

# Organic Salt Effect of Tetramethylammonium Bicarbonate on the Vapor–Liquid Equilibrium of the Dimethyl Carbonate + Methanol System

Changsheng Yang,\* Xia Yin, and Shengyong Ma

Key laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China

**ABSTRACT:** Isobaric vapor–liquid equilibrium (VLE) data for the systems dimethyl carbonate (DMC) + methanol and DMC + methanol + tetramethylammonium bicarbonate (TMAB) at different salt mole fractions (0.04, 0.07, and 0.10) have been measured at 101.32 kPa. The bubble-point data of the system methanol + TMAB have also been measured at different salt mole fractions. The addition of the organic salt TMAB has a salting-out effect on DMC, and the effect would be enhanced with the increasing salt concentration. The VLE data of the salt-containing system were predicted by the modified Wilson and nonrandom two-liquid (NRTL) models proposed by Tan. The average deviations for the mole fraction of the vapor phase and the bubble point by the modified predictive model were:  $\Delta y = 0.011$ ,  $\Delta T = 0.6$  K.

## INTRODUCTION

This work originates from an industrial project where the objective is to synthesize the purified tetramethylammonium hydroxide (TMAH) by the electrolysis of tetramethylammonium bicarbonate (TMAB) in an electrolytic cell, which is presently a common method to prepare the purified TMAH.<sup>1,2</sup> TMAH, which is one of the most widely used products in the electronics industry (used in developing, etching, planarizing, and photoresist stripping),<sup>3–5</sup> is obtained in practice in two stages, namely, the synthesis of intermediate TMAB and subsequently the conversion of this salt into hydroxide by electrolysis. The organic salt TMAB is prepared from the reaction between the trimethylamine gas and the dimethyl carbonate (DMC) containing less metal impurities, using purified methanol as the solvent. The electrolysis process has a strict requirement with the amount of methanol. Therefore, for improved understanding, the chemical-physical properties of the DMC + methanol + TMAB mixture need to be studied to enhance the ability to separate the TMAB-based mixture and establish specific temperature conditions for residue removal.

Recently vapor–liquid equilibrium (VLE) behavior for the binary system DMC + methanol system<sup>6–11</sup> has been widely studied. However, the VLE of the ternary system containing DMC and methanol mainly focused on the effect of the third component, usually an effective extractant (for instance, aniline,<sup>12</sup> dimethyl oxalate,<sup>13</sup> and so on), to enhance the relative volatility between methanol and DMC at atmospheric or pressurized conditions. Meanwhile, Kim et al.<sup>14</sup> have also studied the effect of two ionic liquids on the VLE for the DMC + methanol system at  $T = 333.15$  K. According to the reported results, the azeotrope could effectively be eliminated by the addition of these ionic liquids. Few studies in literature<sup>12–14</sup> involve the salt effect regarding the DMC + methanol system, and no experimental data were found for the ternary system DMC + methanol + TMAB in literature.

It is comprehensible that the thermodynamic behavior of organic salt solutions is much more complicated than that of strong salt solutions since organic salts are weak electrolytes and are partially dissociated in solutions. The coexistence of the particle interactions in a weak salt solution between ion–ion, ion–solvent molecule, ion–salt molecule, solvent molecule–solvent molecule, and salt molecule–solvent molecule is the main reason for the complicated behavior of solutions. Several correlative and predictive models based on the local composition or group-contribution conceptions have been proposed to calculate the VLE of systems formed by mixed solvents and electrolytes. The electrolyte nonrandom two-liquid (NRTL) model of Mock et al.<sup>15</sup> has been widely used to predict the VLE behavior of the ternary system containing salts with different large organic ions by Kurzin et al.<sup>16–19</sup> and Orchillés et al.<sup>20–22</sup> Considering the partially dissociation of the weak electrolyte in the system without water and the sparing solubility between TMAB and DMC, the Wilson and NRTL model modified by Tan,<sup>23,24</sup> which mainly considering the interactions between solvents and salt at the molecular level, are suitable to predict the VLE data of the ternary system in this work. Meanwhile the modified Wilson and NRTL equation gives considerably fewer solvent–solute interaction parameters compared with the approach proposed by other workers based on the consideration of ions and disassociation molecules of the dissolved solutes.

The main goal of this work is to obtain the phase equilibrium data of the systems DMC + methanol and DMC + methanol + TMAB at different salt concentrations at 101.32 kPa. The bubble-point data of the system methanol + TMAB have also been measured at different salt concentrations. The experimental VLE data were predicted by the modified Wilson and NRTL models. A comparison between the predictive and the

Received: July 26, 2011

Accepted: October 31, 2011

Published: November 18, 2011

**Table 1.** Comparison of Boiling Point  $T_b$ /K of Pure Components at Atmospheric Pressure with Literature Data

component	$T_b(101.3 \text{ kPa})/\text{K}$	
	present paper	lit.
methanol	337.8	337.70 <sup>a</sup>
		337.83 <sup>b</sup>
		337.4 <sup>c</sup>
DMC	363.4	363.60 <sup>a</sup>
		363.46 <sup>b</sup>
		363.35 <sup>c</sup>

<sup>a</sup> Reference 6. <sup>b</sup> Reference 9. <sup>c</sup> Reference 11.

experimental vapor mole fraction and temperature for the ternary system showed that the modified Wilson and NRTL equation provided useful estimates.

## EXPERIMENTAL SECTION

**Materials.** Methanol (HPLC grade  $\geq 99.5$  % mass fraction) and DMC (AR grade  $\geq 99.0$  % mass fraction) were supplied by Tianjin Guangfu Technology Development Co. Ltd., China. Methanol was used without further purification. DMC was dried over 3 Å molecular sieves. The purities of the DMC and methanol were tested to be 99.8 % and 99.5 % mass fractions by GC and failed to find any impurities. The boiling point data of the pure components were compared with the published data in Table 1. All materials were degassed using ultrasound before use. TMAB used was prepared in our own laboratory and dried in a vacuum oven at 363 K at reduced pressure for more than 24 h until a constant mass was reached and then stored in the desiccator. Back titration<sup>25</sup> with hydrochloric acid of a known concentration was used for the analysis of bicarbonate/carbonate salt mixtures, and triplicate analysis is needed. The Karl Fischer method was used to measure the water in the TMAB. The result showed that the mass fraction of TMAB was above 98 % and the impurity is tetramethylammonium carbonate (0.5 % mass fraction) and water (1.45 % mass fraction).

**Apparatus and Procedure.** The equilibrium apparatus was a modified Rose-Williams still.<sup>26</sup> In this still, both of the vapor and liquid phases continuously circulate to provide intimate contact of the phases and to ensure that equilibrium can be established rapidly. In each experiment, equilibrium conditions were assumed when constant temperature and pressure were obtained for at least 30 min. The equilibrium temperature was measured with a precision mercury thermometer with the uncertainty of about 0.1 K. The still was connected with a vacuum pump to regulate the system pressure, and the pressure is determined by a U-shaped differential manometer whose fluctuation was held within 0.01 kPa. Ground-glass joints were sealed with Teflon tape to minimize vapor leakage from the system.

The mixture of the TMAB and methanol with known salt concentration obtained by weighing was first put into the still. Then the DMC of required amount was quickly introduced into the equilibrium cell. The first overall mass is about 40 g. The mixture of methanol and DMC with the same composition was introduced into the still to decrease the salt concentration.

Compositions of the condensed vapor and salt-free liquid phase were performed on a BFRL SP-2100A GC with a thermal conductivity detector (TCD) after calibration with standard

**Table 2.** VLE Data for DMC (1) + Methanol (2) at 101.32 kPa

$T/\text{K}$	$x_1$	$y_1$	$T/\text{K}$	$x_1$	$y_1$
337.7	0.055	0.079	338.6	0.483	0.262
337.4	0.084	0.102	339.5	0.553	0.298
337.4	0.106	0.119	341.2	0.643	0.333
337.0	0.151	0.152	343.1	0.732	0.387
337.0	0.218	0.176	347.7	0.845	0.506
337.4	0.355	0.230	351.6	0.901	0.620
337.9	0.416	0.256	356.8	0.956	0.770

solutions prepared gravimetrically. The GC response peaks were treated with the N2000 chromatography station. The chromatographic column (2 m  $\times$  3 mm) was packed with Porapak QS (80 to 100). The flow rate of carrier gas  $\text{H}_2$  was 65 mL  $\cdot$  min<sup>-1</sup>. The column, injector, and detector temperatures were (403.15, 443.15, and 463.15) K, respectively. An injection volume of 0.3  $\mu\text{L}$  was used. At least three analyses were done for each vapor and liquid sample. The accuracy of vapor and liquid mole fractions were about 0.01. The compositions of liquid phase in the system containing salt were prepared gravimetrically using an analytical balance (BP210s) with an accuracy of  $\pm 0.1$  mg.

## RESULTS AND DISCUSSION

**Experimental Data.** Isobaric VLE data obtained at 101.32 kPa for the systems of DMC + methanol and DMC + methanol + TMAB and the bubble-point data of methanol + TMAB were shown in Tables 2 to 4. Figure 1 compared the experimental VLE data for the salt-free system and the published isobaric data<sup>7,9</sup> at 101.3 kPa. The good agreement demonstrated that this equilibrium still is suitable for the determination of VLE data. Figure 2 compared the experimental temperature–composition data for the DMC + methanol system at different salt concentrations and showed the azeotrope shifting. Figure 3 showed the effect of TMAB on the vapor pressure of methanol. The lines were fit by eq 1, and the corresponding parameters were displayed in Table 5.  $R$  is the adjusted  $R^2$ , and the nearer the value comes to 1, the better the regression effect will be. The impact of the different salt concentrations on the VLE was illustrated in Figure 4.

$$P/\text{kPa} = B_1(T/\text{K}) + B_2(T/\text{K})^2 + B_3(T/\text{K})^3 + B_4(T/\text{K})^4 + B_5(T/\text{K})^5 + B_6(T/\text{K})^6 + B_7(T/\text{K})^7 + B_8(T/\text{K})^8 + B_9(T/\text{K})^9 \quad (1)$$

Owing to the sparing solubility of TMAB in the DMC, the salt would precipitate in the DMC-rich region. So the mixture of TMAB and methanol was first put into the still, and then the DMC was introduced into the system. For the system DMC (1) + methanol (2) + TMAB,  $x_s$  is defined as the salt mole fraction in the methanol solvent.  $x_1$  represents the DMC mole fraction in the mixture of DMC and methanol. Figure 2 shows that the azeotropic point was about 0.200 when the salt concentration were at  $x_s = 0.04$  and 0.07 and changed to about 0.300 at  $x_s = 0.10$ . Meanwhile, the experimental data showed the salt effect was strengthened with the increasing concentration of TMAB in the solvent mixture.

**Table 3. VLE Data and Results of the Modified Wilson and NRTL Model for DMC (1) + Methanol (2) at Different TMAB Concentrations**

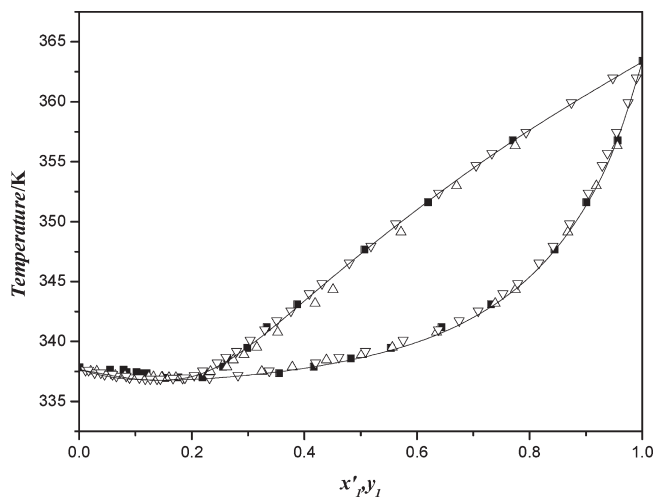
$x_1$	$y_1$	$T$		modified Wilson		modified NRTL	
		K	$\Delta y^a$	$\Delta T^b/K$	$\Delta y^a$	$\Delta T^b/K$	
$x_s = 0.04$							
0.060	0.078	339.6	0.014	0.1	0.007	0.1	
0.120	0.160	339.1	0.014	0.1	0.021	0.2	
0.160	0.178	338.9	0.006	0.1	0.013	0.3	
0.200	0.192	338.9	0.002	0.0	0.005	0.4	
0.300	0.239	339.3	0.005	0.2	0.012	0.2	
0.400	0.269	340.1	0.003	0.5	0.009	0.1	
0.500	0.314	341.4	0.015	1.1	0.019	0.6	
0.650	0.354	344.0	0.008	1.7	0.011	1.0	
0.750	0.402	346.5	0.024	1.9	0.033	1.0	
0.930	0.704	358.0	0.001	3.3	0.019	2.5	
average value			0.009	0.9	0.013	0.6	
$x_s = 0.07$							
0.060	0.085	341.8	0.020	0.2	0.007	0.2	
0.120	0.164	341.2	0.001	0.2	0.015	0.3	
0.160	0.192	341.1	0.001	0.3	0.014	0.3	
0.200	0.210	341.0	0.005	0.3	0.010	0.4	
0.300	0.268	341.2	0.011	0.5	0.025	0.3	
0.400	0.296	341.7	0.007	0.6	0.017	0.3	
0.500	0.339	343.2	0.018	1.6	0.023	0.5	
0.650	0.388	345.6	0.008	2.2	0.001	0.8	
0.750	0.431	347.5	0.010	2.1	0.029	0.4	
0.930	0.669	357.3	0.010	2.5	0.046	1.0	
average value			0.009	1.1	0.019	0.4	
$x_s = 0.10$							
0.060	0.094	344.8	0.027	0.5	0.006	0.2	
0.120	0.182	343.8	0.007	0.5	0.020	0.5	
0.160	0.232	343.6	0.013	0.6	0.040	0.5	
0.200	0.266	343.4	0.023	0.6	0.050	0.6	
0.300	0.302	343.3	0.015	0.6	0.038	0.7	
0.400	0.324	343.9	0.004	1.0	0.022	0.4	
0.500	0.360	345.4	0.010	2.1	0.018	0.4	
0.650	0.427	347.8	0.023	3.2	0.012	1.0	
0.750	0.468	349.7	0.007	3.3	0.023	0.7	
0.850	0.579	353.7	0.021	3.9	0.030	1.1	
0.930	0.711	358.2	0.001	3.3	0.056	1.0	
average value			0.015	1.8	0.031	0.6	

<sup>a</sup>  $\Delta y = (1/N) \sum_i^N |y_{cali} - y_{exp}|$ , <sup>b</sup>  $\Delta T = (1/N) \sum_i^N |T_{cali} - T_{exp}|$ , where  $y_{cal}$  is the equilibrium vapor mole fraction composition calculated from the correlation and  $y_{exp}$  is the corresponding experimental equilibrium vapor composition values for the same equilibrium liquid composition.  $T_{cali}$  is the equilibrium temperature calculated from the correlation, and  $T_{expi}$  is the corresponding experimental temperature values for the same equilibrium liquid composition.  $N$  is the number of experimental data points.

**Calculation of Phase Equilibrium.** The Wilson and NRTL models were used to correlate the experimental VLE data for the DMC + methanol system. Meanwhile, the Tan–Wilson and Tan–NRTL models were applied to predict the experimental

**Table 4. Bubble-Point Data for Methanol + TMAB at Different Salt Concentrations**

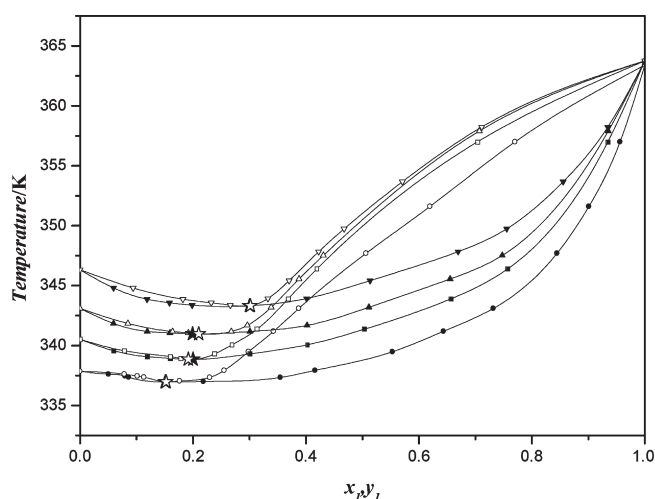
$x_s = 0.04$		$x_s = 0.07$		$x_s = 0.10$	
$T/K$	$P/kPa$	$T/K$	$P/kPa$	$T/K$	$P/kPa$
340.5	101.32	343.1	101.32	346.3	101.32
334.5	78.89	341.5	94.82	344.7	94.82
333.3	74.90	340.1	89.50	343.2	89.50
332.1	70.91	338.5	84.19	340.8	81.53
331.0	67.72	336.8	78.87	338.2	73.55
329.1	62.94	335.1	73.56	336.1	67.71
326.4	56.02	333.1	67.71	334.3	62.92
321.2	45.66	331.3	62.92	329.8	52.29
315.2	34.49	329.2	57.61	326.0	44.31
313.0	31.03	325.7	49.63	319.8	34.48
309.4	25.98	319.8	39.00	318.3	32.35
		317.0	34.48	315.4	28.37
		314.8	31.03		
		312.9	28.37		



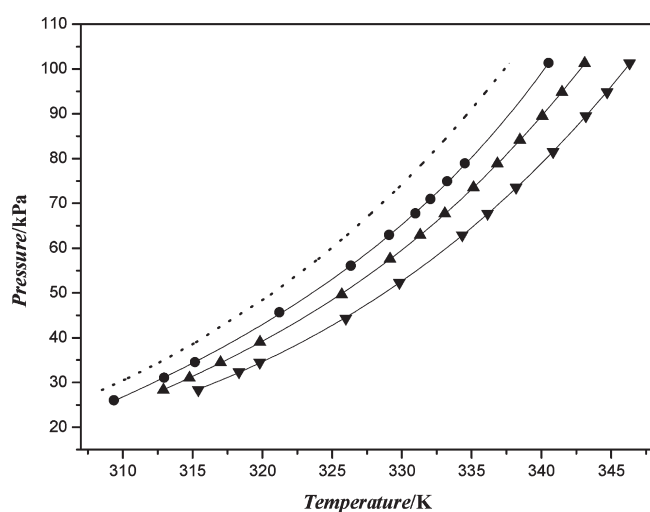
**Figure 1.** DMC (1) + methanol (2) system. Symbols refer to experimental data (■) at 101.32 kPa; △, literature VLE data at 101.3 kPa from Luo et al.;<sup>7</sup> ▽, literature VLE data at 101.3 kPa from Rodríguez et al.<sup>9</sup> Lines: smoothed using the NRTL equation.

data of the DMC + methanol + TMAB system. The exact mathematical forms of the equations are shown in Table 6. Table 7 lists the relevant parameters. In Table 6,  $T_{ci}$ ,  $P_{ci}$ ,  $V_{ci}$ , and  $Z_{ci}$  mean the critical temperature, pressure, volume, and compression factor of the component  $i$ , respectively;  $P_i^o$  is the saturation vapor pressure of the solvent component  $i$  calculated from the Antoine equation at the bubble point  $T_{si}$  of the solvent component  $i$  containing the same concentration of salt at the total pressure  $P$ . Owing to the sparing solubility of TMAB in DMC,  $P_i^o$  equals to the saturation vapor pressure of pure component DMC. In the Wilson equation,  $V_i$ , the molar volume of component  $i$ , was calculated by the Rackett equation.<sup>29</sup>

The estimation of the model parameters were regressed with the least-squares method using the objection function (OF) given by eq 2. The fitted parameters and the average mean deviations between the calculated and experimental vapor-phase



**Figure 2.** DMC (1) + methanol (2) system at different concentrations of TMAB at 101.32 kPa. ● and ○ represent temperature liquid and vapor composition at  $x_s = 0$ ; ■ and □ represent temperature liquid and vapor composition at  $x_s = 0.04$ ; ▲ and △ represent temperature liquid and vapor composition at  $x_s = 0.07$ ; ▼ and ▽ represent temperature liquid and vapor composition at  $x_s = 0.10$ ; ★ and ☆ represent azeotrope liquid and vapor composition at different salt concentrations.



**Figure 3.** Vapor pressure–temperature relationship for the methanol + TMAB system at different salt concentrations: ●,  $x_s = 0.04$ ; ▲,  $x_s = 0.07$ ; ▼,  $x_s = 0.10$ . Solid lines (—) is calculated by eq 1; dotted line (⋯) represents methanol without TMAB, from literature.<sup>27</sup>

mole fraction ( $\Delta y$ ) and bubble point ( $\Delta T$ ) were listed in Table 3.

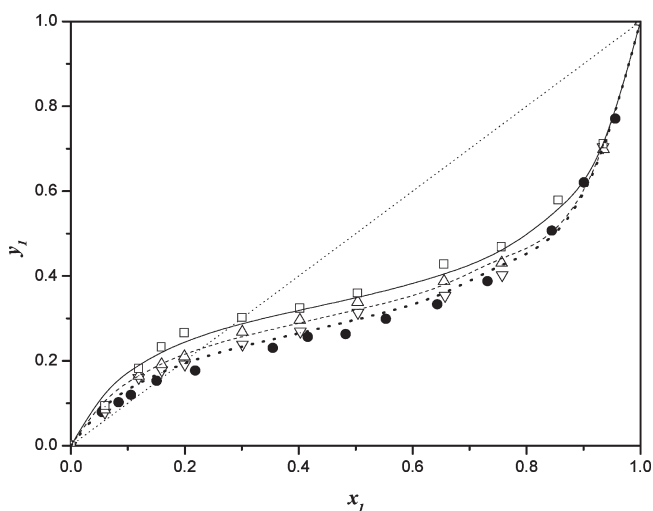
$$\text{OF} = \sum \left[ \left( \frac{\gamma_{\text{exp}} - \gamma_{\text{cal}}}{\gamma_{\text{exp}}} \right)^2 \right] \quad (2)$$

Due to the low total pressure, the vapor phase was assumed to be ideal, and the fugacity coefficients and the Poynting correction were neglected. Thus, it was assumed that the relationship of the vapor and liquid could be expressed by

$$y_i P = P_i^s \gamma_i x_i \quad (3)$$

**Table 5.** Parameters of the Vapor Pressure of the Methanol + TMAB System

	$x_s = 0.04$	$x_s = 0.07$	$x_s = 0.10$
$B_1$	$5.3785 \cdot 10^{-17}$	$-1.5716 \cdot 10^{-16}$	$2.9812 \cdot 10^{-17}$
$B_2$	$8.7194 \cdot 10^{-15}$	$-2.5766 \cdot 10^{-14}$	$4.9275 \cdot 10^{-15}$
$B_3$	$1.2119 \cdot 10^{-12}$	$-3.6214 \cdot 10^{-12}$	$6.9827 \cdot 10^{-13}$
$B_4$	$1.3103 \cdot 10^{-10}$	$-3.9597 \cdot 10^{-10}$	$7.6979 \cdot 10^{-11}$
$B_5$	$8.5019 \cdot 10^{-9}$	$-2.5982 \cdot 10^{-8}$	$5.0927 \cdot 10^{-9}$
$B_6$	$-1.1758 \cdot 10^{-10}$	$3.1202 \cdot 10^{-10}$	$-6.1572 \cdot 10^{-11}$
$B_7$	$6.0354 \cdot 10^{-13}$	$-1.4028 \cdot 10^{-12}$	$2.8052 \cdot 10^{-13}$
$B_8$	$-1.3673 \cdot 10^{-15}$	$2.7966 \cdot 10^{-15}$	$-5.7257 \cdot 10^{-16}$
$B_9$	$1.1574 \cdot 10^{-18}$	$-2.0829 \cdot 10^{-18}$	$4.4408 \cdot 10^{-19}$
$R$	0.9999	0.99997	0.99996



**Figure 4.** Phase diagram ( $x_1$ – $y_1$  diagram) at 101.32 kPa for the DMC (1) + methanol (2) system at different concentrations of TMAB: ●,  $x_s = 0$ ; ▽,  $x_s = 0.04$ ; △,  $x_s = 0.07$ ; □,  $x_s = 0.10$ . Lines are calculated by the modified Wilson model: ⋯,  $x_s = 0.04$ ; - - -,  $x_s = 0.07$ ; —,  $x_s = 0.10$ .

where  $P_i^s$  is the vapor pressure of pure solvent  $i$  at equilibrium temperature ( $i = 1, 2$ ) which were calculated with the Antoine equation,  $y_i$  is the vapor-phase mole fraction, and  $x_i$  is the liquid-phase mole fraction with no salt.  $\gamma_i$  is the activity coefficient of component  $i$ .

The VLE data of the salt-containing system were predicted by the modified Wilson and NRTL models proposed by Tan<sup>23,24</sup> which contain four parameters: two solvent ( $i$ )–solvent ( $j$ ) interaction parameters, which are the same as those found in the original Wilson ( $A_{ij}$ ) or NRTL ( $\alpha_{ij}, \tau_{ij}$ ) equations, and two salt ( $s$ )–solvent ( $i$ ) interaction parameters in the modified Wilson ( $A_{si}$ ) or NRTL ( $\alpha_{is}, \tau_{is}$ ). The solvent ( $i$ )–solvent ( $j$ ) interaction parameters were correlated by the experimental VLE data of the salt-free system using the objection function given by eq 2. As proposed by Tan,<sup>24</sup> the salt ( $s$ )–solvent ( $i$ ) interaction parameters were calculated through the equations in Table 6 and the nonrandomness factor  $\alpha_{is}$  in the modified NRTL equation equal to 0.20.

The organic salt effect on the VLE is associated with the salting-out or salting-in of the solvent components and is usually expressed in terms of an enhancement factor,  $\alpha_s/\alpha_o$ , where  $\alpha_o$  is the relative volatility in absence of salt and  $\alpha_s$  is the relative

Table 6. Mathematical Forms of the Activity Coefficient Equations for the Salt-Free System and the Salt-Containing System

Wilson	$\ln \gamma_i = -\ln(x_i + A_{ij}x_j) + x_j \left( \frac{A_{ij}}{x_i + x_j A_{ij}} - \frac{A_{ji}}{x_j + x_i A_{ji}} \right), \quad A_{ij} = \frac{V_j}{V_i} \exp\left(-\frac{g_{ij} - g_{ii}}{RT}\right)$ $V_i = \frac{RT_{ci}}{P_{ci}} Z_{ci}^{\tau_i}, \quad \tau_i = 1 + (1 - T/T_{ci})^{2/7}, \quad T/T_{ci} \leq 0.75$
NRTL	$\ln \gamma_i = x_j^2 \left[ \frac{G_{ji}^2 \tau_{ji}}{(x_i + x_j G_{ji})^2} + \frac{G_{ij} \tau_{ij}}{(x_j + x_i G_{ij})^2} \right]$ $\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT}, \quad G_{ij} = \exp(-\alpha_{ij} \tau_{ij}), \quad \alpha_{ij} = \alpha_{ji}$
Tan–Wilson	$\ln \gamma_i^s = -\ln(A_{si}x_i + A_{ij}x_j) + x_j \varphi$ $\varphi = \frac{A_{12}}{A_{s1}x_1 + A_{12}x_2} - \frac{A_{21}}{A_{s2}x_j + A_{21}x_1}, \quad A_{si} = \frac{P_i^o}{P}$
Tan–NRTL	$\ln \gamma_i^s = x_j^2 \left[ \frac{G_{ji}^2 \tau_{ji}}{(x_i + x_j G_{ji})^2} + \frac{G_{ij} \tau_{ij}}{(x_j + x_i G_{ij})^2} \right] + \left[ \frac{x_j G_{is} G_{js} (\tau_{is} - \tau_{js})}{(x_i G_{is} + x_j G_{js})^2} \right] + \left[ \frac{x_i G_{is} \tau_{is} + x_j G_{js} \tau_{js}}{x_i G_{is} + x_j G_{js}} \right]$ $\tau_{is} = \frac{g_{is} - g_{ss}}{RT}, \quad G_{is} = \exp(-\alpha_{is} \tau_{is}), \quad g_{is} - g_{ss} = RT \ln(P/P_i^o)_{T_{si}, x_i}, \quad i, j = 1, 2$

Table 7. Antoine Coefficients and Critical Properties for the Pure Components<sup>a</sup>

	Antoine coefficients				critical properties <sup>b</sup>			
	A	B	C	temperature range/K	T <sub>c</sub> /K	P <sub>c</sub> /kPa	V <sub>c</sub> /cm <sup>3</sup> ·mol <sup>-1</sup>	Z <sub>c</sub>
DMC <sup>c</sup>	6.4338	1413.00	-44.25	273.15 to 548.0	539.00	4630.55	250.0	0.2583
methanol <sup>d</sup>	7.14736	1544.804	-37.235	335 to 376	512.84	8092.00	118.0	0.2239

<sup>a</sup> Antoine equation:  $\log(P/\text{kPa}) = A - B/(T/K + C)$ ,  $Z_c = P_c V_c / RT_c$ . <sup>b</sup> Reference 11. <sup>c</sup> Reference 28. <sup>d</sup> Reference 27.

Table 8. Parameters of the Prediction and Correlation with the Modified Wilson and NRTL Model for the DMC (1) + Methanol (2) + TMAB System

$x_s$	modified Wilson model				modified NRTL model	
	$A_{s1}$	$A_{s2}$	$A_{s21}$	$\alpha_s/\alpha_o$	$\tau_{1s}$	$\tau_{2s}$
0.04	1.1175	1.0022	1.1151	0.98/1.42	-0.1111	-0.0022
0.07	1.2331	1.0022	1.2305	1.07/1.46	-0.2096	-0.0022
0.10	1.3923	1.0022	1.3893	1.20/1.79	-0.3310	-0.0022

$g_{12} - g_{11} = 3412.5 \text{ J} \cdot \text{mol}^{-1}$        $\alpha_{12} = \alpha_{21} = 0.4, g_{12} - g_{22} = 3217.2 \text{ J} \cdot \text{mol}^{-1}, g_{21} - g_{11} = 856.0 \text{ J} \cdot \text{mol}^{-1}, \alpha_{1s} = \alpha_{2s} = 0.20$   
 $g_{21} - g_{22} = 862.8 \text{ J} \cdot \text{mol}^{-1}$

volatility in the presence of salt, calculated using liquid compositions on a salt-free basis.  $A_{s21} = A_{s2}/A_{s1}$ <sup>30,31</sup> is the ratio of salt (s)–solvent (i) interaction parameters of the model based on Wilson's local volume fractions concept. As is described in the literature,<sup>23</sup> the larger the value of  $A_{s21}$ , the larger would be the ratio of  $\alpha_s/\alpha_o$ , which would imply larger salting-out of component 1. The results calculated from experimental data were shown in Table 8.  $A_{s21} > 1$  and the increasing value range of  $\alpha_s/\alpha_o$  also demonstrated the phenomenon that TMAB has a salting-out effect on the solvent DMC, and this effect would be enhanced when the salt concentration increased.

Meanwhile, it could be seen from Table 3 that the deviations of the bubble point ( $\Delta T$ ) from the modified NRTL are obviously smaller than the modified Wilson. On the contrary, the deviations of vapor composition ( $\Delta y$ ) from the modified Wilson

model are smaller. The average deviations for the mole fraction of the vapor phase by the modified Wilson model and bubble point by the modified NRTL model at 31 data points of the salt-containing system were  $\Delta y = 0.011$  and  $\Delta T = 0.6$  K. Generally, the modified Wilson and NRTL model are suitable to predict the VLE in the presence of the organic salt such as TMAB.

## CONCLUSION

In this study, isobaric VLE data for the systems DMC + methanol and DMC + methanol + TMAB at different salt mole fractions (0.04, 0.07, and 0.10) at 101.32 kPa have been measured. The bubble-point data of the system methanol + TMAB have also been measured at different salt mole fractions. According to the experimental results, the organic salt TMAB has

a salting-out effect on DMC, and the effect is enhanced with the increasing salt concentration. The VLE data of the ternary system were predicted by the modified Wilson and NRTL models proposed by Tan. The average deviations for the mole fraction of the vapor phase and the bubble point by the modified predictive model were  $\Delta y = 0.011$  and  $\Delta T = 0.6$  K.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: yangchangsheng@tju.edu.cn.

### Funding Sources

We thank the Programme of Introducing Talents of Discipline to Universities (No. B060006) for financial support of this work.

## REFERENCES

- (1) Hale, C. H.; Tanner, A. R.; Hale, B. M. Method for Producing High Purity Quaternary Ammonium Hydroxides. U.S. Patent 4,714,530, 1987.
- (2) Lyon, F. A. Synthesis of Tetramethylammonium Hydroxide. U.S. Patent 2001/0025798 A1, 2001.
- (3) Yagi, O.; Shimizu, S. Synthesis of Highly Purified Tetramethylammonium Hydroxide Solution. *Denki Kagaku Oyobi Kogyo Butsuri Kagaku* **1996**, *64*, 225–231.
- (4) Levitin, G.; Bush, D.; Eckert, C. A.; Hess, D. W. Phase Behavior and Modeling of CO<sub>2</sub>/Methanol/Tetramethylammonium Bicarbonate and CO<sub>2</sub>/Methanol/Tetramethylammonium Bicarbonate/Water Mixtures at High Pressures. *J. Chem. Eng. Data* **2004**, *49*, 599–606.
- (5) Levitin, G.; Myneni, S.; Hess, D. W. Post Plasma Etch Residue Removal Using CO<sub>2</sub>-TMAHCO<sub>3</sub> Mixtures: Comparison of Single-Phase and Two-Phase Mixtures. *J. Electrochem. Soc.* **2004**, *151*, 380–386.
- (6) Comelli, F.; Francesconi, R. Isothermal Vapor–Liquid Equilibria Measurements, Excess Molar Enthalpies, and Excess Molar Volumes of Dimethyl Carbonate + Methanol, + Ethanol, and + Propan-1-ol at 313.15 K. *J. Chem. Eng. Data* **1997**, *42*, 705–709.
- (7) Luo, H. P.; Xiao, W. D.; Zhu, K. H. Isobaric Vapor–Liquid Equilibria of Alkyl Carbonates with Alcohols. *Fluid Phase Equilib.* **2000**, *175*, 91–105.
- (8) Luo, H. P.; Zhou, J. H.; Xiao, W. D.; Zhu, K. H. Isobaric Vapor–Liquid Equilibria of Binary Mixtures Containing Dimethyl Carbonate under Atmospheric Pressure. *J. Chem. Eng. Data* **2001**, *46*, 842–845.
- (9) Rodríguez, A.; Canosa, J.; Domínguez, A.; Tojo, J. Vapour–Liquid Equilibria of Dimethyl Carbonate with Linear Alcohols and Estimation of Interaction Parameters for the UNIFAC and ASOG Method. *Fluid Phase Equilib.* **2002**, *201*, 187–201.
- (10) Fang, Y. J.; Qian, J. M. Isobaric Vapor–Liquid Equilibria of Binary Mixtures Containing the Carbonate Group -OCOO-. *J. Chem. Eng. Data* **2005**, *50*, 340–343.
- (11) Shi, Y. H.; Liu, H. L.; Wang, K.; Xiao, W. D.; Hu, Y. Measurements of Isothermal Vapor–Liquid Equilibrium of Binary Methanol/Dimethyl Carbonate System under Pressure. *Fluid Phase Equilib.* **2005**, *234*, 1–10.
- (12) Hsu, K. Y.; Hsiao, Y. C.; Chien, I. L. Design and Control of Dimethyl Carbonate–Methanol Separation via Extractive Distillation in the Dimethyl Carbonate Reactive-Distillation Process. *Ind. Eng. Chem. Res.* **2010**, *49*, 735–749.
- (13) Ma, X. B.; Liu, X. G.; Li, Z. H.; Xu, G. H. Vapor–Liquid Equilibria for the Ternary System Methanol + Dimethyl Carbonate + Dimethyl Oxalate and Constituent Binary Systems at Different Temperatures. *Fluid Phase Equilib.* **2004**, *221*, 51–56.
- (14) Kim, H. D.; Hwang, I. C.; Park, S. J. Isothermal Vapor–Liquid Equilibrium Data at  $T = 333.15$  K and Excess Molar Volumes and Refractive Indices at  $T = 298.15$  K for the Dimethyl Carbonate + Methanol and Isopropanol + Water with Ionic Liquids. *J. Chem. Eng. Data* **2010**, *55*, 2474–2481.
- (15) Mock, B.; Evans, L. B.; Chen, C. C. Thermodynamic Representation of Phase Equilibria of Mixed-Solvent Electrolyte Systems. *AIChE J.* **1986**, *32* (10), 1655–1665.
- (16) Kurzin, A. V.; Evdokimov, A. N.; Poltoratskiy, G. M.; Platonov, A. Y.; Gusev, V. E.; Golubeva, Y. M. Isothermal Vapor–Liquid Equilibrium Data for the Systems 1,4-Dioxane + Water + Tetrabutylammonium Nitrate and Acetonitrile + Water + Tetrabutylammonium Bromide. *J. Chem. Eng. Data* **2004**, *49*, 208–211.
- (17) Kurzin, A. V.; Evdokimov, A. N.; Antipina, V. B.; Gusev, V. E. Isothermal Vapor–Liquid Equilibrium Data for the System Methanol + Benzene + Sodium Tetrphenylborate. *J. Chem. Eng. Data* **2005**, *50*, 1861–1863.
- (18) Kurzin, A. V.; Evdokimov, A. N.; Antipina, V. B.; Pavlova, O. S.; Gusev, V. E. Isothermal Vapor–Liquid Equilibrium Data for the System Methanol + Toluene + Triphenylbenzylphosphonium Chloride. *J. Chem. Eng. Data* **2007**, *52*, 2174–2176.
- (19) Kurzin, A. V.; Evdokimov, A. N.; Antipina, V. B.; Pavlova, O. S. Vapor–Liquid Equilibrium Data for the System Methanol + Toluene + Tetrabutylammonium Tetrphenylborate. *J. Chem. Eng. Data* **2008**, *53*, 1411–1413.
- (20) Orchillés, V. A.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Ionic Liquids as Entrainers in Extractive Distillation: Isobaric Vapor–Liquid Equilibria for Acetone + Methanol + 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate. *J. Chem. Eng. Data* **2007**, *52*, 141–147.
- (21) Orchillés, V. A.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Isobaric Vapor–Liquid Equilibria for Ethyl Acetate + Ethanol + 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate at 100 kPa. *J. Chem. Eng. Data* **2007**, *52*, 2325–2330.
- (22) Orchillés, V. A.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Isobaric Vapor–Liquid Equilibria for Methyl Acetate + Methanol + 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate at 100 kPa. *J. Chem. Eng. Data* **2007**, *52*, 915–920.
- (23) Tan, T. C. Model for Predicting the Effect of Dissolved Salt on the Vapour Liquid Equilibrium of Solvent Mixtures. *Chem. Eng. Res. Des.* **1987**, *65*, 355–366.
- (24) Tan, T. C. A Modified NRTL Model for Predicting the Effect of Dissolved Solute on the Vapour-Liquid Equilibrium of Solvent Mixtures. *Trans. IChemE* **1990**, *68*, 93–103.
- (25) Levitin, G.; Myneni, S.; Hess, D. W. Reactions Between CO<sub>2</sub> and Tetramethylammonium Hydroxide in Cleaning Solutions. *Electrochem. Solid-State Lett.* **2003**, *6*, 101–104.
- (26) Huang, X. J.; Xia, S. Q.; Ma, P. S.; Song, S.; Ma, B. J. Vapor–Liquid Equilibrium of N-Formylmorpholine with Toluene and Xylene at 101.33 kPa. *J. Chem. Eng. Data* **2008**, *53*, 252–255.
- (27) Stephenson, R. M.; Malanowski, S. *The Handbook of the Thermodynamics of Organic Compounds*; Elsevier: New York, 1987.
- (28) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Smith, N. K. Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Dicyclohexyl Sulfide, Diethylenetriamine, Di-n-octyl Sulfide, Dimethyl Carbonate, Piperazine, Hexachloroprop-1-ene, Tetrakis(dimethylamino) ethylene, N,N'-Bis-(2-hydroxyethyl) ethylenediamine, and 1,2,4-Triazolo[1,5-a]pyrimidine. *J. Chem. Eng. Data* **1997**, *42*, 1037–1052.
- (29) Rackett, H. G. Equation of State for Saturated Liquids. *J. Chem. Eng. Data* **1970**, *15*, 514–517.
- (30) Iliuta, M. C.; Thyron, F. C.; Landauer, O. M. Vapor–Liquid Equilibrium of the Acetone-Methanol System in the Presence of KSCN and Comparison with Other Salts. *Fluid Phase Equilib.* **1997**, *130*, 253–269.
- (31) Iliuta, M. C.; Thyron, F. C. Salt Effect on the Isobaric Vapor–Liquid Equilibrium of the Methyl Acetate + Methanol System. *J. Chem. Eng. Data* **1996**, *41*, 713–717.