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Effect of Cadmium Chloride and Ammonium Chloride Salts on the Enthalpy of Mixing of Pyridine + Water at 303.15 K

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ABSTRACT: In this work, the effect of two dissolved inorganic salts (cadmium chloride, $CdCl_2$; ammonium chloride, NH_4Cl) on the enthalpy of mixing (H^E) of the pyridine + water binary system measured at 303.15 K using an isothermal displacement calorimeter with vapor space is investigated. Compared with the salt-free system, the addition (0.05 mass fraction) of the salts altered the magnitude of H^E values to some extent depending on the mole fraction of x_1. The importance of the solute−solvent and solvent−solvent interactions was demonstrated from the increasing exothermic H^E values with increasing salt concentration (0.10 mass fraction). The experimental values of H^E were fitted into the Redlich−Kister polynomial, and the adjustable parameters obtained by the least-squares method are reported.

INTRODUCTION

Distillation is an energy-intensive process and employs the variation in temperature to separate a liquid and one or more other ingredients that are mixed together. Hence, it is important to understand the thermodynamic properties of liquid mixtures involved in the separation processes such as distillation and absorption in order to carry out a cost-efficient operation. Among the many thermodynamic functions of binary liquid mixtures, the knowledge of the excess enthalpy of mixing (H^E) is important not only for the design of separation processes, but also for the better understanding of molecular interactions existing between a pure component and its mixtures with other solvents, as well as to test and develop some new models and theories that are able to describe the thermodynamic properties of liquids.[1−4] Binary solutions containing salts are increasingly used in distillation due to their influence on the separation processes, and their accurate electrolytic data will help us not only to understand the nature of ion−ion and ion−solvent interactions but also to achieve its practical applicability in various fields. In the extractive distillation case, an inorganic salt acts as a separating agent when dissolved in a binary liquid mixture and can significantly change its equilibrium composition by modifying the relative volatility of the binary mixture accompanied with changes in the free energy of liquid mixture.[5,6]

With the addition of electrolytes to the liquid mixtures, Boone et al.[7] observed an appreciable change in the free energy of the liquid component. Furter and Cook[5] and Jacques and Furter[8] have studied the influence of added salt on the relative volatilities of two-liquid components using 19 inorganic salts. The formation of the associated complexes or clusters of molecules of the volatile component around salt ions and its effect on relative volatilities have been studied extensively by Long and McDevit.[9] An equation derived by Sada et al.[10] indicated the changes in the chemical potential of the solvent components when a salt is added to a solvent mixture. Vercher et al.[11] determined that the addition of salt to the solvent mixture affects the mutual solubility and relative volatility of the two liquid components. Meranda and Furter[12] have observed the gradual shift in the azeotropic composition in certain azeotropic systems by the addition of salts, while certain salts have been found to completely eliminate the azeotrope. Kato et al.[13] found that the addition of an inorganic salt eliminates the azeotrope completely at high salt concentrations. A few more researchers[14,15] have also studied the effect of added salts on the excess enthalpy values of liquid mixtures along with notable contributions from our group.[16−21] The above studies were quite helpful in predicting the phase equilibria of liquid mixtures under the influence of added salts and in understanding the interaction of molecules within the selected liquid mixtures.

As part of our continuing research, the present study investigates the effect of two dissolved inorganic salts (cadmium chloride, $CdCl_2$; ammonium chloride, NH_4Cl) on the H^E of the binary pyridine + water system at 303.15 K. Pyridine is widely used as a solvent, as a waterproofing agent, and in the manufacture of pharmaceuticals and vitamins. A pyridine (0.57 mass fraction) + water mixture forms a minimum boiling azeotrope at 367.15 K and is difficult to separate by conventional distillation methods due to its relative volatility of 1.0. The objective of the present work is to study the effect of selected inorganic salts in enhancing the relative volatility of pyridine from water, which could be useful in their separation by an extractive distillation method in a rectification column. The added inorganic salts (0.05 and 0.10 mass fraction) act as an extractant to separate an otherwise miscible pyridine + water mixture, and the H^E values were measured using a displacement calorimeter as a function of varying mole fraction of pyridine (x_1). 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. Pyridine (≥ 99.9 % purity) and the salts ($CdCl_2$ and NH_4Cl) used in this study were of analytical reagent

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Table 1. Physical Properties of the Solvents and Salts Used

solvent	this work	literature[22]
	boiling point, T_b/K	
pyridine	387.9	388.0
water	373.10	373.15
	ρ/(g·cm^{-3}), 298.15 K	
pyridine	0.9813	0.9819
water	0.9965	0.9970
	(as reported by the supplier)	
salt	melting point, T_m /K	purity
cadmium chloride	837.15	≥ 99.8 %
ammonium chloride	611.15	≥ 99.9 %

grade supplied by E-Merck. Deionized water was purchased from Milli-Q and used as received. Pyridine was further purified by fractional distillation and stored over activated molecular sieves of type 3 Å to remove residual traces of water. The purity of the solvents were checked by measuring their densities (ρ) and boiling points (T_b) using a bicapillary pycnometer and ebulliometer, respectively. After taking into consideration the uncertainty in the measured density and temperature values at ± $1 \cdot 10^{-4}$ and ± 0.1 K, respectively, their purity were found to be in close proximity with the literature values[22] 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.

Preparation of Salt Solutions. The mixtures were prepared by mass using a Mettler H51 balance (precision ± $1 \cdot 10^{-5}$ g). Salts used in the present investigation were first dissolved separately in the solvent to the desired level of concentration in which they are preferentially soluble at 303.15 ± 0.1 K. At this temperature, the material losses due to vaporization were taken to be insignificant. The initial concentrations of salts reported in this work (0.05 and 0.10 mass fractions] are the initial concentrations by mass [mass of salt/(mass of salt + mass of solvent)] before mixing with the other solvent.

Apparatus Used. The calorimeter used in the present investigation is basically the type employed by Tsao and Smith[23] and Murti and Winkle,[24] which is essentially a double-walled Dewar flask of 215 cm^3 volume. The schematic diagram of the experimental setup and the microprocessor design details are described elsewhere.[15] In brief, the H^E values were registered using a custom-made microprocessor (MIPROC)-based digital calorimeter system designed and constructed with assistance from Precision Instrument and Electronics (India) Ltd. It is designed to measure the heat equivalents in calories due to either endothermic or exothermic process when the two liquids are mixed. The calorimeter 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 apparatus and procedures were tested for their reliability by determining H^E values for the non-salt water + methanol binary system at 303.15 K (Figure 1), and the data obtained were found to differ by less than ± 2 % with the literature data.[25]

Experimental Procedure. The experimental procedure adopted in this work is described elaborately in an earlier report,[15] and some of the details are given below. The whole assembly of the calorimeter was placed in a constant-temperature bath in order to minimize the heat losses due to temperature changes. To cover the entire concentration range, the second component (solute) was taken in the calorimeter and the first component (solvent) was slowly added from the buret under constant stirring at around 80 rpm using a magnetic stirrer. The drop or rise in temperature during the mixing of the two components was recorded in the MIPROC system. 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}. Reproducibility of the H^E values was checked by performing the measurements in triplicate for each pyridine + water composition (refer to varying mole fractions of pyridine (x_1) values given in Tables 2 and 3) to obtain the average H^E values with a maximum uncertainty of ± 3 %. The mole fraction of water can be referred to as x_2, whereas x_3 refers to the mole fraction of solute (in Tables 2 and 3), and the sum of $x_1 + x_2 + x_3$ is equal to one with an estimated uncertainty of ± 0.001.

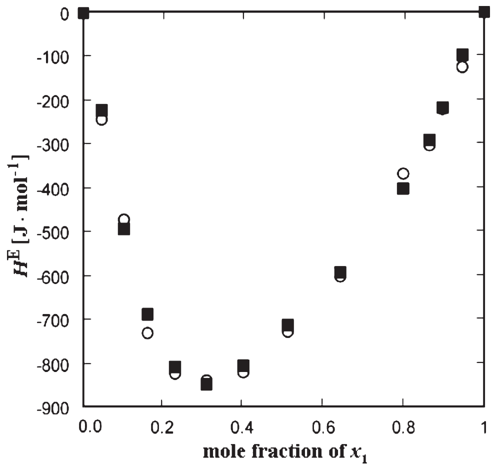

Figure 1. Enthalpy of mixing of water (1) + methanol (2) at 303.15 K: ○, this work; ■, Battler and Rowley.[25]

RESULTS AND DISCUSSION

The experimental H^E values obtained for the pyridine + water system for various concentrations of the two salts used herein are listed in Tables 2 and 3 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 pyridine (polar, aprotic) and water (polar, protic) is negative (exothermic) over the entire composition range, and this explains the strong intermolecular forces of attraction and complex formation on mixing between pyridine and water. The enthalpy of mixing for the salt-free pyridine + water system decreases with increasing mole fraction of pyridine (x_1) from 0.199 to 0.505 (Table 2 and Figure 2) accompanied with an increase in miscibility due to the strong hydrogen bonds or dipole—dipole intermolecular interaction that exist between the lone pair of electrons on pyridine's nitrogen atom and the water molecules. A further increase in x_1 results in an increase in H^E values, indicating that energy is required to overcome the intermolecular forces of attraction between pyridine and water.

Figure 2 illustrates the influence of 0.05 mass fraction of the salts ($CdCl_2$ and NH_4Cl) on the separation feasibility of pyridine + water system. The salts used in the present study altered the magnitude of H^E values along the exothermic direction, which

Table 2. Enthalpy of Mixing Data of the System Pyridine (1) + Water (2) at 303.15 K for the Salt $CdCl_2$[a]

			mass fraction of $CdCl_2$							
no salt			0.05				0.10			
x_1	H^E_{exptl}	H^E_{calcd}	x_1	x_3	H^E_{exptl}	H^E_{calcd}	x_1	x_3	H^E_{exptl}	H^E_{calcd}
mole fraction	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	mole fraction	mole fraction	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	mole fraction	mole fraction	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
0.095	−395.5	−391.5	0.093	0.0229	−464.6	−457.0	0.095	0.0491	−530.8	−530.8
0.199	−866.7	−862.1	0.195	0.0112	−860.5	−856.7	0.197	0.0244	−981.3	−980.7
0.298	−1093.4	−1094.2	0.297	0.0637	−1121.6	−1147.0	0.296	0.0121	−1297.7	−1298.4
0.403	−1230.2	−1234.3	0.403	0.0033	−1339.0	−1331.2	0.402	0.0070	−1497.9	−1497.0
0.505	−1280.9	−1276.1	0.501	0.0016	−1367.3	−1365.7	0.496	0.0037	−1538.0	−1539.6
0.601	−1236.2	−1232.6	0.602	0.0008	−1248.5	−1258.8	0.619	0.0018	−1398.6	−1395.8
0.703	−1129.3	−1128.3	0.705	0.0004	−1018.6	−1028.6	0.705	0.0008	−1166.2	−1167.8
0.807	−870.0	−866.2	0.802	0.0002	−724.7	−714.9	0.801	0.0002	−814.3	−814.9
0.904	−340.2	−341.5	0.912	0.0001	−303.0	−302.4	0.920	0.0001	−310.3	−309.1

[a] x_1 = mole fractions of pyridine. x_3 = mole fractions of solute.

Table 3. Enthalpy of Mixing Data of the System Pyridine (1) + Water (2) at 303.15 K for the Salt NH_4Cl[a]

mass fraction of NH_4Cl							
0.05				0.10			
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	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
0.095	0.0489	−279.6	−274.1	0.097	0.0233	−474.5	−482.3
0.201	0.0249	−751.9	−759.0	0.201	0.0121	−972.6	−958.2
0.305	0.0121	−1141.6	−1127.8	0.298	0.0063	−1256.1	−1267.2
0.397	0.0070	−1241.0	−1249.7	0.401	0.0033	−1408.1	−1413.1
0.501	0.0039	−1251.7	−1257.4	0.502	0.0016	−1415.9	−1423.7
0.621	0.0018	−1060.4	−1069.8	0.610	0.0008	−1244.5	−1252.1
0.709	0.0009	−872.5	−854.1	0.721	0.0004	−956.2	−966.1
0.802	0.0003	−612.6	−616.2	0.805	0.0002	−653.4	−664.0
0.911	0.0001	−266.9	−260.1	0.901	0.0001	−334.8	−337.2

[a] x_1 = mole fractions of pyridine. x_3 = mole fractions of solute.

can be attributed to the further strengthening of hydrogen bonding between pyridine and water in the presence of dissolved salts. A marked decrease in the H^E values was observed in the region of lower mole fraction of x_1, and the reverse trend was noticed in the region of higher mole fraction of x_1 irrespective of the salt type used. The addition of bivalent salt $CdCl_2$ increased the area of heterogeneity to some extent compared with the salt-free system and exhibited the exothermic maximum in the x_1 mole fraction region between 0.4 and 0.6. This trend may be attributed to the contribution from solvation energy of the salt without reducing intermolecular forces of attraction in solvents. In other words, the phase separation may be due to the stronger intermolecular forces between pyridine−Cd^{2+} ion complex than between water−pyridine or water−Cd^{2+} ions. These intermolecular interactions were so strong that they were effective even at low salt concentrations. A closer examination on the effect of 0.05 mass fraction of NH_4Cl salt revealed an insignificantly smaller change in the magnitude of H^E values compared with the salt-free system, and it is more pronounced in the mole fraction region of pyridine between 0.3 and 0.5. This trend implies that the energy required to disrupt the intermolecular forces for the solvation of ions is much more than the energy released. The resultant solvent interaction is expected to be less important than solute−pyridine interaction, and this interaction would not contribute much to the excess enthalpy of a system, because ammonium ions are not expected to have very strong interaction with pyridine.

Figure 3 and Tables 2 and 3 show the effect of increasing salt concentration (0.10 mass fraction) on the H^E values of the pyridine + water system. Increasing addition of the salts $CdCl_2$ and NH_4Cl in the system does bring out a significant change in the H^E values along the negative direction due to the formation of molecular complexes involving hydrogen bonding between pyridine and water molecules. The energy released during salt addition is more than the energy required to disrupt the intermolecular forces of attraction for solvation of ions. During the actual process of separation of two components by extractive distillation, it would be more beneficial if the mole fraction of pyridine is maintained at around 0.5 in the presence of the added

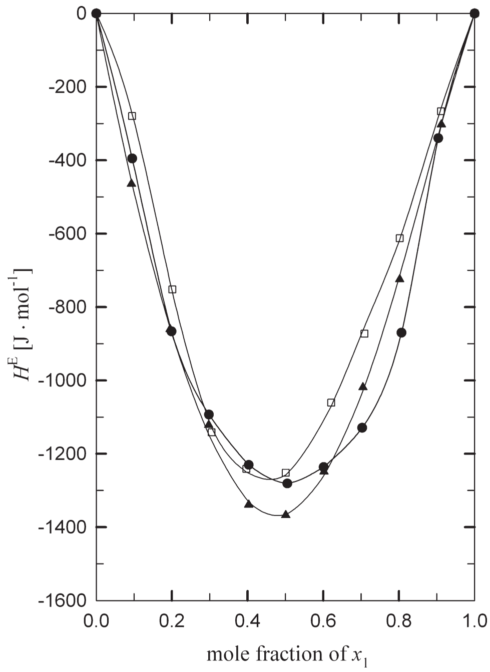

Figure 2. Effect of 0.05 mass fraction of the salts on the H^E of pyridine (1) + water (2) system at 303.15 K against the mole fraction of x_1: ▲, $CdCl_2$; □, NH_4Cl; and ●, salt-free solution. Solid lines and symbols indicate the calculated and experimental H^E values, respectively.

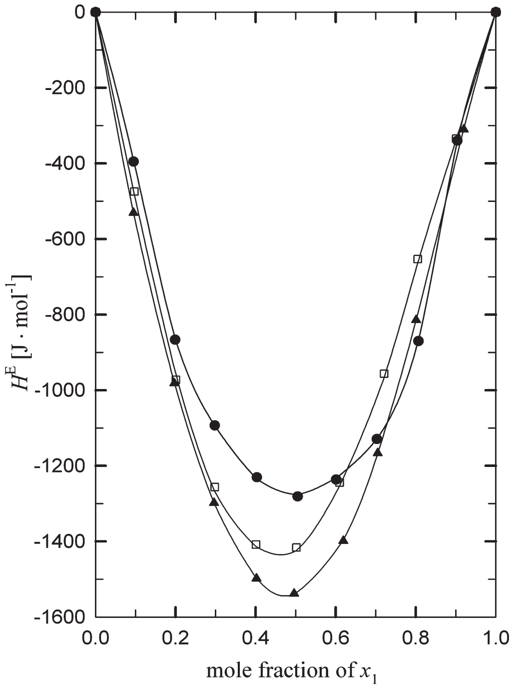

Figure 3. Effect of 0.10 mass fraction of the salts on the H^E of pyridine (1) + water (2) system at 303.15 K against the mole fraction of x_1: ▲, $CdCl_2$; □, NH_4Cl; and ●, salt-free solution. Solid lines and symbols indicate the calculated and experimental H^E values, respectively.

Table 4. Estimated Parameters of eq 1 and Standard Deviation, $\sigma(H^E)$, in eq 2 for the System Pyridine (1) + Water (2) at 303.15 K

salt concn mass fraction	A_0	A_1	A_2	A_3	$\sigma(H_E)$ J·mol^{-1}
no salt	−4775.1	−362.5	−7456.1	1048.2	1.87
0.05 $CdCl_2$	−5739.8	593.0	1285.3	672.6	1.24
0.10 $CdCl_2$	−5745.6	576.2	1279.8	737.7	0.15
0.05 NH_4Cl	−4914.9	2449.0	1716.8	−4860.3	1.57
0.10 NH_4Cl	−5271.8	1962.7	1137.7	−1664.0	1.9

salts. At higher mole fractions of x_1, their separation becomes less formidable. Among the salts used, the divalent salt $CdCl_2$ is preferred over the univalent salt NH_4Cl due to its higher degree of interaction with the pyridine molecules and more contribution toward the separation of pyridine + water mixture compared with the univalent salt NH_4Cl, which exhibited a decreased area of heterogeneity (Figures 2 and 3). Overall, the experimental H^E data of liquid mixtures allow us to draw information on the structure and interactions of mixed solvents with the added salts and serve as a qualitative guide to predict the extent of complex formation in binary liquid mixtures.

Data Correlation and Statistical Analysis. In our study, each set of the experimental H^E values was fitted to the two-component Redlich−Kister polynomial,[26] and the calculated H^E values are presented in Tables 2 and 3. Plots of these representations are shown as solid curves in Figures 2 and 3. This model expresses the excess free energy of mixing as the sum of terms that consist of a function of the mole fractions of each component and an interaction parameter.

$$H^E/\text{J}\cdot\text{mol}^{-1} = x_1x_2 \sum_{i=0}^{j} A_i(2x_1 - 1)^i \qquad (1)$$

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 above equation provides a more accurate representation of the experimental set of data in cases where the representation of data is clearly asymmetric.

The binary parameters (A_i) were evaluated by fitting the experimental H^E values to the above equation by the method of least-squares with each point weighted equally. 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 4), the optimum number of coefficients is ascertained from the examination of the variation in the standard deviation, $\sigma(H^E)$, between the experimental and calculated H^E values, as calculated using eq 2.

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

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.[5,8] The results obtained from this study indicate that the mass of the added salt has a strong effect on the estimated parameters and their corresponding standard deviations, which may have resulted from the interaction between the individual salt and the functional groups present in the pyridine + water system.

CONCLUSION

The effect of two different inorganic salts ($CdCl_2$ and NH_4Cl) on the excess enthalpy of mixing (H^E) of pyridine + water binary system at 303.15 K has been obtained using calorimetric measurements. The added salts preferentially influence the interaction of the pyridine + water mixture resulting in exothermic H^E values. For the addition of 0.05 mass fraction of salts, the phase separation of the pyridine + water binary mixture is largely favored by using the bivalent salt ($CdCl_2$) as observed from the exothermic increase in its H^E values compared with the salt-free system. H^E values increased along the positive direction for the addition of univalent salt (NH_4Cl), 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. At higher salt concentration (0.10 mass fraction), the addition of $CdCl_2$ and NH_4Cl resulted in an increase in exothermic H^E values, which illustrates the lower importance of solvent−solvent interactions than solute−solvent interaction. 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 pyridine + water system in the presence of the selected inorganic salts and to develop new theories or equations of state for use in further studies. The inorganic salts used in this study would be effective in the separation of pyridine from water using extractive distillation by enhancing the relative volatility between pyridine and water and to make separation by rectification possible with only a few theoretical plates.

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NOMENCLATURE

H^E, excess enthalpy of mixing, $J \cdot mol^{-1}$
T_b, boiling point of solvent, K
T_m, melting point of salt, K
x_1, mole fraction of pyridine
x_2, mole fraction of water
x_3, mole fraction of solute

Greek Letters

ρ, density, $g \cdot cm^{-3}$
σ, standard deviation

Subscripts

calcd, calculated
exptl, experimental

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