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Salt Effects on the Isobaric Vapor−Liquid Equilibrium for Four Binary Systems

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An ebulliometer was used to measure the vapor−liquid equilibrium at 101.3 kPa for four binary systems: (1) the acetone−water−$CaCl_2$ system; (2) the 2-propanol−water−potassium acetate system and the 2-propanol−water−KBr system at different salt concentrations; (3) the ethyl acetate−ethanol system saturated with $CaCl_2$; and (4) the acetone−carbon tetrachloride system saturated with $CaCl_2$.The experimental results agree with the common behavior of salt effects on the phase equilibrium. An anomalous crossover between “salting out” and “salting in” effects on acetone had been observed for the acetone−carbon tetrachloride system saturated with $CaCl_2$.

Introduction

The study of the influence of salt on the vapor−liquid equilibrium (VLE) of solvent mixtures is of interest, because adding salt to a mixed solvent mixture will break azeotropes and improve the relative volatility of this mixture. Extractive distillation with salt and salt-containing distillation have been used in practice due to their low energy consumption as well as high efficiency. For example, alcohol is successfully produced from an aqueous solution using extractive distillation with salt. Acetone, ethanol, 2-propanol, ethyl acetate, and carbon tetrachloride are widely used in industry as organic solvents. Research results of salt effects on the VLE for those solvent mixtures have been reported by Wu et al. (1999), Batista and Francesconi (1998), Hashitani and Hirata (1968), and Lliuta et al. (1998). Different kinds of salt will have different influences on the VLE. To develop applications of salt effects and study their regularity, salt effects on the VLE for aqueous binary systems and nonaqueous binary systems must be better understood. The 2-propanol (1)−water (2) system was chosen for study because of the presence of an azeotropic point at 101.3 kPa.

The following binary systems at the pressure 101.3 kPa have been studied in this work: (1) the acetone (1)−water (2)−calcium chloride system; (2) the 2-propanol (1)−water (2)−potassium acetate system and the 2-propanol (1)−water (2)−potassium bromide system at different salt concentrations; (3) the ethyl acetate (1)−ethanol (2) system saturated with calcium chloride; and (4) the acetone (1)−carbon tetrachloride (2) system saturated with calcium chloride.

A limited amount of VLE data for the salt-containing systems presented in this work was found in the literature.

Experimental Section

Materials. Acetone, ethanol, 2-propanol, ethyl acetate, and carbon tetrachloride were analytical grade chemicals and their purity was >99.5 %. Calcium chloride, potassium acetate, and potassium bromide were analytical grade and were dried before use. Twice-distilled water was used. The measured physical properties of the chemicals are compared with published measurements in Table 1.

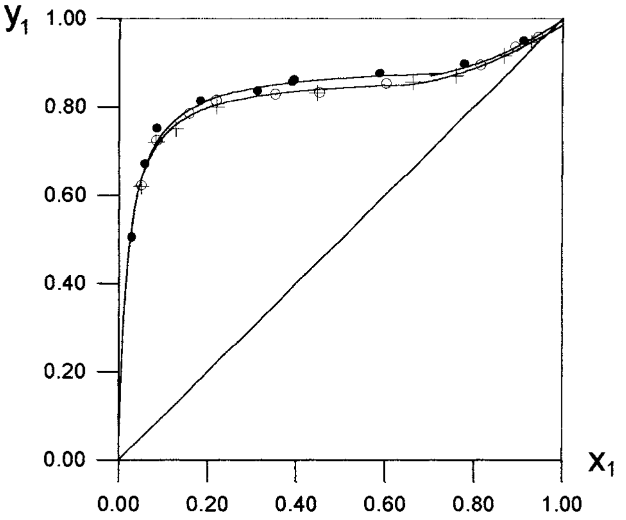

Figure 1. Plot of y_1 versus x_1 for the acetone (1)−water (2)−calcium chloride system: ○, salt-free, experimental; ●, 2.5 wt % $CaCl_2$; +, salt-free (Gmehling and Onken, 1997).

Apparatus and Analytical Method. The vapor−liquid equilibrium conditions for either salt-free or salt-containing systems were measured with a modified ebulliometer. The purpose of the modification was to minimize the volume of condensate so the composition of the solution, which was charged into the still, could be considered the equilibrium composition of the liquid phase during the experiment. Details of the ebulliometer have been described previously (Chen and Hou, 1991).

The boiling temperature was measured with a standard thermometer with 0.1 K graduations.The pressure in the ebulliometer was maintained at 101.3 kPa ± 0.03 kPa with the help of a pressure-control system, which consists of a mercury manometer, a water manometer, two solenoid valves, two electromagnetic relays, two reservoirs, and a vacuum pump.

The compositions of the liquid-phase and vapor-phase samples for the salt-free binary system were analyzed by gas chromatography with a thermal conductivity detector connected to an integrator. For a salt-containing binary system, the composition of the vapor phase could also be

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Table 1. Physical Properties of Chemicals

substance	boiling point, T/K		density (293.15 K)/g·cm^{-3}		refractive index, n_D (293.15 K)	
	lit.[a]	exp	lit.[a]	exp	lit.[a]	exp
ethanol	351.65	351.55	0.7893	0.7891	1.3611	1.3611
2-propanol	355.55	355.60	0.7855	0.7852	1.3776	1.3775
acetone	329.35	329.27	0.7899	0.7897	1.3588	1.3590
ethyl acetate	350.25	350.25	0.9006	0.9005	1.3724	1.3723
carbon tetrachloride	349.90	350.10	1.5748	1.5720	1.4519	1.4520
water	373.15	373.15	0.9982	0.9981	1.3325	1.3325

[a] Lide (1993−1994).

Table 2. Experimental VLE Data of the Acetone (1)−Water (2)−CaCl$_2$ System at 101.3 kPa

salt-free			m_s = 2.5 wt %		
x_1	y_1	T/K	x_1	y_1	T/K
0.0508	0.6215	347.35	0.0293	0.5050	355.45
0.0843	0.7234	342.25	0.0578	0.6702	342.88
0.1563	0.7842	337.85	0.0846	0.7507	346.82
0.2189	0.8140	335.95	0.1826	0.8139	337.16
0.3514	0.8281	335.85	0.3088	0.8352	335.75
0.4503	0.8321	335.85	0.3907	0.8563	335.28
0.6027	0.8519	332.55	0.3950	0.8604	335.45
0.8136	0.9058	330.65	0.5870	0.8753	334.01
0.8924	0.9432	330.05	0.7780	0.8972	331.85
0.9450	0.9692	329.95	0.9116	0.9499	330.35

analyzed by gas chromatography, because the salt is nonvolatile. It is difficult to use gas chromatography to analyze the composition of a liquid phase for a salt-containing system. The composition of the liquid phase at equilibrium was taken to be the original composition of the solution charged into the still. This assumption is reasonable because this still has a large liquid-phase volume and only a small mass of condensate. All salt-containing solutions charged into the still were prepared directly by using an analytical balance, the accuracy of which was ±0.01 mg.

According to an error analysis, the error of the liquid-phase composition is <0.25 % when the ratio between the moles of liquid and the moles of vapor is >200. The structure of the ebulliometer used in this work satisfies the above condition. It is reasonable to assume that the known composition of each prepared solution composition is the same as the equilibrium composition of the liquid phase.

The concentration of salt in the liquid phase for a salt-containing binary system (not in saturation condition) was established by adding measured masses of dried salt to known masses of binary mixtures, which were prepared before starting every run. For nonaqueous binary systems, the saturation conditions of salt in the liquid mixture were ensured by the existence of a slight amount of solid salt in the solution.

Results and Discussion

Calibration of the Ebulliometer. To check the performance of the ebulliometer, the VLE data of the acetone (1)−water (2) system and the 2-propanol (1)−water (2) system at 101.3 kPa were measured with the ebulliometer. The experimental results are given in Tables 2 and 3 and Figures 1 and 2. The results agree well with the data of Gmehling and Onken (1977).

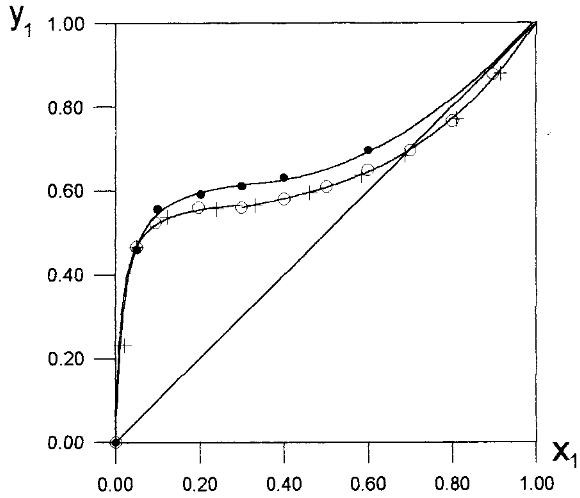

Figure 2. Plot of y_1 versus x_1 for the 2-propanol (1)−water−potassium bromide system: ○, salt-free, experimental; ●, 4.0 wt % KBr; +, salt-free (Gmehling and Onken, 1997).

VLE Results. Isobaric VLE data were measured for three salt-containing systems, acetone (1)−water (2) with 2.5 wt % calcium choride, ethyl acetate (1)−ethanol (2) saturated with calcium chloride, and acetone (1)−carbon tetrachloride (2) saturated with calcium chloride. The experiment results are given in Tables 2 and 4 and in Figures 1, 3, and 4. Isobaric VLE data for the 2-propanol (1)−water (2) system with potassium bromide or with potassium acetate have been measured at various salt concentrations (m_s = 2, 4, 8, 12 wt %). The experimental results are given in Tables 3 and 5 and in Figures 2 and 5.

The thermodynamic consistency of the experimental data of the VLE for the above-measured systems was checked using Herington's (1951) method, and the data were found to be consistent.

The salt effect on the VLE at constant pressure (101.3 kPa) causes a shift of $y-x$ curves when compared with the

Table 3. Experimental VLE Data of the 2-Propanol (1)−Water (2)−KBr System at 101.3 kPa

salt-free			m_s = 2.0 wt %			m_s = 4.0 wt %		
x_1	y_1	T/K	x_1	y_1	T/K	x_1	y_1	T/K
0.0497	0.4656	357.07	0.0000	0.0000	373.22	0.0000	0.0000	373.37
0.0945	0.5234	354.95	0.0501	0.4476	357.84	0.0499	0.4595	358.50
0.1968	0.5600	353.85	0.0999	0.5389	355.65	0.0998	0.5554	355.94
0.2992	0.5601	353.66	0.1996	0.5762	354.43	0.2013	0.5909	354.75
0.3999	0.5806	353.37	0.2996	0.5892	354.27	0.2998	0.6102	354.35
0.5002	0.6097	353.25	0.3994	0.6104	353.91	0.3991	0.6308	353.94
0.5982	0.6487	353.17	0.4996	0.6473	353.59			
0.6992	0.6954	353.15	0.5991	0.6650	353.43			
0.7996	0.7650	353.40						
0.8962	0.8784	354.02						

Table 4. Experimental VLE Data for Two Nonaqueous Binary Systems at 101.3 kPa

ethyl acetate (1)−ethanol (2) saturated with $CaCl_2$			acetone (1)−carbon tetrachloride (2) saturated with $CaCl_2$		
x_1	y_1	T/K	x_1	y_1	T/K
0.0669	0.1594	351.25	0.0354	0.1525	345.37
0.1390	0.3145	349.45	0.1799	0.4300	337.18
0.2583	0.4301	347.65	0.3172	0.6087	333.65
0.3353	0.4998	346.65	0.3962	0.6275	332.34
0.4250	0.5634	345.95	0.4770	0.6712	331.34
0.5146	0.6255	345.55	0.6058	0.7125	330.08
0.6048	0.6670	345.45	0.6905	0.7525	330.10
0.6687	0.7087	345.55	0.7997	0.8225	328.83
0.8148	0.7651	345.95	0.9078	0.9075	328.55
0.9340	0.8851	346.35	0.9612	0.9550	328.65

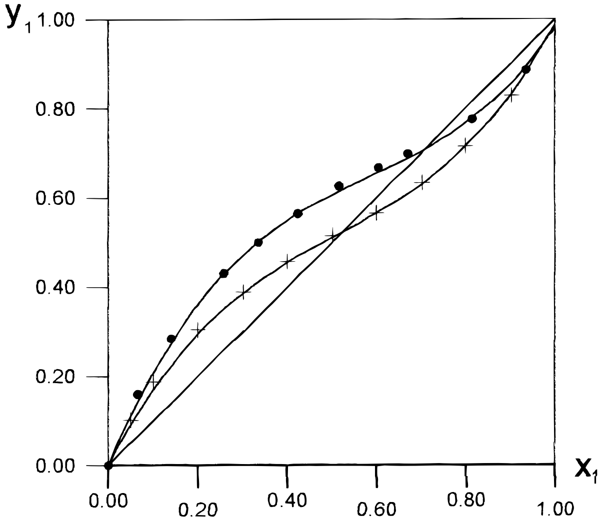

Figure 3. Plot of y_1 versus x_1 for the ethyl acetate (1)−ethanol−calcium chloride system: ●, saturation, $CaCl_2$; +, salt-free (Gmehling and Onken, 1997).

curves for salt-free systems. For the acetone (1)−water (2) system, Figure 1 clearly shows that the relative volatility of acetone to water is increased in the presence of 2.5 wt % $CaCl_2$.

A significant shift in the azeotropic composition occurred for the ethyl acetate (1)−ethanol (2) system saturated with $CaCl_2$. In other words, the azeotropic composition shifts from $x_1 = 0.52$ in the absence of salt to $x_1 = 0.72$ in the presence of salt. The behavior of the salt effect on the system in this work agrees with the observations of Hashitani and Hirata (1968) and Chen and Hou (1991). But different salt concentrations in the liquid phase will result in different VLE data. The acetone (1)−carbon tetrachloride (2) system saturated with $CaCl_2$ exhibits the anomaly of a "crossover effect" (Devasahayam and Srinivasan, 1981), as the composition of the liquid phase varies.

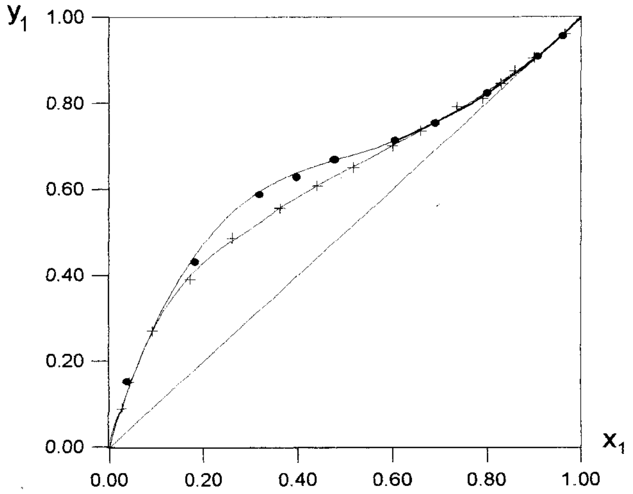

Figure 4. Plot of y_1 versus x_1 for the acetone (1)−carbon tetrachloride (2)−calcium chloride system: ●, saturation, $CaCl_2$; +, salt-free (Bachman and Simons, 1952).

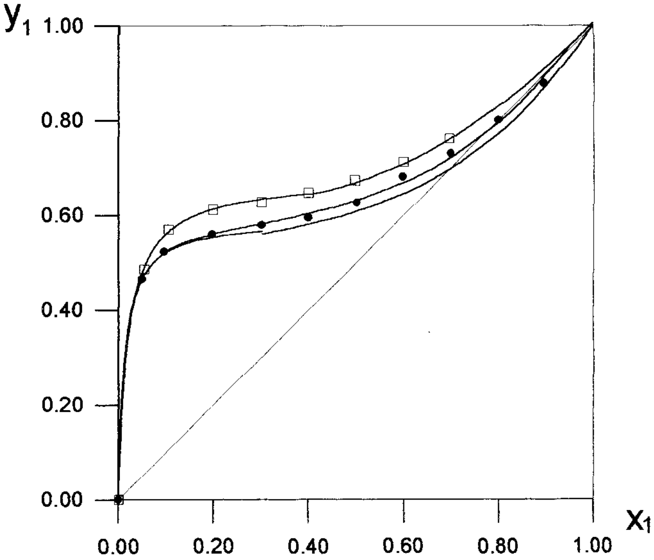

Figure 5. Plot of y_1 versus x_1 for the 2-propanol (1)−water (2)−potassium acetate system: —, salt-free; ●, 4.0 wt % potassium acetate; □, 12.0 wt % potassium acetate.

First, the acetone component is "salted out" (enhancement of relative volatility), and then "salting in" (more soluble) follows in the acetone-rich region. There was a slight shift of the y−x curve for this system.

It can be seen in Figures 2 and 5 that a higher salt concentration is advantageous in eliminating the azeotrope. The relative volatility of 2-propanol to water increases with an increase of salt concentration when the solvent composi-

Table 5. Experimental VLE Data for the 2-Propanol (1)−Water (2)−Potassium Acetate System at 101.3 kPa

m_s = 4.0 wt %			m_s = 8.0 wt %			m_s = 12.0 wt %		
x_1	y_1	T/K	x_1	y_1	T/K	x_1	y_1	T/K
0.0000	0.0000	373.46	0.0000	0.0000	373.86			
0.0999	0.5346	355.20	0.0408	0.4564	358.10	0.0527	0.4916	358.47
0.1994	0.5695	354.13	0.0994	0.5634	355.54	0.1033	0.5661	355.40
0.2999	0.5824	353.86	0.2141	0.5917	354.22	0.1991	0.6085	354.37
0.3982	0.6232	353.55	0.3003	0.6110	353.68	0.2994	0.6186	354.20
0.4980	0.6445	353.46	0.4010	0.6356	353.67	0.3997	0.6457	353.76
0.5995	0.7022	353.36	0.4996	0.6658	353.58	0.4970	0.6742	353.69
0.6972	0.7324	353.45	0.6013	0.7095	353.63	0.5988	0.7121	353.78
0.7946	0.8071	353.87	0.6932	0.7576	353.72	0.6961	0.7947	354.05
0.8999	0.8881	354.41	0.7754	0.8047	354.09			
			0.8924	0.8895	354.86			

tion is fixed. Different kinds of salt have a different influence on the VLE. The azeotropic point of the 2-propanol (1)−water (2)−potassium acetate system will disappear when the salt concentration of the system is 12 wt %.

Conclusions

The ebulliometer was calibrated by measuring the VLE data of two systems and comparing the $x-y-T$ values with literature data. The experimental equipment and measurement method are reasonable. The experimental results agree with the common behavior of salt effects on the VLE. The salt effect on the VLE at 101.3 kPa causes the shift of the $y-x$ curve from that of the salt-free system. The bubble point temperature of a mixture increases with increasing salt concentration.

Literature Cited

Bachman, K. C.; Simons, E. L. Vapor−Liquid Equilibria at Subatmospheric Pressure (Binary System Acetone−Carbon Tetrachloride). *Ind. Eng. Chem.* **1952**, *42*, 202−205.

Batista, S. B.; Francesconi, A. Z. Vapor−Liquid Equilibrium for the Hexane−2-Propanol−Calcium Chloride System at 101.3 kPa. *J. Chem. Eng. Data* **1998**, *43*, 38−39.

Chen, X. Z.; Hou, Y. J. Measurement of Vapor−Liquid Equilibria of Salt-Containing System. *Huagong Zuebao (Chin. Ed.)* **1991**, *42*, 114−118.

Devasahayam, E. M. J. R.; Srinivasan, D. Salt Effects in Vapor−Liquid Equilibria. Effects of Dissolved Salts on the Vapor−Liquid Equilibrium Relationships of Three Miscible Nonaqueous Binary System and One Partially Miscible Binary System. *J. Chem. Eng. Data* **1981**, *26*, 398−401.

Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection;* Chemistry Data Series; DECHEMA: Frankfurt, 1977; Vol. I, Parts 1−2.

Hashitani, M.; Hirata, M. Salt Effect of Calcium Chloride in Vapor−Liquid Equilibrium of the Alcohol−Acetic Ester Systems. *J. Chem. Eng. Jpn.* **1968**, *1*, 116−119.

Herington, E. F. G. Test for Consistency of Experimental Isobaric Vapor−Liquid Equilibrium Data. *J. Inst. Pet.* **1951**, *39*, 357−361.

Lide, D. R. *CRC Handbook of Chemistry and Physics*, 74th ed.; Chemical Rubber Publishing Company: Tokyo, 1993−1994.

Lliuta, M. C.; Lliuta, I.; Landauer, O. M.; Ortansa, M.; Thyrion, F. C. Salt Effect of LiCl on Vapor−Liquid Equilibrium of the Acetone−Methanol System. *Fluid Phase Equilib.* **1998**, *149*, 163−176.

Wu, W. L.; Zhang, Y. M.; Lu, X. H.; Wang, Y. R.; Shi, J.; Lu, B. C. Y. Modification of the Furter Equation and Correlation of the Vapor−Liquid Equilibrium for Mixed−Solvent Electrolyte Systems. *Fluid Phase Equilib.* **1999**, *154*, 301−310.

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