Separation of methanol + dimethyl carbonate azeotropic mixture

Using ionic liquids as entrainers

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Abstract

Isobaric vapor-liquid equilibrium (VLE) data of methanol + dimethyl carbonate, methanol + dimethyl carbonate + 1-Ethyl-3-Methylimidazolium Bromide ([EMIM][Br]) and methanol + dimethyl carbonate + 1-Butyl-3-Methylimidazolium Chloride ([BMIM][Cl]) were measured by a modified Othmer still at 101.3 kPa. The two investigated ionic liquids produced significant effects on the separation of the methanol and dimethyl carbonate azeotropic system. The relative volatility of dimethyl carbonate to methanol was enhanced with the addition of ionic liquid. The two ionic liquids could both eliminate the azeotropic point as their concentration increased to a certain value, but [BMIM][Cl] showed a greater separation effect on methanol and dimethyl carbonate azeotropic system than [EMIM][Br]. Furthermore, the measured data were well correlated with the nonrandom two-liquid (NRTL) model.

Keywords: vapor-liquid equilibrium, ionic liquids, methanol, dimethyl carbonate, NRTL model

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1. Introduction

Dimethyl carbonate (DMC) has been a high-profile agent in recent years because of its excellent properties and extensive applications [1-7]. For example, DMC has favorable solubility and nontoxicity which make it an environmentally friendly solvent. Due to its high oxygen content, DMC could be used as gasoline additives to improve octane number. As a basic organic raw material, methanol has a very wide range of applications [8], such as medicine, solvent, and organic synthesis. In the synthesis process of DMC, methanol is one of the raw materials. Due to the use of excessive methanol, DMC and methanol could form azeotrope which is difficult to be separated.

For separating azeotropic systems, extractive distillation [9-11] is an efficient method and the selection of entrainer is the key to it. Inorganic salts [12-14] and organic solvents [15-16] are traditionally used as entrainers but some bad influence could be caused. For example, the use of inorganic salts could lead to pipeline corrosion and organic solvents may cause environmental pollution and water pollution. Ionic liquids (ILs) as new entrainers have become more and more popular in recent years because of their unique properties, such as negligible vapor pressure, good chemical and thermal stability and tunable structures [17-18]. Now, plenty of ILs have been employed as entrainers to separate azeotropes and their performances reported in literature are uplifting. Zhang et al. [19] investigated the ternary systems of methyl acetate and methanol containing 1-butyl-3-methylimidazolium chloride ($[C_4MIM][Cl]$), or 1-(2-chloroethyl)-3-methylimidazolium chloride ($[CIC_2MIM][Cl]$),

or 1-butyl-3-methylimidazolium bromide ([C₄MIM][Br]). Li et al. [20~21] measured the VLE data based on methanol and DMC containing 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIM][BF₄]), or 1-ethyl-3-methylimidazolium trifluor ([EMIM][OTf]), or 1-butyl-3-methylimidazolium trifluor ([BMIM][OTf]). Cai and Chen et al. [22~23] compared the separation effect of different phosphoric-based ionic liquids on the mixture of methanol and DMC. Ales Blahut et al. [24] studied the effect of 1-ethyl-3-methylimidazolium tetracyanoborate ([EMIM][TCB]) on the azeotropic system of methanol + DMC. The VLE data for the system DMC +methanol with different concentration of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) and 1-ethyl-3-methylimidazolium ethyl sulfate (EMISE) were measured by Hyeon-Deok Kim et al. [25]. [BMIM][Cl] has been tried to separate the azeotropic mixture of methanol and DMC, but only a speculative conclusion that [BMIM][Cl] has remarkable azeotrope breaking capacity was made and no details was given [26].

In this work, two ILs, namely [EMIM][Br] and [BMIM][Cl], were used as entrainers to separate methanol and DMC mixture at 101.3 kPa. The separation effects of these two ionic liquids were compared and the reason for their different performance was analyzed.

2. Experimental section

2.1 Chemicals.

In this experiment, the solvents were methanol, DMC, [EMIM][Br], and [BMIM][Cl]. Methanol and DMC were purchased from Sinopharm group and

examined by gas chromatography. The results proved that their mass fraction was higher than 99.5%. [EMIM][Br] and [BMIM][Cl] were obtained from our own laboratory. Their purities were greater than 99% (mass fraction) which were authenticated by liquid chromatography (Wayee IC6000). The water content checked by Karl Fischer was lower than 0.005 (mass fraction). The ILs were dried at 373 K under vacuum for 48 h before use. The specifications of all the chemicals used in this work are listed in Table 1.

Table 1

The specifications of the chemical samples

Chemical name	Source	purity	Purification method	Analysis method
methanol	SinopharmGroup	0.995	None	GC ^a
DMC	SinopharmGroup	0.995	None	GC ^a
[BMIM][Cl]	Prepared in this work	0.990	Vacuum desiccation	LC ^c KF ^b
[EMIM][Br]	Prepared in this work	0.990	Vacuum desiccation	LC ^c KF ^b

^a GC = gas chromatography.

^b KF = Karl Fisher titration.

^c LC = liquid chromatography.

2.2 Apparatus and procedure

In this experiment, an all-glass dynamic recirculating still (NGW, Wertheim, Germany) described in the previous literature[27] was used to measure the VLE data. This apparatus is mainly composed of heating, cooling, sampling and other parts. Among them a Heating rod was used to heat the apparatus, and a spherical condenser with tap water as condensing medium was used to ensure backflow. The pressure of this apparatus was measured by a manometer whose uncertainty was 0.1 kPa and kept

constant at 101.3 kPa by controlling the pressure of a gas buffer connected to the device. The temperature of this still was measured by a thermometer with a standard uncertainty of 0.01 K.

The experiment data of the binary system of methanol + DMC were obtained by continuously adding methanol to DMC until the mole fraction of DMC was less than 0.04. For the ternary system, a mixture of DMC with a certain mole fraction of IL was prepared firstly and then a mixture of methanol with the same mole fraction of IL was added to the former. Only when the system temperature was constant for more than 30 minutes, could we take the samples of vapor and liquid to analyze.

2.3 Samples analysis

The condensed vapor and liquid phase samples were first inserted into a headspace sampler (G1888 Network headspace sampler, Agilent Technologies) and then analyzed by a gas chromatography (Model 7890A, Agilent Technologies). The GC is equipped with an Agilent 19091J-413 capillary column (30 m in length, 0.32 mm in diameter and 2.5 μm in thickness) and a TCD detector. The carrier gas was H_2 . The operating conditions were as follows: the temperatures of injector, oven and detector were 473K, 353K and 473 K, respectively. The IL content of each liquid sample was measured by calculating the mass difference before and after vaporizing the volatile component in a vacuum desiccator. Each sample was analyzed at least three times. The standard uncertainty of the mole fraction of the components in the liquid and vapor phase is 0.001.

3. Results and discussion

3.1 Experimental data

The VLE data of the binary system of methanol + DMC were measured to check the reliability of our apparatus. Detailed data are shown in Table 2, where T is equilibrium temperature, x_1 is the mole fraction of methanol in the liquid phase and y_1 is the mole fraction of methanol in the vapor phase. It is obvious in Fig. 1 that the experimental data agree well with the data calculated by the NRTL model and the data in literature [20,23]. Therefore, the apparatus in this work is reliable.

Table 2

The isobaric VLE data for the binary system of methanol (1) + DMC (2) at 101.3 kPa.

T/K	x_1	y_1
354.45	0.060	0.287
351.95	0.085	0.353
348.20	0.134	0.455
343.00	0.251	0.590
340.85	0.337	0.654
339.20	0.443	0.706
338.00	0.570	0.740
337.15	0.719	0.794
337.00	0.772	0.810
336.85	0.845	0.844
336.85	0.868	0.868
336.95	0.912	0.895
337.10	0.946	0.928
337.25	0.967	0.958

Standard uncertainty $u(x_1) = u(y_1) = 0.001$, $u(T) = 0.01$ K

Fig. 1. Isobaric VLE diagram for the binary system of methanol (1) + DMC (2) at 101.3 kPa. ○, from Ref [23]; ●, from Ref [20]; ◇, this work; solid line, the data correlated with the NRTL model.

The experimental data of the ternary systems methanol (1) + DMC (2) + [EMIM][Br] (3) and methanol (1) + DMC (2) + [BMIM][Cl] (3) were obtained at 101.3 kPa. The mole fraction of [EMIM][Br] was kept at 0.1, 0.2, and 0.25, while [BMIM][Cl] 0.1, 0.15, and 0.2. The data are listed in Tables 3-4, where T is equilibrium temperature of ternary system, x_3 is the mole fraction of IL in liquid phase, x_1 is the mole fraction of methanol in liquid phase, x_1' is the mole fraction of methanol on an IL-free basis in liquid phase, and y_1 is the mole fraction of methanol in vapor phase.

Table 3

The isobaric VLE data for the ternary system of methanol (1) + DMC (2) + [EMIM][Br] (3) at 101.3 kPa.

T/K	x_3	x_1	x_1'	y_1	α_{12}
357.85	0.11	0.073	0.082	0.112	1.410
354.10	0.11	0.153	0.171	0.233	1.472
351.65	0.11	0.208	0.233	0.304	1.441
347.25	0.10	0.325	0.362	0.435	1.359
345.15	0.10	0.396	0.441	0.499	1.264
343.80	0.10	0.450	0.502	0.534	1.136
342.15	0.10	0.532	0.593	0.601	1.033
341.35	0.11	0.583	0.651	0.651	0.999
340.55	0.10	0.639	0.713	0.699	0.936
339.95	0.11	0.731	0.819	0.780	0.784
339.85	0.11	0.773	0.865	0.818	0.699
340.10	0.10	0.855	0.951	0.911	0.532
353.00	0.21	0.078	0.099	0.057	0.551
352.45	0.20	0.112	0.140	0.090	0.606
350.35	0.20	0.181	0.225	0.153	0.623
347.85	0.21	0.269	0.339	0.253	0.661
345.95	0.21	0.352	0.443	0.342	0.652
344.45	0.20	0.440	0.548	0.432	0.629
343.20	0.20	0.526	0.657	0.531	0.589
342.70	0.20	0.586	0.733	0.605	0.558
342.60	0.20	0.670	0.837	0.727	0.519
343.15	0.20	0.722	0.903	0.824	0.504
344.10	0.21	0.757	0.954	0.895	0.412
351.00	0.25	0.054	0.073	0.026	0.344
350.00	0.25	0.076	0.102	0.041	0.379
348.60	0.25	0.142	0.189	0.085	0.400
347.35	0.25	0.205	0.274	0.144	0.445
346.15	0.25	0.282	0.377	0.237	0.514
345.45	0.25	0.329	0.439	0.282	0.503
344.75	0.25	0.382	0.510	0.345	0.505
344.15	0.25	0.441	0.589	0.418	0.502
343.85	0.25	0.491	0.655	0.483	0.492
343.75	0.25	0.545	0.727	0.558	0.473
343.95	0.25	0.605	0.807	0.653	0.449
344.35	0.25	0.638	0.852	0.709	0.424
345.50	0.24	0.719	0.948	0.876	0.387
346.65	0.25	0.730	0.975	0.935	0.376

Standard uncertainty $u(x_1') = u(x_1) = u(y_1) = 0.001$, $u(T) = 0.01\text{K}$

Table 4

The isobaric VLE data for the ternary system of methanol (1) + DMC (2) + [BMIM][Cl] (3) at 101.3 kPa.

T/K	x_3	x_1	x_1'	y_1	α_{12}
361.35	0.11	0.030	0.034	0.034	0.986
357.00	0.11	0.105	0.118	0.120	1.017
354.25	0.11	0.168	0.189	0.216	1.185
351.65	0.12	0.233	0.265	0.269	1.024
350.00	0.12	0.278	0.315	0.302	0.941
346.60	0.11	0.386	0.436	0.453	1.072
344.55	0.11	0.464	0.521	0.511	0.962
343.35	0.11	0.522	0.587	0.545	0.844
342.25	0.11	0.584	0.656	0.613	0.830
341.15	0.11	0.683	0.769	0.682	0.642
340.85	0.11	0.764	0.861	0.776	0.562
341.10	0.11	0.835	0.937	0.866	0.432
354.45	0.16	0.094	0.112	0.069	0.591
353.65	0.16	0.152	0.181	0.112	0.569
350.55	0.17	0.237	0.285	0.193	0.601
348.15	0.17	0.327	0.392	0.283	0.614
346.45	0.16	0.397	0.472	0.353	0.610
345.15	0.16	0.461	0.552	0.430	0.611
344.25	0.16	0.515	0.613	0.486	0.598
343.60	0.17	0.575	0.691	0.557	0.564
342.95	0.16	0.684	0.817	0.689	0.497
343.15	0.16	0.735	0.877	0.764	0.456
344.20	0.16	0.791	0.947	0.879	0.412
352.55	0.20	0.122	0.154	0.069	0.406
351.35	0.20	0.173	0.216	0.105	0.425
349.25	0.21	0.233	0.294	0.150	0.423
347.55	0.21	0.316	0.398	0.219	0.424
346.45	0.22	0.372	0.478	0.273	0.410
345.65	0.22	0.435	0.555	0.341	0.416
345.15	0.21	0.487	0.618	0.416	0.441
344.55	0.20	0.569	0.715	0.520	0.433
344.85	0.21	0.640	0.809	0.623	0.392
345.45	0.21	0.699	0.880	0.732	0.371
346.50	0.21	0.737	0.931	0.826	0.352

Standard uncertainty $u(x_1') = u(x_1) = u(y_1) = 0.001$, $u(T) = 0.01\text{K}$.

3.2 Calculation of the phase equilibrium

This experiment was carried out at 101.3 kPa, so the assumption of ideal vapor-phase could be made. The equilibrium equation is written as follows:

$$y_i P = x_i \gamma_i P_i^s \quad (1)$$

where y_i represents the mole fraction of the component i in the vapor phase; P represents the total pressure (101.3 kPa in this work); x_i represents the mole fraction of the component i in the liquid phase; P_i^s is the saturated vapor pressure of component i at the equilibrium temperature which could be calculated by the Antoine equation.

$$\log(P_i^s / \text{kPa}) = A - B / (T / K + C) \quad (2)$$

where A , B and C are Antoine parameters; T is equilibrium temperature of ternary system. The parameters (A , B and C) of this equation are listed in Table 5.

Table 5

Antoine parameters for methanol and DMC.

Component	Antoine parameters			Temperature range	
	A_i	B_i	C_i	Min/(K)	Max/(K)
DMC ^a	6.4338	1413.00	-44.25	273.15	548.0
Methanol ^b	7.14736	1544.804	-37.235	335.0	376.0

^a from ref [21], ^b from ref [28]

At present, the nonrandom two-liquid (NRTL) activity coefficient model is usually used to correlate and predict the VLE data of the IL-containing systems and the results are quite satisfactory [29]. NRTL model is expressed by the following equation:

$$\ln \gamma_i = \frac{\sum_{j=1}^N \tau_{ji} G_{ji} x_j}{\sum_{k=1}^N G_{ki} x_k} + \sum_{j=1}^N \frac{x_j G_{ij}}{\sum_{k=1}^N G_{ki} x_k} \left[\tau_{ij} - \frac{\sum_{k=1}^N G_{kj} x_k \tau_{kj}}{\sum_{k=1}^N G_{kj} x_k} \right] \dots \dots \dots (3)$$

$$\tau_{ji} = \frac{\Delta g_{ji}}{RT}, \quad G_{ji} = \exp(-\alpha_{ji} \tau_{ji})$$

where γ_i is the activity coefficient of component i , x_j, x_i and x_k are the mole fractions of components j, i and k , Δg_{ji} is the binary interaction parameter, and T is the equilibrium temperature. The model parameters are obtained by minimizing the average relative deviation (ARD) which is calculated according to the following equation:

$$ARD(\%) = \frac{1}{n} \sum_{i=1}^n \left| \frac{\gamma_i^{exptl} - \gamma_i^{calcd}}{\gamma_i^{exptl}} \right| \times 100 \dots \dots \dots (4)$$

where n is the number of experiment point, γ_i is the activity coefficient of component i , and the superscripts “exptl” and “calcd” represent the experimental and calculated values, respectively. In this work, the NRTL model is also used to correlate the experimental VLE data and the correlated results are listed in Table 6. Then the mean absolute deviations and standard deviations between experimental and calculated values of vapor phase mole fractions and the VLE temperature are listed in Table 7. The results indicate that the NRTL model is suitable to correlate the experimental data.

Table 6

Estimated values of non-randomness factors α_{ij} and binary energy parameters $\Delta g_{i,j}$, $\Delta g_{j,i}$, for the NRTL model.

Component i	Component j	α_{ij}	$\frac{\Delta g_{i,j}}{J/mol}$	$\frac{\Delta g_{j,i}}{J/mol}$	$\frac{ARD}{\%}$
methanol	DMC	0.300 ^a	3115.2 ^a	833.1 ^a	1.98
methanol	[EMIM][Br]	0.277	650.6	2947	1.81
DMC	[EMIM][Br]	0.092	25867	-2432.5	
methanol	[BMIM][Cl]	0.227	110.2	-6012.78	2.96
DMC	[BMIM][Cl]	0.079	26667.5	-4432.5	

^a From ref. [23], $\Delta g_{ij} = g_{ij} - g_{i,i}$, $\tau_{ij} = (g_{ij} - g_{i,i})/RT$

Table 7

Mean absolute deviations $\delta y, \delta T$, and standard deviations $\sigma y, \sigma T$, between experimental and calculated values of vapor phase mole fractions and the VLE temperature

system	δy^a	σy^b	$\delta T^c (K)$	$\sigma T^c (K)$
Methanol + DMC	0.0068	0.0081	0.03	0.05
Methanol + DMC + [EMIM]Br	0.0067	0.0058	0.04	0.07
Methanol + DMC + [BMIM]Cl	0.0065	0.0083	0.07	0.08

n is the number of experimental points.

$$^a \delta y = (1/n) \sum |y_{exptl} - y_{calcd}|, ^b \sigma y = \left[\sum (y_{exptl} - y_{calcd})^2 / (n-1) \right]^{1/2},$$

$$^c \delta T = (1/n) \sum |T_{exptl} - T_{calcd}|, ^d \sigma T = \left[\sum (T_{exptl} - T_{calcd})^2 / (n-1) \right]^{1/2}.$$

The Figs. 2-3 show the y_1 - x_1 diagrams of the ternary systems of methanol (1) + DMC (2) + [EMIM][Br] (3) or [BMIM][Cl] (3). It can be seen that experimental data are in good agreement with the correlated data. What's more, with the addition of IL the content of methanol in the liquid becomes larger. With increasing the amount of IL, the azeotropic point moves down and disappears as the mole fractions of [EMIM][Br] and [BMIM][Cl] are increased to 0.2 and 0.15, respectively. According to the NRTL model, to completely break the azeotropic point of methanol and DMC system the minimum mole fraction of [EMIM][Br] is 0.1461 while that of [BMIM][Cl] only need to reach 0.1168. Thus, it can be concluded that [BMIM][Cl] has better separation effect than [EMIM][Br].

Fig. 2. Isobaric y_1 - x_1 ' diagram for the methanol (1) + DMC (2) + [EMIM][Br] (3) ternary system at 101.3 kPa: dotted line, IL-free system; ■, $x_3 = 0.1$; ●, $x_3 = 0.2$; ▲, $x_3 = 0.25$; solid line, correlated using NRTL model.

Fig. 3. Isobaric y_1 - x_1 ' diagram for the methanol (1) + DMC (2) + [BMIM][Cl] (3) ternary system at 101.3 kPa: dotted line, IL-free system; ■, $x_3 = 0.1$; ●, $x_3 = 0.15$; ▲, $x_3 = 0.2$; solid line, correlated using NRTL model.

Relative volatility α_{12} as an important indication could evaluate the separation effect of entrainer and its defined equation is:

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \quad (5)$$

where y_1 (y_2) and x_1 (x_2) represent the vapor mole fraction and liquid mole fraction of the component 1(2), respectively.

Figs. 4-5 illustrate the relative volatility (α_{12}) of methanol to DMC with different ILs. It is obvious that in the whole-concentration region of methanol, with increasing the concentrations of ILs the relative volatility of methanol to DMC becomes smaller and smaller, until less than 1.0. Compared with [EMIM][Br], [BMIM][Cl] has more

outstanding separation effect.

Fig. 4. Relative volatility α_{12} of methanol (1) to DMC (2) at different mole fraction of [EMIM][Br] at 101.3 kPa: $\diamond$, $x_3 = 0$; $\square$, $x_3 = 0.1$; $\circ$, $x_3 = 0.2$; $\triangle$, $x_3 = 0.25$; solid lines, correlated using NRTL model.

Fig. 5. Relative volatility α_{12} of methanol (1) to DMC (2) at different mole fraction of [BMIM][Cl] at 101.3 kPa: $\diamond$, $x_3 = 0$; $\square$, $x_3 = 0.1$; $\circ$, $x_3 = 0.15$; $\triangle$, $x_3 = 0.2$; solid lines, correlated using NRTL model.

The influence of the two ILs [EMIM][Br] and [BMIM][Cl] on the VLE behavior of the methanol + DMC system might be attributed to the different attractive interactions between ILs and solvents. The ILs could be regarded as organic molten salts, so they are polar compounds. The polarity of methanol is stronger than that of DMC as indicated in table 8 which shows the size of the polarity of the two solvents expressed in $E_T(30)$. According to the principle of “like-dissolves-like”, the attractive interaction of IL with methanol is stronger than that with DMC, resulting in that DMC is more volatile and the relative volatility of DMC to methanol is enhanced. In terms of the

different separation effects of [BMIM][Cl] and [EMIM][Br], as the electronegativity of $[\text{Cl}]^-$ is stronger than that of $[\text{Br}]^-$ and methanol has a functional group $-\text{OH}$ which is not only electron acceptor but also electron donor, the interaction between methanol and $[\text{Cl}]^-$ is stronger than that between methanol and $[\text{Br}]^-$, thus separation effect produced by IL with the $[\text{Cl}]$ anion is stronger. For cation, ILs with a short carbon chain have a stronger interaction with methanol when they have the same anion [21]. In other words, ethyl-based ILs have a stronger interaction with methanol than butyl-based ILs. However, in this work, the separation effect of [EMIM][Br] is weaker than [BMIM][Cl], which might be ascribed to the relative leading role of anion.

Table 8

$E_{\text{T}}(30)$ for methanol and DMC.

Component	$E_{\text{T}}(30)/(\text{kcal/mol})$
methanol	55.4 ^a
DMC	38.2 ^a

^a From ref. [30]

The separation effect of [BMIM][Cl] on the methanol and DMC mixture is compared with other ILs reported in previous literature, including [OMIM][BF₄] [20], [BMIM][OTf] [21], [EMIM][OTf] [21], 1-methyl-3-methylimidazolium dimethylphosphate ([MMIM][DMP]) [22], 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]) [22], 1-butyl-3-methylimidazolium dibutylphosphate ([BMIM][DBP]) [23], [EMIM]TCB [24], [BMIM][BF₄] [25], EMISE [25]. The minimum mole fractions of these ILs to break the azeotrope are 0.2, 0.133, 0.202, 0.074, 0.09, 0.096, 0.08, 0.1 and 0.1, respectively. This shows that the separation effect of [BMIM][Cl] outperforms that of [OMIM][BF₄], [BMIM][OTf]

and [EMIM][OTf] but is inferior to that of [MMIM][DMP], [EMIM][DEP], [BMIM][DBP] [EMIM]TCB, [BMIM][BF₄] and EMISE. However, the price of [BMIM][Cl] is cheaper and its synthesis and purification is easier than all the other reported ILs. So, [BMIM][Cl] may be a more suitable entrainer for the separation of methanol and DMC azeotropic mixture.

4. Conclusions

In this work, the isobaric VLE data for the ternary systems of methanol (1) + DMC (2) + [EMIM][Br] (3) and methanol (1) + DMC (2) + [BMIM][Cl] (3) were measured at 101.3 kPa. The experimental data were well correlated using the NRTL model. Both ILs could enhance the relative volatility of DMC to methanol and break the azeotrope. But the separation effect of [BMIM][Cl] was stronger than that of [EMIM][Br]. When mole fraction of [BMIM][Cl] calculated by NRTL model was about 0.1168, the azeotropic point disappeared. The conclusion is that [BMIM][Cl] could be a potential entrainer to separate the azeotrope system of methanol + DMC.

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List of symbols

A_i, B_i, C_i	Antoine constants of component i
$\Delta g_{ij}, \Delta g_{ji}$	binary energy parameter of NRTL model
x_1'	mole fraction of methanol in liquid phase on an IL-free basis

x_i	mole fraction of solvent i in the liquid phase
y_i	mole fraction of solvent i in the vapor phase
T	equilibrium temperature
P	total pressure in the equilibrium system
P_i^s	Saturated vapor pressure of component i
Greek letters	
α_{12}	relative volatility of component 1 to component 2
α_{ij}	non-randomness parameter of NRTL model
γ_i	activity coefficient of component i
γ_i^{exptl}	the activity coefficient of component i measured by experimental data
γ_i^{calcd}	the activity coefficient of component i calculated with the NRTL model
δ	mean absolute deviation
σ	standard deviation

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