Vapor Pressures of Aqueous Solutions with Mixed Salts of NaCl + KBr and NaBr + KCl

Hsiu-ling Hsu, Yi-chou Wu, and Liang-sun Lee*

Department of Chemical and Material Engineering, National Central University, Chungli 32054, Taiwan

---

The vapor pressures of aqueous NaCl + KBr and NaBr + KCl solutions were measured in the temperature range from 303.15 to 333.15 K and the electrolyte concentration range from 1 to 4 m. The experimental data showed that vapor pressures of these two aqueous mixed electrolyte solutions increase with increasing temperatures and almost linearly decrease with increasing concentrations of electrolyte. The experimental data also showed that, since these two aqueous mixed electrolyte solutions contain the same ions, an identical vapor pressure was observed at the same temperature and electrolyte concentration. This observation is consistent with the well understood fact that the particle interactions are identical in these solutions because the strong electrolytes are completely ionized in solution and have the same effect on the thermodynamic properties of water. The vapor pressures of these solutions were also estimated with the model of two-ionic-parameters for ion activity coefficient estimations proposed by Lin and Lee. The average absolute deviation (AAD) and the average absolute relative deviation (AARD) of NaCl + KBr aqueous solution are 0.05 kPa and 0.41%, respectively, and those of NaBr + KCl aqueous solution are 0.05 kPa and 0.40%, respectively.

Introduction

Electrolyte solutions are encountered commonly in many chemical processes. For instance, the salt-in and salt-out effects in electrolyte solutions have been applied to separate close-boiling mixtures. Electrolyte solutions are also found in reaction processes, in bioengineering processes, in environmental engineering, in the battery industry, and elsewhere.

The thermodynamic properties of aqueous electrolyte solutions are different from those of nonelectrolyte solutions, since the electrolytes in aqueous solutions will dissociate into cations and anions. The particle interactions, including ion−ion, ion−molecule, and molecule-molecule interactions, are more complicated than those in a nonelectrolyte solution in which only molecule−molecule interactions are involved. The vapor pressure of a solution is an important thermodynamic property that can be measured experimentally. For instance, the nonideality of an aqueous solution may be qualitatively shown by the deviation of the vapor pressure of that solution from that of pure water at the same temperature.

In this study, the vapor pressures of the aqueous mixed electrolyte, NaCl + KBr and NaBr + KCl, solutions were measured. In the literature, the vapor pressures of the aqueous mixed electrolyte solutions could be found; for instance, Shiah and Tseng[2] reported those of solutions containing the NaCl + KCl and NaBr + KBr electrolytes and Iyokl et al.[3] reported those of the solution containing LiBr + LiI. The above solutions contained the electrolytes with a common ion. In 1968, Covington et al.[4] reported vapor pressures of the aqueous solutions of NaCl + KBr and NaBr + KCl mixed electrolytes at 298.15 K. In this work, an effort was made to provide more experimental vapor pressures for the above aqueous solutions at different temperatures and electrolyte concentrations. One would have thought that the vapor pressures of the aqueous solutions of these mixed electrolytes should be identical at the same temperature and electrolyte concentration, since the constituent salts are strong electrolytes and will dissociate completely into ions and all particle interactions are identical in solutions. The present experimental data are indeed consistent with this recognized behavior of these aqueous mixed electrolyte solutions.

In this study, the vapor pressures of the aqueous mixed electrolyte solutions were also estimated with a two-ionic-parameter model for ion activity coefficients proposed by Lin and Lee.[1] The estimated results were also listed along with the experimental data and given in the tables and figures for comparison.

Experimental Work

Apparatus. The apparatus used to measure the vapor pressures of the present aqueous mixed electrolyte solutions is a differential static type consisting of two glass vessels. It is the same as the one used for our previous study[5] and will be briefly described here. The vapor pressure of a solution was determined by the pressure difference between a reference liquid and the solution contained separately in two vessels. The whole apparatus was immersed in a tall thermostat with temperature control such that two vessels were maintained at the same temperature with an uncertainty of ±0.1 K. A vacuum test was conducted before each experimental run to find any leakage that could affect the pressure measurements. The temperature was read with a quartz thermometer with an uncertainty of ±0.02 K. The pressure reading has an uncertainty of 0.013 kPa. *N*-Butylphthalate was chosen as the reference liquid, since it has the advantages of being nonhazardous and having a lower vapor pressure than mercury.

During an experiment, one vessel was fed with the mixed aqueous electrolyte solution of the designated composition of equal molarity of each electrolyte and the other vessel was filled with *n*-butylphthalate. The whole apparatus was

---

* Corresponding author. Fax: 886-3-425-2296. E-mail: t3100206@ncu.edu.tw.

10.1021/je020144o CCC: $25.00 © 2003 American Chemical Society
Published on Web 03/11/2003

Table 1. Experimental and Published Vapor Pressures of a LiCl + H_2O Mixture at 303.15 K

m/mol·kg^{-1} of H_2O	P^{sat}_{exp}/kPa	P^{sat}_{exp}/kPa
0.000	4.2423	4.2423
3.010	3.6530	3.6797
5.001	3.1730	3.1760
5.998	2.8423	2.8891
AAD[a]		0.0191

[a] AAD = $\sum_i |P_i^{exp} - P_i^{lit.}|$/number of data.

immersed in a thermostat. Any dissolved gases were expelled with air out of the system by vacuum pumping. It was observed that more than 30 min was required to reach thermal equilibrium. The pressure difference between the two vessels was recorded, and the vapor pressure was then calculated.

The vapor pressures of different concentrations of lithium chloride aqueous solution at 303.15 K have been measured to validate the reliability of the experimental apparatus and the skill with which it was used. The experimental measurements and Hala's data[6] are given in Table 1. The AAD between these two sets of data is 0.0191 kPa.

Chemicals. The chemicals, sodium chloride, sodium bromide, potassium chloride, and potassium bromide, were analytical grade reagent with a purity of +99% and purchased from Merck. Before the experiments, the chemicals were dried in an oven at 353 K for more than 48 h to expel any dissolved gases and moisture. The deionized water used to prepare all solutions was generated from a Millipore water generator with an electric resistivity less than 18.2 MΩ·cm^{-1}.

Experimental Results

In the present study, the vapor pressures of the aqueous solutions of NaCl + KBr and NaBr + KCl were measured from (303.15 to 333.15) K with a 5 K interval and at the designated concentrations of (1, 2, 3, and 4) m. All the experimental data are given in Table 2. The temperature dependence of the vapor pressures of the aqueous NaCl + KBr and NaBr + KCl solutions is also depicted in Figures 1 and 2, respectively. These figures showed that the vapor pressure increases rapidly with increasing temperature. The concentration dependence of the vapor pressure of the aqueous NaCl + KBr and NaBr + KCl solutions is given in Figures 3 and 4, which show that the vapor pressure almost linearly decreases with the increasing concentration of electrolyte. It is obvious that, at the same temperature and concentration, the aqueous solutions of two mixed electrolytes, NaCl + KBr and NaBr + KCl, exhibit an identical vapor pressure. This observation is well understood, since both salts are strong electrolytes and will completely dissociate in solution and thus the particle interaction effect is identical.

Estimation of Vapor Pressure

Most of the published correlation models for the vapor pressures of the aqueous electrolyte solutions emphasize solutions that contain only one electrolyte, for example, the model of Patil et al.,[7] the modified Antoine equation of Sacchetto et al.,[8] and that of Sako et al.[9] Other researchers have proposed models for solutions that contain mixed electrolytes with a common ion, such as Shiah and Tseng[2] and Iyoki et al.[3] However, none of the above models has been applied to mixed electrolyte solutions.

A model, based on consideration of the activity coefficient of each individual ion existing in an electrolyte solution, was proposed by Lin and Lee[1] and was adopted here to estimate the vapor pressures. The derivation for the vapor pressure of an aqueous electrolyte solution and the activity of water required for vapor pressure estimation will be briefly described below.

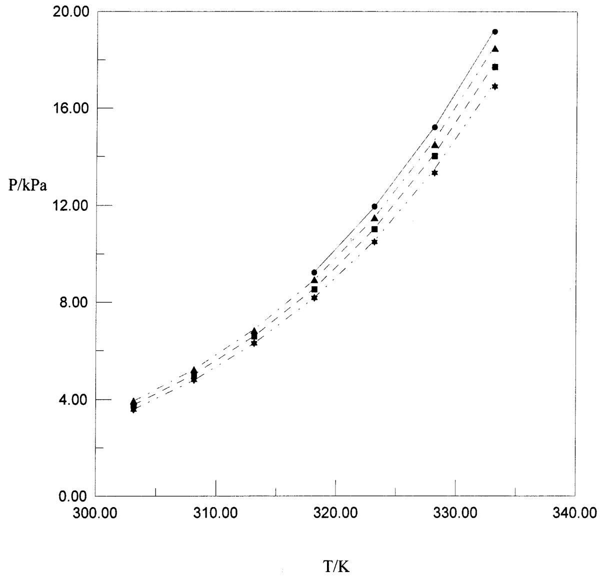

Figure 1. Temperature dependence of the vapor pressure of an NaCl + KBr aqueous solution at different concentrations: ●, 1 m exp (- - -, 1 m calc); ▲, 2 m exp (— · —, 2 m calc); ■, 3 m exp (— — —, 3 m calc); ★, 4 m exp (— · · —, 4 m calc).

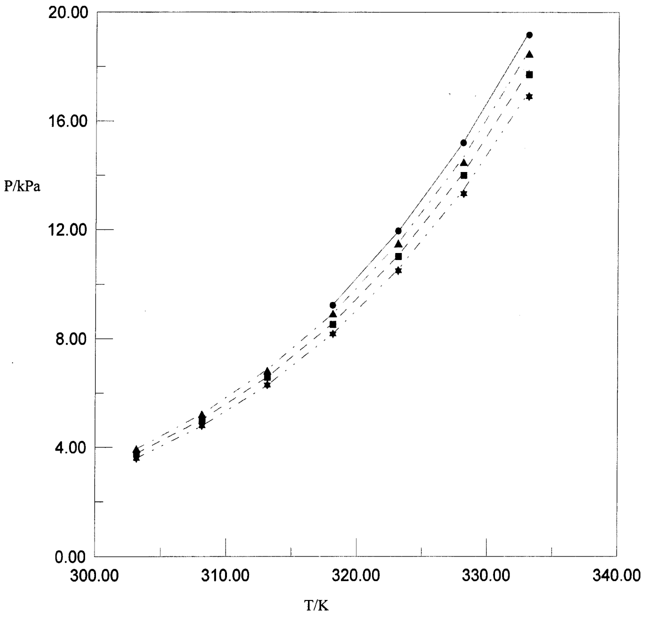

Figure 2. Temperature dependence of the vapor pressure of an NaBr + KCl aqueous solution at different concentrations: ●, 1 m exp (- - -, 1 m calc); ▲, 2 m exp (— · —, 2 m calc); ■, 3 m exp (— — —, 3 m calc); ★, 4 m exp (— · · —, 4 m calc).

At low pressure, the vapor−liquid equilibrium relation for water in an electrolyte solution can be simplified to

$$a_w = \frac{P_w}{P_w^\circ} \tag{1}$$

where a_w is the activity of water and P_w and P_w° are the vapor pressures of solution and pure water, respectively, at the temperature of concern. From eq 1, the vapor pressure of an aqueous solution can be calculated if the activity of water has been determined in advance.

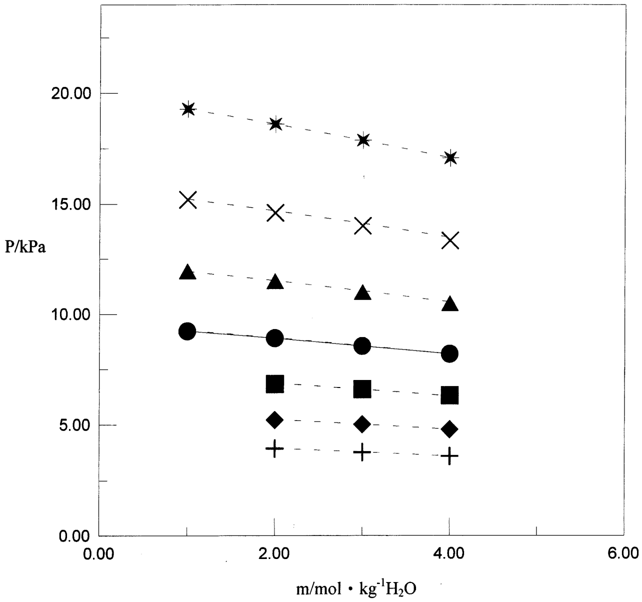

Figure 3. Concentration dependence of the vapor pressure of an NaCl + KBr aqueous solution at different temperatures: +, 303.15 K exp; ◆, 308.15 K exp; ■, 313.15 K exp; ●, 318.15 K exp; ▲, 323.15 K exp; ×, 328.15 K exp; ∗, 333.15 K exp; - - -, calc values.

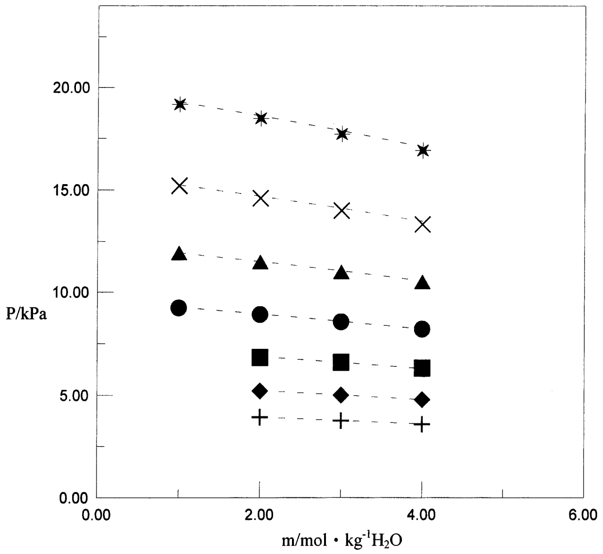

Figure 4. Concentration dependence of the vapor pressure of an NaBr + KCl aqueous solution at different temperatures: +, 303.15 K exp; ◆, 308.15 K exp; ■, 313.15 K exp; ●, 318.15 K exp; ▲, 323.15 K exp; ×, 328.15 K exp; ∗, 333.15 K exp; - - -, calc values.

The Gibbs–Duhem equation for an aqueous mixed electrolyte solution at constant temperature and pressure is expressed as

$$n_w \, d\mu_w + \sum_i n_i \, d\mu_i = 0 \qquad (2)$$

where *i* indicates all the constituent ions in the solution. The chemical potential for water in a solution is

$$d\mu_w = RT \, d \ln a_w \qquad (3)$$

and that for ion *i* is

$$d\mu_i = RT \, d \ln a_i \qquad (4)$$

Then the Gibbs–Duhem equation can be rewritten as

$$\frac{1000}{M_w} d \ln a_w + \sum_i m_i \, d \ln a_i = 0 \qquad (5)$$

where

$$m_i = \frac{1000 n_i}{n_w M_w} \qquad (6)$$

where M_w is the molecular weight of water. Let $m_T = \sum_i m_i$ and $x_i = m_i/m_T$ represent the total molal concentration of all ions in solution and the fraction of an ion, respectively. Since $a_i = m_i \gamma_i$ and ionic strength is expressed as

$$I = \frac{1}{2}\sum_i m_i z_i^2 = \frac{m_T}{2}\sum_i x_i z_i^2 \qquad (7)$$

After some mathematical manipulations, eq 3 may be transformed to

$$d \ln a_w = -\frac{M_w}{1000} dm_T - \frac{M_w}{500} I \frac{\sum_i x_i \, d \ln \gamma_i}{\sum_i x_i z_i^2} \qquad (8)$$

Integrating eq 8 from zero electrolyte concentration to a specific concentration and performing integration by parts, one can obtain the equation for water activity in an aqueous electrolyte solution as

$$\ln a_w = -\frac{m_T M_w}{1000} - \frac{m_T M_w}{1000}\sum_i x_i \ln \gamma_i + \frac{m_T M_w}{1000 I}\sum_i x_i \int_0^I \ln \gamma_i \, dI \qquad (9)$$

To perform the integration, an explicit expression for an activity coefficient is required for the integrand in eq 9. Lin and Lee[1] obtained these final expressions of activity coefficients of cation and anion, given by

$$\ln \gamma_+ = -A_\phi z_+^2 \left[\frac{I^{1/2}}{1 + b_+ I^{1/2}} + \frac{2}{b_+} \ln(1 + b_+ I^{1/2})\right] + \frac{S_+ z_+^2 I^\alpha}{T} \qquad (10)$$

and

$$\ln \gamma_- = -A_\phi z_-^2 \left[\frac{I^{1/2}}{1 + b_- I^{1/2}} + \frac{2}{b_-} \ln(1 + b_- I^{1/2})\right] + \frac{S_- z_-^2 I^\alpha}{T} \qquad (11)$$

where b_i and S_i were defined by Lin and Lee[1] as the approaching parameter and the solvation parameter, respectively, for ion *i*. They concern the approaching distance between two particles and the degree of hydration of an ion in a solution. These two parameters are also called the primary individual ionic parameters and must be determined from correlating the experimental ionic activity coefficients of an aqueous single-electrolyte solution. The parameter α was determined to be the constant value 1.29 by Lin and Lee.[1] The term *I* represents the ionic strength, and A_ϕ is the Debye–Hückel constant. Lin and Lee[1] have given very detailed derivations of both eq 10 and eq 11.

Table 2. Experimental and Estimated Vapor Pressures of Aqueous NaCl + KBr and NaBr + KCl Electrolyte Solutions

NaCl + KBr			P^s/kPa			NaBr + KCl		P^t/kPa		
T	m_{NaCl}	m_{KBr}				m_{NaBr}	m_{KCl}			
K	mol·kg^{-1} of H_2O	mol·kg^{-1} of H_2O	exp	cal	dev	mol·kg^{-1} of H_2O	mol·kg^{-1} of H_2O	exp	cal	dev
318.15	0.501	0.499	9.23	9.26	−0.03	0.501	0.500	9.23	9.26	−0.03
323.15	0.499	0.498	11.95	11.93	0.02	0.499	0.501	11.94	11.93	0.01
328.15	0.496	0.503	15.20	15.23	−0.03	0.501	0.5	15.20	15.23	−0.03
333.15	0.499	0.502	19.17	19.28	−0.11	0.503	0.497	19.17	19.28	−0.11
303.15	0.999	1.001	3.94	3.94	0	1.000	1.002	3.94	3.94	0
308.15	1.001	0.998	5.22	5.23	−0.01	1.002	0.999	5.21	5.23	−0.02
313.15	0.998	1.001	6.82	6.87	−0.05	0.999	0.998	6.83	6.87	−0.04
318.15	1.002	0.999	8.93	8.93	0	1.003	0.009	8.91	8.93	−0.02
323.15	0.998	1.004	11.49	11.51	−0.02	1.002	0.999	11.49	11.51	−0.02
328.15	1.001	0.999	14.59	14.69	−0.1	0.997	1.004	14.60	14.69	−0.09
333.15	1.000	1.001	18.48	18.60	−0.12	1.002	1.000	18.48	18.60	−0.12
303.15	1.500	1.498	3.77	3.78	−0.01	1.502	1.498	3.77	3.78	−0.01
308.15	1.496	1.502	4.99	5.02	−0.03	1.501	1.499	5.01	5.02	−0.01
313.15	1.501	1.498	6.58	6.59	−0.01	1.498	1.500	6.60	6.59	0.01
318.15	1.499	1.501	8.53	8.57	−0.04	1.497	1.503	8.55	8.57	−0.02
323.15	1.496	1.501	11.02	11.05	−0.03	1.499	1.499	11.00	11.05	−0.05
328.15	1.502	1.497	14.01	14.11	−0.1	1.501	1.502	14.00	14.11	−0.11
333.15	1.499	1.502	17.71	17.87	−0.16	1.499	1.503	17.71	17.87	−0.16
303.15	2.000	1.999	3.59	3.60	−0.01	1.999	2.002	3.60	3.60	0
308.15	2.001	1.998	4.80	4.79	0.01	2.001	1.998	4.79	4.79	0
313.15	1.998	2.001	6.30	6.29	0.01	1.999	1.999	6.32	6.29	0.03
318.15	2.000	2.001	8.18	8.19	−0.01	1.999	2.001	8.20	8.19	0.01
323.15	1.999	1.998	10.50	10.55	−0.05	2.003	1.998	10.49	10.55	−0.06
328.15	2.001	1.998	13.33	13.48	−0.15	2.002	1.999	13.33	13.48	−0.15
333.15	1.997	1.998	16.93	17.08	−0.15	1.998	2.001	16.91	17.08	−0.17
			AAD^a = 0.050 kPa			AAD^a = 0.051 kPa				
			AARD^b = 0.41%			AARD^b = 0.40%				

[a] AAD = $\Sigma_i|P^s_{exp} - P^s_{est}|_i/N$. [b] AARD = $\Sigma_i|(P^s_{exp} - P^s_{est})/P^s_{exp}|_i/N \times 100\%$.

Table 3. Approaching and Solvation Parameters[a] of Individual Ions Obtained from Aqueous Single Electrolyte Solutions

electrolyte	ion	B_i	S_i
NaCl	Na^+	7.524	31.080
	Cl^-	1.106	16.246
NaBr	Na^+	3.876	48.955
	Br^-	1.715	13.852
KCl	K^+	1.277	15.257
	Cl^-	3.387	7.615
KBr	K^+	1.412	4.393
	Br^-	2.884	34.818

[a] All parameters are from Lin and Lee.[1]

The integration of eq 9 can be done after substituting the activity coefficient formula into the integrand to obtain

$$\int_0^I \ln \gamma_i \, dI = \frac{-2A_\phi {z_i}^2 I}{b_i} \ln(1 + b_i I^{1/2}) + \frac{S_i {z_i}^2}{(\alpha + 1)T} I^{\alpha+1} \quad (12)$$

The values of the approaching and the solvation parameters of each individual ion were obtained by Lin and Lee[1] and are listed in Table 3 for reference.

The vapor pressures of the present mixed electrolyte solutions were calculated with eqs 1 and 9−12. The estimated values are listed in Table 2 along with the experimental values obtained in this study. Both the experimental and estimated data agree satisfactorily with an average absolute deviation (AAD) and an average absolute relative deviation (AARD) of 0.050 kPa and 0.41%, respectively, for the NaCl + KBr aqueous solutions and with those of 0.050 kPa and 0.40% for the NaBr + KCl solutions, respectively. The very small values of AAD and AARD mean that the model is able to accurately estimate vapor pressures of aqueous mixed electrolyte solutions.

Conclusion

In this study, the vapor pressures of the aqueous mixed electrolyte solutions of NaCl + KBr and NaBr + KCl were measured with a differential static type apparatus in the temperature range between (303.15 and 333.15) K and the electrolyte concentration range between (1 and 4) m. The experimental data showed that both aqueous solutions exhibit identical vapor pressure at the same temperature and concentration of electrolyte and that vapor pressure increases with increasing temperature but decreases with increasing concentration of electrolyte.

The vapor pressures of the above solutions at different conditions were estimated with the two-ionic-parameter model of Lin and Lee.[1] The calculated and the experimental values agree very wellSM, with the AAD and the AARD equal to 0.05 kPa and 0.40%, respectively.

Acknowledgment

The authors acknowledge the financial support of this work by The Chinese Petroleum Corporation through project NSC89-CPC-7-008-004.

Literature Cited

(1) Lin, C. L.; Lee, L. S. A Two-ionic-parameter Approach for Ion Activity Coefficients of Aqueous Electrolyte Solutions. *Fluid Phase Equilib.*, in press.

(2) Shiah, I. M.; Tseng, H. C. Experimental and Theoretical Determination of the Vapor Pressure of NaCl−KCl, NaBr−KBr, and NaCl−$CaCl_2$ Aqueous Solutions at Temperatures from 298 to 343 K. *Fluid Phase Equilib.* **1996**, *124*, 23−249.

(3) Iyokl, S.; Iwasaki, S.; Vemura, T. Vapor Pressure of the Water-Lithium Bromide-Lithium Iodide System. *J. Chem. Eng. Data* **1990**, *40*, 429−433.

(4) Covington, A. K.; Lilley, T. H.; Robinson, R. A. Excess Free Energies of Aqueous Mixtures of Some Alkali Metal Halide Salt Pairs. *J. Phys. Chem.* **1968**, *72*, 2759−2763.

(5) 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* **1998**, *43*, 17−20.

(6) Hala, E. Vapor-Liquid Equilibria of Strong Electrolytes in Systems Containing Mixed Solvent. *Fluid Phase Equilib.* **1983**, *13*, 311−319.
(7) Patil, K. R.; Tripathi, A. D.; Pathak, G.; Katti, S. S. Thermodynamic Properties of Aqueous Electrolyte Solution 1. *J. Chem. Eng. Data* **1990**, *40*, 166−168.
(8) Sacchetto, G. A.; Bombi, G. G.; Macca, C. Vapor Pressure of Very Concentrated Electrolyte solutions 1. *J. Chem. Thermodyn.* **1981**, *13*, 31−40.
(9) Sako, T.; Hakuta, T.; Yoshitome, H. Vapor Pressures of Binary and Ternary Aqueous Solutions. *J. Chem. Eng. Data* **1985**, *20*, 224−228.

Received for review July 23, 2002. Accepted February 1, 2003.

JE020144O