J. Chem. Eng. Data **2010,** *55,* 3567–3571

Effect of Dissolved Inorganic Salts on the Enthalpy of Mixing of the Ethanol + Pyridine System at 303.15 K

R. Tamilarasan

Department of Chemistry, Anna University (Tiruchirappalli, Pattukkottai Campus) 614 701, India

A. Anand Prabu

Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology University, Vellore 632 014, India

Kap Jin Kim*

Department of Advanced Materials Engineering for Information & Electronics, College of Engineering, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, South Korea

M. Dharmendira Kumar*

Department of Chemical Engineering, Alagappa Chettiar College of Technology, Anna University, Chennai 600 025, India

---

This paper presents the effect of five dissolved inorganic salts (sodium chloride, NaCl; calcium chloride, $CaCl_2$; zinc chloride, $ZnCl_2$; cadmium chloride, $CdCl_2$; ammonium chloride, NH_4Cl) on the enthalpy of mixing (H^E) of the binary system ethanol + pyridine measured at 303.15 K using an isothermal displacement calorimeter with vapor space. Compared to the salt-free system, the addition of selected salts (0.05 mass fraction) significantly increased the H^E values along the negative direction in the order of $ZnCl_2 > NaCl > CdCl_2 \approx CaCl_2 > NH_4Cl$. With increasing salt concentration (0.10 mass fraction), the H^E values decreased in the positive direction for the salt $CdCl_2$ and increased in the negative direction for the salt $CaCl_2$ which exemplifies the importance of solute−pyridine interaction. The experimental values of H^E were fitted into the Redlich−Kister equation, and the deviations from the ideal value and binary parameters are reported.

Introduction

In chemical industries, the importance of thermodynamic properties of liquid mixtures involved with separation processes such as distillation and absorption have been well-recognized. Among the many thermodynamic functions, knowledge of the phase equilibria, enthalpies of mixing, and excess functions of mixtures is important not only for the design of separation processes, but also to take decisions regarding the influence of solvents on reaction rates and the suitability of a compound as a capable working fluid.[1] The excess enthalpy of mixing (H^E) remains an important probe to use in understanding the interactions and structure of liquid mixtures. When two or more solvent molecules are associated with one another to form a liquid mixture, it brings about a marked effect in the intermolecular interactions of the solvents. Accurate electrolytic data in aqueous as well as mixed solvent systems are required not only to understand the nature of ion−ion and ion−solvent interactions but also have its practical applicability in various fields.[2] In the extractive distillation case, inorganic salts are used as extractive agents to modify the relative volatility of the binary liquid mixture accompanied with changes in the free energy of liquid mixtures.

In earlier studies, Furter and Cook[3] and Jaques and Furter[4] studied the influence of added salt on the relative volatilities of two liquid components using 19 inorganic salts. The salt effect is believed to be a complex function of salt + solvent interaction and self-interaction among the system components.[2] An equation derived by Sada et al.[5] indicated the changes in the chemical potentials of the solvent components when a salt is added to a solvent mixture. Since there is an interrelation between the excess free energy and the excess enthalpy of liquid mixtures, a few researchers[6−8] have studied the effect of added salts on the excess enthalpy values of liquid mixtures along with notable contributions from our group.[9−14] The above studies using thermodynamic models were quite useful in understanding the interaction of molecules within the selected liquid mixture and predicting the phase equilibria of liquid mixtures under the influence of added salts.

As part of our continuing research, the present study investigates the effect of five dissolved inorganic salts (sodium chloride, NaCl; calcium chloride, $CaCl_2$; zinc chloride, $ZnCl_2$; cadmium chloride, $CdCl_2$; ammonium chloride, NH_4Cl) on the enthalpy of mixing (H^E) of the binary ethanol + pyridine system at 303.15 K. The added inorganic salts (0.05 and 0.10 mass fraction) act as an extractant to separate an otherwise miscible binary solvent mixture, and the H^E values were measured using a displacement calorimeter as a function of varying mole fraction of ethanol (x_1). Since the enthalpy of mixing is dependent on the composition, it is more appropriate to study the changes in

---

* To whom correspondence should be addressed. E-mail address: kjkim@khu.ac.kr. Tel.: +82-31-2012518. Fax: +82-31-2048114. E-mail address: mdkumar@annauniv.edu. Tel.: +91-44-2220 3535. Fax: +91-44-22355373.

10.1021/je1002048

Table 1. Physical Properties of the Solvents and Salts Used

solvent	this work	lit.[15]
	Boiling Point, T_b/K	
ethanol	351.3	351.5
pyridine	387.9	388.0
	ρ/(g·cm^{-3}), 298.15 K	
ethanol	0.7885	0.7893
pyridine	0.9808	0.9819
	(as reported by the supplier)	
salt	melting point, T_m/K	purity
sodium chloride	1073.45	≥ 99.8 %
zinc chloride	565.35	≥ 99.9 %
ammonium chloride	611.15	≥ 99.9 %
calcium chloride	1044.85	≥ 99.9 %
cadmium chloride	837.15	≥ 99.8 %

the enthalpy of mixing rather than the entropy of mixing. The experimental H^E values were fitted into the Redlich−Kister equation, and the deviations from the ideal value and parameters are reported.

Experimental Section

Chemicals Used. Analytical reagent grade ethanol, pyridine, and the salts (NaCl, $CaCl_2$, $ZnCl_2$, $CdCl_2$, and NH_4Cl) used in this investigation were supplied by E-Merck. The solvents were purified by fractional distillation and stored over activated molecular sieves of type 3 Å. The densities (ρ) and boiling points (T_b) of the solvents were measured using a bicapillary pycnometer and ebulliometer, respectively. After taking into consideration the uncertainty in the measured density and temperature values at $\pm 1 \cdot 10^{-4}$ and ± 0.2 K, respectively, the purities of the solvents were found to be in close proximity with the literature values[15] as shown in Table 1. The melting point (T_m) and purity (%) values of the salts used in this study were received from the supplier as given in Table 1. Prior to use, the salts were dried in a vacuum oven at 403.15 K.

Apparatus Used. The calorimeter used in the present investigation is basically of the same type used by Tsao and Smith[16] and Murti and Winkle[17] which is essentially a double-walled Dewar flask of 215 cm^3 volume. The performance of the calorimeter and its reliability for the measurement of the H^E values were ascertained by determining H^E values of a salt-free binary system of water + methanol at 303.15 K (Figure 1), and the data obtained were very consistent (within ± 2 %) with the literature data.[18]

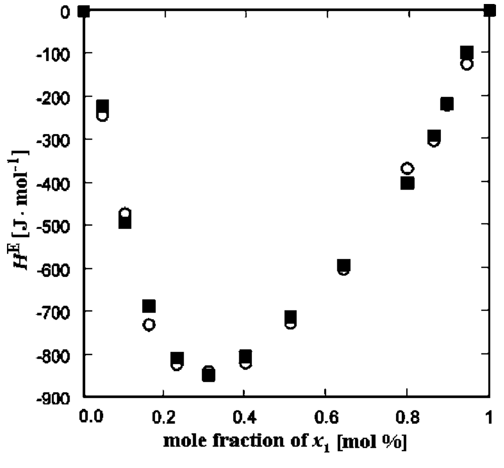

Figure 1. Enthalpy of mixing of water + methanol at 303.15 K: ○, this work; ■, Battler and Rowley.[18]

Table 2. Enthalpy of Mixing Data of the System Ethanol (1) + Pyridine (2) at 303.15 K for the Salt NaCl

no salt			5 % NaCl			
x_1	H^E_{exptl}	H^E_{calcd}	x_1	x_3	H^E_{exptl}	H^E_{calcd}
mole fraction	J·mol^{-1}	J·mol^{-1}	mole fraction	mole fraction	J·mol^{-1}	J·mol^{-1}
0.032	−1.5	−1.6	0.021	0.0479	−1.5	−1.6
0.082	−6.4	−6.3	0.064	0.0435	−12.2	−12.1
0.127	−12.9	−12.6	0.121	0.0388	−40.9	−39.8
0.192	−22.8	−23.3	0.219	0.0333	−110.3	−108.3
0.251	−34.6	−35.3	0.254	0.0294	−132.6	−135.3
0.351	−51.2	−53.7	0.311	0.0253	−179.3	−179.7
0.447	−71.9	−70.1	0.354	0.0216	−210.7	−211.7
0.502	−77.5	−79.1	0.449	0.0170	−266.8	−269.0
0.572	−79.2	−80.4	0.560	0.0124	−311.4	−302.0
0.653	−63.7	−65.2	0.664	0.0084	−284.3	−291.2
0.734	−52.9	−51.7	0.759	0.0051	−243.5	−243.7
0.874	−25.0	−25.2	0.884	0.0020	−134.6	−134.1

Table 3. Enthalpy of Mixing Data of the System Ethanol (1) + Pyridine (2) at 303.15 K for the Salts $ZnCl_2$ and NH_4Cl

5 % $ZnCl_2$				5 % NH_4Cl			
x_1	x_3	H^E_{exptl}	H^E_{calcd}	x_1	x_3	H^E_{exptl}	H^E_{calcd}
mole fraction	mole fraction	J·mol^{-1}	J·mol^{-1}	mole fraction	mole fraction	J·mol^{-1}	J·mol^{-1}
0.063	0.0470	−43.4	−43.2	0.082	0.0458	−14.6	−13.4
0.079	0.0433	−57.0	−55.8	0.185	0.0389	−62.2	−63.5
0.163	0.0381	−126.3	−126.4	0.281	0.0325	−121.4	−123.0
0.214	0.0339	−174.1	−170.0	0.363	0.0268	−164.3	−163.3
0.302	0.0289	−236.1	−235.5	0.471	0.0207	−189.5	−190.5
0.372	0.0246	−275.6	−283.2	0.552	0.0155	−191.2	−189.2
0.453	0.0203	−317.9	−314.1	0.617	0.0117	−178.2	−179.0
0.519	0.0164	−326.3	−319.9	0.716	0.0074	−146.8	−147.0
0.605	0.0124	−300.3	−299.6	0.780	0.0045	−118.5	−119.7
0.683	0.0089	−251.6	−255.1	0.893	0.0016	−63.5	−62.5
0.743	0.0063	−203.4	−207.0				
0.814	0.0038	−141.6	−141.4				

Preparation of Salt Solutions. Salts used in the present investigation were first dissolved separately in the solvent in which they are preferentially soluble to the desired level of concentration at 303.15 ± 0.1 K. At this temperature, the material losses due to vaporization were taken to be insignificant. The concentrations of salts reported in this work [(5 and 10) %] are the initial concentrations by mass [mass of salt/(mass of salt + mass of solvent)] before mixing with the other solvent.

Experimental Procedure. The experimental procedure adopted in this work is described elaborately in our earlier paper.[10] However, some details of the experimental procedure utilized are summarized below. The microprocessor (MIPROC) based digital calorimeter system used in the present study was designed in our laboratory and constructed with assistance from Precision Instrument and Electronics (India) Ltd. The H^E values were registered by the MIPROC which has a built-in program to supply and measure the equivalent electrical energy fed to the liquid mixture and to determine the H^E values and display them digitally in Joules. The value displayed by the MIPROC is divided by the total number of moles of the liquid mixture taken in the calorimeter to obtain the H^E values in J·mol^{-1}. Triplicate samples were prepared for each ethanol + pyridine composition (refer to varying mole fractions of ethanol (x_1) values given in Tables 2 to 5) to ensure reproducibility (within ± 3 %), and the average values are presented. The mole fraction of pyridine can be referred to as x_2, whereas x_3 refers to the mole fraction of solute (in Tables 2 to 5), and the sum of $x_1 + x_2 + x_3$ is equal to one.

Table 4. Enthalpy of Mixing Data of the System Ethanol (1) + Pyridine (2) at 303.15 K for the Salt $CaCl_2$

5 % $CaCl_2$				10 % $CaCl_2$			
x_1	x_3	H^E_{exptl}	H^E_{calcd}	x_1	x_3	H^E_{exptl}	H^E_{calcd})
mole fraction	mole fraction	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	mole fraction	mole fraction	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
0.079	0.0926	−30.8	−30.1	0.112	0.0866	−86.1	−88.8
0.182	0.0831	−105.3	−100.3	0.214	0.0745	−167.5	−166.0
0.281	0.0711	−163.1	−163.0	0.257	0.0659	−203.6	−201.1
0.367	0.0527	−206.4	−212.4	0.305	0.0573	−241.3	−240.5
0.476	0.0419	−260.5	−255.6	0.432	0.0449	−323.1	−329.8
0.569	0.0236	−271.5	−264.1	0.502	0.0360	−357.7	−356.5
0.617	0.0187	−250.5	−256.1	0.591	0.0269	−359.2	−353.2
0.712	0.0111	−209.2	−214.7	0.680	0.0186	−297.9	−300.2
0.793	0.0080	−158.3	−155.8	0.709	0.0138	−270.5	−273.5
0.827	0.0044	−128.7	−127.1	0.807	0.0074	−157.1	−154.5
0.896	0.0015	−66.6	−67.3	0.860	0.0037	−83.3	−84.2
0.939	0.0003	−34.5	−33.8	0.932	0.0009	−19.3	−19.8

Table 5. Enthalpy of Mixing Data of the System Ethanol (1) + Pyridine (2) at 303.15 K for the Salt $CdCl_2$

5 % $CdCl_2$				10 % $CdCl_2$			
x_1	x_3	H^E_{exptl}	H^E_{calcd}	x_1	x_3	H^E_{exptl}	H^E_{calcd}
mole fraction	mole fraction	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	mole fraction	mole fraction	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
0.081	0.0466	−60.1	−59.1	0.084	0.0899	−79.5	−79.8
0.182	0.0407	−144.1	−146.3	0.185	0.0783	−145.2	−148.2
0.286	0.0345	−203.0	−201.6	0.281	0.0668	−198.0	−199.2
0.365	0.0288	−239.2	−236.7	0.362	0.0561	−231.6	−235.4
0.473	0.0226	−265.0	−266.5	0.471	0.0444	−260.5	−266.3
0.565	0.0171	−264.0	−264.5	0.562	0.0339	−265.8	−265.1
0.619	0.0128	−245.0	−248.2	0.615	0.0254	−245.4	−245.7
0.715	0.0080	−196.2	−190.2	0.714	0.0159	−192.2	−192.7
0.796	0.0043	−130.0	−127.3	0.795	0.0085	−121.0	−121.2
0.854	0.0019	−90.0	−93.1	0.821	0.0039	−98.0	−98.1

Results and Discussion

The experimental H^E values obtained for the ethanol + pyridine system for various concentrations of the five salts used herein are listed in Tables 2 to 5 and also represented graphically in Figures 2 and 3. The salt-free data are also given in the figure for the purpose of comparison. It is well-known that the H^E of ethanol (polar, protic) and pyridine (polar, aprotic) is negative (exothermic) over the entire composition range, and this explains the strong intermolecular forces of attraction and complex formation between ethanol and pyridine. The enthalpy of mixing for the salt-free ethanol + pyridine system decreases with the increasing mole fraction of ethanol (x_1) from 0.082 to 0.623 (Table 2 and Figure 2) accompanied with an increase in miscibility. A further increase in x_1 results in an increase in H^E values, indicating that energy is lost in overcoming the inherent intermolecular hydrogen bonding in ethanol.

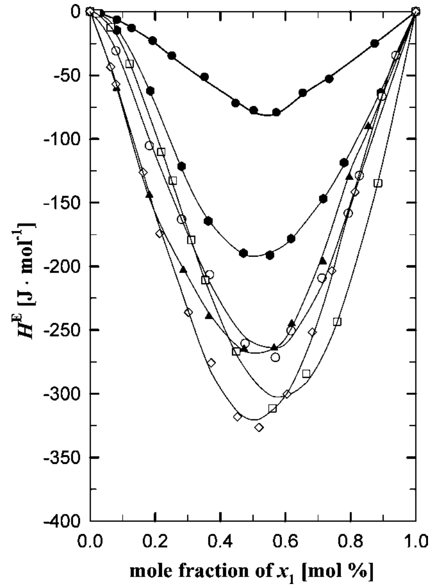

Figure 2. Effect of 5 % mass of the salts: ⬢, NH_4Cl; ○, $CaCl_2$; ▲, $CdCl_2$; □, NaCl; ◇, $ZnCl_2$; and ●, salt-free solution on the H^E of ethanol (1) + pyridine (2) system at 303.15 K against the mole fraction of x_1. Solid lines and symbols indicate the calculated and experimental H^E values, respectively.

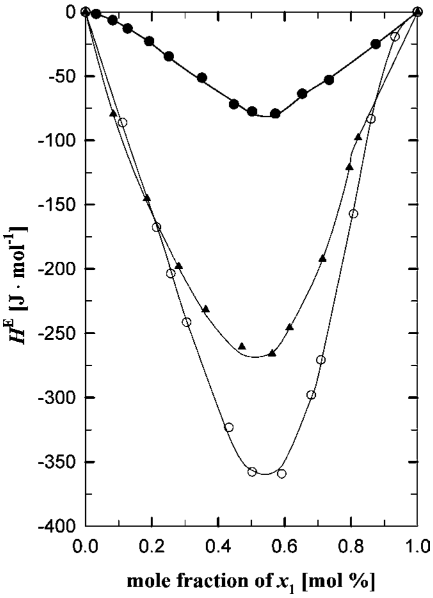

Figure 3. Effect of 10 % mass of the salts: ○, $CaCl_2$; ▲, $CdCl_2$; and □, salt-free solution on the H^E of ethanol (1) + pyridine (2) system at 303.15 K against the mole fraction of x_1. Solid lines and symbols indicate the calculated and experimental H^E values, respectively.

The influence of 5 % mass of the salts (NaCl, $CaCl_2$, $ZnCl_2$, $CdCl_2$, and NH_4Cl) on the separation feasibility of ethanol + pyridine system is evaluated from Figure 2. The salts used in the present study significantly altered the magnitude of H^E values depending on the mole fraction of x_1. In the region of lower mole fraction of x_1, a marked decrease in the H^E values was observed, and the reverse trend was noticed in the region of higher mole fraction of x_1 irrespective of the salt type used. The exothermic maximum was observed in the x_1 mole fraction region between 0.5 and 0.6, which implies higher interaction between the solute and the pyridine compared to the salt-free system. During the actual process of separation of two components by extractive distillation, it would be more beneficial if the mole fraction of ethanol is maintained at around 0.5 in the presence of any of the chosen salts. On the other hand, their separation becomes formidable at higher mole fractions of x_1. As observed from Figure 2, the region of heterogeneity increases to a greater extent in the order of $ZnCl_2 > NaCl > CdCl_2 \approx CaCl_2 > NH_4Cl$ compared to the salt-free ethanol + pyridine binary system. The increase in the original negative H^E values is well-pronounced when x_1 is inbetween 0.3 and 0.7, and this trend may be attributed to the contribution from the solvation energy of the salts without reducing intermolecular forces of attraction in the solvents.

Figure 3 and Tables 4 to 5 show the effect of increasing salt concentration (0.10 mass fraction) on the H^E values of the ethanol + pyridine system. Increasing addition of the salt $CaCl_2$ in the system further increased the H^E values along the negative

Table 6. Estimated Parameters of Equation 1 and Standard Deviation $\sigma(H^E)$ in Equation 2 for the System Ethanol (1) + Pyridine (2) at 303.15 K

salt conc. mass fraction	A_0	A_1	A_2	A_3	$\sigma(H^E)$ $J\cdot mol^{-1}$
no salt	509.4	−913.9	306.2	1098.7	2.08
5 % NaCl	−1157.7	−634.3	555.3	32.5	1.97
5 % $ZnCl_2$	−1280.4	−60.6	844.1	221.9	1.93
5 % NH_4Cl	−762.1	−56.9	621.3	−263.5	1.49
5 % $CaCl_2$	−1040.6	−344.2	624.4	402.7	1.92
10 % $CaCl_2$	−1424.8	−460.3	1193.4	1164.4	1.88
5 % $CdCl_2$	−1076.5	−97.9	625.8	863.7	1.68
10 % $CdCl_2$	−1076.5	−97.8	625.1	863.6	1.43

direction, since the energy released during salt addition is greater than the energy required for overcoming the intermolecular forces for the solvation of ions. Hence, the excess enthalpy is negative for the addition of 10 % $CaCl_2$ salt. In the case of $CdCl_2$, the H^E values increased in the positive direction, implying that the energy required to disrupt the intermolecular forces for the solvation of ions is more than the energy released.

Data Correlation and Statistical Analysis. Jaques and Furter[4] have earlier reported that, when a inorganic salt is added to a binary liquid−liquid mixture, it is not considered as a three-component mixture; instead, this system is treated as a “special binary” in which each of the two “components” is a volatile component saturated individually with the salt. In our study, the effect of added salts on the experimental H^E values was correlated with the H^E values calculated using the two-component Redlich−Kister polynomial.[19] This model expresses the excess free energy of mixing as the sum of terms which consist of a function of the mole fractions of each component and an interaction parameter.

$$H^E/\mathrm{J\cdot mol^{-1}} = x_1 x_2 \sum_{i=0}^{j} A_i (2x_1 - 1)^i \qquad (1)$$

where H^E is the enthalpy of mixing; x_1 and x_2 are the mole fractions of components 1 and 2, respectively; and the A_i are the constants that are functions of temperature and the system properties.

The experimental H^E values were fitted to the above equation by the method of least-squares, with each point weighted equally, and the binary parameters (A_i) were evaluated. The parameter i in A_i from eq 1 represents not the number of components but the number of coefficients (or adjustable parameters) estimated by the least-squared fit method of the experimental H^E values. In each case (first column in Table 6), the optimum number of coefficients is ascertained from the examination of the variation in the standard deviation, $\sigma(H^E)$, as calculated using eq 2. The modeling results are listed in Table 6 along with the standard deviation, $\sigma(H^E)$.

$$\sigma(H^E)/\mathrm{J\cdot mol^{-1}} = \left[\frac{\sum\left(\frac{H^E_{\mathrm{exptl}} - H^E_{\mathrm{calcd}}}{H^E}\right)^2}{(N - K)}\right]^{1/2} \qquad (2)$$

where N and K are the number of data points and the number of parameters, respectively.

The significant advantage of using eq 2 is that it can predict the effect of salt on the H^E values of the binary solvent system without vapor pressure depression data of the solvent−electrolyte system.[3,4] The results obtained from this study showed that the amount of the added salt has a strong effect on the estimated parameters and their corresponding standard deviations, which may have ensued from the interaction between the individual salt and the functional groups present in the ethanol + pyridine system.

Conclusion

The effect of different inorganic salts on the excess enthalpy of mixing (H^E) of an ethanol + pyridine binary system at 303.15 K has been obtained using calorimetric measurements. From the experimental H^E values and statistical data for the addition (5 % by mass) of salts, the phase separation of the binary mixture is largely favored by using $ZnCl_2$ and least favored by using NH_4Cl. The added salts preferentially influence the interaction of the ethanol + pyridine mixture resulting in exothermic H^E values. At high concentrations (0.10 mass fraction), only $CdCl_2$ and $CaCl_2$ are completely soluble in the aforementioned binary system; hence, only these three salts are used for further studies. The H^E values in the presence of $CdCl_2$ increased in the positive direction, which implies that the energy required to overcome the intermolecular forces of attraction for enabling the solvation of ions is more than the energy released during the addition of the salts. The Redlich−Kister model used in the present study represented the experimental data with the required accuracy. Therefore, this model is suitable to predict the excess enthalpy of mixing in the ethanol + pyridine system in the presence of the selected inorganic salts and to develop new theories or equations of state for use in further studies.

Literature Cited

(1) Kojima, K. Thermodynamic analysis of chemical processes: ASOG-based methods for the prediction of excess enthalpy and excess entropy. *J. Chem. Eng. Jpn.* **1994**, *27*, 143–151.

(2) Furter, W. F. *Thermodynamic behavior of electrolytes in mixed solvents; Advances in Chemistry Series 155*; American Chemical Society: Washington, DC, 1976; pp 26−39.

(3) Furter, W. F.; Cook, R. A. Salt effect in distillation−A literature review. *Int. J. Heat Mass Transfer* **1967**, *10*, 23–36.

(4) Jaques, D.; Furter, W. F. Salt effect in vapour liquid equilibrium. Testing thermodynamic consistency of ethanol−water saturated with inorganic salts. *AIChE J.* **1972**, *18*, 343–345.

(5) Sada, E.; Morisue, T.; Miyahara, K. Salt effect in vapour liquid equilibrium of tetrahydrofuran−water system. *J. Chem. Eng. Data* **1975**, *20*, 283–287.

(6) Renon, H. Models for excess properties of electrolyte solutions: Molecular bases and classification, needs and trends for new developments. *Fluid Phase Equilib.* **1996**, *116*, 217–224.

(7) Loehe, J. R.; Donohue, M. D. Recent advances in modeling thermodynamic properties of aqueous strong electrolyte systems. *AIChE J.* **1997**, *43*, 180–195.

(8) Friese, T.; Ulbig, P.; Schulz, S.; Wagner, K. Effect of NaCl or KCl on the excess enthalpies of alkanol + water mixtures at various temperatures and salt concentrations. *J. Chem. Eng. Data* **1999**, *44*, 701–714.

(9) Rajendran, M.; Renganarayanan, S.; Madhavan, P. R.; Srinivasan, D. Effect of dissolved salts on heat of mixing of three miscible binary system. *J. Chem. Eng. Data* **1989**, *34*, 375–382.

(10) Rajendran, M.; Srinivasan, D. Salt effect in heat of mixing: effect of dissolved salts on enthalpy of mixing of 2-propanol−benzene system. *Chem. Eng. Commun.* **1994**, *128*, 109–117.

(11) Kumar, M. D.; Rajendran, M. Enthalpy of mixing of methanol + benzene + mercuric chloride at 303.15 K. *J. Chem. Eng. Data* **1999**, *44*, 248–250.

(12) Tamilarasan, R.; Prabu, A. A.; Kumar, M. D.; Yoo, C. K. Salt effect on the enthalpy of mixing of 1,4-dioxane + formic acid at 303.15 K. *J. Chem. Eng. Data* **2008**, *53*, 966–969.

(13) Tamilarasan, R.; Prabu, A. A.; Raajenthiren, M.; Kumar, M. D.; Yoo, C. K. Effect of dissolved salts on the enthalpy of mixing of methanol + formic acid system at 303.15 K. *J. Chem. Eng. Data* **2009**, *54*, 4–7.

(14) Tamilarasan, R.; Prabu, A. A.; Raajenthiren, M.; Kumar, M. D.; Yoo, C. K. Determination and correlation of excess enthalpies of mixing of ethyl acetate/benzene mixtures containing dissolved inorganic salts at 303.15 K. *J. Chem. Eng. Jpn.* **2009**, *42*, 485–489.

(15) Timmermanns, J. *Physico-chemical constants in concentrated solutions*; Wiley-Interscience: New York, 1980.

(16) Tsao, C. C.; Smith, J. M. Heat of mixing of liquids. *Chem. Eng. Prog. Symp. Ser.* **1953**, *49*, 107–117.

(17) Murti, O. S.; Winkle, M. V. Vapour liquid equilibria and heat of mixing of *N*-octane-ethyl benzene-cello solve system. *AIChE J.* **1957**, *3*, 517–524.

(18) Battler, J. R.; Rowley, R. L. Excess enthalpies between 293 and 323 K for constituent binaries of ternary mixtures exhibiting partial miscibility. *J. Chem. Thermodyn.* **1985**, *17*, 719–732.

(19) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

Received for review March 4, 2010. Accepted July 27, 2010. This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (R11-2005-065). One of the authors, A. A. Prabu, also wishes to thank DST-SERC, New Delhi, India for its financial support (100/IFD/9726/2009-2010 dated 2/2/2010).

JE1002048