Articles

Effect of Dissolved Salts on the Enthalpy of Mixing of the Methanol + Formic Acid System at 303.15 K

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This paper presents the effect of four dissolved inorganic salts (sodium chloride, cadmium chloride, zinc chloride, and ammonium chloride) on the enthalpy of mixing of the binary system methanol + formic acid measured at 303.15 K using an isothermal displacement calorimeter with vapor space. A significantly increasing trend in excess enthalpy values for the salt cadmium chloride, an insignificant but small increase in the excess enthalpy for the salt zinc chloride, and a smaller but similar decrease in the excess enthalpy values with the addition of sodium chloride and ammonium chloride were noticed. The experimental values of the enthalpy of mixing were fitted into a modified Redlich−Kister equation, and the deviations and parameters are reported. Importance of the solute−formic acid interaction is demonstrated by the enhanced excess enthalpy of mixing (H^E) values in the positive direction with increasing salt (ammonium chloride) concentration.

Introduction

In many chemical engineering processes such as distillation and absorption, knowledge about the electrolyte's influence on the phase equilibria is of significant importance. In the extractive distillation case, inorganic salts are used as extractive agents to modify the relative volatility of the binary mixture accompanied with changes in the free energy of liquid mixtures. In earlier studies, Furter and Cook[1] and Jaques and Furter[2] studied the influence of added salt on the relative volatilities of two liquid components using 19 inorganic salts. Formation of associated complexes or clusters of molecules of the volatile component around the salt ions and its effect on relative volatilities have been studied extensively by Long and McDevit.[3] The salt effect is also believed to be a complex function of salt + solvent interaction and self-interaction among the system components.[4] 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. Regarding azeotropic mixtures, the phase equilibria changes can be used to design more effective and economical distillation operations because the azeotrope can be shifted or can even be broken by using salt as an extractive agent.[6]

Since there is an interrelation between the excess free energy and the excess enthalpy of liquid mixtures, a few researchers[7−9] have studied the effect of added salts on the excess enthalpy values of liquid mixtures along with notable contributions from our group.[10−15] The above studies using thermodynamic models were quite useful in understanding the interaction of molecules within the selected liquid mixture and to predict 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 four dissolved salts (sodium chloride, cadmium chloride, zinc chloride, and ammonium chloride) on the enthalpy of mixing of the binary methanol + formic acid system. The experimental values were fitted into a modified Redlich−Kister equation, and the deviations and parameters are reported.

Experimental Section

Chemicals Used. Analytical reagent grade methanol, formic acid, and the salts (sodium chloride, cadmium chloride, zinc chloride, and ammonium chloride) used in this investigation were supplied by E-Merck. The solvents were purified by fractional distillation, and their purity was checked by comparing measured densities (ρ) and boiling points (T_b) with those reported in the literature.[16] Their densities were measured using a bicapillary pycnometer, and their boiling points were measured using an ebulliometer giving a precision of ± 0.2 K. The salts were dried before use, and their melting point and purity (%) values were received from the supplier. The physical properties of solvents and salts used in this study were found to be in close proximity with the literature values as shown in Table 1.

Apparatus Used. The calorimeter used in the present investigation is basically of the same type used by Tsao and Smith[17] and Murti and Winkle,[18] 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 enthalpy of mixing values were ascertained by determining the enthalpy of mixing values of the nonsalt binary system water + methanol at 303.15 K (Figure 1), and the data compare well (within 2 %) with literature data.[19]

Preparation of Salt Solutions. Salts used in the present investigation were first dissolved separately in the solvent in

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Table 1. Physical Properties of the Solvents and Salts Used

solvent	this work	lit.[16]
	boiling point, T_b /K	
methanol	337.8	337.2
formic acid	373.6	373.7
	ρ/(g·cm^{-3}), 298.15 K	
methanol	0.7820	0.7825
formic acid	1.2210	1.2200

salt	(as reported by the supplier) melting point, T_m/K	purity
sodium chloride	1073.45	≥ 99.8 %
cadmium chloride	841.25	≥ 99.8 %
zinc chloride	566.35	≥ 99.9 %
ammonium chloride	612.85	≥ 99.9 %

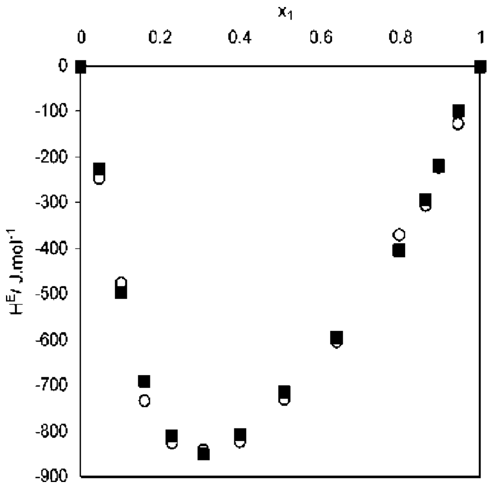

Figure 1. Enthalpy of mixing of water + methanol at 303.15 K: ○, this work; ■, Battler and Rowley.[19]

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 values of the enthalpies of mixing 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 values of enthalpy of mixing 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 enthalpy of mixing values in Joules per mole. Some of the experimental runs were repeated to check the reproducibility of the data, and they were found to be within ± 3 %.

Results and Discussion

The experimental excess enthalpy data obtained for the methanol + formic acid system under various salt conditions are given in the form of tables and also represented graphically as detailed below. Both methanol and formic acid are polar solvents, and it is well-known that their excess enthalpy of mixing value is negative (exothermic). This illustrates the complex formation and strong intermolecular forces of attraction between formic acid and methanol dipoles through the hydrogen bonding. The enthalpy of mixing for the salt-free methanol + formic acid system decreases with increasing mole fraction of methanol from 0.068 to 0.550 (Table 2) accompanied with an increase in miscibility. A further increase in the methanol mole fraction increases the enthalpy value, which indicates the expenditure of energy for breaking the inherent intermolecular hydrogen bonding in methanol.

Table 2. Enthalpy of Mixing Data of the System Methanol (1) + Formic Acid (2) at 303.15 K for the Salt NaCl

no salt			5 % NaCl			
	H^E_{exptl}	H^E_{calcd}			H^E_{exptl}	H^E_{calcd}
x_1	J·mol^{-1}	J·mol^{-1}	x_1	x_3	J·mol^{-1}	J·mol^{-1}
0.068	−19.3	−19.7	0.060	3.79·10^{-2}	−18.2	−17.6
0.116	−31.4	−32.2	0.114	3.34·10^{-2}	−31.9	−32.7
0.187	−50.4	−49.4	0.186	2.87·10^{-2}	−53.6	−52.3
0.305	−77.9	−76.3	0.305	2.31·10^{-2}	−79.1	−80.7
0.355	−85.8	−86.2	0.354	1.95·10^{-2}	−90.1	−89.8
0.415	−95.3	−96.0	0.414	1.58·10^{-2}	−96.1	−98.0
0.475	−100.9	−101.8	0.470	1.25·10^{-2}	−101.9	−102.1
0.550	−104.7	−104.5	0.549	9.17·10^{-3}	−100.3	−101.0
0.655	−94.6	−95.8	0.605	6.59·10^{-3}	−94.2	−95.0
0.745	−76.2	−77.7	0.675	4.17·10^{-3}	−80.0	−81.6
0.795	−62.4	−63.4	0.720	2.44·10^{-3}	−70.3	−70.1

Table 3. Enthalpy of Mixing Data of the System Methanol (1) + Formic Acid (2) at 303.15 K for the Salts $CdCl_2$ and $ZnCl_2$

5 % $CdCl_2$				5 % $ZnCl_2$			
		H^E_{exptl}	H^E_{calcd}			H^E_{exptl}	H^E_{calcd}
x_1	x_3	J·mol^{-1}	J·mol^{-1}	x_1	x_3	J·mol^{-1}	J·mol^{-1}
0.057	3.84·10^{-2}	−41.5	−42.1	0.056	3.80·10^{-2}	−18.2	−17.9
0.113	3.32·10^{-2}	−83.6	−81.7	0.107	3.36·10^{-2}	−32.2	−32.7
0.180	2.80·10^{-2}	−124.3	−127.6	0.189	2.86·10^{-2}	−56.2	−54.2
0.301	2.19·10^{-2}	−201.3	−202.8	0.307	2.31·10^{-2}	−81.2	−83.0
0.352	1.78·10^{-2}	−226.9	−226.8	0.427	1.77·10^{-2}	−101.3	−103.7
0.413	1.38·10^{-2}	−251.3	−252.7	0.465	1.47·10^{-2}	−106.8	−107.5
0.468	1.02·10^{-2}	−264.3	−265.8	0.547	1.10·10^{-2}	−108.9	−109.4
0.550	8.42·10^{-3}	−266.0	−267.1	0.602	8.26·10^{-3}	−105.2	−105.2
0.602	6.69·10^{-3}	−255.3	−255.6	0.675	5.57·10^{-3}	−91.1	−92.7
0.675	4.03·10^{-3}	−219.0	−220.8	0.712	3.76·10^{-3}	−82.1	−83.5
0.782	1.69·10^{-3}	−157.9	−158.8	0.820	1.62·10^{-3}	−50.2	−48.7
0.860	7.34·10^{-4}	−109.5	−110.9	0.961	2.45·10^{-4}	−4.32	−5.21

Table 4. Enthalpy of Mixing Data of the System Methanol (1) + Formic Acid (2) at 303.15 K for the Salt NH_4Cl

5 % NH_4CL				10 % NH_4CL			
		H^E_{exptl}	H^E_{calcd}			H^E_{exptl}	H^E_{calcd}
x_1	x_3	J·mol^{-1}	J·mol^{-1}	x_1	x_3	J·mol^{-1}	J·mol^{-1}
0.051	3.85·10^{-2}	−15.2	−15.2	0.054	7.40·10^{-2}	−15.2	−15.5
0.105	3.34·10^{-2}	−29.6	−29.6	0.102	6.48·10^{-2}	−26.9	−26.2
0.190	2.78·10^{-2}	−50.1	−49.3	0.190	5.41·10^{-2}	−41.6	−41.4
0.305	2.18·10^{-2}	−69.6	−71.3	0.302	4.23·10^{-2}	−55.6	−57.1
0.401	1.63·10^{-2}	−89.6	−88.2	0.421	3.20·10^{-2}	−72.5	−70.6
0.517	1.12·10^{-2}	−98.6	−99.1	0.547	2.21·10^{-2}	−77.5	−78.3
0.622	8.02·10^{-3}	−92.3	−93.2	0.602	1.59·10^{-3}	−78.1	−78.1
0.701	4.55·10^{-3}	−77.6	−78.4	0.715	9.01·10^{-3}	−69.2	−68.6
0.801	1.99·10^{-3}	−50.8	−51.2	0.820	3.98·10^{-3}	−47.6	−48.4
0.921	1.13·10^{-4}	−20.2	−21.2	0.901	1.35·10^{-3}	−27.8	−27.1

The influence of the salts (NaCl, $CdCl_2$, $ZnCl_2$, and NH_4Cl) on the excess enthalpy of mixing for the methanol + formic acid system is illustrated in Tables 2 to 4. Figure 2 shows the enthalpy values of the system with 5 % mass of the salts NaCl, $CdCl_2$, $ZnCl_2$, and NH_4Cl. The salt-free data are also given in the figure for the purpose of comparison. An insignificant change in magnitude of the enthalpy values was observed for the salts used in this system with the exception of $CdCl_2$, which exhibited a significantly decreased excess enthalpy value compared to the salt-free system. As observed from Figure 2, the addition of

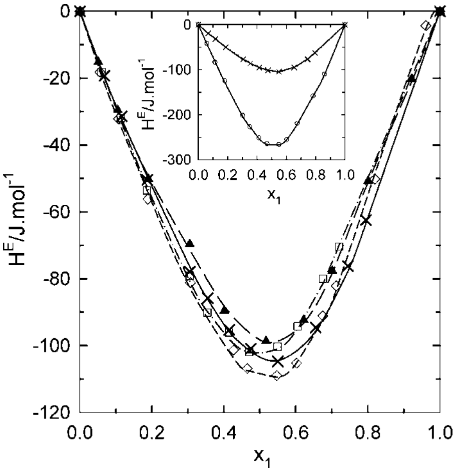

Figure 2. Effect of 5 % mass of the salts □, NaCl; ○, $CdCl_2$ (see inset); ◇, $ZnCl_2$; and ▲, NH_4Cl; and ×, salt-free solution on the enthalpy of mixing of methanol (1) + formic acid (2) at 303.15 K. Solid and dashed lines indicate calculated value.

$CdCl_2$ increases the original negative values of excess enthalpy to a considerable extent, which may be attributed to the contribution from solvation energy of the salts without reducing intermolecular forces in the solvents. A closer examination on the effect of the other salts revealed a slightly decreased excess enthalpy values for the salt $ZnCl_2$, which is more pronounced in the mole fraction region of methanol between 0.45 and 0.55. In the case of $CdCl_2$, its solvation energy is expected to play a significant role, and the ionic radii order follows as Cd^{2+} = 0.95 Å > Zn^{2+} ≈ 0.74 Å. Cd^{2+} ions having large ionic radii can facilitate coordination of solvents with minimum interligand (solvent) repulsive forces. But, around smaller Zn^{2+} ions, comparatively more interligand forces are expected on its coordination sphere, providing less negative enthalpy of mixing.[4] The monovalent salts NaCl and NH_4Cl exhibited a marginally increased enthalpy of mixing values compared to the salt-free system. In our case, the solvent−solvent interaction is expected to be less important than solute−formic acid interaction aided by an expected repulsion among formic acid in the solvation sphere which would also reduce the total solvation energy released.

The effect of increasing salt concentration (10 % by mass) on the H^E values of the methanol + formic acid system was studied using the salt NH_4Cl as shown in Figure 3. Increasing addition of the salt NH_4Cl in the system further increased the excess enthalpy values along 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. The Redlich−Kister 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.[20] In this study, the effect of added salts on the experimental enthalpy data (H^E) was correlated with values calculated using the Redlich−Kister polynomial.

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

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.

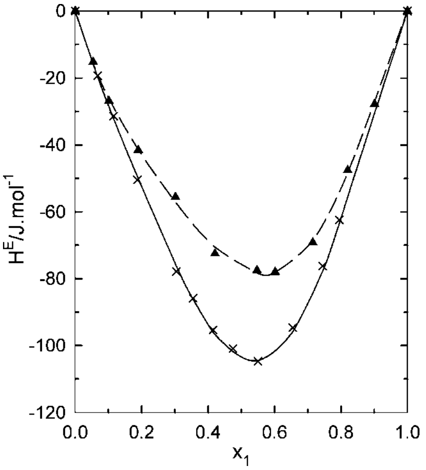

Figure 3. Effect of 10 % mass of the bivalent salt ▲, NH_4Cl; and ×, salt-free solution on the enthalpy of mixing of methanol (1) + formic acid (2) at 303.15 K. Solid and dashed lines indicate calculated value.

Table 5. Estimated Parameters of Equation 1 and Percentage of Standard Deviation % $\sigma(H^E)$ of the System Methanol (1) + Formic Acid (2) at 303.15 K

salt conc. (wt %)	% $\sigma(H^E)$	A_0	A_1	A_2	A_3
no salt	1.58	−416.89	−87.49	231.41	221.89
5 % NaCl	1.99	−410.81	0.99	260.8	149.21
5 % $CdCl_2$	1.85	−1076.46	−97.89	625.83	409.8
5 % $ZnCl_2$	1.98	−437.53	−64.11	232.16	201.97
5 % NH_4Cl	1.44	−384.72	−157.7	−81.66	8.57
10 % NH_4Cl	1.88	−306.42	−105.8	16.9	147.87

The experimental H^E values were fitted to the following equation by the method of least-squares, with each point weighted equally, and the binary parameters (A_i) have been evaluated. The modeling results are listed in Table 5 along with the percentage standard deviation (σ). The values of the percentage standard deviation σ are computed from the following equation and shown in Table 5.

$$\%\ \sigma(H^E) = \left[\frac{\sum \left(\frac{H^E_{\mathrm{exptl}} - H^E_{\mathrm{calcd}}}{H^E} \cdot 100 \right)^2}{(N - K)} \right]^{1/2} \tag{2}$$

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

Conclusion

The effect of different inorganic salts on the excess enthalpy of mixing (H^E) of a methanol + formic acid system at 303.15 K has been obtained using calorimetric measurements. The experimental H^E study and its statistical analysis show that $CdCl_2$ exhibits more negative enthalpy of mixing values for the binary mixture followed by an insignificant but smaller increase in negative enthalpy of mixing for the salt $ZnCl_2$. With increasing salt concentration, NH_4Cl shows more positive H^E values compared to the salt-free system which exemplifies the less importance of solvent−solvent interactions than solute−formic acid interaction. The above results also imply that the energy required to disrupt the intermolecular forces for the solvation of ions is more than the energy released. The Redlich−Kister model used in the present study represented the experimental data with the required accuracy, and therefore this model is suitable to predict the excess enthalpy of mixing in a methanol + formic acid binary mixture in the presence of the selected inorganic salts and develop new theories or equations of state for use in further studies.

Literature Cited

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

(2) 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.

(3) Long, F. A.; McDevit, W. F. Activity coefficients of nonelectrolytes solutes in aqueous salt solutions. *Chem. Rev.* **1952**, *51*, 119–169.

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

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

(6) Gironi, F.; Lamberti, L. Vapour-liquid equilibrium data for the water-2-propanol system in the presence of dissolved salts. *Fluid Phase Equilib.* **1995**, *105*, 273–286.

(7) 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.

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

(9) 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.

(10) 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.

(11) Rajendran, M.; Renganarayanan, S.; Srinivasan, D. Salt effect in phase equilibria and heat of mixing: effect of dissolved inorganic salts on the liquid-liquid equilibria of ethyl acetate - 2, propanol - water system and the vapour liquid equilibria of its constituent binaries. *Fluid Phase Equilib.* **1991**, *70*, 65–106.

(12) 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.

(13) 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.

(14) Kumar, M. D.; Rajendran, M. Salt effect on enthalpy of mixing of water + methanol at 303.15 K. *Fluid Phase Equilib.* **1999**, *164*, 217–224.

(15) 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.

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

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

(18) 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.

(19) 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.

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

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