Articles

Isobaric Vapor−Liquid Equilibrium of Acetone + Methanol System in the Presence of Calcium Bromide

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This paper gives experimental vapor−liquid equilibrium (VLE) measurements of the acetone + methanol system in the presence of calcium bromide ($CaBr_2$). The influence of the addition of $CaBr_2$ on the VLE was investigated using an Othmer recirculation-type still. The VLE data were presented in terms of the enhancement factor. Furthermore, an assessment of thermodynamic models is presented by applying thermodynamic consistency test as well as the Wilson activity coefficient model, coupled with several equations of state, to the measured data. Analysis of the results suggests that adding $CaBr_2$ to acetone + methanol system leads to a crossover behavior; a mixture of salt-in and salt-out effects. In particular, the addition of 0.3 M $CaBr_2$ was found to eliminate the azeotropic point of acetone + methanol system.

Introduction

A knowledge of vapor−liquid equilibrium (VLE) of solutions is vital for the design and optimization of distillation and absorption columns. In azeotropic systems or close boiling-point mixtures, the separation of the system components is difficult by conventional distillation techniques. Other advanced techniques might be used to separate such mixtures. Pressure distillation, azeotropic distillation, reactive distillation, and extractive distillation are examples of these techniques. Moreover, salt distillation is one of the viable options to shift or eliminate the azeotropic point. The salt as a third component, called an entrainer, is added to alter the relative volatility of the liquid mixture whereas the salt may exhibit a salt-in and/or a salt-out effect on the components.[1] Salt-out effect results when the volatility of one component increases; while salt-in effect results when the volatility of the other component decreases. Therefore, the overall effect is to increase the relative volatility and to shift the azeotropic point or to break it. It is worth mentioning that the concentration of salt normally used in the VLE systems is very low and would not result in corrosion problems.

The literature is rich in systems involving VLE data in the presence of different organic and inorganic salts. Ohe[2] has collected the available published data at that time in a data book to cover the salt effect. To predict salt effect, Ohe[2] has applied the preferential solvation method to the collected data. The formation of preferential solvates between the salt and one of the volatile components was confirmed.[2]

Salt addition to binary mixtures influences the boiling point, the solubilities of the two liquid components, and the equilibrium vapor phase composition. One of the explanations for the salt effect is that dissolved salt particles tend preferentially to attract one type of solvent molecules more strongly than the other.[2] The more polar component molecules are usually preferentially attracted by the electrostatic field of the ions; hence, the vapor composition is enriched by the less polar component. Three types of anomalous behaviors have been recognized by Meranda and Furter.[3] One of these is the crossover in salt effect between salting-in and salting-out. Such a phenomenon has been noticed by Dernini et al.[4] for the acetone−methanol system through adding NaI, NaSCN, or KSCN salts to the mixture at saturation concentration. Iliuta and Thyrion[5] noticed the crossover phenomenon for the acetone + methanol system by adding NaI salt even at concentrations below saturation.

The VLE behavior of a certain system in the presence of one salt differs from that in the presence of another salt. It is not easy to theoretically anticipate the effect of salts on the VLE; as such experimental data are of great importance. The four objectives of this work were to (1) obtain experimental VLE data for the methanol + acetone system and compare them to other data found in the literature, (2) compare VLE data in the absence of salt and in the presence of $CaBr_2$ salt, (3) study the effect of $CaBr_2$ concentration on the VLE behavior of the methanol + acetone system, and (4) examine the ideality of the vapor phase of the acetone + methanol mixture.

Materials and Methods

Apparatus. The apparatus used for measuring VLE data is the Othmer recirculation-type still with certain modification so as to maintain constant mole fraction in the liquid phase. The apparatus shown in Figure 1 is composed mainly of (1) 1 L distillation flask, placed over a stirring hot plate and surrounded by a heating tape; (2) three-way stopcock, which joins the condenser chamber to the return line; (3) capillary tube, which is used for circulation of the

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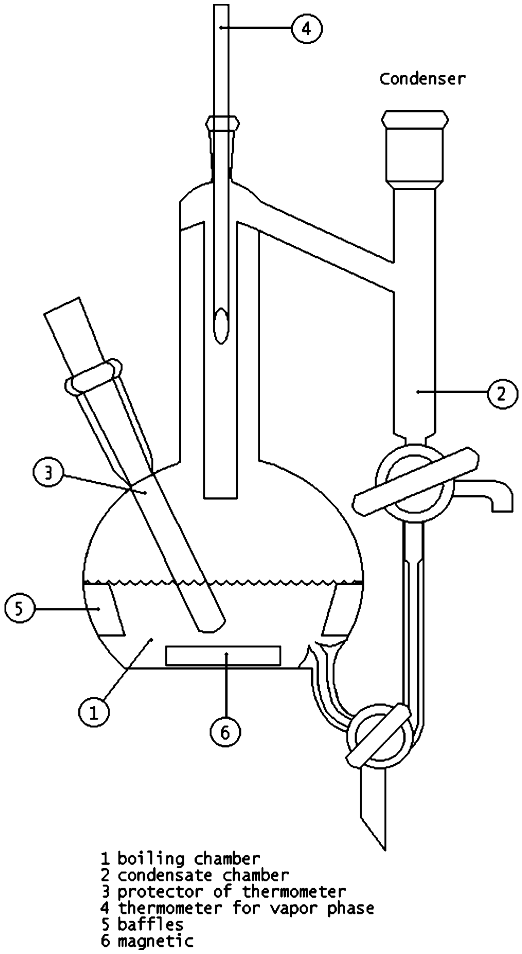

Figure 1. Sketch of Othmer apparatus.

liquid from the three-way stopcock to the flask; (4) thermometers to measure the temperatures of the vapor and of the boiling liquid; and (5) condenser of helical form connected to the distillation flask.

This still is similar to the design of Furter[6] incorporating various modifications to the Othmer recirculation-type still. The Othmer-type still was modified in order to minimize the volume of condensate so as maintain constant liquid mole fraction during the experiment. The main feature of the present still is the high ratio of flask volume to condensate volume. As such, the composition of the equilibrium liquid sample does not significantly vary and is almost the same as the initial charged to the still. An internal vapor jacket is placed in the neck of the flask to prevent entrainment. Further details of the still and the experimental procedure can be found elsewhere.[7]

Chemicals. The chemicals used are of analytical grade; acetone (99.5 wt %, Frutarom (UK) LTD) and methanol (99.8 wt %, Frutarom (UK) LTD) were dried with molecular sieves. The purity was checked with gas chromatography. The purity was greater than 99.9 wt % and 99.7 wt % for acetone and methanol, respectively.

Experimental Procedure. Certain amounts of acetone and methanol were mixed in the distillation flask to achieve a desired concentration. The mixture was stirred for about 30 min to ensure complete mixing. Cooling water was circulated through the condenser. After that, the heating tape and the stirring heat plate were turned on, and the heating rate was gradually increased to attain boiling. The still was then allowed to operate until equilibrium was reached. The time needed to reach equilibrium was about 60 min. Samples of vapor condensate were withdrawn from the three-way stopcock and kept into well-sealed vials. The procedure was repeated at different concentrations. When salt was involved in the experiments, a specified weight of salt was mixed with the acetone−methanol mixture to achieve the required salt concentration.

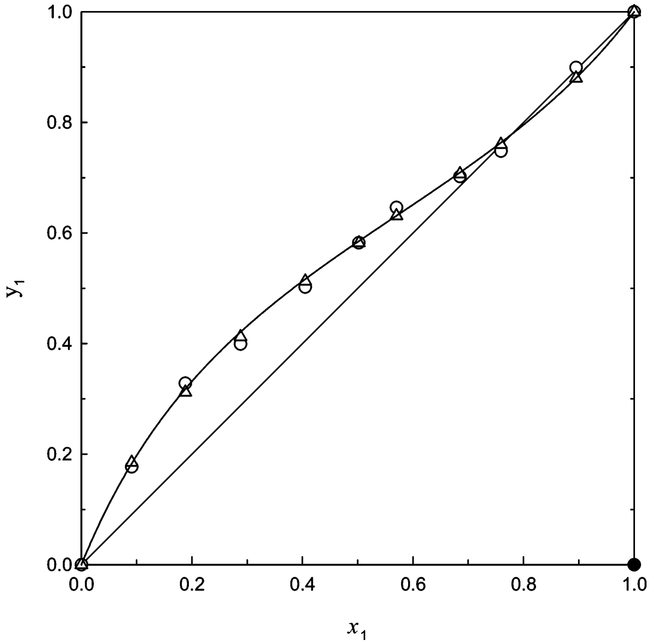

Figure 2. Phase diagram (x_1−y_1 diagram) for acetone (1) + methanol (2) system. Solid line, Wilson model; ○, this work; △, literature.[2]

Isobaric vapor liquid equilibrium data were collected at atmospheric pressure, which was measured by a mercury column barometer with an uncertainty of ± 2 mmHg. The equilibrium temperature was measured with a standard thermometer with an uncertainty of ± 0.1 °C. After circulation for 1 h, we checked whether the readings of the vapor and liquid thermometers are the same. If temperature readings are stable, we monitored again the change of that temperature during the next 15 min from that instant. If the temperature readings were maintained constant, we regarded the system to be in equilibrium. At this condition, the measured temperature was considered to be an equilibrium temperature.

Sample Analysis. Samples of the vapor condensate were taken from the three-way stopcock and kept into closed vials in a refrigerator for analysis. Concentrations of methanol and acetone in these samples were measured using Varian 3400-GC equipped with an FID detector. The operating temperatures of the GC were 200 °C for the column; 250 °C for the injector; and 300 °C for the detector. The peak area-calibration curve for the acetone−methanol system was prepared by injecting samples of known composition. The GC experimental results were reproducible within ± 1 %.

Results and Discussion

The isobaric VLE data for the methanol + acetone system obtained in this work and those reported in the literature[2] are shown in Figure 2. Furthermore, these data are tabulated in Table 1; where x_1 is the acetone mole fraction calculated based on salt-free basis. Comparing the results obtained to that reported in the literature, a maximum difference of 2 % was observed, indicating that the experimental apparatus and the procedure used in this

Table 1. Vapor−Liquid Equilibrium Data for Acetone (1) + Methanol (2)

x_1	y_1 (this work)	y_1 (literature[2])	temperature, t/°C
0	0	0	64.6
0.091	0.187	0.185	61.7
0.188	0.328	0.318	59.6
0.288	0.399	0.419	58.1
0.405	0.502	0.513	56.9
0.502	0.582	0.582	56.3
0.570	0.646	0.628	55.9
0.685	0.702	0.708	55.5
0.759	0.762	0.763	55.4
0.895	0.891	0.881	55.6
1.0	1.0	1.0	56.2

work are precise enough for performing such measurements. The results of this work and those of literature (Figure 2) indicate that the acetone−methanol system forms an azeotrope at acetone mole fraction of 0.76. These data were obtained at an assumed constant atmospheric pressure.

Wilson equation as an activity coefficient model was applied to the acetone−methanol VLE data. In the activity coefficient approach, the basic VLE relationship is represented by

$$\phi_i^{v} y_i P = x_i \gamma_i f_i^{l} \tag{1}$$

The vapor-phase fugacity coefficient (ϕ_i^{v}) is computed from an equation of state. The determination of the liquid-phase fugacity (f_i^{l}) depends on the definition of the reference state for the liquid, which is defined as pure component in the liquid state at temperature and pressure of the system. According to this definition, γ_i, the liquid activity coefficient of component i, approaches unity as x_i approaches unity. The gas phase of the acetone−methanol system was assumed ideal, and the ideal gas equation of state was used for this purpose. The ideal gas equation of state is an approximate model, which is adequate for many engineering calculations involving gases at low pressures. To account for any possible deviation from the ideal gas behavior, other more complex equations of state including the Redlich−Kwong (R−K) cubic equation of state[8] and the Hayden−O'Conell (HOC) virial equation of state were used.[8] The combination of any of these equations of state with Wilson model is called a thermodynamic property method. The thermodynamic property methods including Wilson-ideal, Wilson-R−K, and Wilson-HOC were used to compute the liquid-phase boiling point curve. The predicted and experimental curves are concurring each other as shown in the $T-x$ diagram (Figure 3). As seen in Figure 3, the predictions of the Wilson-ideal, Wilson-R−K, and Wilson-HOC property methods are close to each other. This confirms that the acetone−methanol vapor mixture at the given conditions behaves as an ideal gas and that ϕ_i^{v} is close to unity. Applicability of Wilson model using ideal gas equation of state is also shown on the $x-y$ diagram (Figure 2).

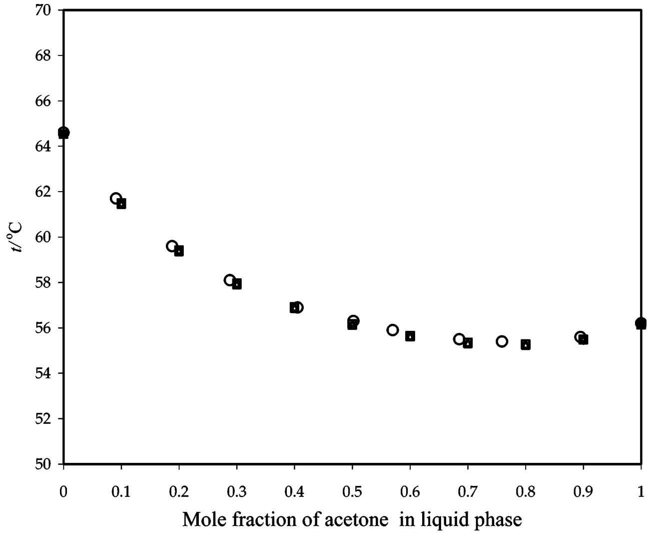

Figure 3. Wilson prediction of $T-x$ diagram using different forms of equation of state. ○, experimental data; ◇, Wilson-ideal gas; □, Wilson-RK; △, Wilson-HOC.

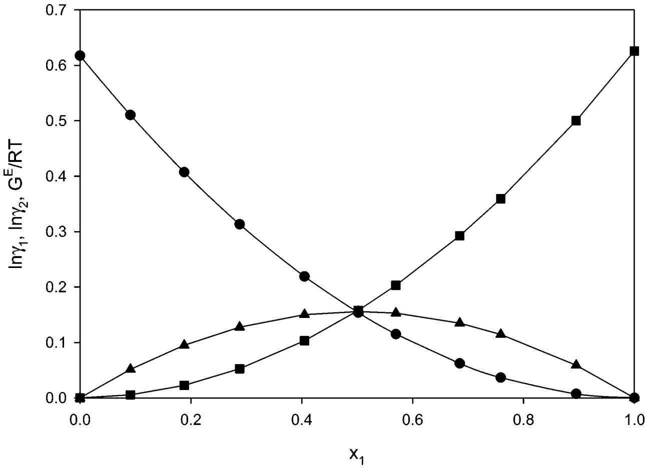

Figure 4. Liquid-phase properties from VLE data at 1 atm for acetone (1) + methanol (2) system. ●, ln γ_1; ■, ln γ_2; ▲, G^E/RT.

Table 2. Activity Coefficients for Acetone (1) + Methanol (2) System

x_1	y_1	t/°C	ln γ_1	ln γ_2	G^E/RT	ln(γ_1/γ_2)
0	0	64.6	0.617371	0	0	
0.091	0.187	61.7	0.510283	0.005316	0.051268	0.504967
0.188	0.328	59.6	0.407106	0.022534	0.094834	0.384572
0.288	0.399	58.1	0.313063	0.05252	0.127557	0.260543
0.405	0.502	56.9	0.218955	0.103147	0.150049	0.115808
0.502	0.582	56.3	0.153791	0.15778	0.155777	−0.00399
0.570	0.646	55.9	0.114972	0.202967	0.15281	−0.08799
0.685	0.702	55.5	0.062088	0.292508	0.13467	−0.23042
0.759	0.762	55.4	0.036531	0.359026	0.114252	−0.3225
0.895	0.891	55.6	0.007014	0.499991	0.058777	−0.49298
1.0	1.0	56.2	0	0.625773	0	

Summary of activity coefficients calculations and values of G^E/RT ($G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$) at different temperatures are listed in Table 2. It should be emphasized that ln γ_1, ln γ_2, and G^E/RT are properties of the liquid phase. Figure 4 shows how ln γ_1, ln γ_2, and G^E/RT vary with composition for acetone + methanol binary system at a specified temperature. In such case, where ln $\gamma_i \geq 0$, the liquid phase shows positive deviation from ideal-solution behavior. The curve for the dimensionless Gibbs energy (G^E/RT) (Figure 4) is a typical one for binary system exhibiting positive deviation, where value of G^E/RT goes to zero at both $x_1 = 0$ and $x_1 = 1.0$, which is consistent with Gibbs−Duhem equation at each end.

Consistency of thermodynamic data can be assessed using either the slope test or the Redlich−Kister test. The slope test is based on the following form of Gibbs−Duhem equation:

$$\frac{\mathrm{d} \ln \gamma_1}{\mathrm{d}x_1} = -\frac{x_2}{x_1}\frac{\mathrm{d} \ln \gamma_2}{\mathrm{d}x_1} \quad \text{(at constant } T \text{ and } P\text{)} \tag{2}$$

Thus, for thermodynamic data to be consistent, the follow-

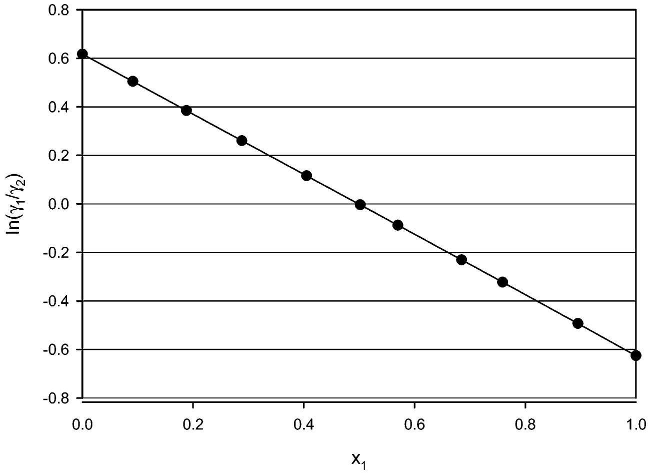

Figure 5. Plot of $\ln(\gamma_1/\gamma_2)$ vs liquid composition, x_1.

Table 3. Vapor−Liquid Equilibrium Data for Acetone (1) + Methanol (2) at Different $CaBr_2$ Concentrations

	0.05 M $CaBr_2$		0.1 M $CaBr_2$		0.3 M $CaBr_2$	
x_1	y_1 (acetone)	t/°C	y_1 (acetone)	t/°C	y_1 (acetone)	t/°C
0	0	56.21	0	56.2	0	56.2
0.091	0.488	55.3	0.451	55.3	0.382	55.9
0.188	0.656	54.1	0.625	54.6	0.625	55.1
0.288	0.687	56.2	0.678	56.7	0.678	56.3
0.405	0.766	54.0	0.770	54.5	0.780	54.9
0.502	0.820	54.3	0.808	54.4	0.810	54.0
0.570	0.853	55.2	0.851	55.7	0.852	55.5
0.685	0.876	56.2	0.868	56.0	0.880	55.8
0.731	0.870	56.2	0.883	56.8	0.900	56.1
0.749	0.859	58.3	0.870	58.6	0.902	57.4
0.840	0.780	60.5	0.801	54.4	0.930	56.6
0.959	0.710	61.3	0.814	52.9	0.985	57.1
1.0	1.0	64.65	1.0	64.65	1.0	64.65

ing observations should be verified from the plots of $\ln \gamma_1$, $\ln \gamma_2$ versus x_1, based on eq 2:

(i) At any value of x_1, the $\ln \gamma_1$ and $\ln \gamma_2$ curves should have opposite slopes.

(ii) At $x_1 = x_2$, the slopes should be equal and opposite.

(iii) Each curve has zero slope as x_i goes to 1.0.

It is seen that the plots of $\ln \gamma_1$ and $\ln \gamma_2$ presented in Figure 4 satisfy these observations; thus, the VLE data of the acetone−methanol system are consistent according to this test.

According to Redlich−Kister test, the Gibbs−Duhem equation takes the form

$$\int_{x_1=0}^{x_1=1} \ln(\gamma_1/\gamma_2)\,\mathrm{d}x_1 = 0 \qquad (3)$$

Thus, if the area under the $\ln(\gamma_1/\gamma_2) - x_1$ curve turns to zero, then the VLE data are thermodynamically consistent according to this test. Plot of $\ln(\gamma_1/\gamma_2)$ versus x_1 is shown in Figure 5. It can be observed that the area above the x_1-axis is almost the same as that below the x_1-axis. Thus the VLE data of acetone + methanol system is also thermodynamically consistent according to this test.

The VLE data of acetone + methanol system in the presence of 0.05 M $CaBr_2$ are shown in Table 3 and Figure 6. It is seen that the presence of 0.05 M $CaBr_2$ shifts up the VLE curve, but had not removed or eliminated the azeotropic composition. The azeotropic point was only shifted from 0.76 to 0.8 mole fraction. Thereafter, the crossover phenomenon was noticed where acetone concentration in the vapor phase was lowered below the corresponding VLE values. Nonetheless, the resulted $x-y$ curve is more favorable for distillation processes. Figure 7 shows the VLE data at various $CaBr_2$ concentrations. The presence of $CaBr_2$ at a concentration of 0.3 M completely eliminated the azeotropic point as shown in Figure 7. The relative volatility of acetone in the presence of 0.3 M $CaBr_2$ was greater than that in the presence of 0.1 M and 0.05 M $CaBr_2$. This means that the salting effect increases with salt concentration. This trend was expected since the increase in salt concentration increases the intermolecular forces between the salt and the highly polar component (methanol) in the mixture.[2] Thus, the salting-out effect of the lower polarity component (acetone) increases as the salt molarity increases.

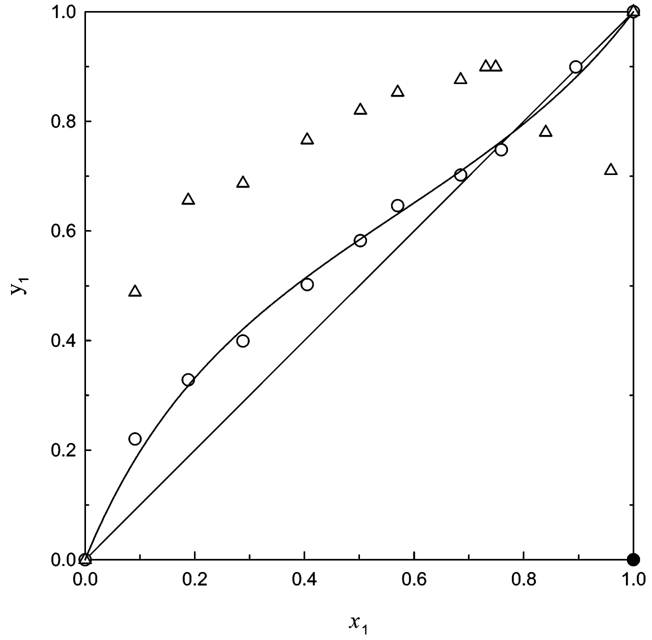

Figure 6. Phase diagram (x_1-y_1 diagram) for acetone (1) + methanol (2) system for salt free and in the presence of 0.05 M $CaBr_2$. Solid line, Wilson model; ○, salt free; △, 0.05 M $CaBr_2$.

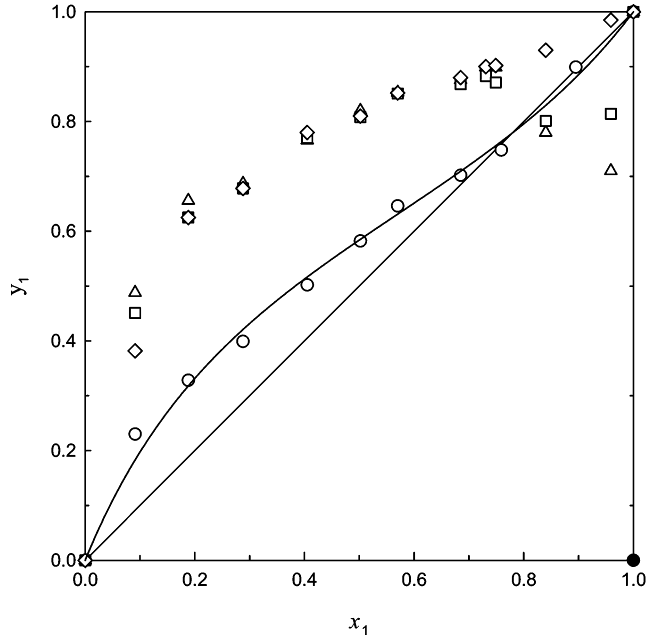

Figure 7. Phase diagram (x_1-y_1 diagram) for acetone (1) + methanol (2) system at different concentrations of $CaBr_2$. Solid line, Wilson model; ○, salt free; △, 0.05 M $CaBr_2$; □, 0.1 M $CaBr_2$; ◇, 0.3 M $CaBr_2$.

Iliuta and Thyrion[9] showed that the azeotropic point of the acetone + methanol system was shifted from 0.783 to 0.915 mole fraction of acetone and 0.98 when NaI salt was added at 0.01 M and 0.015 M, respectively; however, at salt concentrations higher than 0.015, the azeotrope of the mixed solvent system disappeared. They also reported that, by adding NaSCN salt, the azeotropic point was shifted, respectively, to 0.834 and 0.99 mole fraction of acetone at 0.01 M and 0.03 M salt concentrations. At higher NaSCN concentration, again the azeotrope of the mixed solvent system disappeared. The results of Illiuta and Thyrion about the effect of NaI and NaSCN salts and the results of this work concerning the effect of $CaBr_2$ salt clearly show the possibility of breaking the azeotrope of the acetone−methanol system.

Calcium bromide is soluble in both acetone and methanol and is more soluble in methanol.[2] Meranda and Furter[3] considered the salting-in on acetone as an anomalous behavior as compared to the usual trend of salt effect. Iliuta and Thyrion[9] attributed the crossover in the salt effect phenomenon to the change in the preferential solution of ions with liquid composition.

The VLE data of acetone + methanol system in the presence of $CaBr_2$ can be explained in terms of the enhancement factor (φ) defined as

$$\varphi = \frac{\alpha_s}{\alpha_0} \tag{4}$$

where α_s and α_0 are the relative volatilities of acetone in the presence and in the absence of $CaBr_2$, respectively. The relative volatility can be determined using the equation

$$\alpha = \frac{y_1/x_1}{y_2/x_2} \tag{5}$$

where the subscripts 1 and 2 hold for acetone and methanol, respectively. Values of φ at different $CaBr_2$ concentrations are presented in Figure 8. It is seen that all values of the enhancement factor decreased with an increase in acetone concentration. Most of the enhancement factor values remained above 2.0 for salt concentrations tested, except those above the azeotrope composition. At salt concentrations of 0.05 M and 0.1 M, the enhancement factor falls to less than unity after the azeotrope composition; this is due do the crossover behavior when using these salt concentrations. Basically, as the value of φ approaches unity, the salt has insignificant effect on the VLE data. As all of the enhancement factor values are greater than two, this would indicate that $CaBr_2$ improved the separation of acetone + methanol mixture.

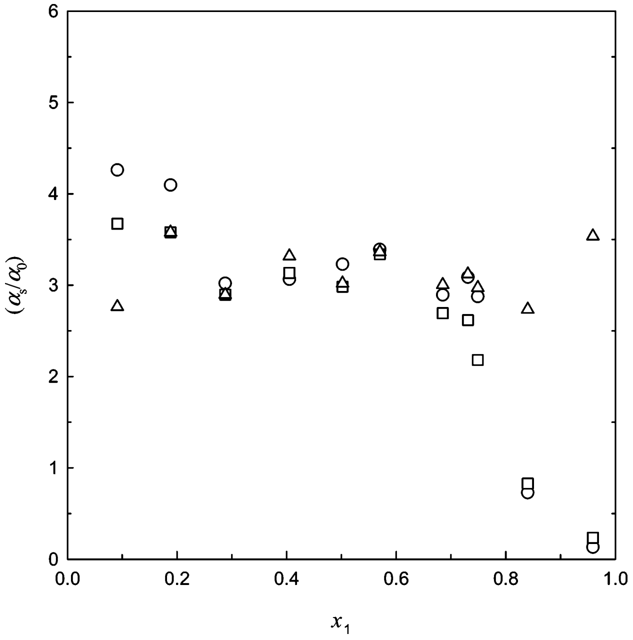

Figure 8. Enhancement factor versus liquid composition at different $CaBr_2$ concentrations. ○, 0.05 M $CaBr_2$; □, 0.1 M $CaBr_2$; △, 0.3 M $CaBr_2$
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Conclusions

Vapor−liquid equilibrium of acetone + methanol system exhibited a positive deviation from the ideal behavior. The VLE data of the acetone + methanol system obtained in this work are thermodynamically consistent. The influence of calcium bromide addition on the VLE of the acetone + methanol system has been investigated. The crossover phenomenon, which is a combination of salting-out and salting-in effects was noticed in the presence of 0.05 M $CaBr_2$ but was not encountered at higher concentrations. Increasing the $CaBr_2$ concentration from (0.05 to 0.3) M significantly altered the VLE of the system. The azeotropic point of the acetone + methanol system was completely eliminated at the 0.3 M $CaBr_2$ concentration. The gas phase of the acetone + methanol system was confirmed to follow the ideal gas behavior at the given experimental conditions.

Literature Cited

(1) Furter, W. Production of fuel-grade ethanol by extractive distillation employing the salt effect. *Sep. Purif. Methods* **1993**, *21*, 1−21.
(2) Ohe, S. *Vapor-Liquid Equilibrium Data*: *Salt Effect*; Elsevier: Amsterdam, 1991.
(3) Meranda, D.; Furter, W. F. Salt effect on vapor−liquid equilibria: some anomalies. *AICHE J.* **1974**, *20*, 103−108.
(4) Dernini, S.; De, Santis, R.; Marrelli, L. Salt effects in isobaric vapor−liquid equilibria of acetone + methanol system. *J. Chem. Eng. Data* **1976**, *21*, 170−173.
(5) Iliuta, M. C.; Thyrion, F. C. Vapor−liquid equilibria of the acetone + methanol + inorganic salt system. *Fluid Phase Equilib.* **1995**, *103*, 257−284.
(6) Furter, N. F. Correlation and prediction of salt effect in vapor−liquid equilibrium. *Adv. Chem. Ser.* **1976**, *155*, 26−35.
(7) Subbaiah, T. Salt effect in vapor liquid equilibria. *J. Chem. Technol. Biotechnol.* **1993**, *57*, 163−168.
(8) Prausnitz, J. M.; Anderson, T.; Grens, E.; Eckert, C.; Hsieh, R.; O'Connell, J. *Computer Calculations for Multicomponent Vapor−Liquid and Liquid−Liquid Equilibria*; Prentice Hall: Englewood Cliffs, NJ, 1980.
(9) Iliuta, M. C.; Thyrion, F. C. Salt effects on vapor−liquid equilibrium of acetone + methanol system. *Fluid Phase Equilib.* **1996**, *121*, 235−252.

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