J. Chem. Eng. Data **1998,** *43,* 17−20

Vapor Pressures and Enthalpies of Vaporization of Aqueous Solutions of Benzyltrimethylammonium Chloride, Benzyltriethylammonium Chloride, and Benzltributylammonium Chloride

Liang-sun Lee* and Chiou-chen Lee

Department of Chemical Engineering, National Central University, Chung-li, Taiwan 32054, Republic of China

In this study, the vapor pressures of aqueous solutions of three organic salts, benzyltrimethylammonium chloride, benzyltriethylammonium chloride, and benzyltributylammonium chloride, were measured from 298.15 K to 333.15 K, and the enthalpies of vaporization were estimated by the Clausius−Clayperon equation. The concentrations of salts ranged from 0.5 m (mol·1000 g solvent^{-1}) to saturation depending on the solubility of the salt.

Introduction

Organic salts are important chemicals used as surfactants, intermediate chemicals, reaction catalysts, prohibitors to undesired reactions, and supporting electrolytes in electrochemical processes. Recently, the application of organic salts as catalysts in phase-transfer catalytic reactions has drawn much attention. The advantages of this process include the mild reaction conditions of room temperature and atmospheric pressure and high reaction rate. The applications of phase-transfer catalytic reactions reported in the literature are: synthesis of alcoholic and esteric compounds, elimination reactions, reduction reactions, carboxylic reactions, and synthesis of organic metal complex. The phase-transfer catalysts usually used are quaternary ammonium salts and quaternary phosphonium salts. Due to the wide applications of organic salts, it is important to understand the thermodynamic behavior of their solutions. Since organic salts are weak electrolytes and partially dissociate into ions in solutions, the thermodynamic behavior of weak electrolyte solutions is more complicated than that of strong electrolyte solutions.

Very few studies have been reported on weak electrolyte solutions. In this study, the vapor pressures of benzyltrimethylammonium chloride, benzyltriethylammonium chloride, and benzyltributylammonium chloride solutions were measured experimentally and correlated by the Patil model. The enthalpies of vaporization of these solutions were determined by Clausius−Clapeyron equation.

Correlation Model

The complicated thermodynamic behavior of weak electrolyte solutions is attributed to the presence of undissociated salt molecules in addition to ions and solvent molecules in solution. In this study, the empirical correlation model of Patil et al. (1990), which was originally proposed to correlate the vapor pressures of the aqueous solutions of strong electrolytes, is used to correlate our vapor pressure data. The Patil model (1990) has the form

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

where P is the vapor pressure of the solution, T is the absolute temperature, and $A(m)$, $B(m)$, and $C(m)$ are polynomials of salt concentration in molality in the following form:

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

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

$$C(m) = C_0 + C_1 m + C_2 m^2 + C_3 m^3$$

Experimental Work

Apparatus. A simple, easy-to-operate, and reliable differential static glass apparatus was constructed for our measurements. With this apparatus, vapor pressures were measured by the pressure difference between a reference liquid and the aqueous organic salt solutions contained in separate vessels (250 cm^3 in volume) at the same temperature. This apparatus has the advantages of high accuracy even at very dilute concentration. The effect of temperature variations are minimal on the pressure reading since both vessels are kept at the same temperature. A disadvantage of this apparatus is that it is unsuitable for high vapor pressure mixtures. While experiments are being conducted, the apparatus must be checked with a level to keep horizontal, and no leakage is allowed. The accuracy of the pressure reading was 0.013 kPa. The pressure measurement medium was chosen to be *n*-butyl phthalate. It has the following advantages over mercury: (1) lower vapor pressure at the same temperature; (2) much lower density so that pressure readings were more sensitive to concentration and temperature changes; (3) not poisonous. The water bath temperature was controlled to within ±0.1 K. Temperatures were read with a quartz thermometer

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* To whom the correspondence should be addressed.

S0021-9568(97)00134-9 CCC: $15.00

Table 1. Vapor Pressures of LiCl + H_2O of Experimental and Literature at 303.15 K

m/mol·1000 g solvent^{-1}	$P_{\mathrm{exp}}^{\mathrm{sat}}$ /kPa	$P_{\mathrm{lit}}^{\mathrm{sat}}$ /kPa^{a}
0.000	4.2423	4.2423
3.010	3.6424	3.6797
4.999	3.1731	3.1891
5.998	2.8424	2.8891
7.856	2.3345	2.3398
10.168	1.7359	1.7199
12.693	1.2132	1.1999
ADD		0.0187

[a] Hala (1983).

Table 2. Vapor Pressures of Benzyltrimethylammonium Chloride Aqueous Solutions

m^{a}	P^{sat}/kPa	m^{a}	P^{sat}/kPa	m^{a}	P^{sat}/kPa
		T = 298.15 K			
0.000	3.17	2.494	2.96	5.494	2.70
0.101	3.12	2.994	2.89	5.994	2.63
0.601	3.07	3.493	2.87	6.493	2.59
0.995	3.05	3.993	2.81	6.993	2.53
1.495	3.03	4.493	2.78		
1.964	3.01	4.993	2.73		
		T = 303.15 K			
0.000	4.24	2.462	3.96	5.467	3.63
0.103	4.18	2.965	3.92	5.967	3.56
0.497	4.13	3.473	3.88	6.467	3.51
1.000	4.11	3.981	3.82	6.966	3.45
1.485	4.08	4.478	3.75		
1.979	4.01	4.979	3.69		
		T = 313.15 K			
0.000	7.38	2.494	6.85	5.495	6.22
1.000	7.28	2.995	6.76	5.994	6.04
0.496	7.25	3.494	6.61	6.494	5.95
0.996	7.17	3.993	6.57	6.994	5.78
1.495	7.05	4.495	6.46		
1.995	6.98	4.994	6.28		
		T = 323.15 K			
0.000	12.33	2.470	11.38	5.414	10.34
0.130	12.19	2.967	11.27	5.917	10.10
0.494	12.03	3.467	11.05	6.417	9.83
0.988	11.93	3.923	10.92	6.917	9.59
1.488	11.78	4.425	10.72		
1.984	11.59	4.921	10.54		
		T = 333.15 K			
0.000	19.92	2.502	18.23	5.504	16.20
0.103	19.54	3.003	17.97	6.005	15.80
0.503	19.39	3.503	17.69	6.505	15.36
1.002	19.12	4.005	17.37	7.006	14.95
1.503	18.85	4.506	16.99		
2.002	18.57	5.005	16.66		

[a] m is in units of mol·1000 g solvent^{-1}.

Table 3. Vapor Pressures of Benzyltriethylammonium Chloride Aqueous Solutions

m^{a}	P^{sat}/kPa	m^{a}	P^{sat}/kPa	m^{a}	P^{sat}/kPa
		T = 298.15 K			
0.000	3.17	1.999	2.99	4.496	2.68
0.102	3.12	2.498	2.88	4.996	2.62
0.500	3.11	2.998	2.83	5.452	2.52
0.999	3.06	3.487	2.79	5.995	2.47
1.500	3.03	3.995	2.73		
		T = 303.15 K			
0.000	4.24	2.005	4.00	4.503	3.52
0.099	4.18	2.504	3.93	5.004	3.38
0.500	4.14	3.004	3.85	5.504	3.23
1.003	4.11	3.503	3.77	6.005	3.00
1.503	4.08	4.003	3.64		
		T = 313.15 K			
0.000	7.38	2.003	6.96	4.505	6.32
0.101	7.30	2.504	6.79	5.005	6.17
0.501	7.24	3.004	6.72	5.505	5.86
0.999	7.13	3.504	6.58	6.001	5.70
1.499	7.04	4.004	6.43		
		T = 323.15 K			
0.000	12.33	1.999	11.61	4.500	10.92
0.100	12.19	2.498	11.51	5.001	10.77
0.501	12.13	2.998	11.37	5.501	10.63
1.002	11.96	3.496	11.22	6.000	10.44
1.500	11.84	4.001	11.06		
		T = 333.15 K			
0.000	19.92	2.000	18.84	4.503	17.38
0.100	19.60	2.502	18.60	5.000	17.11
0.499	19.45	3.000	18.23	5.500	16.92
1.000	19.38	3.501	17.92	6.008	16.72
1.499	19.03	4.001	17.65		

[a] m is in unit of mol·1000 g solvent^{-1}.

Table 4. Vapor Pressures of Benzyltributylammonium Chloride Aqueous Solutions

m^{a}	P^{sat}/kPa	m^{a}	P^{sat}/kPa	m^{a}	P^{sat}/kPa
		T = 298.15 K			
0.000	3.17	2.006	3.03	4.511	2.78
0.100	3.14	2.422	2.98	5.006	2.75
0.501	3.12	3.004	2.95	5.509	2.72
1.000	3.09	3.501	2.91	6.010	2.67
1.502	3.08	4.003	2.83		
		T = 303.15 K			
0.000	4.24	2.000	4.01	4.484	3.75
0.099	4.19	2.498	3.95	4.982	3.73
0.503	4.15	2.994	3.87	5.480	3.69
1.067	4.10	3.494	3.81	5.974	3.61
1.502	4.08	3.990	3.77		
		T = 313.15 K			
0.000	7.38	2.002	6.98	4.505	6.56
0.104	7.28	2.499	6.86	5.006	6.45
0.503	7.22	3.001	6.73	5.506	6.32
1.003	7.14	3.503	6.70	6.002	6.17
1.503	7.10	4.004	6.65		
		T = 323.15 K			
0.000	12.33	2.001	11.65	4.502	10.91
0.100	12.13	2.501	11.52	5.003	10.78
0.502	12.03	3.002	11.36	5.503	10.56
1.003	11.86	3.502	11.29	6.002	10.09
1.502	11.73	4.003	11.06		
		T = 333.15 K			
0.000	19.92	1.985	18.83	4.481	17.56
0.099	19.57	2.486	18.56	4.976	17.16
0.500	19.43	2.987	18.30	5.474	16.66
0.993	19.29	3.487	18.14	5.975	16.33
1.486	19.03	3.986	17.87		

[a] m is in units of mol·1000 g solvent^{-1}.

(Hart Scientific Microthermo, Model 1502) with accuracy of ±0.02 K. One of the vessels was filled with a mixture of salt and solvent (water) prepared by mass, and the another vessel was filled with *n*-butyl phthalate. The air was then pumped out of the system to expel dissolved gas. Then the whole apparatus was immersed into a thermostat for more than 30 min to reach thermal equilibrium. The pressure difference between two vessels was recorded. The vessel containing the aqueous weak salt solution was separated from the apparatus, and its mass was determined again to obtain the concentration of the solution.

This apparatus was tested by making measurements on the vapor pressures of lithium chloride aqueous solutions of seven concentrations at a temperature of 303.15 K as given in Table 1. The average absolute deviations (AAD) of the experimental data sets were 0.018 kPa compared to the experimental values of Hala (1983). This experimental test showed that the present apparatus and operations would provide reliable experimental data.

Table 5. Correlation Parameters of the Model of Patil et al. (Eq 2)[a]

	BTMAC	BTEAC	BTBAC
A_0	6.093 679	6.087 867	6.595 536
A_1	0.297 622	2.159 088	2.454 802
A_2	−0.011 390	−1.213 621	−0.984 915
A_3	0.006 221	0.166 756	0.092 163
B_0	−1001.355	−1001.950	−1323.715
B_1	−207.35 07	−1354.871	−1576.329
B_2	74.464 03	759.547 4	634.490 8
B_3	−4.349 036	−103.856 6	−60.003 28
C_0	−199 240.9	−198 398.7	−147 513.5
C_1	34 759.70	211 305.6	251 567.6
C_2	−12 171.83	−118 709.6	−101 943.2
C_3	746.9925	16 133.89	9 729.252

[a] BTMAC, benzyltrimethylammonium chloride; BTEAC, benzltriethylammonium chloride; BTBAC, benzyltributylammonium chloride.

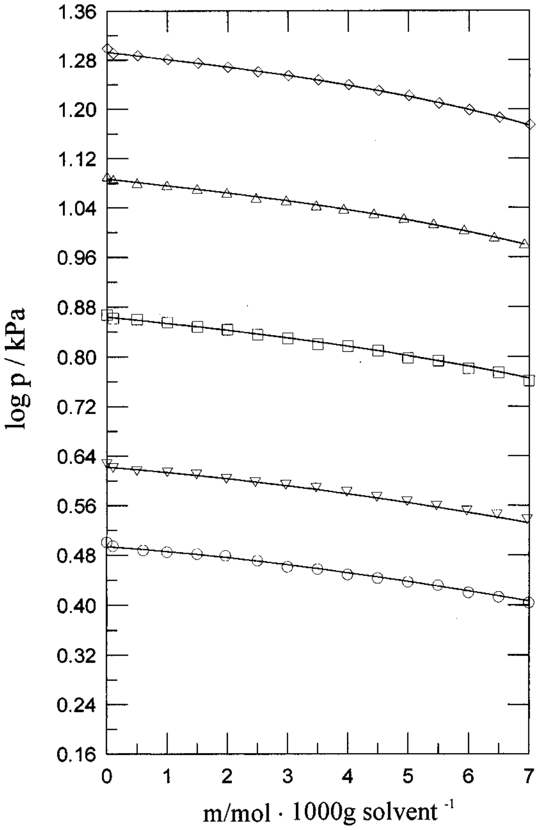

Figure 1. Vapor pressures of benzyltrimethylammonium chloride aqueous solutions: ○, 298.15 K; ▽, 303.15 K; □, 313.15 K; △, 323.15 K; ◇, 333.15 K; —, Patil et al. model.

Experimental Materials

Benzyltrimethylammonium chloride, benzyltriethylammonium chloride, and benzyltributylammonium chloride purchased from Merck Co. were analytical reagent grade with a purity of +99%. The organic salts were dried in a vacuum oven at 353 K for more than 48 h to purge dissolved gases and moisture. The aqueous solutions were prepared by the deionized and degassed distilled water with electric resistance less than 18.2 MΩ·cm^{-1}.

Experimental Results and Discussion

The vapor pressures of the aqueous solutions of three organic salts were measured at 298.15 K, 303.15 K, 313.15 K, 323.15 K, and 333.15 K. For each temperature, 14 or 16 vapor pressure measurements of different concentrations, dependent on the solubilities of salts, were conducted. The concentrations of organic salts range from 0.5 m (mol·1000 g solvent^{-1}) to saturation. All the experimental results are given in Tables 2−4.

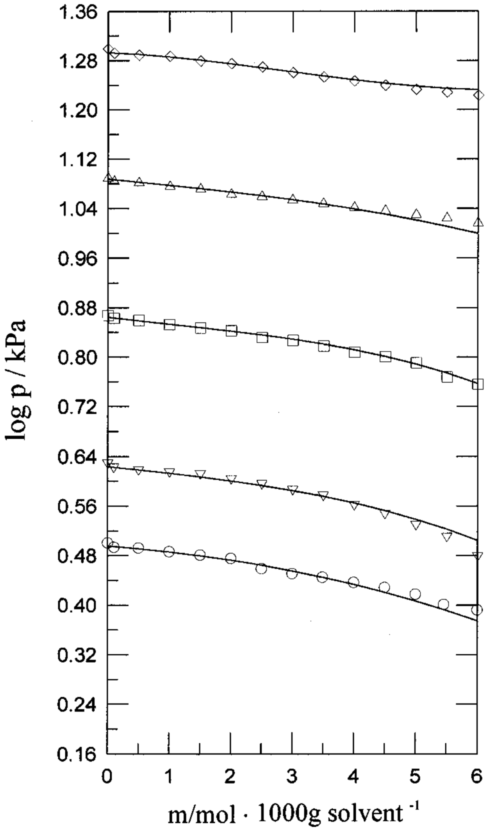

Figure 2. Vapor pressures of benzyltriethylammonium chloride aqueous solutions: ○, 298.15 K; ▽, 303.15 K; □, 313.15 K; △, 323.15 K; ◇, 333.15 K; —, Patil et al. model.

The model of Patil et al. (1990) was employed to fit our experimental data by a nonweighted least-squares fitting method. The degree of polynomials for concentration parameters in the model was the optimum value after several trials. The correlation parameters are given in Table 5. The average absolute deviations (AAD) of the correlations for benzyltrimethylammonium chloride, benzyltriethylammonium chloride, and benzyltributylammonium chloride aqueous solutions are 0.03 kPa, 0.04 kPa, and 0.03 kPa, respectively.

For benzyltrimethylammonium chloride aqueous solution, the experimental results and the values calculated by Patil's model are plotted in Figure 1. The vapor pressures for benzyltriethylammonium chloride and benzyltributylammonium chloride aqueous solutions are plotted in Figures 2 and 3, respectively. These figures include vapor pressures of five different temperatures; thus, the vertical axis is divided into five vapor pressure intervals. All the figures show that these three organic salts exhibit very similar change of vapor pressure with salt concentration.

Calculations of Enthalpies of Vaporization

The Clausius−Clapeyron equation is a general equation originally relating vapor pressure, temperature, volume change, and enthalpy of vaporization of a pure liquid. If the enthalpy of vaporization of a liquid is independent of

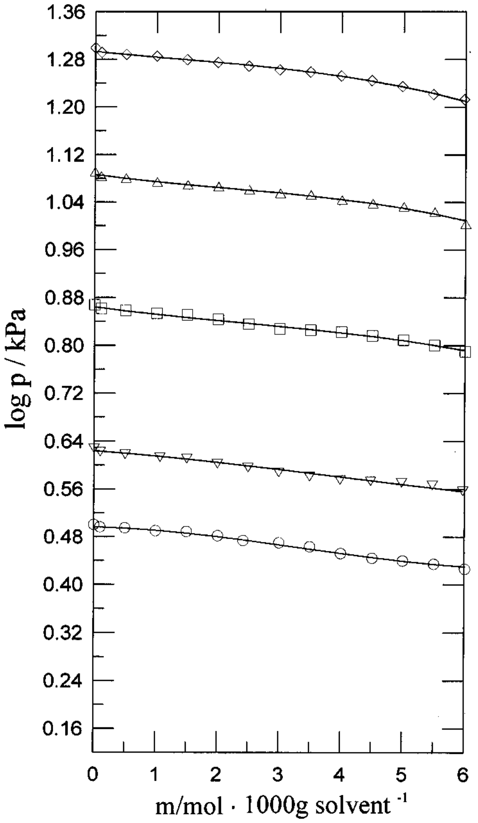

Figure 3. Vapor pressures of benzyltributylammonium chloride aqueous solutions: ○, 298.15 K; ▽, 303.15 K; □, 313.15 K; △, 323.15 K; ◇, 333.15 K; —, Patil et al. model.

temperature and the volume of the liquid is much smaller than that of the gas, then the Clausius–Clapeyron equation becomes

$$\log P = \frac{-\Delta_{\mathrm{vap}}H}{2.303RT} + c \tag{3}$$

where p is the vapor pressure, $\Delta_{\mathrm{vap}}H$ is the enthalpy of vaporization, T is the absolute temperature, and R is the gas constant. The linear relationship between log P and $1/T$ shows that the enthalpies of vaporization of these aqueous solution are temperature independent over the temperature range studied. The estimated values of the enthalpies of vaporization detrmined from the slope for the solutions studied are given in Table 6.

Table 6. Enthalpies of Vaporization of Organic Salt Aqueous Solutions[a]

	$\Delta_{\mathrm{vap}}H$/kJ·mol^{-1}		
m/mol·kg solvent^{-1}	BTMAC	BTEAC	BTBAC
0.0	43.40	43.40	43.40
1.0	43.28	43.52	43.22
2.0	43.00	43.42	43.20
3.0	43.03	44.00	43.26
4.0	42.88	44.31	43.56
5.0	42.65	45.05	43.17
6.0	42.29	45.62	42.51
7.0	41.78		

[a] BTMAC, benzyltrimethylammonium chloride; BTEAC, benzyltriethylammonium chloride; BTBAC, benzyltributylammonium chloride.

Conclusion

In this study, the vapor pressures of aqueous solutions of three organic salts at different temperatures were measured by a differential static apparatus. The experimental data were correlated with the empirical model of Patil et al. (1990).

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Received for review May 27, 1997. Accepted September 18, 1997.⊗

JE9701341

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1997.