

# Isobaric Vapor Liquid Equilibrium for the Methanol + Ethanol + Water + Ammonium Bromide System

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The binary vapor–liquid equilibrium (VLE) data for salt-containing systems including methanol/ethanol/water/ $\text{NH}_4\text{Br}$  were determined and correlated. The method of combining titration analysis and gas chromatographic analysis was used to determine concentrations in the liquid phase for salt-containing multicomponent systems. The optimal parameters of the NRTL model, which were obtained by correlating data of the binary systems, were used to predict salt-containing VLE data for the ternary and the quaternary systems, and the experimental VLE data were compared with the predicted data. The results show that predicted data agree well with experimental data.

## Introduction

The study of vapor–liquid equilibrium (VLE) data for salt-containing systems is important for both salt-containing distillation and salt-containing extractive distillation. Simple and accurate VLE models are needed for industrial design. To evaluate these models, one generally compares the salt-containing multicomponent experimental VLE data with the predicted data. Because of the difficulty of determining the salt concentration in the liquid phase for salt-containing multicomponent systems, these experimental data are scarce, especially for salt-containing VLE data for quaternary systems (Sander et al., 1984). In salt-containing extractive distillation processes, where an extractive agent is made up of a salt and a solvent, it is necessary to deal with the VLE problem of salt-containing quaternary systems (Fu, 1996). Undoubtedly, VLE data for salt-containing multicomponent systems are very valuable for evaluating salt-containing VLE models. This paper aims at studying VLE data for  $\text{NH}_4\text{Br}$ -containing systems and includes the following contents:

1. the determination and correlation of VLE data for the binary systems of methanol/ $\text{NH}_4\text{Br}$ , ethanol/ $\text{NH}_4\text{Br}$ , and water/ $\text{NH}_4\text{Br}$ ;
2. the determination and prediction of VLE data for the ternary system of ethanol/water/ $\text{NH}_4\text{Br}$ ;
3. the determination and prediction of VLE data for the quaternary system of methanol/ethanol/water/ $\text{NH}_4\text{Br}$ ;
4. discussions on the salt effect on the above systems.

## Experimental Section

The purity of both methanol and ethanol were 99.95 mass %, the purity of  $\text{NH}_4\text{Br}$  was 99.5 mass %, and distilled water was used.

**1. Experimental Equipment and Measurement Method.** **1.1. The Determination of VLE Data for Salt-Containing Binary Systems.** A small boiling instrument was used to determine VLE data for salt-containing binary systems of methanol/ $\text{NH}_4\text{Br}$ , ethanol/ $\text{NH}_4\text{Br}$ , and water/ $\text{NH}_4\text{Br}$ , as in the method introduced in the literature (Qi et al., 1990). The temperature was measured with a mercury-in-glass thermometer ( $1/10$  °C

division), and the exposed part of the thermometer was corrected. A device consisting of a 2200 pressure sensor and PDRC-1C/2C display supplied by the MKS Corporation (Andover, MA), with a precision of  $\pm 13.3$  Pa, was used to measure the pressure directly. Pressure was controlled by a needle valve. The range of pressure fluctuation was less than 40.0 Pa. Experimental data are shown in Tables 1, 2, and 3.

**1.2. Determination of VLE Data for Salt-Containing Multicomponent Systems.** The measurement methods of pressure and temperature are the same as described in Section 1.1. Multicomponent VLE data were determined by the improved Drorak–Boublik double-cycle VLE still. The VLE data for ternary and quaternary systems of ethanol/water/ $\text{NH}_4\text{Br}$  and methanol/ethanol/water/ $\text{NH}_4\text{Br}$  are presented in Tables 4 and 5.

**2. Analysis Method.** For salt-containing binary systems, concentrations of salt and solvent in the equilibrium liquid phase can be determined by means of weighing salt and solvent, and the detention part in the vapor phase was treated (Qi et al., 1990). The salt was regarded as a nonvolatile component, so  $y_{\text{solvent}} = 1$  and  $y_{\text{salt}} = 0$ .

The equilibrium compositions in the vapor phase of salt-containing multicomponent systems were analyzed with chromatography. The type of gas chromatography is SP2305, and the type of integrator is HP3390A (both made in Beijing Analysis Equipment Corporation, China). A thermoconductivity detector was used, installed with a 1 m, 6 mm in diameter stainless steel separation column, which was packed with Chromosorb-105 60–80 mesh. The injector and oven temperatures were 200 and 160 °C, respectively. The detector electric current was 150 mA. It is difficult to determine the liquid-phase composition owing to the existence of salt. This paper proposed a method of combining titration analysis and gas chromatographic analysis (CTGC) to determine equilibrium compositions in the liquid phase.

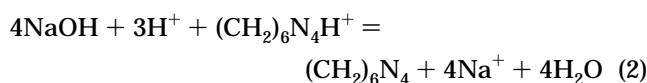
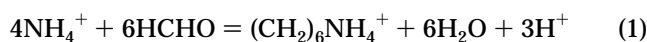
Solvent components  $X_i$  (salt-free) in the liquid phase can be analyzed by gas chromatography. Salt concentration in liquid samples can also be obtained by combining titration analysis.

**Table 1.** VLE Data for the Binary System of Methanol/  
NH<sub>4</sub>Br (NRTL)<sup>a</sup>

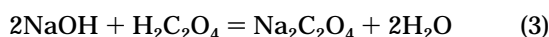
<i>P</i> /kPa	Δ <i>P</i> /kPa	<i>t</i> /°C	Δ <i>t</i> /°C	<i>x</i> <sub>1</sub>	Δ <i>x</i> <sub>1</sub>
99.998	0.039	64.50	-0.09	0.9784	-0.0001
93.331	0.023	62.80	-0.05	0.9784	-0.0001
86.665	0.067	60.85	-0.13	0.9784	-0.0002
79.998	0.060	58.90	-0.11	0.9784	-0.0002
73.332	0.007	56.90	-0.01	0.9784	0.0
66.665	0.016	54.60	-0.03	0.9784	0.0
59.999	-0.013	52.15	0.00	0.9784	0.0
53.332	-0.002	49.45	0.02	0.9784	0.0004
46.666	-0.036	46.45	0.04	0.9784	0.0001
39.999	-0.051	43.05	0.05	0.9784	0.0001
99.998	-0.012	65.00	0.03	0.9568	0.0
93.331	0.009	63.20	-0.02	0.9568	0.0
86.665	0.028	61.30	-0.06	0.9568	-0.0001
79.998	0.040	59.30	-0.07	0.9568	-0.0001
73.332	0.032	57.20	-0.05	0.9568	-0.0001
66.665	-0.063	55.10	0.10	0.9568	0.0002
59.999	0.047	52.40	-0.07	0.9568	-0.0001
53.332	-0.083	49.90	0.11	0.9568	0.0002
46.666	-0.049	46.80	0.06	0.9568	0.0001
39.999	-0.069	43.40	0.07	0.9568	0.0001
99.998	0.032	65.68	0.07	0.9275	0.0002
93.331	0.021	63.90	0.05	0.9275	0.0001
86.665	0.002	61.95	-0.03	0.9275	-0.0001
79.998	0.024	59.95	-0.04	0.9275	-0.0001
73.332	-0.011	57.90	0.02	0.9275	0.0
66.665	-0.008	55.60	0.01	0.9275	0.0
59.999	-0.002	53.12	0.02	0.9275	0.0001
53.332	-0.081	50.50	0.11	0.9275	0.0003
46.666	0.005	47.30	-0.01	0.9275	0.0
39.999	-0.045	43.95	0.05	0.9275	0.0001
99.998	-0.024	66.00	0.05	0.9146	0.0001
93.331	-0.007	64.20	0.01	0.9146	0.0
86.665	0.031	62.25	-0.06	0.9146	-0.0002
79.998	0.039	60.25	-0.07	0.9146	-0.0002
73.332	0.052	58.10	-0.09	0.9146	-0.0002
66.665	0.008	55.90	-0.01	0.9146	0.0
59.999	0.011	53.40	-0.02	0.9146	0.0
53.332	-0.011	50.70	-0.01	0.9146	0.0
46.666	0.021	47.60	-0.02	0.9146	-0.0001
39.999	0.013	44.20	0.00	0.9146	0.0
mean	0.037		0.06		0.0001

<sup>a</sup> Δ*g*<sub>12</sub> = 6543.21 J/mol, Δ*g*<sub>21</sub> = -2624.37 J/mol, α<sub>12</sub> = 1.00.

NH<sub>4</sub><sup>+</sup> titration analysis was done in salt-containing solution as shown in the following reactions (Center of Analytical Chemistry, 1978):



Phenolphthalein was used as an indicator. The equivalent concentration of NaOH standard solution was determined by H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. The reaction formula is given by eq 3.



This process can be stated as follows:

1. Solvent component *X<sub>i</sub>* (salt-free) in the liquid phase can be obtained by gas-chromatographic analysis, and at the same time it can be translated to mass percent (*W<sub>i</sub>*).
2. Analyze the salt equivalent concentration (*N<sub>s</sub>*) in the liquid phase by titration.
3. Calculate the salt mass percent *W<sub>s</sub>* in the liquid phase with the following equation:  $W_s = [N_s M_s / (N_s M_s + 1000 \rho_{\text{mix solvent}})]\%$ , where  $\rho_{\text{mix solvent}} = \sum W_i \rho_i$ .

**Table 2.** VLE Data for the Binary System of Ethanol/  
NH<sub>4</sub>Br (NRTL)<sup>a</sup>

<i>P</i> /kPa	Δ <i>P</i> /kPa	<i>t</i> /°C	Δ <i>t</i> /°C	<i>x</i> <sub>1</sub>	Δ <i>x</i> <sub>1</sub>
99.890	0.053	78.07	-0.01	0.9949	0.0
93.331	0.093	76.36	-0.02	0.9949	0.0
86.665	0.027	74.54	-0.01	0.9949	0.0
79.998	-0.187	72.63	0.04	0.9949	0.0001
73.332	0.040	70.48	-0.01	0.9949	0.0
66.665	0.093	68.20	-0.02	0.9949	0.0
59.999	0.280	65.70	-0.04	0.9949	-0.0001
53.332	0.453	62.96	-0.06	0.9949	-0.0001
46.666	0.453	59.95	-0.05	0.9949	-0.0001
39.999	0.453	56.55	-0.05	0.9949	-0.0001
99.998	0.120	78.27	-0.03	0.9811	0.0
93.331	0.040	76.56	-0.01	0.9811	0.0
86.665	-0.053	74.74	0.01	0.9811	0.0
79.998	-0.029	72.83	0.05	0.9811	0.0001
73.332	-0.240	70.71	0.04	0.9811	0.0
66.665	-0.067	68.40	0.01	0.9811	0.0
59.999	0.080	65.90	-0.01	0.9811	0.0
53.332	0.560	63.10	-0.07	0.9811	-0.0001
46.666	1.067	60.00	-0.02	0.9811	-0.0001
99.998	-0.040	78.48	0.01	0.9658	0.0
93.331	-0.107	76.76	0.02	0.9658	0.0
86.665	-0.213	74.94	0.04	0.9658	0.0
79.998	-0.480	73.03	0.09	0.9658	0.0001
73.332	-0.453	70.91	0.08	0.9658	0.0001
66.665	-0.307	68.60	0.05	0.9658	0.0001
59.999	-0.200	66.10	0.03	0.9658	0.0
53.332	0.360	63.28	-0.05	0.9658	0.0
46.666	1.013	60.15	-0.12	0.9658	-0.0001
99.998	0.173	78.58	-0.04	0.9540	-0.0001
93.331	0.320	76.81	-0.07	0.9540	-0.0001
86.665	0.0	75.04	0.0	0.9540	0.0
79.998	-0.027	73.08	0.01	0.9540	0.0
73.332	-0.227	71.01	0.04	0.9540	0.0001
mean	0.360		0.05		0.0001

<sup>a</sup> Δ*g*<sub>12</sub> = 7805.66 J/mol, Δ*g*<sub>21</sub> = -2479.67 J/mol, α<sub>12</sub> = 1.00.

4. Calculate the salt mass (*S<sub>w</sub>*) based on 1 mol of mixed solvent by solving the following equation:  $W_s = S_w / (\sum X_i M_i + S_w)$ ,  $n_s = S_w / M_s$ .

5. Determine the mole fraction *x<sub>i</sub>* of solvent components with the following equation:  $x_i = x_i / (1 + 2n_s)$ . Determine the mole fraction *x<sub>s</sub>* of salt ions with the following equation:  $x_s = 2n_s / (1 + 2n_s)$ , where  $n_s = S_w / M_s$ .

Three liquid samples were made by a weighting method for the system of methanol/water/salt to evaluate the above method. The results as follows:

weighting samples			CTGC method		
<i>X<sub>meth.</sub></i>	<i>X<sub>water</sub></i>	<i>X<sub>salt</sub></i>	<i>X<sub>meth.</sub></i>	<i>X<sub>water</sub></i>	<i>X<sub>salt</sub></i>
0.1932	0.7826	0.0242	0.1956	0.7829	0.0215
0.5040	0.4551	0.0409	0.5042	0.4548	0.0410
0.8523	0.1147	0.0330	0.0852	0.1170	0.0309

The absolute error for the above-mentioned method is about 0.003. The error is similar to that in chromatogram analysis for general VLE experiments, so the method can be used to analyze components in the liquid phase.

### Correlation of VLE Data for Binary System

VLE data for binary systems in this quaternary system were correlated by using the salt-containing local composition model (SCLCM) (Fu, 1991) and the vapor-liquid equilibrium model ( $y_i P_s = \gamma_i x_i p_i^\circ$ ). The vapor phase was assumed as an ideal gas. For salt-containing binary systems, the salt was regarded as a nonvolatile component ( $y_s = 0$  and  $j_{\text{solvent}} = 1$ ). The formula mentioned above was rewritten as  $P_s = \gamma_i x_i p_i^\circ$ . A salt molecule or salt ion can be taken as the least particle to define the mole fraction in the liquid phase. The two definitions have a little effect

**Table 3. VLE Data for the Binary System of Water/  
NH<sub>4</sub>Br (NRTL)<sup>a</sup>**

P/kPa	ΔP/kPa	t/°C	Δt/°C	x <sub>1</sub>	Δx <sub>1</sub>
99.998	0.387	99.87	-0.08	0.9870	-0.0002
93.331	0.440	97.94	-0.08	0.9870	-0.0002
86.665	0.520	95.89	-0.09	0.9870	-0.0002
79.998	0.520	93.72	-0.09	0.9870	-0.0002
73.332	0.547	91.39	-0.08	0.9870	-0.0002
66.665	0.440	88.90	-0.06	0.9870	-0.0001
59.999	-0.613	86.36	0.08	0.9870	0.0002
53.332	0.120	83.23	-0.01	0.9870	0.0
46.666	-0.200	79.95	0.02	0.9870	0.0
39.999	-0.013	76.16	0.0	0.9870	0.0
99.998	0.080	100.12	-0.02	0.9797	0.0
93.331	0.547	98.09	-0.10	0.9797	-0.0002
86.665	0.280	96.11	-0.05	0.9797	-0.0001
79.998	0.360	93.92	-0.06	0.9797	-0.0001
73.332	0.360	91.59	-0.06	0.9797	-0.0001
66.665	0.187	89.11	-0.03	0.9797	-0.0001
59.999	0.213	86.37	-0.03	0.9797	-0.0001
53.332	0.267	83.36	-0.03	0.9797	-0.0001
46.666	-0.253	80.11	0.03	0.9797	0.0001
39.999	-0.347	76.36	0.03	0.9797	0.0001
99.998	1.293	100.70	-0.18	0.9487	-0.0005
93.331	0.173	98.87	-0.03	0.9487	-0.0001
86.665	0.320	96.87	-0.06	0.9487	-0.0002
79.998	-0.067	94.77	0.01	0.9487	0.0
73.332	-0.173	92.45	0.03	0.9487	0.0001
66.665	-0.120	89.91	0.02	0.9487	0.0
59.999	-0.080	87.16	0.01	0.9487	0.0
53.332	-0.080	84.14	0.01	0.9487	0.0
46.666	-0.347	80.84	0.04	0.9487	0.0001
39.999	-0.733	77.12	0.07	0.9487	0.0002
99.998	-0.707	102.00	0.14	0.9200	0.0005
93.331	0.107	99.86	-0.02	0.9200	-0.0001
86.665	0.0	97.83	0.0	0.9200	0.0
79.998	0.0	95.64	0.0	0.9200	0.0
73.332	-0.320	93.36	0.05	0.9200	0.0002
66.665	-0.093	90.78	0.01	0.9200	0.0
59.999	-0.173	88.04	0.02	0.9200	0.0001
53.332	-0.360	85.05	0.04	0.9200	0.0001
46.666	-10.040	81.81	0.11	0.9200	0.0004
39.999	-10.173	78.04	0.11	0.9200	0.0004
99.998	-10.413	103.00	0.29	0.8985	0.0001
93.331	0.347	100.60	-0.07	0.8985	-0.0003
86.665	0.293	98.56	-0.05	0.8985	-0.0002
79.998	0.547	96.31	-0.09	0.8985	-0.0004
73.332	0.480	93.98	-0.07	0.8985	-0.0003
66.665	0.573	91.43	-0.08	0.8985	-0.0003
59.999	0.480	88.69	-0.07	0.8985	-0.0003
53.332	0.507	85.67	-0.06	0.8985	-0.0002
46.666	0.480	82.32	-0.05	0.8985	-0.0002
39.999	0.213	78.58	-0.02	0.8985	-0.0001
mean	0.480		0.08		0.0003

<sup>a</sup> Δg<sub>12</sub> = 6541.12 J/mol, Δg<sub>21</sub> = -762.29 J/mol, α<sub>12</sub> = 1.00.

on predicting precision (Fu, 1994). In this article, the definition of a salt ion as the least particle was adopted. It is  $x_{\text{solvent}} = n_j / (\sum n_i + \sum n_{\text{salt}}^+)$  and  $x_{\text{salt}} = \sum n_{\text{salt}}^+ / (\sum n_i + \sum n_{\text{salt}}^+)$ . The NRTL model was used to calculate activity coefficients  $\gamma_i$ .

The optimal parameters of the NRTL model were determined with the correlating method based on maximum likelihood theory (Anderson et al., 1978). The objective function is

$$F = \sum_i^m \left[ \frac{(P^e - P^s)^2}{\sigma_{P_i}^2} + \frac{(T^e - T^s)^2}{\sigma_{T_i}^2} + \frac{(x_{1i}^e - x_{1i}^s)^2}{\sigma_{x_{1i}}^2} + \frac{(y_{1i}^e - y_{1i}^s)^2}{\sigma_{y_{1i}}^2} \right] \quad (4)$$

For the salt-containing binary system, the salt was re-

**Table 4. VLE Data for Ternary System of Ethanol/Water/  
NH<sub>4</sub>Br (97.330 kPa)**

T/K	ΔT/K	x <sub>1</sub>	x <sub>2</sub>	y <sub>1</sub>	y <sub>2</sub>	Δy <sub>1</sub>	Δy <sub>2</sub>
350.86	0.04	0.9305	0.0419	0.9582	0.0418	-0.0019	0.0019
350.87	0.09	0.9221	0.0534	0.9474	0.0526	-0.0019	0.0019
350.96	0.05	0.8941	0.0705	0.9333	0.0667	-0.0020	0.0020
351.01	0.05	0.8625	0.0995	0.9086	0.0914	-0.0024	0.0024
351.01	0.0	0.8045	0.1594	0.8604	0.1396	-0.0027	0.0027
351.11	0.02	0.7538	0.2131	0.8209	0.1791	-0.0022	0.0022
351.25	-0.02	0.6919	0.2774	0.7823	0.2177	0.0028	-0.0028
351.41	0.03	0.6537	0.3211	0.7525	0.2475	0.0016	-0.0016
351.72	-0.04	0.5892	0.3797	0.7346	0.2654	0.0148	-0.0148
352.42	-0.13	0.4571	0.5208	0.6708	0.3292	0.0215	-0.0215
352.44	-0.13	0.4515	0.5285	0.6642	0.3358	0.0187	-0.0187
353.63	0.04	0.3351	0.6461	0.6203	0.3797	0.0225	-0.0225
353.71	-0.23	0.3047	0.6754	0.5970	0.4030	0.0113	-0.0113
355.25	-0.86	0.1754	0.8067	0.5512	0.4488	0.0335	-0.0335
355.95	-0.95	0.1497	0.8320	0.5246	0.4754	0.0282	-0.0282
364.25	-0.64	0.0362	0.9494	0.2849	0.7151	0.0214	-0.0214
367.70	-0.31	0.0185	0.9669	0.1746	0.8254	0.0142	-0.0142
mean	0.21					0.0121	0.0121

garded as a nonvolatile component,  $y_{\text{solvent}} = 1$ , and  $y_{\text{salt}} = 0$ . The last item on the right-hand side of eq 4 is zero. In eq 4  $\sigma^2$  is the estimated variance of each of the measured variables, i.e., pressure, temperature, and liquid and vapor phase mole fractions. These variances can be estimated from probable experimental uncertainties (Anderson and Prausnitz, 1978). Here, assumed standard deviations in the measured variables were  $\sigma_{P_i} = 133.3$  Pa,  $\sigma_{T_i} = 0.05$  K,  $\sigma_{x_{1i}} = 0.0010$ , and  $\sigma_{y_{1i}} = 0.0030$ .

The correlation results for the binary VLE data are shown in Tables 1, 2, and 3. Of course, the data for other binary systems were needed in order to predict VLE for ternary and quaternary systems in this paper. The data for binary systems of methanol/ethanol, methanol/water, and ethanol/water were taken from the literature (Gmehling and Onken, 1977). The maximum likelihood method was used again to correlate the literature data and determine the optimal parameters of the NRTL model in order to predict the multicomponent salt-containing VLE data.

### Prediction of the Multicomponent System VLE

The aforementioned parameters were used to predict VLE data for ternary and quaternary systems with the SCLCM method (Fu, 1991), and the predicted values were compared with the experimental data. The deviations of temperature and vapor-phase composition for the ternary system of ethanol/water/NH<sub>4</sub>Br are shown in Table 4. The predicted results of the system show that the CTGC method proposed in this paper, which can be used to determine salt-containing liquid-phase composition, is reasonable.

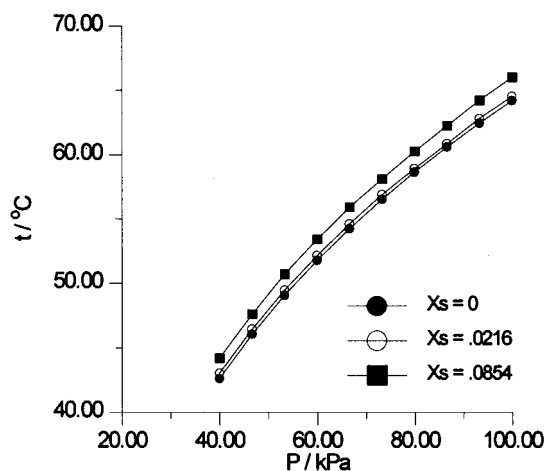
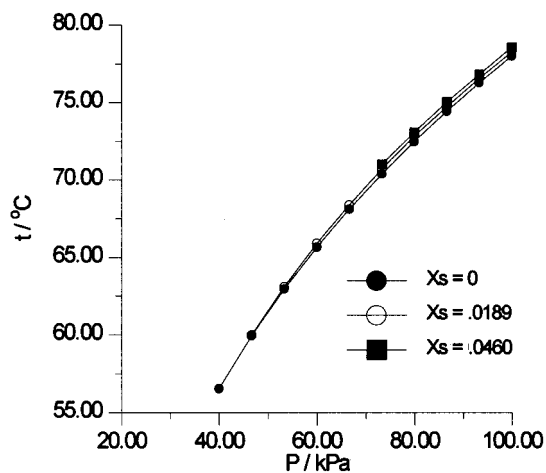
Similar work has been done for the salt-containing quaternary system of methanol/ethanol/water/NH<sub>4</sub>Br, and the results are shown in Table 5. The results indicate that the predictive precision of the quaternary system is similar to that of the ternary system. SCLCM can be used to predict VLE for quaternary systems satisfactorily.

### Discussion on Salt Effect on Vapor Liquid Equilibrium

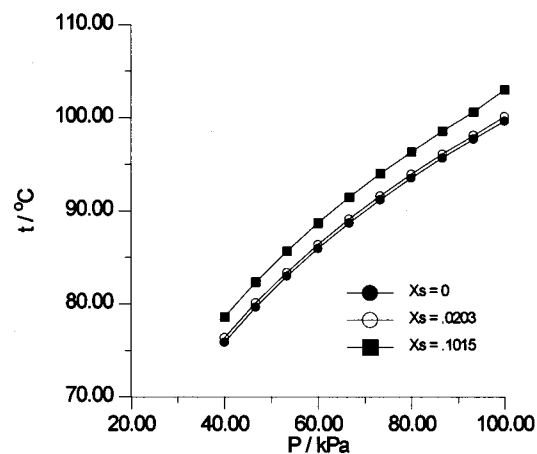
**Salt Effect on the Vapor Pressure of Pure Solvent.** The salt effect on the vapor pressure of methanol, ethanol, and water is shown in Figures 1–3. Clearly, their vapor pressure decreases with the increase of salt mole fraction. For the system of ethanol and water, it is desirable that the salt effect on vapor of ethanol is weaker, while it is stronger for water. It leads to increase the relative

**Table 5.** VLE Data for Quaternary System of Methanol/Ethanol/Water/ $\text{NH}_4\text{Br}$  (97.330 kPa)

$T/K$	$\Delta T/K$	$x_1$	$x_2$	$x_3$	$y_1$	$y_2$	$y_3$	$\Delta y_1$	$\Delta y_2$	$\Delta y_3$
355.45	-0.37	0.1466	0.0250	0.8123	0.4645	0.0987	0.4368	0.0097	0.0150	-0.0247
353.23	-0.37	0.0543	0.2471	0.6761	0.1257	0.4968	0.3775	0.0156	0.0078	-0.0233
352.12	-0.19	0.0436	0.3877	0.5467	0.0910	0.5760	0.3330	0.0162	0.0001	-0.0163
349.85	-0.33	0.1782	0.3211	0.4681	0.3041	0.4397	0.2562	0.0039	0.0154	-0.0193
351.31	-0.37	0.1406	0.2460	0.5880	0.2744	0.4043	0.3213	0.0123	0.0043	-0.0166
350.70	-0.38	0.1185	0.3578	0.5011	0.2157	0.4842	0.3001	0.0162	-0.0079	-0.0083
350.45	-0.35	0.1059	0.4271	0.4432	0.1794	0.5358	0.2848	0.0076	-0.0065	-0.0011
350.20	-0.25	0.0928	0.5157	0.3695	0.1548	0.5896	0.2556	0.0091	-0.0108	0.0016
350.20	-0.25	0.0643	0.6140	0.2967	0.1062	0.6691	0.2247	0.0055	-0.0106	0.0051
350.10	-0.10	0.0541	0.7104	0.2130	0.0772	0.7399	0.1829	-0.0077	-0.0054	0.0131
349.85	-0.04	0.0561	0.8015	0.1226	0.0987	0.7886	0.1127	0.0092	-0.0173	0.0081
355.35	-0.17	0.0092	0.1853	0.7917	0.0298	0.5102	0.4600	0.0074	-0.0001	-0.0072
356.27	-0.33	0.0310	0.1247	0.8310	0.0678	0.4664	0.4658	-0.0207	0.0496	-0.0289
355.66	-0.42	0.0672	0.1049	0.8132	0.1715	0.3650	0.4635	-0.0185	0.0311	-0.0126
358.00	-0.52	0.0559	0.0655	0.8587	0.1453	0.3299	0.5248	-0.0472	0.0609	-0.0137
359.19	-0.77	0.0453	0.0511	0.8864	0.1364	0.3075	0.5561	-0.0382	0.0626	-0.0244
355.15	-0.43	0.0832	0.1077	0.7893	0.1846	0.3721	0.4433	-0.0407	0.0555	-0.0148
352.02	0.04	0.1711	0.1542	0.6551	0.3325	0.3075	0.3600	-0.0200	0.0168	0.0032
349.60	-0.11	0.2692	0.1310	0.5788	0.4851	0.2251	0.2898	-0.0165	0.0227	-0.0062
348.99	0.30	0.3089	0.1355	0.5359	0.5186	0.2074	0.2740	-0.0236	0.0188	0.0047
343.25	0.76	0.6214	0.0636	0.2893	0.8108	0.0592	0.1300	-0.0128	0.0051	0.0077
342.40	0.68	0.6671	0.0506	0.2553	0.8341	0.0507	0.1152	-0.0198	0.0101	0.0097
341.85	0.52	0.6878	0.0592	0.2254	0.8483	0.0421	0.1096	-0.0127	-0.0038	0.0165
342.45	0.59	0.6611	0.0411	0.2711	0.8446	0.0320	0.1234	-0.0104	-0.0016	0.0119
mean	0.35							0.0167	0.0183	0.0125

**Figure 1.** Salt effect on vapor pressure of methanol.**Figure 2.** Salt effect on vapor pressure of ethanol.

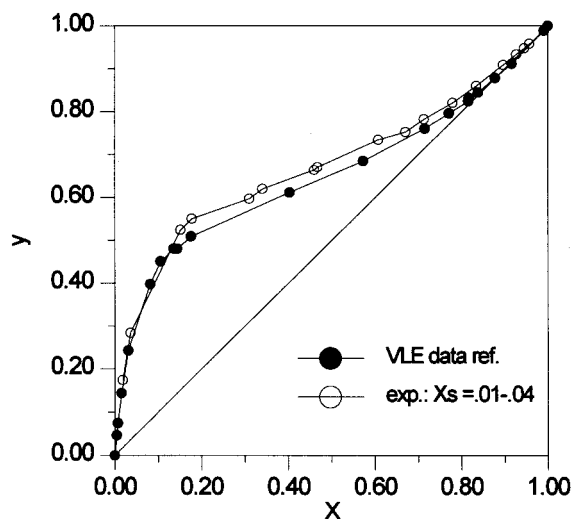
volatility of them. So, it is possible to eliminate the azeotrope entirely. The  $\text{NH}_4\text{Br}$  effect on vapor pressure of water is bigger than that of ethanol. It can be concluded that the relative volatility of ethanol and water will be increased in the presence of the salt as in the above

**Figure 3.** Salt effect on vapor pressure of water.

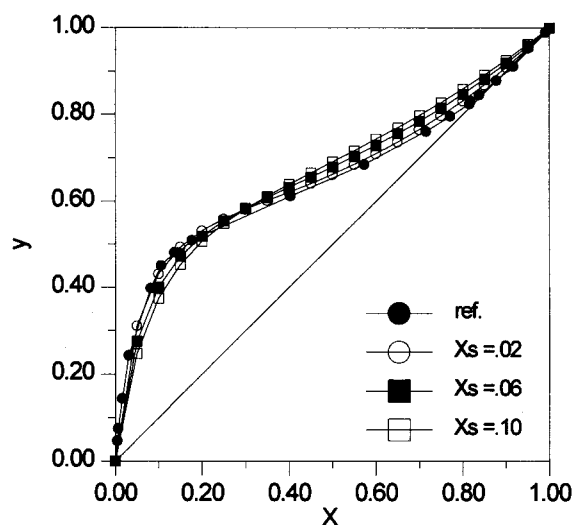
discussion. This can be confirmed by experimental results discussed in the next section.

**Salt Effect on the Relative Volatility of Ethanol and Water.** The  $x$ - $y$  diagram for binary system of ethanol/water (Gmehling and Onken, 1977) and the  $X$ - $y$  diagram for the ternary system of ethanol/water/ $\text{NH}_4\text{Br}$  (this work, salt-free) are shown in Figure 4. The curve of this work is not smooth because the salt mole fraction is not a constant. Figure 4 clearly shows that the relative volatility of ethanol and water is increased in the presence of  $\text{NH}_4\text{Br}$ . Different salt mole fractions have different influences on the VLE. The  $X$ - $y$  diagram of values predicted by the SCLCM method are plotted on Figure 5 at  $x_s = 0.02, 0.06, \text{ and } 0.10$ . It can be seen that higher salt mole fraction is advantageous in eliminating the azeotrope because the relative volatility is increased with increase of salt mole fraction.

**Salt and Methanol Effect on the System of Ethanol and Water.** Various combination for this quaternary system can be calculated by means of parameters of the NRTL model for every binary system. For example, the change of relative volatility of ethanol and water can be examined in the presence of methanol. This kind of  $X$ - $y$  phase diagram (methanol-free) is shown in Figure 6 at  $x_{\text{meth.}} = 0.10, 0.15, \text{ and } 0.20$ . Similarly, the change of relative



**Figure 4.** Experimental phase diagrams for the system of ethanol/water/ $\text{NH}_4\text{Br}$  (salt-free).



**Figure 5.** Calculated  $X$ - $y$  phase diagram for the system of ethanol/water/ $\text{NH}_4\text{Br}$  at 97.330 kPa and at different salt mole fractions (salt-free).

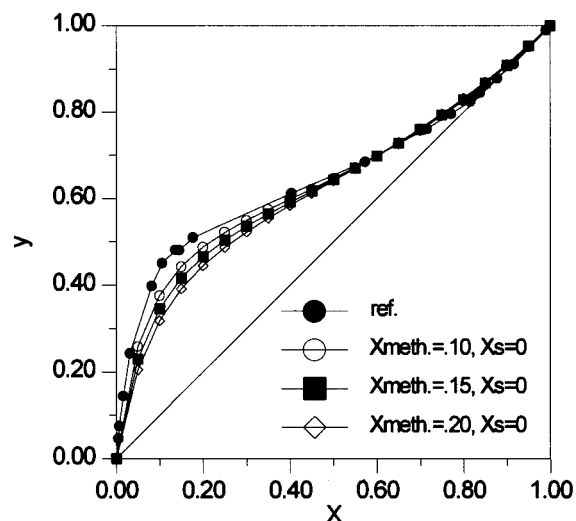
volatility of them can also be examined in the presence of methanol and salt.  $x_s = 0.05$  and  $x_{\text{meth.}} = 0.05, 0.10,$  and  $0.15$  ( $x_{\text{meth.}} + x_s = 0.10, 0.15,$  and  $0.20$ ) are selected to calculate the VLE of the quaternary system on a comparable basis (see Figures 6 and Figure 7). The  $X$ - $y$  phase diagram for the system of ethanol and water (methanol + salt-free) is shown in Figure 7. It can be seen that the azeotrope cannot be eliminated by adding methanol, while it is possible in the presence of methanol and salt together. Similar discussion is very valuable for salt-containing extractive distillation processes, which have an industrial background (Fu, 1996).

### Conclusion

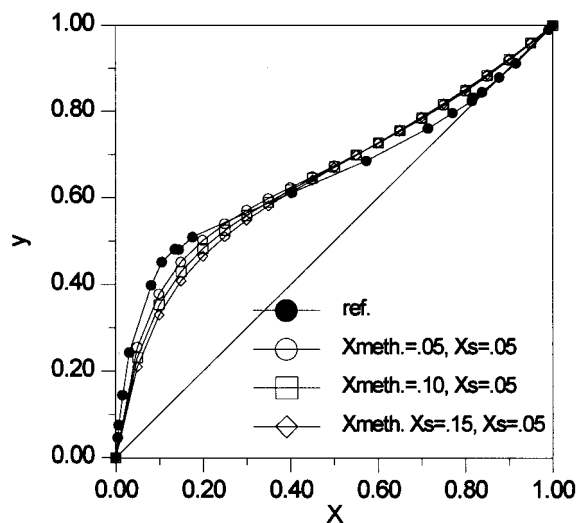
1. The CTGC method is reasonable for determining salt-containing liquid-phase composition and has acceptable accuracy.

2. The salt-containing local composition model is suitable to calculate VLE data for salt-containing systems in this paper.

3. For salt-containing quaternary systems, the salt-containing local composition model has a similar predicting precision as that of a ternary system.



**Figure 6.** Calculated  $X$ - $y$  phase diagram for the system of ethanol/water/methanol at 97.330 kPa and at different methanol mole fractions (methanol-free).



**Figure 7.** Calculated  $X$ - $y$  phase diagram for the system of ethanol/water/methanol/ $\text{NH}_4\text{Br}$  at 97.330 kPa and at different (methanol + salt) mole fractions (methanol + salt-free).

4. Vapor pressures of methanol, ethanol, and water are decreased with increase of the salt mole fraction. Relative volatilities of ethanol and water are increased with increase of the salt mole fraction.

### Acknowledgment

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### Glossary

$M$  = molecular weight  
 $N$  = equivalent concentration  
 $n$  = mole number  
 $P$  = total pressure, kPa  
 $T$  = temperature, K  
 $t$  = temperature,  $^{\circ}\text{C}$   
 $X$  = liquid mole fraction (salt-free)  
 $x$  = liquid mole fraction  
 $y$  = vapor mole fraction

### Greek Letters

$\alpha$  = NRTL model nonrandomness constant

$\gamma$  = activity coefficient  
 $\sigma$  = standard deviation  
 $\Delta$  = difference between exp. and cal.  
 $\Delta g_{ij}$  = NRTL model parameter, J/mol

#### Superscripts

c = calculation value  
e = experimental value  
° = saturated vapor pressure

#### Subscripts

*i* = solvent component  
*P* = pressure  
*s* = salt  
*T* = temperature  
*w* = weight  
 $x_1$  = liquid-phase component 1  
 $y_1$  = vapor phase component 1

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