Experimental determination and correlation of enthalpy of mixing of binary methanol + ethyl acetate system in the presence of dissolved inorganic salts at 303.15 K

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ARTICLE INFO	ABSTRACT
Article history: Received: 21 February 2011; Received in revised form: 20 March 2011; Accepted: 29 March 2011; **Keywords** Excess Enthalpy, Calorimeter, Inorganic Salts, Methanol, Ethyl acetate.	This paper presents the effect of five dissolved inorganic salts ($NaCl$, $CaCl_2$, $ZnCl_2$, $CdCl_2$ and NH_4Cl) on the endothermic enthalpy of mixing of the binary methanol + ethyl acetate system has been investigated at 303.15 K, using an isothermal batch calorimeter with vapour space. The endothermic excess enthalpies of mixing values are significantly increases for the addition of $ZnCl_2$, $CdCl_2$ and $CaCl_2$. For the addition of $NaCl$ and NH_4Cl salts are insignificantly decreases the endothermic excess enthalpy values. The experimental values of the enthalpy of mixing were fitted into a Redlich – Kister equation, the deviations and parameters were reported. The experimental and correlation results reveals that the importance of the solvent- solvent and solute-solvent interaction by the enhanced excess enthalpy of mixing (H^E) values in the positive direction with increasing concentration of the salts.

Introduction

The various thermodynamic properties like excess enthalpy, excess volume and excess free energy of a pure solvent and its mixtures are helpful to better understand as well as explain the molecular interaction between the components. Different types of phase equilibria and excess thermodynamic properties of liquid mixtures are used to validate and develop new models as well as new theories that are able to describe the thermodynamic behavior of liquids. Excess thermodynamic functions have been used as a qualitative guide to predict the extent of complex formation in binary liquid mixtures. Literature survey reveals that excess enthalpy of mixing data of electrolyte solution particularly in the mixed solvent system are lacking. Accurate electrolytic data in aqueous as well as mixed solvent system are required for the study of real behavior of binary systems and also frequently described by Prausnitz, *et al.,* (1999) through excess properties. An important technique in extractive distillation is the use of salts as on extractive agent to modify the relative volatility of the binary mixtures. Furter and Cook (1967) and Jaques and Furter (1972) have studied the influence of added salt on the relative volatilities of two liquid components using 19 inorganic salts. Chen and co-workers (1982, 1986a, 1986b) described the salt effects in terms of the interaction between each salt ion and each of the solvent components. The addition of inorganic salt to the binary solvent mixture affects the boiling point, the mutual solubility of the liquid components, and the relative volatility of pure as well as mixed solvent systems were studied by Vercher *et. al.*, (2005) and Mock *et al.,* (1986).

Salt enhanced distillation employing a dissolved form of a salt as separating agent in a mixed solvent consisting of two miscible liquids is a promising but relatively little used extractive technique for achieving azeotropic and other difficult separations are studied by Zhao *et al.,* (1995). Relative volatility and azeotropy like properties are influenced by the addition of salts. For the addition of salt as an extractive agent the azeotrope can be shifted or can even be broken was studied by Gironi and Lambert (1995). Some of the salts have been found to completely eliminate the azeotrope. Since there is an interrelation, between the excess free energy and the excess enthalpy of liquid mixtures are observed by Lim *et al.,*(2001). 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 Mc Devit (1952). Furter (1976) has reported that the salt and solvent interaction among all the components of the system. An equation has been derived by Sada *et al.,* (1975) indicating the changes in the chemical potential of the solvent components when a salt is added to a mixed solvent. Meranda and Furter (1974) have observed a gradual shift in the azeotropic composition in certain azeotropic systems by the addition of salts. Certain salts have been found to completely eliminate the azeotrope. Very little information on the measurements of the excess enthalpy of mixing of binary mixtures in the presence of dissolved inorganic salts has been reported along with notable contributions from our group(Rajendran et al. 1988, 1989,1991,1994; Dharmendirakumar et al. 1999a,1999b and Tamilarasan et al. 2008,2009a, 2009b, 2009c, 2010a,2010b). It is therefore of interest to investigate the effect of dissolved inorganic salts on enthalpy of mixing of liquid mixtures, which are the commercial importance. In this investigation the effect of five dissolved inorganic salts (Sodium chloride, Calcium chloride, Zinc chloride, Cadmium chloride and Ammonium chloride) on the enthalpy of mixing of the binary methanol +

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ethyl acetate has been studied experimentally.

Experimental Section
Chemicals Used.

Analytical reagent grade methanol, ethyl acetate and the salts (sodium chloride, calcium chloride, cadmium chloride, zinc chloride and ammonium chloride) used in this investigation were supplied by E-Merck. The solvents were purified by fractional distillation. Their densities were measured using a bicapillary pycnometer and their boiling points were measured using an ebulliometer giving a precision of ± 0.2 K. After taking into consideration the uncertainty in the measured density and temperature values at $\pm 1 \times 10^{-4}$ and ± 0.2 K, respectively, the purity of the solvents were found to be in close proximity with the literature values(Timmermanns, 1990) as shown in Table 1. The melting point (Tm) 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

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. The concentrations of salts reported in this work (5% and 10%) are the initial mass concentrations [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 (Rajendran, 1989) 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. 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 non-salt water + methanol binary system at 303.15 K (Figure 1), and the data compared well (within 2 %) with the literature data (Battler and Rowley,1985).

Triplicate samples were prepared for each methanol + ethyl acetate composition (refer to varying mole % methanol (x_1) values given in Tables 2 to 5) to ensure reproducibility (within ± 3 %), and the average values are presented. The mole fraction of ethyl acetate 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.
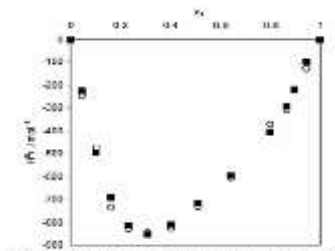

Figure 1. Enthalpy of mixing of water + methanol at 303.15 K:
○, this work; ■, Battler and Rowley

Results and Discussion

The experimental excess enthalpy data obtained for the methanol + ethyl acetate system under various salt conditions are given in the form of tables and also represented graphically as detailed below. The enthalpy of mixing of this system is endothermic. Both the solvents are polar in nature, Hence solvent-solvent interaction is very weak. The mixing is due to the weak Vander waals forces of attraction and dipole-induced dipole interaction between the solvents. The influence of salts NaCl, CaCl$_2$, ZnCl$_2$, CdCl$_2$, and NH$_4$Cl on the excess enthalpy of mixing of this system is illustrated in Tables 2 to 5. Figure 2 shows the enthalpy values of the system with 5 % mass of the salts NaCl, CaCl$_2$, ZnCl$_2$, CdCl$_2$, and NH$_4$Cl. The salt-free data are also given in the figure for the purpose of comparison. The addition of 5% salts, which increases the endothermic enthalpy values compared to the salt – free system, this is because due to the salt - solvent (methanol) interaction is more favour than that of solvent-solvent interactions.
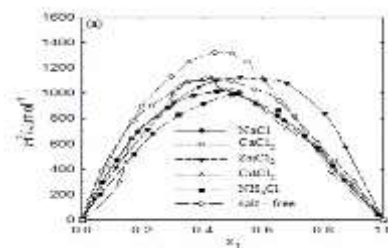

Figure. 2 Effect of 5 % mass of the salts on the enthalpy of mixing (H^E) of Methanol + Ethyl acetate system at 303.15 K against the mole fraction of x$_1$.

A closer examination on the effect of the other salts compared to the salt ZnCl$_2$ revealed that a significantly increasing excess enthalpy values illustrates the complex formation and strong intermolecular forces of attraction between ethyl acetate and methanol dipoles with the metal ions. The smaller Zn^{2+} ions have more inter-ligand forces are expected on its coordination sphere, providing more positive enthalpy of mixing is more pronounced in the mole fraction region of methanol between 0.215 and 0.607. Addition of 5% NaCl and NH$_4$Cl which decreases the endothermic enthalpy values is due to the solvent-solvent interaction is expected to be less important than solute-solvent interaction aided by an expected repulsion among ethyl acetate in the salvation 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 + ethyl acetate system was studied using a salt CaCl$_2$ as shown in Figure 3. The addition of 10% CaCl$_2$ slightly increase in the excess enthalpy of mixing is well pronounced when x_1 is between 0.198 and 0.496, this trend may be due to contribution from the solvation energy of the salt with the solvents.
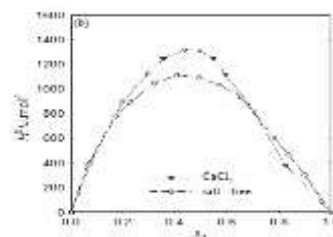

Figure. 3 Effect of 10 % mass of the salt on the enthalpy of mixing (H^E) of Methanol + Ethyl acetate system at 303.15 K against the mole fraction of x$_1$.

Data Correlation and Statistical Analysis

The Redlich-Kister (1948) 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. In this study, the effect of added salts on the experimental enthalpy data (H^E) was correlated with H^E values calculated using the Redlich-Kister polynomial(1948).

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

where H^E is the enthalpy of mixing; x_1 and x_2 are the mole fractions of the solvents 1 and 2, respectively; and A_i is a constant that is a function of temperature and the system properties.

The experimental H^E values were fitted with Eq. (1) by the least-squares method with each point weighted equally, and the binary parameters (A_i) were evaluated. The modeling results are listed in Table 6 along with the percentage standard deviation ($\%\sigma(H^E)$). The values of the percentage standard deviation σ are computed from Eq. (2) and shown in Table 6.

$$\%\sigma(H^E) = \left[\frac{\sum \left(\frac{H^E_{\text{exp}\,tl} - H^E_{\text{calcd}}}{H^E} \bullet 100 \right)^2}{(N - K)} \right]^{1/2} \qquad (2)$$

where N and K are the number of data points and the number of parameters, respectively. The results obtained 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 solvents present in methanol + ethyl acetate system.

Conclusion

The effect of different inorganic salts on the excess enthalpy of mixing (H^E) of a methanol + ethyl acetate system at 303.15 K has been obtained using calorimetric measurements. The experimental H^E study and its statistical analysis show that the enthalpies of mixing value of the system for both salt-free and salt systems are positive. In the salt-free system the ability of polar methanol to associate with ethyl acetate via polarization would require prior inhibition of the intermolecular association of methanol by an expenditure of energy. The positive value of the enthalpy of mixing supported this conclusion. The same positive but higher value of the enthalpy of mixing observed when the salt is added evidently confirms the existence of methanol – metal ion complexes prior to the mixing of methanol with ethyl acetate. This may be due to the requirement of an additional expenditure of energy that could be required to liberate to coordinated methanol from the coordination sphere in order to bring into association with ethyl acetate.

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Table 1: Physical Properties of Solvent and salts Used

Solvent	T_b / K		$\rho/(g\ cm^{-3})$	
	This work	Lit. 15	This work	Lit.15
Methanol	337.60	337.20	0.7821	0.7825
Ethyl acetate	350.23	350.10	0.9165	0.9140

Salt	As reported by the supplier	
	Melting point, T_m / K	Purity
Sodium chloride	1073.45	$\geq$ 99.8 %
Calcium chloride	1044.85	$\geq$ 99.9 %
Cadmium chloride	841.25	$\geq$ 99.8 %
Zinc chloride	566.35	$\geq$ 99.9 %
Ammonium chloride	612.85	$\geq$ 99.8 %

Table 2: Enthalpy of Mixing Data for the System Methanol +Ethyl acetate at 303.15 K for the Salt NaCl

	No Salt		NaCl 5%			
X_1	H^E J.mol-1 (Expt.)	H^E J.mol-1 (Calcd.)	X_1	X_3	H^E J.mol^{-1} (Expt.)	H^E J.mol^{-1} (Calcd.)
0.065	389.11	384.60	0.065	5.090×10^{-2}	293.70	293.50
0.170	780.02	676.40	0.115	4.657×10^{-2}	470.70	478.20
0.230	897.97	904.20	0.185	3.990×10^{-2}	694.10	685.00
0.321	1047.17	1049.20	0.286	3.373×10^{-2}	888.60	890.40
0.408	1111.06	1109.50	0.370	2.807×10^{-2}	983.60	985.00
0.494	1097.04	1092.10	0.445	2.270×10^{-2}	1012.50	1013.50
0.572	1028.72	1031.70	0.516	1.769×10^{-2}	995.70	992.60
0.653	936.96	925.20	0.670	1.138×10^{-2}	784.90	795.50
0.780	608.39	611.50	0.739	7.337×10^{-2}	661.90	648.80
0.837	467.77	465.70	0.868	2.932×10^{-2}	312.60	317.80
0.900	302.00	300.20	0.981	2.416×10^{-4}	039.60	038.20
0.981	067.98	069.50				

Table 3: Enthalpy of Mixing Data for the System Methanol +Ethyl acetate at 303.15 K for the Salt CaCl₂

		CaCl₂ 5%				CaCl₂ 10%	
X_1	X_3	H^E J.mol^{-1} (Expt.)	H^E J.mol^{-1} (Calcd.)	X_1	X_3	H^E J.mol^{-1} (Expt.)	H^E J.mol^{-1} (Calcd.)
0.045	5.218×10^{-2}	311.20	313.00	0.028	9.870×10^{-2}	156.90	156.40
0.102	4.697×10^{-2}	605.90	596.20	0.080	8.952×10^{-2}	419.80	417.30
0.218	4.046×10^{-2}	909.60	920.40	0.198	6.938×10^{-2}	896.90	885.90
0.314	3.475×10^{-2}	1052.20	1050.50	0.296	6.034×10^{-2}	1128.90	1150.70
0.408	2.833×10^{-2}	1121.70	1120.30	0.354	5.412×10^{-2}	1245.90	1250.20
0.475	2.339×10^{-2}	1152.20	1145.70	0.439	4.302×10^{-2}	1318.90	1311.00
0.517	2.117×10^{-2}	1138.00	1141.20	0.496	3.625×10^{-2}	1308.90	1291.50
0.651	1.618×10^{-2}	1076.10	1085.70	0.547	2.885×10^{-2}	1245.90	1231.90
0.742	9.951×10^{-3}	975.20	944.10	0.596	2.176×10^{-2}	1114.60	1138.30
0.791	7.421×10^{-3}	796.60	826.60	0.705	1.220×10^{-2}	812.90	819.80
0.905	5.861×10^{-3}	441.60	434.70	0.826	5.366×10^{-3}	378.90	371.60
0.931	7.792×10^{-4}	326.90	323.70	0.957	1.014×10^{-3}	017.10	016.50

Table 4 : Enthalpy of Mixing Data for the System Methanol +Ethyl acetate at 303.15 K for Salts ZnCl₂ and CdCl₂

		ZnCl₂ 5%				CdCl₂ 5%	
X_1	X_3	H^E J.mol^{-1} (Expt.)	H^E J.mol^{-1} (Calcd.)	X_1	X_3	H^E J.mol^{-1} (Expt.)	H^E J.mol^{-1} (Calcd.)
0.041	5.225×10^{-2}	162.90	162.80	0.064	5.181×10^{-2}	302.90	301.60
0.112	4.677×10^{-2}	412.90	415.90	0.169	4.545×10^{-2}	642.90	657.80
0.217	4.066×10^{-2}	712.60	721.40	0.231	4.016×10^{-2}	821.20	813.10
0.304	3.487×10^{-2}	925.60	911.90	0.320	3.462×10^{-2}	996.50	981.90
0.386	2.948×10^{-2}	1049.30	1039.20	0.405	2.924×10^{-2}	1089.90	1087.80
0.442	2.473×10^{-2}	1094.10	1096.80	0.497	2.345×10^{-2}	1102.10	1132.30
0.524	1.960×10^{-2}	1122.90	1136.80	0.573	1.814×10^{-2}	1119.80	1107.80
0.605	1.476×10^{-2}	1104.50	1121.90	0.657	1.356×10^{-2}	1026.20	1007.70
0.678	1.045×10^{-2}	1076.10	1057.90	0.698	1.106×10^{-2}	1011.90	1023.80
0.804	5.593×10^{-3}	839.30	816.10	0.785	5.947×10^{-2}	718.20	708.40
0.873	2.648×10^{-3}	574.90	599.40	0.832	3.317×10^{-3}	549.80	561.40
0.975	2.989×10^{-4}	139.80	141.50	0.902	1.038×10^{-3}	321.20	322.40

Table 5: Enthalpy of Mixing Data for the System Methanol +Ethyl acetate at 303.15 K for the Salt NH₄Cl.

	NH₄Cl 5%		
X_1	X_3	H^E J.mol^{-1} (Exp)	H^E J.mol^{-1} (Pre)
0.061	5.187×10^{-2}	201.60	200.60
0.172	4.554×10^{-2}	512.90	519.20
0.235	4.028×10^{-2}	680.90	669.20
0.32	3.461×10^{-2}	826.50	828.80
0.401	2.914×10^{-2}	911.40	927.30
0.496	2.318×10^{-2}	987.60	966.10
0.575	1.841×10^{-2}	921.50	930.70
0.651	1.370×10^{-2}	860.10	838.60
0.648	1.249×10^{-2}	822.60	843.30
0.781	6.055×10^{-3}	570.40	567.10
0.831	3.337×10^{-3}	426.90	435.90
0.905	1.042×10^{-3}	239.80	233.10

Table 6; The Estimated Parameters of Equation (1) and the Percentage of Standard Deviation % σ (H^E) of the System Methanol + Ethyl acetate at 303.15 K

System	Salt conc.	A_0	A_1	A_2	A_3	% σ H^E
	5% NaCl	4005.36	-945.12	-533.71	-617.61	1.56
	5% CaCl₂	4599.26	188.98	1870.30	-1736.49	1.82
	10% CaCl₂	5153.18	-1680.52	-2503.12	-1471.40	1.66
Methanol + Ethyl acetate	5% ZnCl₂	4522.66	706.47	495.92	195.42	1.98
	5% CdCl₂	4530.08	71.14	-405.14	1304.55	1.69
	5% NH₄Cl	3863.61	-186.62	-1119.56	-501.40	1.96