

Vapor Pressures and Enthalpies of Vaporization of Aqueous Solutions of Triethylammonium Chloride, 2-Hydroxyethylammonium Chloride, and Tris(hydroxymethyl)aminomethane Hydrochloride

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The vapor pressures of the aqueous solutions of three organic salts, triethylammonium chloride, 2-hydroxyethylammonium chloride, and tris(hydroxymethyl)aminomethane hydrochloride were measured from 298.15 K to 333.15 K and regressed by the Patil et al. model. The vapor pressure data were used to calculate enthalpies of vaporization by the Clausius–Clayperon equation. The concentration of salt is from 0.5 mol·kg⁻¹ to saturation depending on the solubility of that salt. The vapor pressures of the present aqueous solutions are not much different from those of three organic salts in our previous study.

Introduction

Organic salts are important in the chemical industry. They are used as intermediate chemicals, reaction catalysts, surfactants, inhibitors to undesired reaction, and supporting electrolytes in electrochemical processes. Recently, organic salt used as catalyst in phase-transfer catalytic reaction has been widely discussed, e.g., Wang and Weng (1995, 1996), Starks et al. (1994). The advantages of this reaction system include the mild reaction conditions at room temperature and atmospheric pressure and high reaction extent. The phase-transfer catalysts usually used are quaternary salts, such as quaternary ammonium salts and quaternary phosphonium salts, and macrocyclic ethers. It is important to understand the thermodynamic behavior of organic salt solutions for their application in chemical industry. The thermodynamic behavior of weak electrolyte solutions is more complicated than that of strong electrolytes since organic salts are weak and partially dissociate into ions in solutions in which exist ions, solvent molecules, and organic salt molecules.

In the previous paper (Lee and Lee, 1998), we reported the vapor pressures and enthalpies of vaporization of the structurally similar organic salts, benzyltrimethylammonium chloride, benzyltriethylammonium chloride, and benzyltributylammonium chloride. In this study the vapor pressures of triethylammonium chloride, 2-hydroxyethylammonium chloride, and tris(hydroxymethyl)aminomethane hydrochloride were measured. These three organic salts have different molecular structure, physical properties, and solubilities in water.

The experimental data of vapor pressures are regressed by the Patil et al. model (1990). The enthalpies of vaporization of these solutions were estimated from the vapor pressure data by the Clausius–Clapeyron equation.

Correlation Model

The presence of ions, solvent molecules, and undissociated salt molecules complicates the thermodynamic behavior of weak electrolyte solutions. To theoretically correlate

Table 1. Vapor Pressures of LiCl + H₂O at 333.15 K

<i>m</i> /mol·Kg ⁻¹	<i>P</i> _{exp} ^{sat} /kPa	<i>P</i> _{exp} ^{sat} /kPa ^a
0.000	19.9157	19.9157
0.885	19.2491	19.2891
1.605	18.6891	18.7211
2.187	18.2492	18.2025
2.628	17.8092	17.7800
3.144	17.2226	17.2506
3.418	16.9826	17.0386
4.108	16.1827	16.1747
4.507	15.6494	15.7054
4.952	15.1827	15.1454
ADD ^b		0.0333

^a Hala (1983). ^b ADD = $\sum_{i=1}^N |P_{exp}^{sat} - P_{lit}^{sat}|/N$.

the experimental data of weak electrolyte solutions is not an easy task since the dissociation constant of a weak salt in solvent is difficult to determine. So far, we have not succeeded in the development of such model. In this study, the empirical correlation model of Patil et al. (1990), which was originally proposed to correlate the vapor pressures of aqueous solutions of strong electrolytes, is applied to correlate our experimental data. The Patil et al. model was adopted after the correlation results were compared with those of the model of Sako et al. (1985). The Patil et al. model has the form

$$\log P/\text{kPa} = A(m) + \frac{B(m)}{TK} + \frac{C(m)}{(TK)^2} \quad (1)$$

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

$$\begin{aligned} A(m) &= A_0 + A_1m + A_2m^2 + A_3m^3 \\ B(m) &= B_0 + B_1m + B_2m^2 + B_3m^3 \\ C(m) &= C_0 + C_1m + C_2m^2 + C_3m^3 \end{aligned} \quad (2)$$

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Table 2. Vapor Pressures of Triethylammonium Chloride Aqueous Solutions

$m/\text{mol}\cdot\text{kg}^{-1}$	$P^{\text{sat}}/\text{kPa}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$P^{\text{sat}}/\text{kPa}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$P^{\text{sat}}/\text{kPa}$
$T=298.15\text{ K}$					
0.000	3.17	2.512	3.02	5.512	2.76
0.102	3.14	3.012	2.98	6.004	2.73
0.504	3.11	3.512	2.87	6.051	2.68
1.005	3.10	4.012	2.86	7.010	2.65
1.504	3.08	4.511	2.82		
2.006	3.07	5.012	2.81		
$T=303.15\text{ K}$					
0.000	4.24	2.511	3.93	5.513	3.52
0.102	4.18	3.012	3.88	6.011	3.47
0.502	4.16	3.511	3.84	6.511	3.42
1.001	4.09	4.010	3.80	7.013	3.37
1.506	4.04	4.509	3.64		
2.010	3.97	5.011	3.62		
$T=313.15\text{ K}$					
0.000	7.38	2.504	6.69	5.491	5.84
0.103	7.27	3.004	6.56	5.994	5.75
0.504	7.17	3.503	6.42	6.492	5.62
1.008	7.07	3.997	6.31	6.990	5.40
1.504	6.96	4.497	6.15		
2.001	6.86	4.994	6.03		
$T=323.15\text{ K}$					
0.000	12.33	2.496	11.04	5.494	9.72
0.103	12.11	2.996	10.83	5.997	9.46
0.502	11.88	3.489	10.69	6.502	9.20
1.064	11.74	3.994	10.40	7.010	8.93
1.501	11.54	4.494	10.21		
1.997	11.31	4.992	9.97		
$T=333.15\text{ K}$					
0.000	19.92	2.499	18.16	5.155	16.37
0.102	19.62	2.999	17.88	6.018	16.04
0.504	19.48	3.503	17.72	6.518	15.71
1.006	19.21	4.006	17.38	7.023	15.44
1.508	18.88	4.512	17.01		
2.015	18.59	5.015	16.74		

Experimental Work

Apparatus. The apparatus, a differential static glass apparatus, has been described in detail by Lee and Lee (1998). The vapor pressures are measured by the pressure difference between a reference liquid and the aqueous electrolyte solutions contained in two separate vessels at the same temperature. All the connections of this apparatus have been so tightly sealed that no leakage was detected by vacuum test before each experimental run. The accuracy of pressure reading is 0.013 kPa. *N*-butylphthalate is chosen as reference liquid since it has more advantages over mercury. The measured temperature was controlled within $\pm 0.1\text{ K}$. Temperatures were read with a quartz thermometer with an accuracy of $\pm 0.02\text{ K}$. For experiments, one of vessel was fed with mixture of accurately weighed salt and water and another was fed with *n*-butylphthalate, and air was pumped out of the system to expel dissolved gases. 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.

The reliability of this apparatus had been tested by the measurements of seven vapor pressures of lithium chloride aqueous solutions at 333.15 K as given in Table 1. The average absolute deviation of the experimental data set was 0.03 kPa compared to the experimental values of Hala (1983).

Experimental Materials. Triethylammonium chloride, 2-hydroxyethylammonium chloride, and tris(hydroxymethyl)aminomethane hydrochloride from Merck Co. were

Table 3. Vapor Pressures of 2-Hydroxyethylammonium Chloride Aqueous Solutions

$m/\text{mol}\cdot\text{kg}^{-1}$	$P^{\text{sat}}/\text{kPa}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$P^{\text{sat}}/\text{kPa}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$P^{\text{sat}}/\text{kPa}$
$T=298.15\text{ K}$					
0.000	3.17	3.491	2.86	7.501	2.64
0.097	3.12	3.999	2.77	7.994	2.61
0.501	3.11	4.497	2.75	8.494	2.57
1.005	3.08	4.993	2.73	8.994	2.54
1.494	3.07	5.493	2.71	9.494	2.51
1.990	3.01	5.996	2.70	9.994	2.46
2.488	2.96	6.496	2.68		
2.994	2.95	7.003	2.66		
$T=303.15\text{ K}$					
0.000	4.24	3.495	3.79	7.495	3.28
0.100	4.14	3.997	3.75	7.995	3.21
0.501	4.10	4.495	3.69	8.493	3.14
0.999	4.05	4.995	3.60	8.996	3.06
1.499	4.00	5.498	3.55	9.495	3.01
1.996	3.93	5.998	3.49	9.994	2.92
2.495	3.88	6.495	3.41		
2.995	3.81	6.994	3.35		
$T=313.15\text{ K}$					
0.000	7.38	3.502	6.44	7.509	5.31
0.101	7.22	4.003	6.33	8.010	5.16
0.502	7.11	4.504	6.19	8.511	5.05
1.001	7.03	5.006	6.07	9.011	5.00
1.502	6.94	5.508	5.90	9.513	4.93
2.001	6.79	6.009	5.72	10.014	4.80
2.501	6.66	6.507	5.59		
3.002	6.51	7.007	5.52		
$T=323.15\text{ K}$					
0.000	12.33	3.508	10.55	7.502	8.70
0.101	12.13	4.008	10.42	8.038	8.58
0.502	11.90	4.504	10.12	8.504	8.26
1.005	11.67	5.003	9.84	9.003	8.13
1.507	11.44	5.503	9.61	9.503	7.86
2.009	11.13	6.001	9.46	10.002	7.68
2.508	11.06	6.501	9.14		
3.007	10.84	7.002	8.95		
$T=333.15\text{ K}$					
0.000	19.92	3.515	17.24	7.463	14.32
0.097	19.57	4.010	16.93	7.993	13.78
0.504	19.33	4.507	16.62	8.493	13.20
1.008	18.90	5.000	16.12	8.993	12.68
1.513	18.66	5.499	15.86	9.499	12.10
2.015	18.15	6.003	15.50	9.993	11.56
2.513	18.04	6.493	15.07		
3.017	17.63	6.993	14.74		

analytical reagent grade with a purity of +99%. They 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 using deionized and degassed distilled water with electric resistance less than $18.2\text{ M}\Omega\cdot\text{cm}^{-1}$.

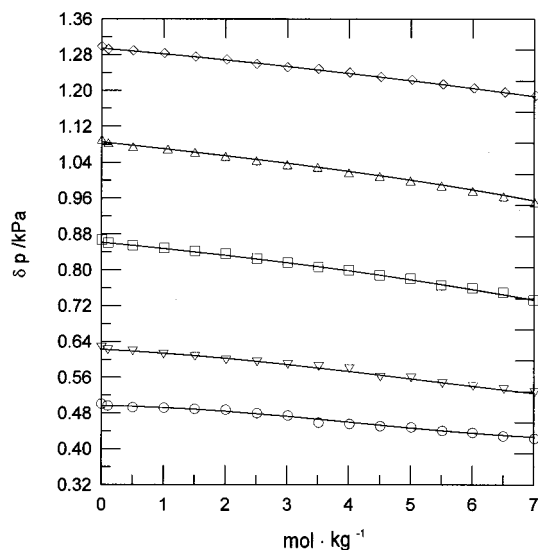
Experimental Results and Discussion

In the present study, the vapor pressures of aqueous solutions of triethylammonium chloride, 2-hydroxyethylammonium chloride, and tris(hydroxymethyl)aminomethane hydrochloride were measured at 298.15 K, 303.15 K, 313.15 K, 323.15 K, and 333.15 K. The concentration of solutions of each organic salt ranged from $0.5\text{ mol}\cdot\text{kg}^{-1}$ to the saturated solubility of that salt in water. Thus, very extensive experimental data have been collected and given in Table 2 to Table 4.

To correlate the experimental data, the model of Patil et al. (1990) was applied along with a nonweighted least-squares fitting method. The degree of polynomials of the concentration parameters of model was empirically determined to be the optimum value. Table 5 gives all the correlation parameters of model. The correlation for triethylammonium chloride aqueous solution has an average

Table 4. Vapor Pressures of Tris(hydroxymethyl)-aminomethane Hydrochloride Aqueous Solutions

$m/\text{mol}\cdot\text{kg}^{-1}$	$P^{\text{sat}}/\text{kPa}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$P^{\text{sat}}/\text{kPa}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$P^{\text{sat}}/\text{kPa}$
$T = 298.15 \text{ K}$					
0.000	3.17	1.999	2.94	4.501	2.68
0.101	3.14	2.499	2.90	5.001	2.60
0.501	3.10	3.000	2.85	5.501	2.55
0.998	3.07	3.501	2.80	6.000	2.52
1.499	3.00	4.001	2.72		
$T = 303.15 \text{ K}$					
0.000	4.24	2.007	3.92	4.507	3.54
0.101	4.18	2.507	3.86	5.007	3.51
0.506	4.13	3.007	3.77	5.507	3.41
1.006	4.07	3.507	3.69	6.008	3.35
1.507	4.03	4.007	3.65		
$T = 313.15$					
0.000	7.38	2.002	6.81	4.503	6.15
0.010	7.24	2.502	6.62	5.003	6.02
0.501	7.13	3.003	6.48	5.503	5.96
1.003	6.97	3.504	6.39	6.002	5.85
1.503	6.68	4.004	6.30		
$T = 323.15 \text{ K}$					
0.000	12.33	2.011	11.13	4.521	10.31
0.104	12.12	2.525	10.91	5.033	10.11
0.500	12.01	2.996	10.77	5.471	9.98
1.001	11.70	3.519	10.69	6.004	9.86
1.505	11.36		10.52		
$T = 333.15 \text{ K}$					
0.000	19.92	2.002	18.36	4.506	17.03
0.101	19.56	2.054	17.94	5.009	16.71
0.500	19.24	3.004	17.80	5.509	16.38
1.032	18.69	3.504	17.49	6.011	15.68
1.506	18.67	4.004	17.30		

**Figure 1.** Vapor pressures of triethylammonium chloride aqueous solutions: \circ , 298.15 K; ∇ , 303.15 K; \square , 315.15 K; \triangle , 323.15 K; \diamond , 333.15 K; —, Patil model.

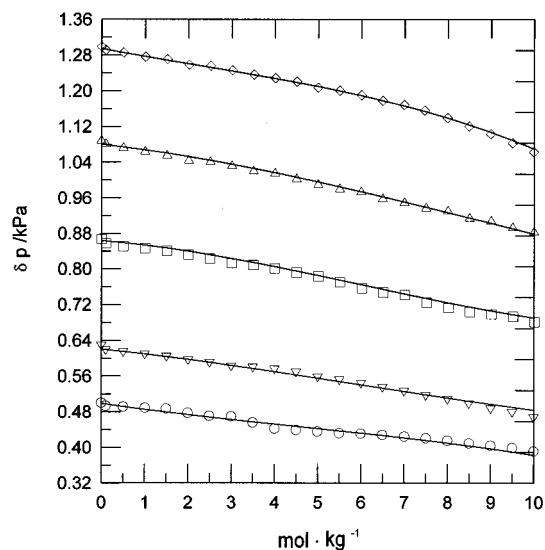
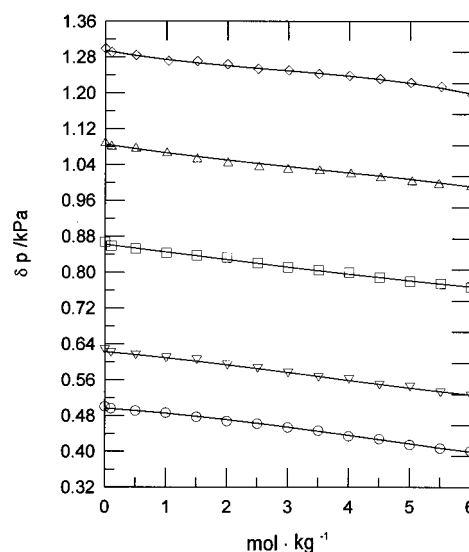
absolute deviation (AAD) of 0.04 kPa. For 2-hydroxyethylammonium chloride and tris(hydroxyethyl)aminomethane hydrochloride aqueous solutions, the AADs are 0.06 kPa and 0.04 kPa, respectively.

For triethylammonium chloride aqueous solution the experimental data and the calculated values by the Patil et al. model are plotted in Figure 1. This figure includes vapor pressures of five different temperatures; thus, the vertical axis is divided into five vapor pressure intervals. The vapor pressure vs temperature for 2-hydroxyethylammonium chloride aqueous solutions are plotted in Figure 2, and those of tris(hydroxyethyl)aminomethane hydrochloride aqueous solutions are plotted in Figure 3. All the

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

	TEAC	2-HEAC	TRIS
A_0	7.628170	10.14146	7.641816
A_1	2.183007	-2.783560	-0.049352
A_2	-0.395661	1.012594	0.504063
A_3	0.050547	-0.072459	-0.087266
B_0	-1970.019	-3562.851	-1979.180
B_1	-1414.311	1734.523	-23.33847
B_2	255.8520	-638.4133	-297.5799
B_3	-32.51897	45.46873	52.90124
C_0	-46635.77	205109.1	-45050.00
C_1	227524.1	-270944.7	10505.07
C_2	-41375.43	100403.8	43740.80
C_3	5223.995	-7120.746	-8002.961

^a TEAC, triethylammonium chloride; 2-HEAC, 2-hydroxyethylammonium chloride; TRIS, tris(hydroxymethyl)aminomethane hydrochloride.

**Figure 2.** Vapor pressures of 2-hydroxyethylammonium chloride aqueous solutions: \circ , 298.15 K; ∇ , 303.15 K; \square , 315.15 K; \triangle , 323.15 K; \diamond , 333.15 K; —, Patil model.**Figure 3.** Vapor pressures of tris(hydroxymethyl)aminomethane chloride aqueous solutions: \circ , 298.15 K; ∇ , 303.15 K; \square , 315.15 K; \triangle , 323.15 K; \diamond , 333.15 K; —, Patil model.

figures show that these three organic salts exhibit very similar behavior of vapor pressure at various concentrations.

Table 6. Enthalpies of Vaporization of Organic Salt Aqueous Solutions^a

<i>m</i> /mol·kg ⁻¹	$\Delta_{\text{vap}}H/\text{kJ}\cdot\text{mol}^{-1}$		
	TEAC	2-HEAC	TRIS
0.0	43.40	43.40	43.40
1.0	43.00	43.20	43.10
2.0	42.77	42.78	43.19
3.0	42.52	42.33	43.29
4.0	42.26	41.85	43.39
5.0	41.97	41.33	43.50
6.0	41.67	40.78	43.62
7.0	41.35	40.18	43.75
8.0		39.52	
9.0		38.81	

^a TEAC, triethylammonium chloride; 2-HEAC, 2-hydroxyethylammonium chloride; TRIS, tris(hydroxymethyl)aminomethane hydrochloride.

Calculations of Enthalpies of Vaporization

The Clausius–Claperon equation describes the thermodynamic property changes of enthalpy and volume of a pure liquid attributed to phase change. For a phase change from liquid to vapor, the Clausius–Claperon equation can be simplified as eq. 3 if the volume of liquid is much smaller than that of vapor and the enthalpy of vaporization is independent of temperature.

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

where P is the vapor pressure at temperature T , $\Delta_{\text{vap}}H$ is the enthalpy of vaporization, and R is the universal gas constant. This equation can be applied to the mixtures of present study. From our experimental data, we can construct diagrams showing the linear slope of $\log P$ vs $1/T$ drawings and determining the enthalpies of vaporization. All these diagrams are not shown here since all the experimental information is given in the tables and figures. The estimated values of enthalpies of vaporization of present weak salt solutions are given in Table 6.

Conclusion

The vapor pressures of aqueous solutions of triethylammonium chloride, 2-hydroxyethylammonium chloride, and

tris(hydroxymethyl)aminomethane hydrochloride at different temperatures were measured by a differential static apparatus. The experimental data were correlated with the empirical model of Patil et al. (1990). The enthalpies of vaporization of three organic salts at different concentrations were calculated using the Clausius–Clayperon equation.

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