

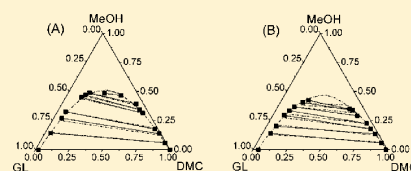
Liquid–Liquid Equilibria for the System Dimethyl Carbonate + Methanol + Glycerol in the Temperature Range of (303.15 to 333.15) K

Huajun Wang^{*,†,‡} and Pengfei Lu[†]

[†]School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, P. R. China

[‡]Hubei Key Laboratory of Material Chemistry & Service Failure, Huazhong University of Science and Technology, Wuhan 430074, P. R. China

ABSTRACT: Liquid–liquid equilibria (LLE) data of the ternary system dimethyl carbonate + methanol + glycerol were measured from (303.15 to 333.15) K. The equilibrium data are correlated with the nonrandom two-liquid (NRTL) model. The reliability of this model is tested by comparison with the experimental results. On the other hand, LLE and vapor–liquid equilibria (VLE) of the binary system dimethyl carbonate + glycerol were also measured under isopiestic pressure (101.3 kPa) and predicted using the NRTL model, with the adjusted parameters obtained from the LLE data of the ternary system dimethyl carbonate + methanol + glycerol. The predicted VLE and LLE for the binary system agreed well with the experimental data.



1. INTRODUCTION

Currently, large amounts of glycerol (GL) as a byproduct of the plant oil methanolysis are produced for the biodiesel production and are continually increasing.¹ The utilization of GL has become a research focus to promote the development of the biodiesel industry. Therefore, more and more value-added GL derivatives have been reported in the scientific and patent literature.² Among these products, glycerol carbonate (GC) is a promising one due to its potential uses. GC is a stable and colorless liquid with low toxicity, good biodegradability, and a high boiling point and is useful in various fields. For example, it can be used as a polar high boiling solvent, a surfactant component, and an intermediate for many kinds of polymers such as polyesters, polycarbonates, polyamides, and so on.³

Several processes for the synthesis of GC have already been discovered. GC can be obtained from direct carboxylation of GL with carbon dioxide under supercritical conditions,¹ from a carbamylation–carbonation reaction between GL and urea,^{4,5} or from transesterification of GL with ethylene carbonate.² In these reactions, however, some disadvantages are found: the first reaction has low yields of GC, while the second reaction must be carried out at vacuum to separate continuously ammonia; furthermore, the separation of products is difficult in the third reaction.^{6,7} An alternative process for producing GC is the transesterification of GL with dimethyl carbonate (DMC) because the carbonate source DMC is a green reagent which can be manufactured by an environmentally safe method and the reaction condition is milder.⁸

The combined process of reaction distillation and extraction distillation for the synthesis of GC from GL and DMC through transesterification has been investigated by authors and the other researchers.⁹ Unfortunately, the design and calculation of the combined process are limited by the lack of data on the thermodynamic behavior of the system containing DMC, methanol (MeOH), GL, and GC. To the best of our knowledge,

only the vapor–liquid equilibria (VLE) of the binary system DMC + MeOH and GL + MeOH have been reported in the literature.^{10–17}

As part of a series, the purpose of this work is to supply some basic thermodynamic data for the above system for the study of the combined process. In this work, the liquid–liquid equilibria (LLE) for the ternary system DMC + MeOH + GL are measured from (303.15 to 333.15) K. On the other hand, LLE and VLE for the binary system DMC + GL are also measured. The LLE data of the ternary system presented are correlated using the nonrandom two-liquid (NRTL) model. Finally, the reliability of this model is tested by a comparison with the experimental results.

2. EXPERIMENTAL SECTION

Materials. DMC (Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China), GL (Sinopharm Chemical Reagent Co., Ltd., China), and MeOH (Sinopharm Chemical Reagent Co., Ltd., China) used were of ≥ 99.0 % purity, respectively. The purities of tetraethylene glycol (Acros Organics) and *n*-butanol (Shanghai Zhanyun Chemical Co., Ltd., Shanghai, China) were 99.5 % and 99.0 %, respectively. Prior to the measurements, the purities of all of these chemicals were checked by gas chromatography, and the mass fractions were found to be better than 99.0 %. They were used without further purification.

Equilibrium Measurements. A 50 mL round-bottom three-neck glass flask fitted with a magnetic stirrer, two sampling devices, and a thermometer was used to measure the LLE for the ternary system. The accuracy of the temperature measurements was ± 0.01 K. The energy was applied to the test flask with the constant temperature water bath. During the operation, a given

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Table 1. Experimental LLE Data on Mole Fractions (x) and Selectivities (S) of the Ternary System DMC (1) + MeOH (2) + GL (3) at 101.3 kPa

T/K	DMC-rich phase			GL-rich phase			selectivity (S)
	x_1	x_2	x_3	x_1	x_2	x_3	
303.15	0.9326	0.0595	0.0079	0.0417	0.1422	0.8161	53.45
	0.8513	0.1381	0.0106	0.0602	0.2699	0.6700	27.64
	0.8003	0.1773	0.0224	0.0625	0.3260	0.6114	23.54
	0.6416	0.3130	0.0454	0.1176	0.4494	0.4330	7.83
	0.6020	0.3450	0.0530	0.1372	0.4692	0.3936	5.97
	0.5522	0.3940	0.0539	0.1584	0.4880	0.3537	4.32
	0.4033	0.4674	0.1293	0.2719	0.4848	0.2433	1.54
313.15	0.9289	0.0591	0.0120	0.0425	0.1271	0.8305	47.00
	0.7725	0.2030	0.0244	0.0781	0.3548	0.5671	17.29
	0.7126	0.2459	0.0415	0.1057	0.3875	0.5068	10.62
	0.6942	0.2629	0.0429	0.0966	0.4021	0.5013	10.99
	0.5951	0.3323	0.0726	0.1383	0.4507	0.4110	5.84
	0.5136	0.3861	0.1002	0.1709	0.4766	0.3525	3.71
	0.4954	0.3898	0.1149	0.1688	0.4826	0.3485	3.63
323.15	0.8922	0.0932	0.0145	0.0529	0.1587	0.7884	28.72
	0.8422	0.1429	0.0149	0.0543	0.2164	0.7293	23.49
	0.7681	0.1898	0.0420	0.0778	0.2956	0.6266	15.38
	0.6913	0.2469	0.0618	0.1077	0.3358	0.5565	8.73
	0.5917	0.3218	0.0865	0.1408	0.4023	0.4569	5.25
	0.5419	0.3605	0.0976	0.1689	0.4378	0.3933	3.90
	0.4756	0.3809	0.1435	0.1645	0.4330	0.4025	3.29
333.15	0.9263	0.0570	0.0167	0.0627	0.1404	0.7970	36.39
	0.8405	0.1365	0.0229	0.0709	0.2021	0.7270	17.55
	0.7869	0.1765	0.0366	0.0847	0.2955	0.6198	15.55
	0.7336	0.2254	0.0410	0.1039	0.3353	0.5608	10.50
	0.6306	0.2915	0.0779	0.1249	0.3669	0.5082	6.35
	0.5737	0.3377	0.0886	0.1675	0.4055	0.4270	4.11
	0.5443	0.3490	0.1067	0.2002	0.4240	0.3758	3.30

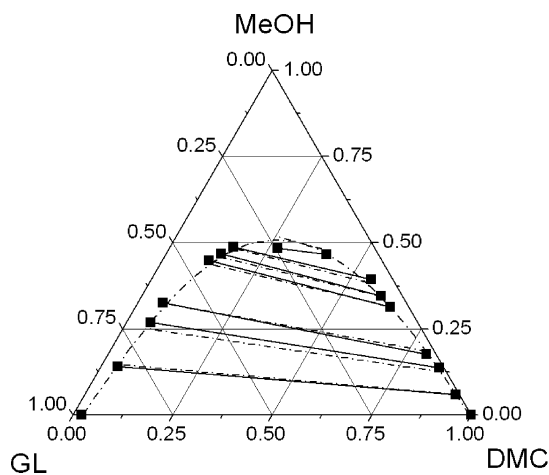


Figure 1. Ternary LLE of the DMC (1) + MeOH (2) + GL (3) system at 303.15 K. (■—■), experimental tie-line data; ---, tie-lines and binodal curve predicted using the NRTL model with the parameters of Table 4.

liquid mixture was charged into the test flask, which was filled almost completely, and heated to the desired temperature. Then, the liquid mixture was stirred for at least 2 h with the stirring speed of 600 rpm and set for at least 3 h at the constant temperature. Under the above conditions, the LLE were reached for the both phases as confirmed by the preparatory experiments.

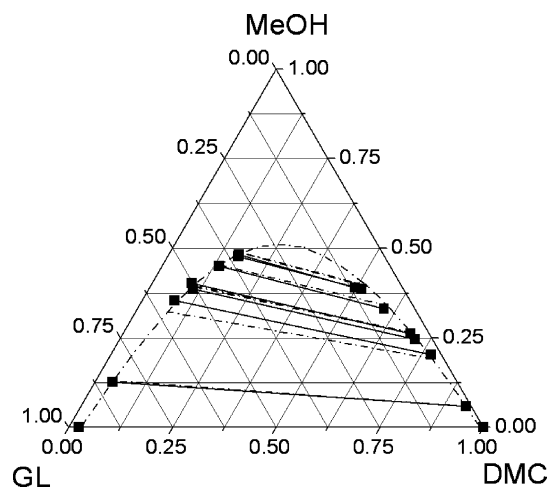


Figure 2. Ternary LLE of the DMC (1) + MeOH (2) + GL (3) system at 313.15 K. (■—■), experimental tie-line data; ---, tie-lines and binodal curve predicted using the NRTL model with the parameters of Table 4.

At the end of the setting period, the samples of the equilibrium were taken out from the both phases, respectively. All of the components were analyzed by the gas chromatograph (Agilent GC1790) equipped with a flame ionization detector (FID) and a capillary column DM-FFAP (30 m long, 0.25 mm i.d.). The internal standard method was used. Nitrogen (99.999 % pure, Sichuan Tianyi Science & Technology Co., Ltd.,

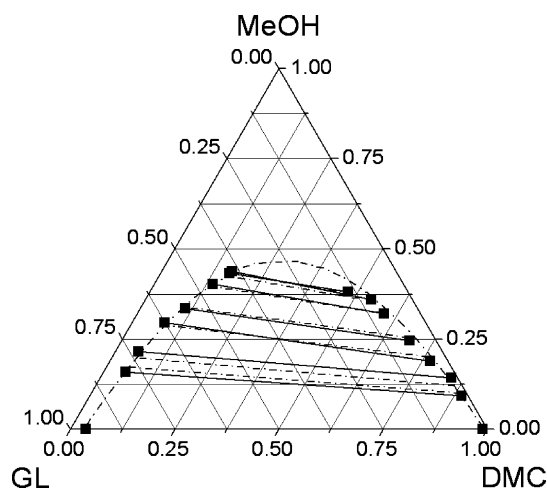


Figure 3. Ternary LLE of the DMC (1) + MeOH (2) + GL (3) system at 323.15 K. (■—■), experimental tie-line data; ---, tie-lines and binodal curve predicted using the NRTL model with the parameters of Table 4.

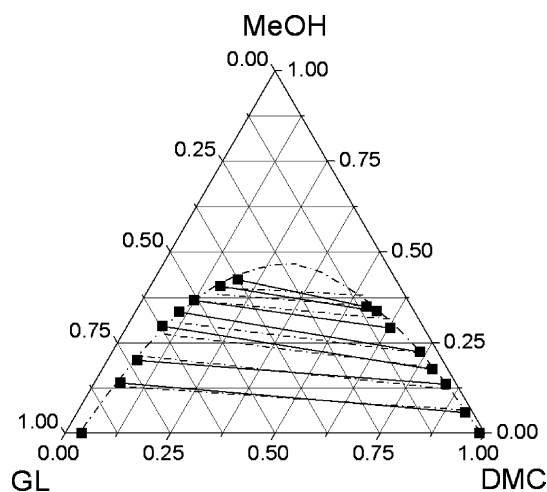


Figure 4. Ternary LLE of the DMC (1) + MeOH (2) + GL (3) system at 333.15 K. (■—■), experimental tie-line data; ---, tie-lines and binodal curve predicted using the NRTL model with the parameters of Table 4.

Sichuan, China) was used as the carrier gas with a flow rate of $30 \text{ mL}\cdot\text{min}^{-1}$ at 0.3 MPa. The temperatures of the injector and the detector were (250 and 270) °C, respectively. The temperature of the column was programmed to have a 2 min initial hold at 70 °C, a $15 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ ramp from (70 to 250) °C, and a 15 min hold at 250 °C. A good peak separation was achieved under these conditions for all components. *n*-Butanol was used as the internal standard to determine DMC and MeOH, while tetraethylene glycol was used as the internal standard to determine GL. In the internal standard method, gas chromatography calibration plots were obtained by employing six sample mixtures of known compositions as the standard reference. The compositions of these standard samples were obtained through weighing with an electronic balance, having an accuracy of $\pm 0.0001 \text{ g}$. The mass of each component in the sample was determined from the calibration and converted to mole fraction. At least three analyses were performed for each sample to obtain a mean value. The standard uncertainties of the mole fractions were less than 0.009.

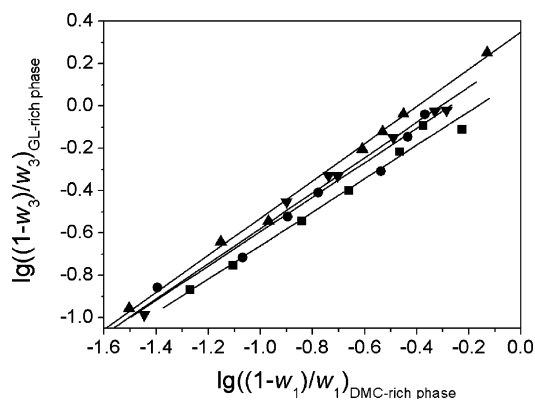


Figure 5. Othmer–Tobias plots for the DMC (1) + MeOH (2) + GL (3) system at all temperatures. Experimental data: ▲, 303.15 K; ▼, 313.15 K; ■, 323.15 K; ●, 333.15 K. Curve fit: solid lines.

Table 2. Parameters of Othmer–Tobias Correlation Equation 1 (*a*, *b*) and Correlation Factor (*R*²) for the Ternary System DMC (1) + MeOH (2) + GL (3)

<i>T</i> /K	<i>a</i>	<i>b</i>	<i>R</i> ²
303.15	0.3495	0.8785	0.9984
313.15	0.2573	0.8354	0.9958
323.15	0.1333	0.7923	0.9912
333.15	0.2205	0.8134	0.9904

Table 3. Root-Mean-Square Deviation (*rmsd*) of the Data Correlation for the Ternary System DMC (1) + MeOH (2) + GL (3) at 323.15 K with the Different Values of the Nonrandomness Parameter α_{ij} in the NRTL Model

no.	value of α_{ij}	<i>rmsd</i> (%)
1	$\alpha_{12} = \alpha_{23} = \alpha_{13} = 0.3$	1.18
2	$\alpha_{12} = \alpha_{23} = \alpha_{13} = 0.2$	2.33
3	$\alpha_{23} = 0.3, \alpha_{12} = \alpha_{13} = 0.2$	1.16
4	α_{ij} are regressed simultaneously with Δg_{ij} ($\alpha_{12} = 0.16, \alpha_{13} = 0.29, \alpha_{23} = 0.15$) ^a	1.24

^aValues of parameter α_{ij} which were obtained by regression.

To investigate the suitability of the model parameters obtained from LLE data of the ternary system DMC + MeOH + GL for the prediction of the VLE, some VLE data of the binary system DMC + GL were also measured. The experimental method of VLE has been reported in the previous work.¹⁸

3. RESULTS AND DISCUSSION

Experimental Data. The LLE data of the ternary system DMC (1) + MeOH (2) + GL (3) at (303.15, 313.15, 323.15, and 333.15) K and atmospheric pressure with the selectivity are shown in Table 1. All concentrations are expressed in mole fraction. In Figures 1 to 4, the experimental data at all research temperatures are plotted, respectively, together with the tie-lines and binodal curve calculated using the NRTL model. The system exhibits type I liquid–liquid phase behavior, having one pair of partially miscible components (DMC + GL) and two pairs of completely miscible components (DMC + MeOH and MeOH + GL) in the temperature range investigated. As can be observed in Figures 1 to 4, the size of the two-phase region decreases with the temperature, but the effect is small. The ternary system studied

Table 4. NRTL Binary Interaction Parameters for the Ternary System DMC (1) + MeOH (2) + GL (3)

T/K	i-j	α_{ij}	NRTL parameter		rmsd (%)
			Δg_{ij}	Δg_{ij}	
			J·mol ⁻¹	J·mol ⁻¹	
303.15	1-2	0.2	-8387.68	3365.09	1.02
	1-3	0.2	10512.05	5165.65	
	2-3	0.3	-661.63	-8067.17	
313.15	1-2	0.2	-2997.68	4433.83	1.15
	1-3	0.2	9490.01	5117.18	
	2-3	0.3	-427.59	-2012.43	
323.15	1-2	0.2	-5181.37	15306.87	1.16
	1-3	0.2	12091.69	6085.64	
	2-3	0.3	-3062.42	2106.39	
333.15	1-2	0.2	6102.29	-1532.00	1.63
	1-3	0.2	8515.12	5966.74	
	2-3	0.3	3997.77	-384.05	

Table 5. Optimized Temperature-Independent NRTL Binary Interaction Parameters for the Ternary System DMC (1) + MeOH (2) + GL (3) Fitted to All Isotherms

i-j	α_{ij}	NRTL parameter		rmsd (%)
		Δg_{ij}	Δg_{ij}	
		J·mol ⁻¹	J·mol ⁻¹	
1-2	0.2	-9901.11	3588.69	1.88
1-3	0.2	10017.82	5141.07	
2-3	0.3	-1082.03	-8824.08	

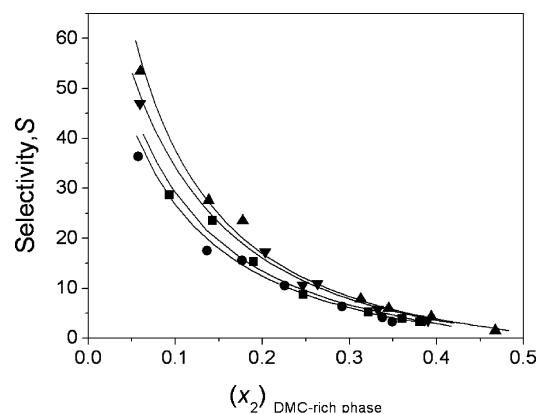
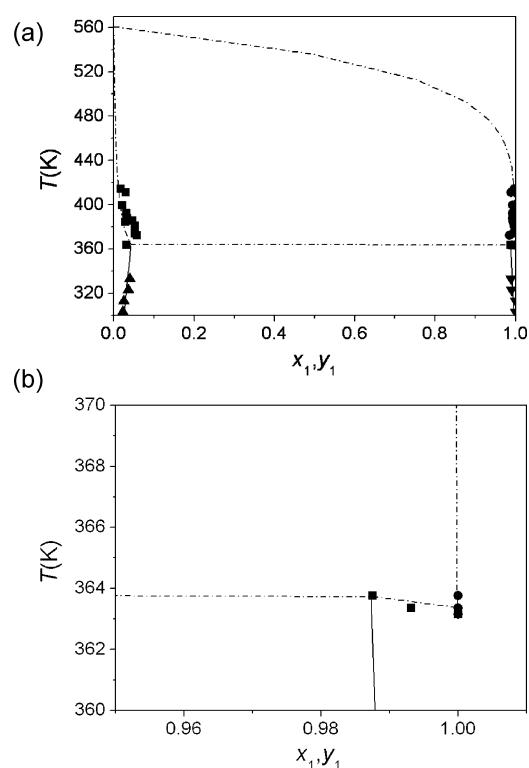
presents a wide two-phase region that is important, together with the slope of the tie-lines, when establishing the selectivity of GL.

The Othmer–Tobias equation was used to check the reliability of experimental results.¹⁵ This equation is listed as

$$\left[\log \left(\frac{1-w_3}{w_3} \right) \right]_{\text{GL-rich phase}} = a + b \left[\log \left(\frac{1-w_1}{w_1} \right) \right]_{\text{DMC-rich phase}} \quad (1)$$

where w_1 is the mass fraction of DMC in the DMC-rich phase; w_3 is the mass fraction of GL in the GL-rich phase; a and b are the constants in eq 1. Figure 5 shows the plot of $\log((1-w_3)/w_3)_{\text{GL-rich phase}}$ against $\log((1-w_1)/w_1)_{\text{DMC-rich phase}}$ at all temperatures for the ternary system. The values of a and b and the correlation factor (R^2) are given in Table 2. All of the values of R^2 are >0.99 . This shows that the experimental data in this work are reliable.

Data Correlation of the DMC (1) + MeOH (2) + GL (3) System. In this work, the NRTL model¹⁹ was used to correlate the experimental data for the research ternary system. There are two effective binary interaction parameters for a pair of substances. So, six effective binary interaction parameters are required for a ternary system. On the other hand, the ASPEN Plus Simulator not only is the tool of flowsheeting, but it also has a strong property analysis system and data regression system as well.²⁰ So, the ASPEN Simulator²¹ was used to calculate the optimum sets of the binary interaction parameters and predict the LLE behavior of the research system in this work.

**Figure 6.** Effect of temperature on measured and calculated selectivity S for the DMC (1) + MeOH (2) + GL (3) system. Experimental data: ▲, 303.15 K; ▼, 313.15 K; ■, 323.15 K; ●, 333.15 K. Prediction by the NRTL model with the parameters of Table 4: solid lines.**Figure 7.** (a) VLE and LLE experimental and predicted results for the DMC (1) + GL (3) system at 101.3 kPa. (b) The partial amplification drawing of the top. Experimental LLE data: ▲, GL phase; ▼, DMC phase; solid lines, calculated by the NRTL model with the parameters of Table 5. Experimental VLE data: ■, liquid phase; ●, vapor phase; ---, predicted by NRTL model with the parameters of Table 5.

The regression method used in the ASPEN simulator was the generalized least-squares method based on the maximum likelihood principle.^{20,22} The new Britt–Luecke algorithm²³ was employed to obtain the model parameters with the Deming initialization method.²⁴ The objective function used is

$$\text{OF} = \sum_{k=1}^M \sum_{j=1}^2 \sum_{i=1}^2 \left[\frac{(T_k^{\text{exp}} - T_k^{\text{cal}})^2}{\sigma_T^2} + \frac{(x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}})^2}{\sigma_x^2} \right] \quad (2)$$

Table 6. LLE Deviation between Experimental and Predicted Results on Mole Fractions (x_1) for the Binary System DMC (1) + GL (3) at 101.3 kPa

T/K	DMC-rich phase		GL-rich phase	
	experimental results	deviation with NRTL model ^a	experimental results	deviation with NRTL model ^a
	x_1	Δx_1^b	x_1	Δx_1^b
303.15	1.0000	0.0052	0.0222	-0.0040
313.15	1.0000	0.0062	0.0246	-0.0040
323.15	0.9898	-0.0030	0.0363	0.0051
333.15	0.9888	-0.0028	0.0395	0.0056
mean deviation ^c		0.0043		0.0047

^aPredicted by the NRTL model with the parameters of Table 5. ^b $\Delta x_1 = x_1^{\text{exp}} - x_1^{\text{cal}}$. ^cMean deviation = $\sum_{i=1}^n |\Delta x_1|/n$ ($n = 4$).

Table 7. VLE Deviation between Experimental and Predicted Results on Mole Fractions (x_1, y_1) for the Binary System DMC (1) + GL (3) at 101.3 kPa

T/K	experimental results		deviation with NRTL model ^a		
	x_1	y_1	$\Delta T^b/K$	$\Delta T/T^{\text{exp}}$ (%)	Δy_1^b
363.15	1.0000	1.0000	-0.22	-0.06	0.0000
363.36	0.9932	1.0000	-0.22	-0.06	0.0001
363.75	0.9875	1.0000	0.03	0.01	0.0001
363.79	0.0313	0.9914	-7.95	-2.19	-0.0083
372.43	0.0569	0.9859	6.70	1.80	-0.0140
374.39	0.0520	0.9939	8.66	2.31	-0.0060
381.03	0.0528	0.9962	15.30	4.02	-0.0037
384.82	0.0287	0.9941	6.81	1.77	-0.0056
387.94	0.0338	0.9932	15.21	3.92	-0.0066
390.30	0.0259	0.9998	6.99	1.79	0.0002
394.34	0.0251	0.9998	9.91	2.51	0.0003
399.87	0.0206	0.9926	11.88	2.97	-0.0067
414.34	0.0171	0.9963	10.00	2.41	-0.0020
416.28	0.0141	0.9997	7.25	1.74	0.0022
mean deviation ^c			7.65	1.96	0.0040

^aPredicted by the NRTL model with the parameters of Table 5. ^b $\Delta T = T^{\text{exp}} - T^{\text{cal}}$, $\Delta y_1 = y_1^{\text{exp}} - y_1^{\text{cal}}$. ^cMean deviation = $\sum_{i=1}^n |\Delta T|/n$ or mean deviation = $\sum_{i=1}^n |\Delta y_1|/n$ ($n = 14$).

where M is the number of tie-lines, x^{exp} and T^{exp} indicate the experimental mole fraction and temperature, and x^{cal} and T^{cal} are the calculated mole fraction and temperature, respectively. The subscripts i, j , and k denote, respectively, the component, phase, and tie-line. σ_T and σ_x are the standard deviation of the temperature and the mole fraction of component i , respectively, and their values were taken as: $\sigma_T = 0.01$ K, $\sigma_x = 0.009$.

The data correlations were made as following two steps for the NRTL model. First, when the binary interaction parameters, Δg_{ij} , were regressed, the value of the nonrandomness parameter, α_{ij} , was investigated with the following four cases: (1) all of the α_{ij} were set to 0.3; (2) all of the α_{ij} to 0.2; (3) $\alpha_{23} = 0.3$, $\alpha_{12} = \alpha_{13} = 0.2$; (4) all of the α_{ij} were regressed simultaneously with Δg_{ij} . The results are listed in Table 3. In this work, the root-mean-square deviation (rmsd) in the phase composition was calculated as

$$\text{rmsd} = 100 \left(\sum_{k=1}^M \sum_{j=1}^2 \sum_{i=1}^3 \frac{(x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}})^2}{6M} \right)^{1/2} \quad (3)$$

Table 8. VLE Deviation between Experimental and Predicted Results on Mole Fractions (x_2, y_2) for the Binary System DMC (1) + MeOH (2) at 101.3 kPa

T/K	experimental results ^a		deviation with NRTL model ^b		
	x_2	y_2	$\Delta T^c/K$	$\Delta T/T^{\text{exp}}$ (%)	Δy_2^c
361.99	0.0103	0.0523	1.44	0.40	-0.0433
359.93	0.0252	0.1258	2.74	0.76	-0.0753
357.45	0.0457	0.2065	3.73	1.04	-0.0952
355.71	0.0620	0.2669	3.97	1.12	-0.0890
354.69	0.0709	0.2950	3.88	1.09	-0.0856
352.38	0.0958	0.3613	3.65	1.04	-0.0729
349.83	0.1291	0.4379	3.05	0.87	-0.0450
347.97	0.1582	0.4818	2.41	0.69	-0.0317
346.56	0.1834	0.5202	1.82	0.52	-0.0139
344.85	0.2210	0.5687	1.07	0.31	0.0098
343.99	0.2472	0.5915	0.73	0.21	0.0186
342.57	0.2913	0.6238	0.04	0.01	0.0305
341.74	0.3251	0.6488	-0.33	-0.10	0.0415
340.99	0.3619	0.6703	-0.63	-0.18	0.0487
340.11	0.4247	0.6960	-0.85	-0.25	0.0509
339.18	0.4916	0.7206	-1.15	-0.34	0.0492
338.69	0.5386	0.7394	-1.24	-0.37	0.0482
338.21	0.5800	0.7547	-1.39	-0.41	0.0451
337.55	0.6622	0.7806	-1.45	-0.43	0.0294
337.18	0.7181	0.7955	-1.47	-0.44	0.0131
336.97	0.7684	0.8123	-1.40	-0.42	-0.0019
336.95	0.8160	0.8332	-1.20	-0.36	-0.0130
336.88	0.8617	0.8560	-1.10	-0.33	-0.0242
336.89	0.8824	0.8736	-1.02	-0.30	-0.0231
336.98	0.9104	0.8931	-0.85	-0.25	-0.0265
337.11	0.9341	0.9166	-0.67	-0.20	-0.0226
337.25	0.9549	0.9406	-0.49	-0.14	-0.0173
337.39	0.9726	0.9614	-0.32	-0.10	-0.0129
337.60	0.9889	0.9833	-0.09	-0.03	-0.0061
mean deviation ^d			1.52	0.44	0.0374

^aVLE experimental data were obtained from the literature.¹⁴ ^bPredicted by the NRTL model with the parameters of $T/K = 333.15$ in Table 4. ^c $\Delta T = T^{\text{exp}} - T^{\text{cal}}$, $\Delta y_2 = y_2^{\text{exp}} - y_2^{\text{cal}}$. ^dMean deviation = $\sum_{i=1}^n |\Delta T|/n$ or mean deviation = $\sum_{i=1}^n |\Delta y_2|/n$ ($n = 29$).

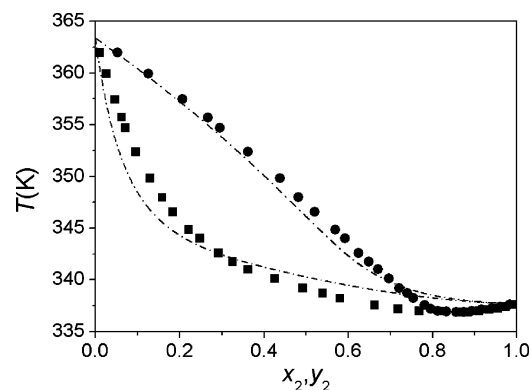


Figure 8. VLE experimental and predicted results for the DMC (1) + MeOH (2) system at 101.3 kPa: ■, liquid phase; ●, vapor phase; ---, predicted by the NRTL model with the parameters of $T/K = 333.15$ in Table 4 (VLE experimental data were obtained from the literature¹⁴).

As shown in Table 3, the best results were obtained when $\alpha_{23} = 0.3$ and $\alpha_{12} = \alpha_{13} = 0.2$ with 1.16 % of the rmsd. Second, the binary interaction parameters were calculated separately using the above method when $\alpha_{23} = 0.3$ and $\alpha_{12} = \alpha_{13} = 0.2$ at each

Table 9. VLE Deviation between Experimental and Predicted Results on Mole Fractions (x_2 , y_2) for the Binary System MeOH (2) + GL (3) at (32.02 and 45.3) kPa

experimental results ^a			deviation with NRTL model ^b		
T/K	x_2	y_2	ΔT^c /K	$\Delta T/T^{\text{exp}}$ (%)	Δy_2^c
$p/\text{kPa} = 32.02$					
521.80	0.0000	0.0000	1.06	0.20	0.000000
356.95	0.1000	0.999882	5.39	1.51	0.000018
340.25	0.2000	0.999981	5.17	1.52	0.000010
331.90	0.3000	0.999994	4.77	1.44	0.000006
326.60	0.4000	0.999997	4.21	1.29	0.000004
322.80	0.5000	0.999998	3.51	1.09	0.000002
319.80	0.6000	0.999999	2.65	0.83	0.000002
317.35	0.7000	0.999999	1.79	0.56	0.000001
315.15	0.8000	1.0000	0.94	0.30	0.000002
313.05	0.9000	1.0000	0.23	0.07	0.000001
311.00	1.0000	1.0000	-0.04	-0.01	0.000000
mean deviation ^d			2.70	0.80	0.000004
$p/\text{kPa} = 45.3$					
533.40	0.0000	0.0000	1.38	0.26	0.000000
370.35	0.1000	0.999722	8.55	2.31	-0.000060
351.85	0.2000	0.999955	7.62	2.17	0.000001
342.45	0.3000	0.999985	6.68	1.95	0.000004
336.40	0.4000	0.999993	5.67	1.69	0.000004
332.00	0.5000	0.999997	4.57	1.38	0.000004
328.50	0.6000	0.999998	3.37	1.03	0.000003
325.65	0.7000	0.999999	2.24	0.69	0.000003
323.10	0.8000	0.999999	1.15	0.36	0.000002
320.75	0.9000	1.0000	0.31	0.10	0.000001
318.50	1.0000	1.0000	-0.05	-0.02	0.000000
mean deviation ^d			3.78	1.08	0.000007

^aVLE experimental data were obtained from the literature.¹⁰

^bPredicted by the NRTL model with the parameters of $T/\text{K} = 333.15$ in Table 4. ^c $\Delta T = T^{\text{exp}} - T^{\text{cal}}$, $\Delta y_2 = y_2^{\text{exp}} - y_2^{\text{cal}}$. ^dMean deviation = $\sum_{i=1}^n |\Delta T|/n$ or mean deviation = $\sum_{i=1}^n |\Delta y_2|/n$ ($n = 11$).

temperature. The results are given in Table 4. With the use of these parameters, the tie-lines and binodal curve for the DMC (1) + MeOH (2) + GL (3) system predicted using the NRTL model can be obtained (shown in Figures 1 to 4).

Although a good fit is obtained for all temperatures, the parameters determined for each temperature have no relation between them. So, to obtain a unique set of parameters valid for the range of temperatures studied, a simultaneous correlation of all of the experimental LLE data of this system was carried out. Table 5 lists the optimized NRTL binary interaction parameters obtained in a simultaneous correlation of all data assuming temperature-independent parameters. As shown in Table 5, the rmsd values are little higher than when the individual correlation at each temperature was made. However, the all rmsd values are less than 2.0 % in Tables 4 and 5. This suggests that the NRTL model provides an adequate representation of the phase behavior of the ternary system DMC (1) + MeOH (2) + GL (3) at all temperatures.

Selectivity. In the process of reaction distillation for the synthesis of GC, how to separate DMC from the mixture of both DMC and MeOH is one of the key technologies. Among the various proposals, the method of using extraction and distillation with organic solvents to separate DMC from this mixture is a good one. On the other hand, the effectiveness of a solvent can be expressed by the selectivity S . In fact, the effectiveness of MeOH extraction by GL is given by its

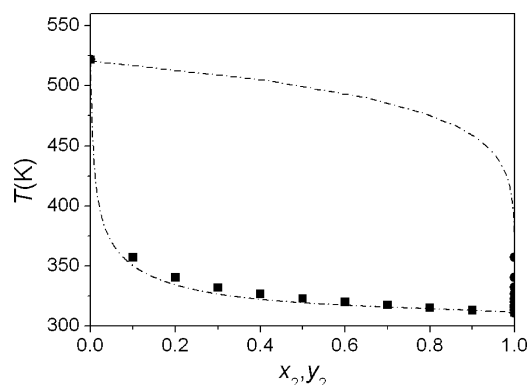


Figure 9. VLE experimental and predicted results for the MeOH (2) + GL (3) system at 32.02 kPa: ■, liquid phase; ●, vapor phase; ---, predicted by the NRTL model with the parameters of $T/\text{K} = 333.15$ in Table 4 (VLE experimental data were obtained from the literature¹⁰).

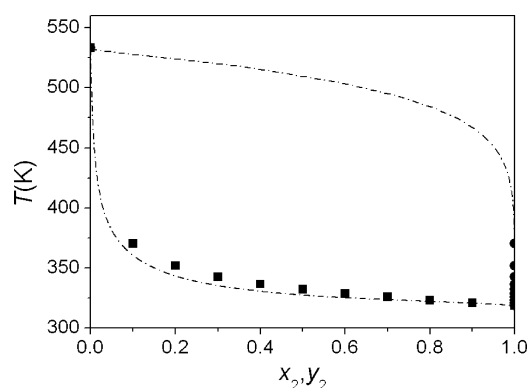


Figure 10. VLE experimental and predicted results for the MeOH (2) + GL (3) system at 45.3 kPa: ■, liquid phase; ●, vapor phase; ---, predicted by the NRTL model with the parameters of $T/\text{K} = 333.15$ in Table 4 (VLE experimental data were obtained from the literature¹⁰).

selectivity, which is an indication of the ability of GL to separate MeOH from DMC, and is given by

$$S = \frac{(x_2/x_1)_{\text{GL-rich phase}}}{(x_2/x_1)_{\text{DMC-rich phase}}} \quad (4)$$

where the subscripts 1 and 2 represent DMC and MeOH, respectively. As shown in Table 1, the selectivity values are greater than 1 for the research system. This means that extraction of MeOH by GL is possible. The selectivity values decreased as the concentration of MeOH increased. Therefore, the higher the concentration of MeOH in feed, the lower the selectivity of GL. Figure 6 shows the extracting power of GL at each temperature, and it can be observed that the higher the temperature, the lower the selectivity. Similar behavior was also correctly predicted using the NRTL model as shown in the same figure. In Figure 6, a good agreement between the experimental and calculated selectivity values is shown.

Prediction of VLE and LLE for the DMC (1) + GL (3) System. In this work, an attempt was made to examine the capability for predicting the isobaric VLE of the partially miscible system DMC (1) + GL (3) using the parameters determined from the LLE data of the ternary system DMC (1) + MeOH (2) + GL (3). The predicted VLE and LLE data by the ASPEN Simulator, using the binary interaction parameters (pair 1–3) obtained by correlation with the NRTL model, are

compared with the experimental values in Figure 7. Tables 6 and 7 show the deviations between experimental and predicted results for the DMC (1) + GL (3) system in detail. The standard uncertainties of the mole fractions x_i , y_i , and the equilibrium temperature T of the experimental VLE data of the DMC (1) + GL (3) system were less than (0.005, 0.003, and 0.01) K, respectively. As can be observed the NRTL model is capable of reproducing the VLE and LLE of this system, and the agreement between experimental and predicted VLE and LLE values is good.

Using the same method, the VLE data for the two completely miscible systems (DMC (1) + MeOH (2) and MeOH (2) + GL (3)) are also predicted by the ASPEN Simulator with the binary interaction parameters (pair 1–2 and pair 2–3, respectively). The results are shown in Tables 8 and 9 and Figures 8 to 10. The VLE experimental data for the two binary systems, DMC (1) + MeOH (2) and MeOH (2) + GL (3), are taken from the references 14 and 10, respectively. The results also indicated that there is good agreement between the experimental data and the calculations by the NRTL model for the two binary systems.

4. CONCLUSIONS

The LLE of the DMC + MeOH + GL system have been measured at different temperatures. This system has one pair of partially miscible components (DMC + GL) and two pairs of completely miscible components (DMC + MeOH and MeOH + GL) in the temperature range investigated. The binary interaction parameters in the NRTL model were obtained by correlating the LLE data. The correlation with the NRTL equation fits the experimental data satisfactorily. The simultaneous correlation of the four isothermal data sets gives a unique set of parameters in the range of the temperature considered. Finally, the VLE for the three binary systems DMC + GL, DMC + MeOH, and MeOH + GL were predicted using the NRTL model, with the adjusted parameters obtained from the LLE data. These predictions were successful when compared with the experimental VLE data.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wanghuajun@mail.hust.edu.cn. Tel.: +86 27 87543732. Fax: +86 27 87543632.

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LIST OF ABBREVIATIONS

LLE	liquid–liquid equilibria
NRTL	nonrandom two-liquid model
rmsd	root-mean-square deviation (eq 3)
VLE	vapor–liquid equilibria
DMC	dimethyl carbonate
GL	glycerol
GC	glycerol carbonate
MeOH	methanol

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