

Determination and Modeling of Isobaric Vapor—Liquid Equilibria for the Methylcarbamate + Methyl-*N*-phenyl Carbamate System at Different Pressures

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ABSTRACT: The vapor pressures of methylcarbamate (MC) and methyl *n*-phenyl carbamate (MPC), at different temperatures ranging from (341.45 to 418.45) K, have been measured using the quasi-static ebulliometric method. The experimental data were fitted to the Antoine equation with the overall average absolute deviation of pressure of 0.06 kPa. Isobaric vapor-liquid equilibrium (VLE) data were also determined for the MC and MPC system at (1.00, 2.00, 4.00, 6.00, and 8.00) kPa by the same method and were correlated with nonrandom two-liquid (NRTL) and Wilson models. The both model parameters were obtained with the overall average absolute deviation of temperature 0.82 K and 0.81 K. The relative volatility of the binary system was calculated and was more than 1 by far, indicating that high-purity MPC can be obtained from the binary mixture by distillation technology.



INTRODUCTION

Diphenylmethane diisocyanate (MDI) is a major raw material for the manufacturing of polyurethanes which have been widely used in the production of elastomer, elastic fiber, foamed plastic polyurethanes, and so on.¹ The current world production capacity is around 5.67 million tons per annum. China is the second largest producer and the largest consumer with 30 % of the global capacity.¹ There are several processes for manufacturing MDI, but the phosgene process is dominant at industrial scale, representing 90 % of the total production capacity at present² due to its mature technology and economic feasibility. In this phosgene process, MDI is produced by a noncatalytic reaction between the corresponding amine and phosgene. Besides generating waste salt and organic halogen compound as a byproduct,³ the phosgene, COCl₂, used as the carbonylization reagent in the reaction, is very toxic and corrosive. Therefore, there has been increasing interest in developing an alternative, phosgene-free process synthesis of isocyanates.⁴ As in the earlier study, some methods simply consist of the replacement of phosgene by less dangerous carbonylating agents like carbonates or triphosgene. In the reductive carbonylation process, the nitroaromatic precursors were directly used to give isocyanates or carbamates, the latter being subsequently cracked into isocyanates.³ However, the thermal decomposition of corresponding carbamates to obtain isocyanates is thought to be one of the most attractive methods used in the industrial sector.^{2,5,6} Methyl *n*-phenyl carbamate (MPC), one of the main carbamates, is an important chemical intermediate for synthesizing MDI in the decomposition process. Many studies⁷⁻¹² have been done about the synthesis of MPC in recent years. In our laboratory, a new process for the synthesis of MPC was proposed, and four steps were included: First, methylcarbamate (MC) was derived from the reaction of urea and methanol with a high conversion and yield. Second,

excess MC reacted with aniline using the chlorobenzene and methanol as solvent to form MPC. The mixtures after the reaction contained mainly methanol, chlorobenzene, MC, and MPC. Third, the methanol and chlorobenzene were separated easily by vacuum distillation, and then the mixtures of the MC and MPC remained. Finally, the high-purity MPC could be obtained by another vacuum distillation, which was a key step for separation. As we know, the separation of the mixtures requires knowledge of the thermodynamic properties and the vapor—liquid equilibria.^{13,14} However, these data are scarce for the MC and MPC systems, and even the vapor pressures of MPC are not documented.

Both MC and MPC are white crystals at room temperature, and their melting points are 327.15 K and 325.00 K, respectively.¹⁵ Zeng et al.¹⁶ measured the heat capacity, standard enthalpy of formation, and standard entropy of MC. Zhu et al.¹⁷ studied the decomposition of MPC to phenyl isocyanate at (463 to 513) K. The Antoine constants *A*, *B*, and *C* of MC, reported in the Landolt–Bornstein database,¹⁸ are 11.0909, 3883, and 0, respectively. Some other basic thermodynamic properties of the MC and MPC are published in the Landolt–Bornstein database.

In the present work, all measurements were undertaken using the quasi-static ebulliometric method.^{19–21} The experimental apparatus was established, and the accuracy was verified by measuring the vapor pressures of the water, ethylene glycol, and *n*-decane at reduced pressures. The vapor pressures of MC and MPC were measured and fitted to the Antoine equation. In addition, isobaric T-p-x data were determined for the MPC and MC systems at (1.00, 2.00, 4.00, 6.00, and 8.00) kPa and

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were correlated with the nonrandom two-liquid (NRTL) and Wilson models.

EXPERIMENTAL SECTION

Chemicals. The chemicals used in this work include: ethylene glycol (CAS Registry No. 107-21-1), mass fraction \geq 99 %, from Sinopharm Chemical Reagent Co., Ltd.; *n*-decane (CAS Registry No. 124-18-5), mass fraction \geq 99 %, from Tokyo Chemical Industry (Shanghai) Co., Ltd.; and MC (CAS Registry No. 598-55-0) from Shandong Hi-tech Chemical Group Co., Ltd. The purity was checked by gas chromatography (GC-2010 plus, Shimadzu), and the GC analysis did not show any observable impurities. MPC (CAS Registry No. 2603-10-3) was synthesized in our laboratory; the purity also was checked by GC, and the GC analysis did not show any observable impurities.

The water used in the experiment was deionized water.

Synthesis of MPC. Aniline reacted with excess MC using the chlorobenzene as solvent to form MPC, phenylurea, and diphenylurea. The conversion of aniline was nearly 99 %, and the selectivity was about 70.0 %, 14.5 %, and 14.5 %. Then, the methanol was taken into the same reactor and reacted with the most of phenylurea and diphenylurea to form MPC. All results were undertaken using a 25 L batch pot with the TiO₂ catalyst. The mixtures after the reaction, which contained mainly methanol, chlorobenzene, MC, and MPC, were treated by rotary evaporation for a long time. The crude product MPC was obtained when most of the methanol, chlorobenzene, and MC were evaporated. Finally, the high-purity MPC was obtained by recrystallization in cyclohexane more than once.

Apparatus and Procedure. In this study, the experiments were carried out with an all-glass inclined ebulliometer (the average coefficient of evaporation is about 0.018 %). Figure 1



Figure 1. Experimental apparatus for VLE measurement. 1, heating bar; 2, magnetic stirrer; 3, inclined ebulliometer; 4, condenser; 5, mercury thermometer; 6, mercury manometer; 7, Pirani vacuum gauge; 8, needle valve; 9, vacuum pump; 10, buffer vessel.

shows a schematic of the experiment apparatus. It was composed of an inclined ebulliometer, a mercury thermometer, a condenser, a buffer vessel, a mercury manometer, a pirani vacuum gauge, a needle valve, and a vacuum pump (Oerlikon Leybold Vacuum). The vacuum pump could get an extremely low pressure of 0.013 Pa. The inclined ebulliometer was connected to a buffer vessel (approximately 10 L), and the system pressures were controlled by the needle valve. The condenser was cooled with a circulating water (approximately 330 K) to minimize the most of condensed vapor because the

evaporation of solvent would change the initial concentration of the samples. Meanwhile, it should keep the vapor from freezing. The pressures were measured using a mercury manometer with an accuracy of 0.1 kPa when pressures were more than 1.00 kPa and using a Pirani vacuum gauge with a relative accuracy of 10 % when pressures were less than 1.00 kPa. A mercury thermometer, with an accuracy of 0.1 K, was used for measuring the equilibrium temperature.

The isobaric T-p-x data of the samples were measured as follows: the samples were melting at about 333.15 K, which were analyzed by GC, and charged into the inclined ebulliometer with approximately 85 mL. The system pressures were adjusted to the desired pressures, and then the samples were heated and stirred vigorously with a magnetic stirrer to stem super heating and get homogeneous mixing. A mixture of liquid and vapor were sprayed gradually to the thermometer sleeve. When the reading of the mercury thermometer was almost stable about 15 min, the vapor—liquid equilibria were established, and meanwhile the temperature and pressure were recorded.

Verification of Procedure. The experimental apparatus and procedure for isobaric T-p-x data measurement were verified by determining the vapor pressures of water, ethylene glycol, and *n*-decane and comparing the experimental data with literature.²² Data were measured for the ethylene glycol and *n*-decane at pressures ranging from (0.20 to 12.00) kPa and for the water at pressures ranging from (1.20 to 12.00) kPa, respectively. The agreement between the experimental data (listed in Table 1) and the literature is excellent, as shown in

Table 1. Vapor Pressures of the Water, n-Decane, and Ethylene Glycol^a

wa	iter	n-de	ecane	ethylen	e glycol
T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
280.20	1.29	299.25	0.1732	336.45	0.2527
282.23	1.34	306.95	0.3091	345.00	0.4838
287.90	1.82	309.15	0.4116	355.15	0.9002
292.36	2.13	316.26	0.6545	369.25	1.69
296.13	2.78	326.10	1.04	374.45	2.13
300.70	3.47	340.05	1.95	378.95	2.66
304.80	4.54	347.90	2.97	384.45	3.57
306.67	4.82	353.32	3.80	388.10	4.40
309.65	5.90	358.67	4.82	391.45	5.33
312.07	6.75	362.85	5.92	394.56	6.01
314.95	7.78	365.13	6.96	397.25	7.14
316.65	8.45	370.40	8.23	404.05	9.20
317.90	9.45	377.13	10.48	408.25	11.34
320.04	10.62	379.93	12.00		
322.75	11.78	382.83	13.25		
Standard	uncertaintie	es u are u(I	() = 0.1 K at	nd $u(p) = 0$.1 kPa.

Figure 2. The average absolute temperature deviation of the water, ethylene glycol, and *n*-decane are 0.97 K, 0.94 K, and 1.21 K. In view of the above, it was considered to be reliable to measure the boiling points of samples with the new established apparatus and procedure from (0.20 to 12.00) kPa.

RESULTS AND DISCUSSION

Thermodynamic Modeling. When the phase equilibrium is established, the fugacity of the vapor is equal to the liquid. The rigorous, fundamental relation for vapor–liquid equilibria is as follows:²³



Figure 2. Comparison between the measured and the published vapor pressures of water, *n*-decane, and ethylene glycol. Symbols indicate experimental data in this work: \blacktriangle , water; \blacksquare , *n*-decane; \blacktriangledown , ethylene glycol; solid lines, literature.

$$\phi_i^{\rm V} y_i p = x_i \gamma_i \phi_i^{\rm S} p_i^{\rm S} \exp\left[\frac{V_i^{\rm L}(p-p_i^{\rm S})}{RT}\right]$$
(1)

where *R* is the universal gas constant, *p* and *T* are the system pressure and absolute temperature, x_i and y_i are the mole fractions of liquid and vapor phase, respectively, γ_i is the activity coefficient of component *i* in the liquid, ϕ_i^{V} is the fugacity coefficient of component *i* of vapor phase, and p_i^{S} is the saturated vapor pressure of pure component *i*, which is determined by the experiment in this work. V_i^{L} is the molar volume of pure liquid, and ϕ_i^{S} is the fugacity coefficient of the pure component *i* at saturation.

When the total system pressure is relatively low, the vapor phase is treated as ideal gas, and the second viral coefficient was omitted. The Poynting pressure correction factor $\exp[(V_i^L(p - p_i^S))/RT]$, ϕ_i^V , and ϕ_i^S are often near unity. Thus, the simplification of the vapor-liquid equilibrium relation is obtained as:

$$y_i p = x_i \gamma_i p_i^{\rm S} \tag{2}$$

The saturated vapor pressures could be calculated by the Antoine equation:

$$\ln(p_i^S/kPa) = A_i - \frac{B_i}{C_i/K + T/K}$$
(3)

where A_i , B_i , and C_i are three parameters for the Antoine equation and are regressed with the experiment in this work. In the NRTL model,^{24,25} the activity coefficient of

In the NRTL model,^{24,25} the activity coefficient of component γ_i is written as:

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_j}{\sum_k x_k G_{ki}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{nj} G_{mj}}{\sum_k x_k G_{ki}} \right)$$
(4)

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{5}$$

$$\alpha_{ij} = \alpha_{ji} \tag{6}$$

where α_{ij} is the nonrandomness factor and τ_{ij} is the interaction parameter, which is given by:

$$\tau_{ij} = a_{ij} + b_{ij}/T \tag{7}$$

The adjustable parameters in the NRTL model are the nonrandomness factor α_{ij} , a_{ij} , and b_{ij} . In practice, the value of α_{ij} is usually 0.3 for an ordinary nonideal system, and a_{ij} and b_{ij} could be regressed with the T-p-x experimental data. In the Wilson model,^{24,26} the activity coefficient of

In the Wilson model, $\gamma_i^{2\tau,20}$ the activity coefficient of component γ_i is written as:

$$\ln \gamma_{ij} = 1 - \ln(\sum_{j} A_{ij} x_j) - \sum_{j} \frac{A_{jj} x_j}{\sum_k A_{jk} x_k}$$
(8)

where:

$$\ln A_{ij} = a_{ij} + b_{ij}/T \tag{9}$$

The binary parameters a_{ij} and b_{ij} must be determined from T-p-x data regression. Naturally, it could predict the VLE data at different pressures and temperature with the binary parameters.

In this study, Aspen plus software is applied to regress the binary parameters a_{ij} and b_{ij} with the maximum-likelihood principle,²⁴ and the objective function is:

$$F_{\rm OB} = \sum_{n=1}^{\rm NDG} w_n \sum_{i=1} \left[\left(\frac{T_i^{\rm exp} - T_i^{\rm est}}{\sigma_T} \right)^2 + \left(\frac{p_i^{\rm exp} - p_i^{\rm est}}{\sigma_P} \right)^2 + \left(\frac{x_{i,j}^{\rm exp} - x_{i,j}^{\rm est}}{\sigma_X} \right)^2 \right]$$

$$\left. + \left(\frac{x_{i,j}^{\rm exp} - x_{i,j}^{\rm est}}{\sigma_X} \right)^2 \right]$$
(10)

where σ is standard deviation of the indicated data, w_n is the weight of data group n ($w_n = 1$, for each data group n), and x is the liquid composition. The subscript i is data for data point i, and j is fraction data for component j. The superscript exp is experimental data, est is estimated data, NDG is the number of data groups in the regression case (NDG = 5, for (1.00, 2.00, 4.00, 6.00, and 8.00) kPa). In this work, the standard deviation is 0.1 K for temperature, 0.1 % for pressure, and 1 % for the liquid composition.

The relative volatility is defined as:

$$\alpha = \frac{y_i / x_i}{y_j / x_j} \tag{11}$$

where y and x are the mole fractions of the components in the vapor and liquid phase.

In this work, the T-p-x data determined at (1.00, 2.00, 4.00, 6.00, and 8.00) kPa were correlated with the NRTL and Wilson models to obtain the T-p-x-y data for the system. Both models were derived from the Gibbs–Duhem relation as written for the Gibbs free energy of the liquid phase.^{25,26} Therefore, the T-p-x-y data reported in this paper have passed the thermodynamic consistency test.

Vapor Pressures of MC and MPC. The vapor pressures of the MC and MPC are listed in Table 2. Data were measured for MC at pressures ranging from (1.00 to 14.00) kPa and for MPC at pressures ranging from (0.20 to 2.20) kPa, respectively. The vapor pressures of MPC, ranging from (2.20 to 8.00) kPa, are calculated by using the extrapolation, because of its instability at more than 2.2 kPa. The Antoine constants of them, listed in Table 3, are regressed with the experimental data with the overall average absolute pressure deviation of 0.06 kPa. Figures 3 and 4 show that the Antoine equations are able to describe the vapor pressures of MC and MPC well. Therefore,

М	С	M	PC
T/K	p/kPa	T/K	p/kPa
341.45	1.31	372.50	0.2093
350.90	1.91	374.46	0.2248
356.06	2.50	376.90	0.2540
360.75	3.55	379.05	0.3080
364.43	4.19	380.65	0.3343
367.00	4.48	383.31	0.3891
371.70	5.42	385.85	0.4487
373.85	6.23	387.85	0.4996
377.23	7.14	390.35	0.5609
384.90	9.83	391.76	0.5914
387.17	10.96	394.05	0.6510
390.50	12.39	395.80	0.7190
393.75	13.99	397.05	0.7885
		397.05	0.7897
		399.63	0.9364
		399.83	0.9418
		402.15	1.06
		409.85	1.29
		412.90	1.54
		415.90	1.97
		418.45	2.13
^a Standard uncert	ainties u are $u(T)$) = 0.1 K u(n) =	01 kPa

Table 2. Vapor Pressures of MC and MPC^{a}

Table 3	Antoine	Constants	of MC	and MPC
I able 5.	Antome	Constants		and Mr C

	Α	В	С	R^{a}			
MC	13.77	3222.65	-104.04	0.9994			
MPC	17.87	6691.34	-27.75	0.9953			
^a Correlation coefficient.							



Figure 3. Vapor pressures of MC. $\mathbf{\nabla}$, experimental data; solid line, calculated data using the Antonie constants.

the values calculated using the Antoine constants could be applied to the NRTL and Wilson models.

Vapor–Liquid Equilibria for the MC and MPC System. The T-p-x data for the binary system MC and MPC were determined at (1.00, 2.00, 4.00, 6.00, and 8.00) kPa with the quasi-static ebulliometric method. All measurements were kept below 393.15 K to make the MPC stable. The liquid mole fraction of MC approximately ranged from (0.15 to 0.95) at (1.00, 2.00, and 4.00) kPa, (0.30 to 0.95) at 6.00 kPa, and (0.50



Figure 4. Vapor pressures of MPC. ▲, experimental data; solid line, calculated data using the Antonie constants.

to 0.95) at 8.00 kPa, respectively. The experimental results are presented graphically in Figure 5, respectively and listed in



Figure 5. VLE phase diagram of the MC (1) and MPC (2) system at (1.00, 2.00, 4.00, 6.00, and 8.00) kPa. The liquid mole fraction of MC is the experimental data in this work: \blacktriangle , 1.00 kPa; \blacktriangledown , 2.00 kPa; \diamondsuit , 4.00 kPa; \bigcirc , 6.00 kPa; \blacksquare , 8.00 kPa; solid lines, *T*-*x* curves predicted by the NRTL; dashed lines, *T*-*x* curves predicted by the Wilson.

Table 4. The liquid compositions x_i is considered to be equal to the feed compositions z_i approximately for the quasi-static ebulliometric method, and the vapor compositions could be calculated from the properties of the liquid phase alone.^{27,28}

The T-p-x data were correlated with the NRTL and Wilson models, and the binary parameters obtained are listed in Table 5. As for the NRTL model, the nonrandomness factor α_{ij} was kept constant at 0.3, which is ordinary for the nonpolar system. The absolute deviations between regressed and experimental data are tabulated in Table 6. The average absolute deviation of pressure is close to zero for the both models. The average absolute deviation of temperature, 0.46 K for the NRTL model, is more than 0.20 K for the Wilson model, but the average absolute deviation of x_1 , 0.0099 for the NRTL model, is less than 0.0239.

According to the Gibbs phase rule, the degree of freedom is 2 for the binary vapor—liquid equilibria. Thus, when the liquid

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Table 4. VLE Data for the MC (1) and MPC (2) System at Different Pressures (below 393.15 K)^a

experime	ntal data		ľ	NRTL model				Ι	Wilson model		
T ^{exp} /K	x_1^{exp}	y_1^{cal}	$T^{\rm cal}/{ m K}$	$\Delta T^b/K$	γ_1	γ ₂	y_1^{cal}	T ^{cal} /K	$\Delta T^{b}/K$	γ_1	γ ₂
					1.00 1	kPa					
340.45	0.9497	1.0000	338.56	1.89	0.983	0.064	1.0000	338.77	1.68	0.972	0.063
341.13	0.8983	0.9997	340.26	0.87	0.947	0.143	0.9997	340.63	0.50	0.928	0.173
342.60	0.8181	0.9986	343.10	0.50	0.892	0.322	0.9982	343.43	0.83	0.876	0.389
345.65	0.7743	0.9973	344.63	1.02	0.868	0.429	0.9968	344.88	0.77	0.856	0.501
346.90	0.7177	0.9948	346.54	0.36	0.845	0.560	0.9941	346.67	0.23	0.838	0.626
349.70	0.6331	0.9892	349.30	0.40	0.825	0.722	0.9884	349.26	0.44	0.826	0.770
354.45	0.5575	0.9819	351.71	2.74	0.823	0.829	0.9814	351.57	2.88	0.828	0.860
355.15	0.4732	0.9710	354.42	0.73	0.836	0.910	0.9710	354.22	0.93	0.845	0.926
356.95	0.3108	0.9378	360.20	3.25	0.926	0.988	0.9383	360.06	3.11	0.934	0.990
368.00	0.1579	0.8701	367.97	0.03	1.172	1.005	0.8692	368.08	0.08	1.167	1.005
AAD^{c}				1.18					1.15		
251.57	0.0440	0.0004	251.50	0.02	2.00 1	kPa	0.0004	251 (1	0.05	0.004	0.440
351.56	0.9440	0.9994	351.59	0.03	0.995	0.432	0.9994	351.61	0.05	0.994	0.448
351.67	0.8963	0.9985	352.76	1.09	0.987	0.538	0.9984	352.79	1.12	0.985	0.565
354.65	0.8257	0.9964	354.61	0.04	0.975	0.682	0.9962	354.63	0.02	0.973	0.713
355.05	0.7625	0.9935	350.31	1.26	0.967	0.788	0.9933	350.31	1.26	0.967	0.814
357.43	0./22/	0.9912	357.39	0.04	0.966	0.843	0.9910	357.37	0.06	0.966	0.865
358.50	0.0345	0.9848	359.81	1.31	0.971	0.934	0.9847	359.//	1.27	0.973	0.945
302.04	0.5429	0.9739	302.41 264 19	0.57	0.993	1.012	0.9759	302.37 264.16	0.55	0.995	0.994
260.25	0.4838	0.9687	270.20	0.62	1.01/	1.012	0.9087	270.22	0.00	1.019	1.012
380 50	0.5108	0.9372	378.36	2.14	1.139	1.031	0.9309	378.68	1.87	1.154	1.029
ΔΔD ^c	0.13/9	0.8738	378.30	2.14	1.405	1.018	0.8733	3/8.08	0.75	1.402	1.018
1010				0.70	4.00]	kPa			0.75		
366.83	0.9494	0.9981	365.59	1.24	1.000	1.126	0.9981	365.59	1.24	1.000	1.131
367.55	0.9030	0.9961	366.59	0.96	1.002	1.153	0.9961	366.59	0.96	1.002	1.153
368.85	0.8254	0.9919	368.32	0.53	1.008	1.179	0.9919	368.32	0.53	1.008	1.174
369.90	0.7582	0.9875	369.86	0.04	1.018	1.187	0.9877	369.87	0.03	1.018	1.178
371.15	0.6953	0.9828	371.36	0.21	1.032	1.185	0.9830	371.38	0.23	1.032	1.175
372.30	0.6376	0.9778	372.79	0.49	1.049	1.178	0.9780	372.82	0.52	1.049	1.167
376.23	0.5371	0.9673	375.47	0.76	1.094	1.156	0.9675	375.54	0.69	1.092	1.147
378.60	0.4773	0.9596	377.22	1.38	1.131	1.139	0.9597	377.31	1.29	1.127	1.131
381.75	0.3108	0.9286	383.17	1.42	1.301	1.087	0.9282	383.34	1.59	1.292	1.083
391.60	0.1579	0.8659	392.07	0.47	1.656	1.038	0.8652	392.17	0.57	1.647	1.038
AAD^{c}				0.75					0.77		
					6.00 1	kPa					
375.96	0.9615	0.9979	374.21	1.75	1.001	1.461	0.9979	374.21	1.75	1.001	1.444
375.53	0.8934	0.9937	375.69	0.16	1.004	1.429	0.9938	375.69	0.16	1.004	1.411
378.75	0.8190	0.9885	377.36	1.39	1.013	1.390	0.9887	377.36	1.39	1.013	1.372
379.17	0.7549	0.9835	378.86	0.31	1.024	1.355	0.9837	378.86	0.31	1.024	1.338
380.70	0.7126	0.9798	379.89	0.81	1.034	1.332	0.9801	379.88	0.82	1.034	1.316
381.90	0.6365	0.9723	381.84	0.06	1.056	1.290	0.9727	381.82	0.08	1.057	1.275
385.45	0.5338	0.9601	384.76	0.69	1.099	1.235	0.9606	384.70	0.75	1.102	1.223
387.82	0.4742	0.9513	386.66	1.16	1.133	1.204	0.9520	386.57	1.25	1.138	1.193
392.05	0.3108	0.9161	393.21	1.16	1.2/5	1.124	0.9179	392.89	0.84	1.293	1.117
AAD				0.83	8 00 1	-Do			0.82		
382.18	0.9566	0 9972	380 89	1 29	0.00 I 1 001	1 568	0 9972	380 80	1 20	1 001	1 550
382.10	0.2020	0.9972	382.30	0.05	1.001	1.500	0.9972	382.30	0.05	1.001	1.559
384.49	0.82.01	0.9869	384.04	0.45	1.011	1.459	0.9870	384.01	0.48	1.012	1.450
385.85	0.7596	0.9815	385.54	0.31	1.019	1.414	0.9817	385.48	0.37	1.022	1.405
386.90	0.7101	0.9767	386.83	0.07	1.028	1.380	0.9770	386.74	0.16	1.032	1.370
388.46	0.6233	0.9669	389.29	0.83	1.048	1.322	0.9676	389.09	0.63	1.057	1.312
391.95	0.5357	0.9548	392.09	0.14	1.074	1.269	0.9560	391.73	0.22	1.091	1.258
AAD^{c}				0.45					0.46		
AAD^d				0.82					0.81		

^{*a*}Standard uncertainties *u* are u(T) = 0.1 K, u(p) = 0.1 kPa, and $u(x_1) = 0.0010$. ^{*b*}Absolute deviation of the temperature. ^{*c*}Average absolute deviation. ^{*d*}Overall average absolute deviation.

Table 5. Binary Parameters of NRTL and Wilson Models for the MC (1) and MPC (2) Systems

	α_{12}	<i>a</i> ₁₂	<i>a</i> ₂₁	b_{12}/K	b_{21}/K
NRTL model	0.3	-13.2462	27.4717	4957.1047	-10105.4690
Wislon model		-20.4498	7.5452	7528.2023	-2865.6628

mole fraction of MC and the pressures are fixed, other variable quantities such as temperatures, the vapor compositions and liquid activity coefficients could be calculated and are listed in Table 4. The T-x curves predicted by NRTL and Wilson models are presented graphically in Figure 5 as well.

The average absolute deviations of the temperature (AAD) between calculated and experimental data are listed in Table 4. It could be seen that the results calculated by NRTL and Wilson model are approached for the MC and MPC systems at

Table 6	. Absolute	Deviations	between	Experimental	and	Regressed	Data	with	NRTL	and	Wilson	Models
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e	experimental dat	ta		NRTL		Wilson		
T^{exp}/K	p ^{exp} /kPa	x_1^{exp}	$ T^{exp} - T^{est} /K$	$ p^{\exp} - p^{est} /kPa$	$ x_1^{exp} - x_1^{est} $	$ T^{exp} - T^{est} /K$	$ p^{\exp} - p^{est} /kPa$	$ x_1^{exp} - x_1^{est} $
340.45	1.00	0.9497	1.76	0.00	0.0014	0.14	0.00	0.0658
341.13	1.00	0.8983	0.74	0.00	0.0027	0.04	0.00	0.0128
342.60	1.00	0.8181	0.35	0.00	0.0040	0.10	0.00	0.0211
345.65	1.00	0.7743	0.62	0.00	0.0113	0.11	0.00	0.0210
346.90	1.00	0.7177	0.19	0.00	0.0051	0.04	0.00	0.0060
349.70	1.00	0.6331	0.16	0.00	0.0075	0.09	0.00	0.0113
354.45	1.00	0.5575	0.64	0.00	0.0656	0.73	0.00	0.0704
355.15	1.00	0.4732	0.21	0.00	0.0158	0.28	0.00	0.0202
356.95	1.00	0.3108	1.28	0.00	0.0509	1.16	0.00	0.0481
368.00	1.00	0.1579	0.01	0.00	0.0002	0.03	0.00	0.0005
351.56	2.00	0.9440	0.02	0.00	0.0000	0.01	0.00	0.0014
351.67	2.00	0.8963	0.98	0.00	0.0026	0.18	0.00	0.0313
354.65	2.00	0.8257	0.04	0.00	0.0003	0.00	0.00	0.0008
355.05	2.00	0.7625	0.88	0.00	0.0126	0.24	0.00	0.0354
357.43	2.00	0.7227	0.03	0.00	0.0007	0.01	0.00	0.0021
358.50	2.00	0.6345	0.64	0.00	0.0231	0.31	0.00	0.0333
362.04	2.00	0.5429	0.11	0.00	0.0091	0.09	0.00	0.0077
363.56	2.00	0.4838	0.19	0.00	0.0138	0.18	0.00	0.0128
369.35	2.00	0.3108	0.33	0.00	0.0129	0.34	0.00	0.0140
380.50	2.00	0.1579	0.88	0.00	0.0158	0.76	0.00	0.0137
366.83	4.00	0.9494	1.18	0.01	0.0007	0.24	0.00	0.0733
367.55	4.00	0.9030	0.89	0.01	0.0019	0.20	0.00	0.0413
368.85	4.00	0.8254	0.45	0.00	0.0032	0.12	0.00	0.0195
369.90	4.00	0.7582	0.04	0.00	0.0005	0.01	0.00	0.0016
371.15	4.00	0.6953	0.13	0.00	0.0029	0.05	0.00	0.0063
372.30	4.00	0.6376	0.26	0.00	0.0085	0.14	0.00	0.0141
376.23	4.00	0.5371	0.22	0.00	0.0186	0.21	0.00	0.0172
378.60	4.00	0.4773	0.42	0.00	0.0301	0.40	0.00	0.0284
381.75	4.00	0.3108	0.51	0.00	0.0213	0.55	0.00	0.0235
391.60	4.00	0.1579	0.17	0.00	0.0035	0.21	0.00	0.0043
375.96	6.00	0.9615	1.67	0.02	0.0005	0.33	0.00	0.1535
375.53	6.00	0.8934	0.13	0.00	0.0003	0.03	0.00	0.0052
378.75	6.00	0.8190	1.13	0.02	0.0091	0.31	0.00	0.0518
3/9.17	6.00	0.7549	0.22	0.00	0.0033	0.07	0.00	0.0102
380.70	6.00	0./126	0.51	0.01	0.0110	0.20	0.00	0.0254
381.90	6.00	0.6365	0.03	0.00	0.0010	0.02	0.00	0.0022
385.45	6.00	0.5338	0.18	0.00	0.0161	0.21	0.00	0.0177
387.82	6.00	0.4/42	0.31	0.00	0.0241	0.36	0.01	0.0264
392.05	8.00	0.3108	0.35	0.01	0.0162	0.27	0.00	0.0122
202.18	0.00 8.00	0.9300	1.21	0.02	0.0005	0.25	0.00	0.0803
302.33	0.00 8.00	0.0939	0.04	0.00	0.0001	0.01	0.00	0.0019
205 05	0.UU 8.00	0.8201	0.30	0.01	0.0029	0.10	0.00	0.0102
303.83 386.00	8.00 8.00	0.7590	0.21	0.00	0.0032	0.08	0.00	0.0114
200.90	8.00 8.00	0./101	0.04	0.00	0.0008	0.05	0.00	0.0040
201.05	8.00 8.00	0.0255	0.02	0.01	0.0130	0.15	0.00	0.0107
ADD^a	0.00	0.5557	0.46	0.00	0.0099	0.20	0.00	0.0239

^{*a*}Average absolute deviation.

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all studied pressures. At the same time, Figure 5 also shows that the T-x curves of the both models are almost coincident. Moreover, the overall average absolute deviation of the temperature is nearly 0.82 K and 0.81 K. Therefore, the prediction accuracy of the NRTL model is the same as the Wilson model. The AAD is different at all studied pressures. The AAD has a maximum at 1 kPa, possibly because it was difficult to control the experiment conditions at a low pressure of 1.00 kPa. The ADD is less than 1.00 K at all studied pressures except that it is less than 1.20 K at 1.00 kPa. Comparing the T-x experimental data and T-x curves in Figure 5, the conclusion could be drawn that both models could describe the vapor-liquid equilibria very well.

Figure 5 also shows that T-x curves decline rapidly with the liquid compositions of MC from (0 to 0.30) and slowly from (0.30 to 1.00). The reason for this is that the boiling point of pure MC and MPC is very different at the same pressure. Figure 6 shows the y-x diagram, and the degree of separation is



Figure 6. y-x diagram of the MC (1) and MPC (2) systems at (1.00, 4.00, and 8.00) kPa calculated using the Wilson model.

much larger at lower pressure. Besides, the relative volatility (α) of the mixture is calculated by the Wilson model and illustrated in Figure 7, respectively. It could be seen that the relative



Figure 7. Relative volatility (α) of MC (1) and MPC (2) at (1.00, 2.00, 4.00, 6.00, and 8.00) kPa.

volatility decreases slowly with the liquid mole compositions of MC from (0 to 0.30) at (1.00, 2.00, 4.00, 6.00, and 8.00) kPa and does not change virtually from (0.30 to 1.00) at (4.00, 6.00, and 8.00) kPa, but increases rapidly at (1.00 and 2.00) kPa. Meanwhile, with the pressures decreasing, the relative volatility increases gradually. Figure 7 also shows that it is much easier to get the high-purity MPC from the binary system by using distillation technology at (1.00 and 2.00) kPa.

CONCLUSIONS

New vapor pressures of MC and MPC have been measured using the quasi-static ebulliometric method, and the Antoine constants were obtained via regression of experimental data. The isobaric VLE data for the MC and MPC system have been determined at (1.00, 2.00, 4.00, 6.00, and 8.00) kPa by the same method as well. Both NRTL and Wilson models could describe the MC and MPC system very well. The relative volatility of the binary system is calculated and is more than 1 by far, so the conclusion can be drawn that it is easy to get the high purity MPC from the binary system by distillation technology at low pressures.

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Notes

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NOMENCLATURE

 ϕ_i^{V} , fugacity coefficient; $\gamma_{i\nu}$ activity coefficient of component *i* in the liquid; $x_{i\nu}$ mole fractions of liquid; $y_{i\nu}$ mole fractions of vapor; *R*, universal gas constant; *p*, system pressure; *T*, absolute temperature; p_i^{S} , saturated vapor pressure of pure component *i*; V_i^{L} , molar volume of pure liquid; ϕ_i^{S} , fugacity coefficient of the pure component *i* at saturation; $A_{i\nu} B_{i\nu}$ and $C_{i\nu}$ three parameters for the Antoine equation; $\alpha_{ij\nu}$ nonrandomness factor; $a_{ij\nu} b_{ij\nu}$ binary parameters of the NRTL and Wilson models; F_{OB} , objective function; σ , standard deviation of the indicated data; w, weight of data group; _{NDG}, number of data groups in the regression case

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