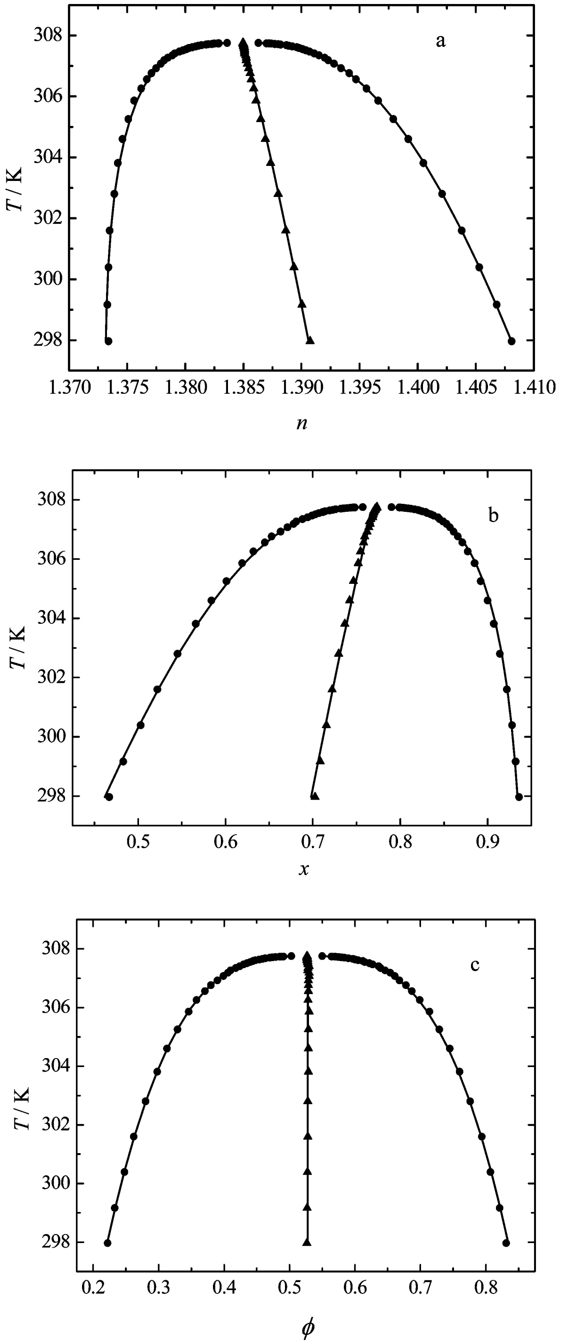

Figure 2. Coexistence curves of (a) temperature against refractive index (T, n), (b) temperature against mole fraction (T, x), and (c) temperature against volume fraction (T, ϕ) for {x dimethyl carbonate + $(1-x)$ n-tetradecane}. ▲, experimental values of diameter ρ_d of the coexisting phases; ●, experimental values of general density variables ρ of the coexisting phases; −, general density variables ρ(calcd) and diameters ρ_d(calcd) of the coexisting phases calculated from a combination of eq 5 to eq 6 with coefficients listed in Tables 7 and 8.

Table 4. Refractive Indexes n at Wavelength $\lambda = 632.8$ nm for Pure Dimethyl Carbonate, n-Decane, and n-Tetradecane at Various Temperatures T

T/K	n	T/K	n	T/K	n	T/K	n
			Dimethyl Carbonate				
277.336	1.3749	284.240	1.3718	301.768	1.3637	307.113	1.3612
278.704	1.3743	285.534	1.3712	302.822	1.3632	308.136	1.3607
280.058	1.3737	286.927	1.3706	303.910	1.3627		
281.535	1.3730	299.638	1.3647	304.986	1.3622		
282.921	1.3724	300.685	1.3642	306.043	1.3617		
			n-Decane				
278.874	1.4169	281.303	1.4158	283.616	1.4148	286.064	1.4137
280.096	1.4163	282.481	1.4153	284.818	1.4142	287.228	1.4132
			n-Tetradecane				
299.637	1.4248	301.681	1.4240	303.746	1.4231	305.780	1.4222
300.669	1.4244	302.713	1.4235	304.750	1.4226	306.857	1.4218
307.907	1.4213						

Table 5. Refractive Indexes n at Wavelength $\lambda = 632.8$ nm for {x Dimethyl Carbonate + $(1-x)$ n-Decane} and {x Dimethyl Carbonate + $(1-x)$ n-Tetradecane} at the Temperatures (287.95 and 308.14) K, Respectively

n	x	n	x	n	x	n	x
			x Dimethyl Carbonate + $(1-x)$ n-Decane				
1.4095	0.101	1.4030	0.300	1.3958	0.501	1.3880	0.686
1.4062	0.204	1.3995	0.401	1.3917	0.605	1.3821	0.800
1.3762	0.903						
			x Dimethyl Carbonate + $(1-x)$ n-Tetradecane				
1.4235	0.000	1.4107	0.300	1.3966	0.600	1.3729	0.899
1.4179	0.100	1.4067	0.399	1.3898	0.708	1.3632	1.000
1.4145	0.201	1.4019	0.500	1.3826	0.801		

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

$$1/\phi = (1 - K) + K/x \tag{3a}$$

$$K = (d_1M_2/d_2M_1) \tag{3b}$$

where d is mass density; M is the molar mass; and subscripts 1 and 2 relate to dimethyl carbonate and n-alkane, respectively. The values of d_1 and d_2 were obtained from Lange's Handbook of Chemistry.[13] 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.

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

$$|\rho_2 - \rho_1| = B\cdot\tau^{\beta} \tag{4}$$

where $\tau = (T_c - T)/T_c$; T_c is the critical temperature; 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; B is the critical amplitude; and β is the critical exponent. 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 4, with all points equally weighted to obtain β and B. The results are listed in Table 6. The values of β are in very good agreement with that of other (polar liquid + n-alkane) systems we reported previously and the theoretical prediction of 0.3255[2] for the temperature range $(T_c - T) < 1$ K.

With the critical exponents β and Δ to be fixed at the theoretical values ($\beta = 0.3255$, $\Delta = 0.5$),[2] a least-squares program was used to fit the Wegner equation

$$|\rho_2 - \rho_1| = B\cdot\tau^{\beta} + B_1\cdot\tau^{\beta+\Delta} + \cdots \tag{5}$$

to obtain the parameters B and B_1. The results are summarized in Table 7.

It was known that the diameter ρ_d of a coexistence curve at least is the sum of the three terms of $\tau^{1-\alpha}$, $\tau^{2\beta}$, and τ, where α characterizes the divergence as the critical point is approached of the heat capacity at constant volume for pure fluids. These terms were thought as a direct consequence of complete scaling,[2] while the presence of the term $\tau^{2\beta}$ was attributed to a wrong choice for the order parameters in the past.[14,15] 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

$$\rho_d = \rho_c + D\cdot\tau^{z} \tag{6}$$

with an apparent exponent Z being fixed at the values 1, $(1 - \alpha) = 0.89$, and $2\beta = 0.651$ in separate fitting procedures. The results are compared in Table 8.

In Table 8, 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 eq 3a and eq 3b.

The goodness of fit to eq 6 may be indicated by the reduced chi-squared value χ^2/N (N is the number of degrees of freedom of the fitting).[16] The uncertainties of optimal parameters reported in Table 8 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 ± 0.002 and ± 0.003, respectively. These uncertainties together with the uncertainty of 0.0001 in measurements of refractive index were used to estimate χ^2/N, which are also listed in Table 8. 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 has 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 goodness of the parameter, the smaller the difference, the better the parameter is.

For both (dimethyl carbonate + n-decane) and (dimethyl carbonate + n-tetradecane), we found that the fits for order parameter ϕ have a similar reduced chi-squared value for all three terms, while for the order parameter x the value of fits with $1 - \alpha$ was significantly larger than that with 2β (i.e.,

Table 6. Values of Critical Amplitude B and Critical Exponent β for Coexistence Curves of (T, n), (T, x), and (T, ϕ) for {x Dimethyl Carbonate + $(1 - x)$ n-Decane} and {x Dimethyl Carbonate + $(1-x)$ n-Tetradecane} in Equation 4

order parameter	$T_c - T < 1$ K		$T_c - T < 10$ K	
	B	β	B	β
	x Dimethyl Carbonate + $(1-x)$ n-Decane			
n	0.078 ± 0.002	0.327 ± 0.003	0.076 ± 0.001	0.325 ± 0.001
x	1.67 ± 0.04	0.329 ± 0.003	1.69 ± 0.02	0.331 ± 0.002
ϕ	1.89 ± 0.05	0.326 ± 0.003	1.86 ± 0.02	0.323 ± 0.002
	x Dimethyl Carbonate + $(1-x)$ n-Tetradecane			
n	0.108 ± 0.002	0.325 ± 0.003	0.108 ± 0.001	0.324 ± 0.001
x	1.38 ± 0.03	0.328 ± 0.002	1.46 ± 0.02	0.335 ± 0.002
ϕ	1.90 ± 0.03	0.325 ± 0.002	1.89 ± 0.02	0.324 ± 0.001

Table 7. Parameters of Equation 5 for Coexistence Curves of (T, n), (T, x) and (T, ϕ) for {x Dimethyl Carbonate + $(1-x)$ n-Decane} and {x Dimethyl Carbonate + $(1-x)$ n-Tetradecane}

order parameter	x Dimethyl Carbonate + $(1-x)$ n-Decane		x Dimethyl Carbonate + $(1-x)$ n-Tetradecane	
	B	B_1	B	B_1
n	0.0765 ± 0.0001		0.1084 ± 0.0002	
	0.0776 ± 0.0002	-0.010 ± 0.002	0.1103 ± 0.0003	-0.017 ± 0.002
x	1.655 ± 0.003		1.408 ± 0.006	
	1.624 ± 0.004	0.29 ± 0.03	1.338 ± 0.002	0.63 ± 0.02
ϕ	1.873 ± 0.004		1.903 ± 0.004	
	1.910 ± 0.005	-0.34 ± 0.04	1.938 ± 0.005	-0.31 ± 0.04

Table 8. Parameters of Equation 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 + $(1-x)$ n-Decane} and {x Dimethyl Carbonate + $(1-x)$ n-Tetradecane}[a]

	(T, n)	(T, x)	(T, ϕ)
	x Dimethyl Carbonate + $(1-x)$ n-Decane		
ρ_c(exptl)	1.3883 ± 0.0001	0.691 ± 0.001	0.493 ± 0.002
	$Z = 1$		
ρ_c	1.3883 ± 0.00001	0.684 ± 0.0006	0.491 ± 0.0002
D	0.161 ± 0.001	-2.03 ± 0.06	0.05 ± 0.02
χ^2/N	0.131	1.874	0.151
	$Z = 2\beta = 0.651$		
ρ_c	1.3879 ± 0.00006	0.689 ± 0.0002	0.490 ± 0.0003
D	0.046 ± 0.001	-0.60 ± 0.01	0.02 ± 0.01
χ^2/N	5.336	0.211	0.135
	$Z = 1 - \alpha = 0.89$		
ρ_c	1.3882 ± 0.00001	0.685 ± 0.0004	0.491 ± 0.0002
D	0.108 ± 0.001	-1.38 ± 0.03	0.04 ± 0.02
χ^2/N	0.374	0.911	0.146
	x Dimethyl Carbonate + $(1-x)$ n-Tetradecane		
ρ_c (exptl)	1.3851 ± 0.0001	0.775 ± 0.001	0.528 ± 0.002
	$Z = 1$		
ρ_c	1.3850 ± 0.00001	0.770 ± 0.0006	0.528 ± 0.0002
D	0.183 ± 0.001	-2.32 ± 0.06	-0.01 ± 0.02
χ^2/N	0.125	8.066	0.332
	$Z = 2\beta = 0.651$		
ρ_c	1.3846 ± 0.00006	0.775 ± 0.0002	0.528 ± 0.0003
D	0.052 ± 0.002	-0.67 ± 0.01	0.002 ± 0.01
χ^2/N	7.007	0.838	0.334
	$Z = 1 - \alpha = 0.89$		
ρ_c	1.3849 ± 0.00001	0.771 ± 0.0004	0.528 ± 0.0002
D	0.123 ± 0.001	-1.57 ± 0.03	-0.005 ± 0.02
χ^2/N	0.460	3.486	0.334

[a] ρ_c(exptl) is the critical value of the order parameter determined by the techniques described in the text.

the difference between the χ^2/N values of the fits with $1 - \alpha$ and 2β for x is larger than that for ϕ), 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 significantly smaller for ϕ than that for the other two parameters, which is consistent with what the symmetry shows: 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. Comparing the values of χ^2/N for the binary mixtures of (dimethyl carbonate + n-decane) and (dimethyl carbonate + n-tetradecane), we found that the difference between the χ^2/N values of the fits with $1 - \alpha$ and 2β for x increases significantly with an increase of the number of carbon atoms in n-alkane molecules compared with that for ϕ. It indicates that as the number of carbon atoms increases the contribution of the 2β term for order parameter x becomes more significant than ϕ, thus the order parameter ϕ becomes more favorable. It is consistent with the observations and the analyses for the binary system of nitrobenzene + n-alkanes.[1,2,17] 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.

A combination of eq 5 and eq 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, 0.3255, and 0.5, respectively for both {x dimethyl carbonate + $(1-x)$ n-decane} and {x dimethyl carbonate + $(1-x)$ n-tetradecane} and taking the values of D, ρ_c, B, and B_1 from Tables 7 and 8. ρ_d, ρ_1, and ρ_2 were calculated from eq 7 and eq 8. The values are shown as lines in Figures 1 and 2. The values from calculation are in good agreement with experimental results.

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