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Vapor Pressure of Ethanol + Benzyltributylammonium Chloride Solution and Vapor−Liquid Equilibrium of Ethanol + Water + Benzyltributylammonium Chloride Mixture at Atmospheric Pressure

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In this study, the vapor pressures of benzyltributylammonium chloride and ethanol solutions were measured from 298.25 K to 318.15 K, and the enthalpies of vaporization of this mixture were estimated by the Clausius−Clapeyron equation. The vapor−liquid equilibria of the ethanol and water mixtures with 2 *m* and saturated concentrations of the same organic salt were measured with an Othmer type equilibrium cell under atmospheric pressure. The uncertainty of the calibration is ±0.0019 mole fraction for the water + ethanol mixture and that of temperature is 0.1 K.

Introduction

Organic salts are important and are usually used as intermediate chemicals, reaction catalysts, inhibitors to undesired reactions, supporting electrolytes, and surfactants. In addition to the above applications, use of organic salts to phase transfer catalytic reactions has invited extensive discussion recently. This type of reaction is applied to the synthesis of alcoholic and esteric compounds, elimination reactions, reduction reactions, carboxylic reactions, and syntheses of organic metal complexes. The advantages of phase transfer catalytic reactions include the mild reaction conditions of room temperature and atmospheric pressure. For such broad applications of organic salts, it is necessary to investigate the thermodynamic behavior of solutions containing these salts. 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.

Recently, the vapor pressures of the aqueous solutions of several organic salts such as chlorides of benzyltrimethylammonium, benzyltriethylammonium, benzyltributylammonium, triethylammonium, and (2-hydroxyethyl)ammonium and trihydroxy(methylamino)methane hydrochloride, have been reported by Lee and Lee (1998a,b). In this study, the vapor pressures of ethanol and benzyltributylammonium chloride solutions and the vapor−liquid equilibria (VLE) of ethanol−water−benzyltributylammonium chloride mixtures at atmospheric pressure were measured. The experimental vapor pressure data were correlated by the Patil model. The enthalpies of vaporization of these solutions were estimated by the Clausius−Clapeyron equation. On the other hand, we failed to correlate the experimental VLE data, and only the experimental data and the phase diagram of this solution were reported in this study.

Vapor Pressure Measurements

Apparatus. The equipment for vapor pressure measurement is identical to the one used by Lee and Lee (1998a,b), which is simple, easy-to-operate, and reliable. The vapor pressures were determined by measuring the pressure difference between an organic salt solution and a reference liquid which was chosen to be *n*-butylphthalate due to these advantages over mercury: lower vapor pressure at the same temperature; much lower density so that pressure readings were more sensitive to concentration and temperature changes; and not poisonous. The accuracy of the pressure reading was 0.013 kPa. The water bath temperature was controlled within ±0.1 K. The construction and the operation of this apparatus have been described in detail by Lee and Lee (1998a,b) and need not be repeated here. This apparatus was tested by measuring the vapor pressure of lithium chloride aqueous solutions of seven different concentrations at 303.15 K. The absolute average deviation (AAD) of the experimental data from the experimental values of Patil et al. (1990) was 0.019 kPa. This test showed the reliability of this apparatus and experimental procedure.

Correlation Model. Owing to the existence of undissociated salt molecules, it is quite complicated to develop a predictive model to estimate the vapor pressures of such organic salt solutions. In this study, the empirical correlation model of Patil et al. (1990) was adopted to fit the vapor pressure data of the present study. The Patil model was originally proposed for strong electrolyte solutions. However, it performed fairly well for aqueous solutions of organic salt as reported in the studies of Lee and Lee (1998a,b). The Patil model is in the form

$$\log P = A(m) + \frac{B(m)}{T} + \frac{C(m)}{T^2} \tag{1}$$

where *P* is the vapor pressure of solution in kPa, *T* is the

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absolute temperature in K, m is the molality, and $A(m)$, $B(m)$, and $C(m)$ are the following polynomials:

$$A(m) = A_0 + A_1 m + A_2 m^2 + A_3 m^3$$

$$B(m) = B_0 + B_1 m + B_2 m^2 + B_3 m^3$$

$$A(m) = C_0 + C_1 m + C_2 m^2 + C_3 m^3 \qquad (2)$$

Vapor−Liquid Equilibrium Measurements

Apparatus. A static Othmer type condensed vapor recirculating still was used for the present study. This type of apparatus requires longer phase equilibrium time than a flow or semiflow type apparatus; however, it has the advantages of simple construction, easy operation, and low cost. It was designed so that liquid entrainment was avoided and heat loss from both liquid and vapor phases was prevented by insulation. The vapor and liquid temperatures were measured with mercury thermometers which have a scale with 0.1 °C divisions. The pressure was measured with a Fortin mercury barometer with an accuracy of 0.013 kPa (0.1 mmHg). The liquid mixture was fed into the still and heated by an electric heater. The power supplied maintains about 6 $\text{mL}\cdot\text{min}^{-1}$ of liquid to vaporize, condense, and recirculate it back to the still. It required about 1 h to reach a new equilibrium state after vapor and liquid temperatures became identical and stable. About 1 μL of both liquid and vapor samples were taken with syringes and injected into a GC for composition analysis.

The GC used in this study is made by China Chromatograph Co. in Taipei. For the present mixture, the detector is a TCD, the column is an 80/100 Porapak Q, 4 m × $^1/_8$ in. The optimum operation conditions were as follows: the injection temperature was 170 °C; the oven temperature was 150 °C; the detector temperature was 140 °C; the detector current was 220 mA; the carrier gas was nitrogen with a flow rate of 50 mL/min. A precolumn packed with fiberglass was connected to prevent salt from getting into the main column.

The mole fraction of each component in solution was determined by a calibration curve prepared prior to the experiments. The calibration curve relating the peak area ratio from GC analysis to the mole fraction of the constituent component was made with gravimetrically prepared samples over the entire composition range for a binary mixture. The uncertainty of calibration is ±0.0019 mole fraction for water + ethanol mixtures.

Materials. The benzyltributylammonium chloride was analytical reagent grade with a purity of 99+% from Merck Co. This salt was dried in a vacuum oven at 353 K for more than 24 h to expel the dissolved gases and moisture. Ethanol was GR grade and from Merck Co. with a purity of 99+%. The distilled water was deionized and degassed to give an electric resistance less than 18.2 $\text{M}\Omega\cdot\text{cm}^{-1}$.

Vapor Pressure Measurements

The vapor pressures of the benzyltributylammonium chloride−ethanol mixtures were measured for different concentrations at 298.15 K, 303.15 K, 308.15 K, 313.15 K, and 318.15 K. The experimental data are given in Table 1.

The experimental vapor pressures were fitted by the Patil model (Patil et al., 1990) with a nonweighted least-squares method. The degree of the polynomials for concentration parameters in the model was optimized after several trials. The correlation parameters of this mixture are given in Table 2. The absolute average deviation (AAD) of the correlation of this mixture is 0.14 kPa. The experimental and the calculated values by the Patil model were plotted in Figure 1.

Table 1. Vapor Pressures of Ethanol−Benzyltributylammonium Chloride Solutions

m^a	$P^{\text{sat.}}$/kPa	m^a	$P^{\text{sat.}}$/kPa	m^a	$P^{\text{sat.}}$/kPa
		$T = 298.15$ K			
0.000	7.62	2.140	6.55	4.664	4.60
0.099	7.47	2.539	6.25	5.196	4.03
0.510	7.39	3.094	5.80	5.827	3.22
1.064	7.09	3.529	5.49		
1.523	6.92	4.025	5.15		
		$T = 303.15$ K			
0.000	10.11	1.597	8.93	3.554	7.07
0.101	9.92	2.071	8.28	4.095	6.47
0.520	9.86	2.454	8.01	4.750	5.80
1.007	9.50	2.991	7.52		
		$T = 308.15$ K			
0.000	13.29	1.463	12.22	3.300	9.49
0.099	13.13	1.902	11.89	3.822	9.04
0.501	13.04	2.433	11.21	4.255	8.66
0.983	12.52	2.827	10.64		
		$T = 313.15$ K			
0.000	17.31	0.015	16.44	2.454	14.60
0.097	17.15	1.515	15.96	2.970	13.72
0.519	16.99	2.008	15.54	3.562	12.73
		$T = 318.15$ K			
0.000	22.36	1.042	21.16	2.358	18.68
0.101	22.04	1.426	19.98	2.884	17.16
0.502	21.88	1.875	19.59		

[a] m is the molality in units of $\text{mol}\cdot(1000\ \text{g of solvent})^{-1}$.

Table 2. Correlation Parameters of the Patil Model and Enthalpies of Vaporization of Ethanol−Benzyltributylammonium Chloride Solutions

param		concn/m	$\Delta_{\text{vap}}H/(\text{kJ}\cdot\text{mol}^{-1})$
A_0	12.240 17	0.5	42.84
A_1	18.908 67	1.0	43.16
A_2	7.689 239	1.5	42.63
A_3	−0.272 255	2.0	44.51
B_0	−4665.547	2.5	44.03
B_1	11 835.66	3.0	43.74
B_2	−4885.960	3.5	43.72
B_3	196.5062		
C_0	381 496.4		
C_1	−1851 514.0		
C_2	773 800.0		
C_3	−34 545.90		

Enthalpies of Vaporization

The Clausius−Clapeyron equation, which relates vapor pressure, temperature, change of volume, and enthalpy of vaporization, was originally developed for pure substances. We have applied this equation to calculate the enthalpies of vaporization of the present organic salt solution, as was done by Lee and Lee (1998a,b) for organic salt aqueous solutions.

If the enthalpy of vaporization of a liquid is independent of temperature and the volume of liquid phase is negligible compared to the vapor phase, then the Clausius−Clapeyron equation can be simplified to the form

$$\log P = \frac{-\Delta_{\text{vap}}H}{2.303RT} + c \qquad (3)$$

where P, T, and $\Delta_{\text{vap}}H$ are vapor pressure, absolute temperature, and enthalpy of vaporization, respectively. It is clear that a plot of $\log P$ vs $1/T$ of the experimental data

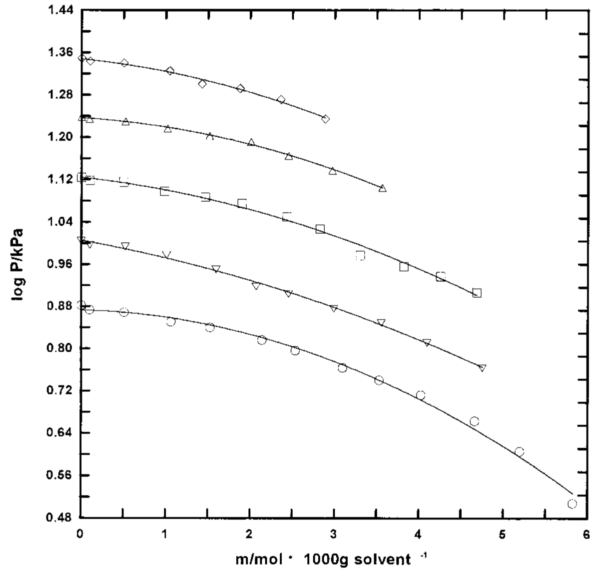

Figure 1. Vapor pressures of ethanol−benzyltributylammonium chloride mixtures.

Table 3. Experimental VLE Data of Ethanol (1)−Water (2) Solutions with 2 *m* Benzyltributylammonium Chloride

P/kPa	T/K	x_1	y_1	γ_1	γ_2
101.13	373.6	0.000	0.000		1.004
101.14	368.7	0.010	0.152	7.897	1.008
101.26	365.2	0.064	0.237	2.180	1.092
101.19	365.0	0.052	0.233	2.657	1.092
101.11	363.7	0.089	0.277	1.935	1.125
101.21	361.6	0.121	0.311	1.726	1.204
101.11	360.3	0.181	0.385	1.499	1.213
101.09	358.7	0.256	0.444	1.298	1.285
101.45	357.3	0.334	0.485	1.146	1.404
101.25	357.2	0.446	0.565	1.004	1.432
101.05	356.6	0.499	0.588	0.955	1.535
101.09	356.6	0.573	0.637	0.901	1.587
101.05	356.0	0.638	0.691	0.898	1.632
101.03	355.7	0.681	0.713	0.878	1.741
101.29	355.5	0.808	0.827	0.865	1.757
101.01	355.5	0.831	0.841	0.856	1.835
101.11	355.5	0.904	0.909	0.850	1.849
101.13	355.4	0.918	0.917	0.844	1.974
101.26	355.4	0.976	0.970	0.843	2.448
101.11	355.5	1.000	1.000	0.845	

at a specific concentration is linear, as seen in our previous studies (Lee and Lee, 1998a,b). Thus, the enthalpies of vaporization of different compositions were estimated with eq 3 and given in Table 2.

Experimental VLE Measurements

The VLE experiments of ethanol−water−benzyltributylammonium chloride were carried out in a static type equilibrium cell under atmospheric pressure. The effect of atmospheric pressure variation on VLE was negligible since it varied within only ±0.26 kPa. The experimental VLE data of 2 *m* and saturated organic salt concentrations are listed in Tables 3 and 4, respectively. The last two columns of these two tables are the experimental activity coefficients, γ_i, of ethanol and water, respectively. The experimental activity coefficient is estimated with the phase equilibrium equation

$$y_i\hat{\phi}_i^v P = x_i\gamma_i p_i^s\phi_i^s \tag{4}$$

Table 4. Experimental VLE Data of Ethanol (1)−Water (2) Solutions with Saturated Benzyltributylammonium Chloride

P/kPa	T/K	x_1	y_1	γ_1	γ_2
101.14	430.3	0.000	0.000		0.176
101.26	422.8	0.121	0.218	0.185	0.191
101.35	417.0	0.222	0.354	0.192	0.210
101.34	416.2	0.251	0.407	0.198	0.204
101.31	409.7	0.373	0.603	0.236	0.196
101.03	407.3	0.451	0.621	0.215	0.229
101.14	398.4	0.631	0.796	0.254	0.240
101.45	394.7	0.734	0.842	0.258	0.289
101.33	389.2	0.894	0.946	0.282	0.295
101.19	386.7	0.943	0.985	0.301	0.166
101.34	383.9	1.000	1.000	0.315	

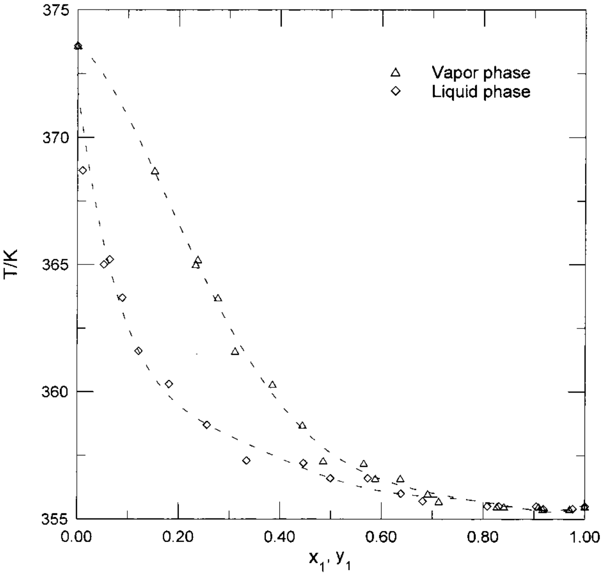

Figure 2. Experimental VLE data of ethanol (1)−water (2) mixture with 2 *m* benzyltributylammonium chloride.

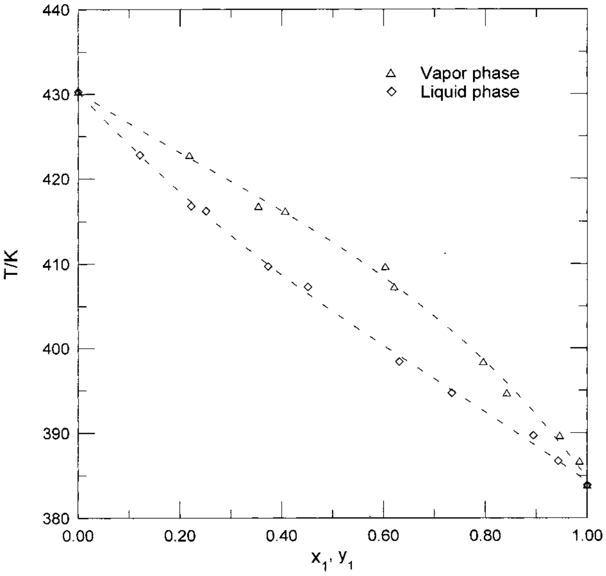

Figure 3. Experimental VLE data of ethanol (1)−water (2) mixture with saturated benzyltributylammonium chloride.

Figures 2 and 3 are the T−x−y phase diagrams of 2 *m* and saturated salt concentration, where x and y are mole fractions on a salt free basis. The saturated salt concentration is dependent on the solubility of the salt in the solvent mixture (approximately 4 *m* to 5 *m*). It is interesting to observe that benzyltributylammonium chloride shifts the VLE curve of the ethanol−water mixture away from the diagonal line so that an azeotrope would disappear if an

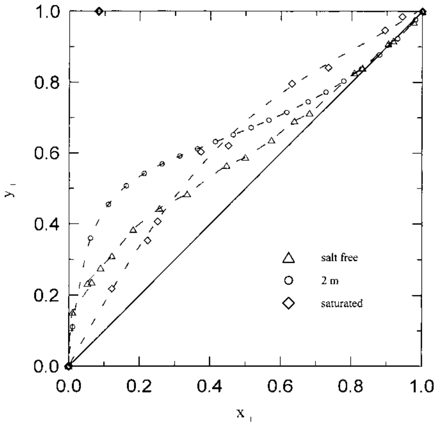

Figure 4. Experimental *x*−*y* diagram of ethanol (1)−water (2) mixture with 2 *m* and saturated benzyltributylammonium chloride.

adequate amount of salt was added, as shown in Figure 4. This is similar to the phase behavior when the inorganic salt such as LiCl, $CuCl_2$, or NaCl was added to this mixture.

Conclusions

In this study, the vapor pressures of ethanol−benzyltributylammonium chloride mixtures were measured at different concentrations and temperatures. The experimental data were correlated with the empirical model of Patil et al. The enthalpies of vaporization of this mixture at different salt concentrations were also calculated.

We attempted to ascertain experimentally the effect of an organic salt, benzyltributylammonium chloride, on the VLE of ethanol−water solutions. It is observed that this organic salt can shift and finally break away the azeotrope of ethanol−water mixtures just as an inorganic salt does.

Literature Cited

Lee, L. S.; Lee, C. C. Vapor pressures and Enthalpies of Vaporization of Aqueous Solutions of Benzyltrimethylammonium Chloride, Benzyltriethylammonium Chloride, and Benzyltributylammonium Chloride. *J. Chem. Eng. Data* **1998a**, *43*, 17−20.

Lee, L. S.; Lee, C. C. Vapor pressures and Enthalpies of Vaporization of Aqueous Solutions of Triethylammonium Chloride, 2-Hydroxyethylammonium Chloride, and Tris(hydroxymethyl)aminomethane Hydrochloride. *J. Chem. Eng. Data* **1998b**, *43*, 469−472.

Patil, K. R.; Tripathi, A. D.; Pathak, G.; Katti. S. S. Thermodynamic Properties of Aqueous Electrolyte Solutions. 1. Vapor Pressure of Aqueous Solutions of LiCl, LiBr, and LiI. *J. Chem. Eng. Data* **1990**, *35*, 166−168.

Sako, T.; Hakuta, T.; Yoshitome, H. Vapor Pressure of Binary and Ternary Aqueous Solutions. *J. Chem. Eng. Data* **1985**, *30*, 224−248.

Weng, H. S.; Wang, G. H. Tri-Liquid-Phase Transfer Catalysis. *J. Chin. Inst. Chem. Eng.* **1996**, *27*, 419−426.

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