J. Chem. Eng. Data 2000, 45, 11−14

Salt Effect on Enthalpy of Mixing of Methanol + Ethyl Acetate at 303.15 K

M. Dharmendira Kumar and M. Rajendran*

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

The effect of three dissolved salts, namely sodium iodide, magnesium nitrate, and mercuric chloride, on the endothermic enthalpy of mixing of the binary system methanol + ethyl acetate has been investigated at 303.15 K in an isothermal batch calorimeter with vapor space. The influence of the salt sodium iodide is more pronounced at higher concentrations of the salt while the salt magnesium nitrate brought about an enhancement in the enthalpy of mixing values even at a lower concentration. The salt mercuric chloride, on the other hand, has been found to reduce the enthalpy values of the system. The experimental values of the enthalpy of mixing were fitted into a modified Redlich−Kister equation, and deviations and parameters are reported.

Introduction

In recent years there has been considerable progress in the experimental investigation of the thermodynamic properties under the influence of salts dissolved in liquid mixtures. These thermodynamic properties have been used as a qualitative guide to predict the extent of complex formation in binary liquid mixtures. An important technique in extractive distillation is the use of salts as extractive agents to modify the relative volatility of binary mixtures (Furter and Cook, 1967; Jaques and Furter, 1972). The most likely effect is that the salt would induce the formation of associated complexes or clusters of molecules of the volatile component about its ions (Long and McDevit, 1952) and that the salt effect is believed to be a complex function of salt and solvent interaction and self-interaction among all the components of the system (Furter, 1976). An equation has been derived indicating the changes in the chemical potentials of the solvent components when a salt is added to a mixed solvent (Sada et al., 1975). While a number of works on the effect of dissolved salts on VLE and LLE have been reported, only a few measurements of the excess enthalpy of the binary mixture in the presence of dissolved inorganic salts have been reported (Rajendran et al., 1988, 1989a, 1989b, 1991, 1994; Dharmendira Kumar and Rajendran, 1999a, 1999b; Nowicke et al., 1997). In this investigation the effect of the salts sodium iodide, magnesium nitrate, and mercuric chloride on the enthalpy of mixing of methanol + ethyl acetate has been studied at 303.15 K.

Experimental Section

Chemicals Used. Methanol, ethyl acetate, and the salts were of analytical reagent grade and supplied by E-merck. The solvents were further purified by fractional distillation and the salts were dried in a desiccator for more than 24 h before use. The purities of the compounds were also checked by comparing measured normal boiling points with those reported in the literature (Riddick et al.,1986; Timmermans, 1980). Boiling points were measured using a Swietoslawski-type ebulliometer with an accuracy of ±0.2 K. The measured values are given in Table 1 along with literature values (Timmermans, 1980).

Table 1. Physical Properties of Solvents Used

	normal boiling point, T_b/K	
solvent	this work	lit. (Timmermans, 1980)
methanol	337.72	337.70
ethyl acetate	359.8	360.1

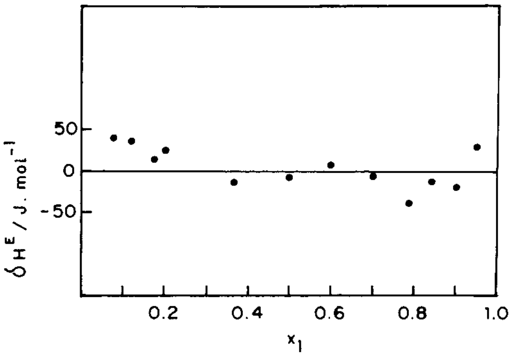

Figure 1. Enthalpy of mixing for the system water (1) + methanol (2) at 303.15 K: Comparison of reported data of Battler and Rowley (1995) with experimental work.

Experimental Apparatus. The calorimeter was of the type employed by earlier workers (Taso and Smith, 1953; Murti and VanWinkle, 1957). The description of the apparatus was given by Rajendran et al. (1989). The performance of the calorimeter and its reliability for the measurement of enthalpy of mixing values were ascertained by determining the enthalpy of mixing for water + methanol at 303.15 K. The results compared well, within 2%, with literature data (Battler and Rowley, 1985), as shown in Figure 1. The standard experimental procedure followed has been described in our earlier paper (Rajendran et al.,

---

* To whom correspondence should be addressed. E-mail: mrajendran@annauniv.edu.

10.1021/je990074u CCC: $19.00

Table 2. Enthalpy of Mixing Data for the System Methanol (1) + Ethyl Acetate (2) at 303.15 K for the Salt NaI[a]

salt-free		5 mass % NaI			10 mass % NaI		
x_1	H^E/J·mol^{-1}	x_1	x_3	H^E/J·mol^{-1}	x_1	x_3	H^E/J·mol^{-1}
0.065	389	0.030	1.750×10^{-3}	472	0.057	1.337×10^{-4}	570
0.170	780	0.055	5.790×10^{-3}	648	0.096	4.647×10^{-4}	610
0.230	897	0.091	1.837×10^{-2}	753	0.145	1.087×10^{-3}	1535
0.321	1047	0.188	5.451×10^{-2}	805	0.201	2.067×10^{-3}	1874
0.408	1111	0.262	1.173×10^{-1}	864	0.300	4.946×10^{-3}	2029
0.494	1097	0.308	1.592×10^{-1}	866	0.398	9.405×10^{-3}	2037
0.572	1028	0.390	2.351×10^{-1}	775	0.500	1.590×10^{-2}	1828
0.653	936	0.487	3.607×10^{-1}	662	0.600	2.476×10^{-2}	1472
0.780	608	0.563	4.982×10^{-1}	507	0.682	3.571×10^{-2}	921
0.837	467	0.714	7.849×10^{-1}	292	0.802	5.248×10^{-2}	821
0.900	302	0.831	9.240×10^{-1}	177	0.850	6.917×10^{-2}	201
0.981	67						

[a] x_1, mole fraction; x_3, mass fraction.

Table 3. Enthalpy of Mixing Data for the System Methanol (1) + Ethyl Acetate (2) at 303.15 K for the Salt Mg(NO$_3$)$_2$[a]

5 mass % Mg(NO$_3$)$_2$			10 mass % Mg(NO$_3$)$_2$		
x_1	x_3	H^E/J·mol^{-1}	x_1	x_3	H^E/J·mol^{-1}
0.048	5.334×10^{-5}	677	0.047	1.192×10^{-4}	753
0.097	2.226×10^{-4}	1171	0.090	5.384×10^{-4}	1393
0.142	5.042×10^{-4}	1723	0.184	1.799×10^{-3}	1945
0.193	9.339×10^{-4}	1991	0.275	4.376×10^{-3}	2112
0.235	1.873×10^{-3}	2092	0.365	9.615×10^{-3}	2008
0.376	4.218×10^{-3}	1903	0.451	1.444×10^{-2}	1736
0.466	7.099×10^{-3}	1497	0.544	2.087×10^{-2}	1380
0.555	1.102×10^{-2}	1242	0.636	3.272×10^{-2}	1004
0.642	1.626×10^{-2}	805	0.722	5.103×10^{-2}	669
0.732	2.333×10^{-2}	594	0.788	6.097×10^{-2}	502
0.821	3.283×10^{-2}	412	0.807	7.318×10^{-2}	470
0.921	4.122×10^{-2}	230	0.855	7.807×10^{-2}	340

[a] x_1, mole fraction; x_3, mass fraction.

1989). The total volume of the calorimeter is 215 mL. The salt was first dissolved to the required mass in the solvent in which it is preferentially soluble at the temperature 303.15 ± 1 K. The mass values of salt reported in this work (5% and 10% mass) are in the methanol component. These concentrations are the initial concentration of salt in methanol before mixing with ethyl acetate. Some of the experimental runs were repeated to check the reproducibility of the data, which was found to be within ±3% error.

Results and Discussion

The enthalpy values of the binary miscible systems methanol + ethyl acetate were measured experimentally using salts the NaI, Mg(NO$_3$)$_2$, and HgCl$_2$ individually (Tables 2−4).

Figure 2 shows the enthalpy values of the system with 5% mass of NaI, Mg(NO$_3$)$_2$, and HgCl$_2$. The salt-free data are also given in the figure. It can be observed from the figure that the salts NaI and HgCl$_2$ show a reduction in the values of H^E compared to the salt-free data. While the salt Mg(NO$_3$)$_2$ enhances the H^E values to a large extent. The values of H^E at equimolar composition (0.5 mole fraction) are 1100 J mol^{-1} for the salt-free data, 650 J mol^{-1} for NaI, 800 J mol^{-1} for HgCl$_2$, and 1300 J mol^{-1} for Mg(NO$_3$)$_2$. It may further be observed that the peak values get shifted to 0.25 mole fraction of the liquid mixture in the case of NaI and Mg(NO$_3$)$_2$.

Table 4. Enthalpy of Mixing Data for the System Methanol (1) + Ethyl Acetate (2) at 303.15 K for the Salt HgCl$_2$[a]

5 mass % HgCl$_2$			10 mass % HgCl$_2$		
x_1	x_3	H^E/J·mol^{-1}	x_1	x_3	H^E/J·mol^{-1}
0.198	4.026×10^{-4}	460	0.107	7.602×10^{-5}	133
0.327	1.351×10^{-3}	698	0.198	1.942×10^{-4}	360
0.426	2.436×10^{-3}	787	0.324	3.307×10^{-4}	543
0.491	3.079×10^{-3}	808	0.481	1.532×10^{-3}	677
0.547	4.612×10^{-3}	810	0.536	3.489×10^{-3}	682
0.593	5.596×10^{-3}	801	0.597	8.104×10^{-3}	671
0.621	1.088×10^{-2}	790	0.653	1.448×10^{-2}	642
0.654	1.478×10^{-2}	769	0.707	2.097×10^{-2}	611
0.686	1.917×10^{-2}	755	0.729	2.836×10^{-2}	594
0.703	2.341×10^{-2}	742	0.743	3.641×10^{-2}	579
0.721	2.556×10^{-2}	719	0.819	4.909×10^{-2}	502
0.754	2.931×10^{-2}	705	0.892	5.857×10^{-2}	251
0.841	3.564×10^{-2}	418	0.912	6.553×10^{-2}	209
0.880	4.392×10^{-2}	319	0.934	7.323×10^{-2}	146
			0.957	8.155×10^{-2}	88

[a] x_1, mole fraction; x_3, mass fraction.

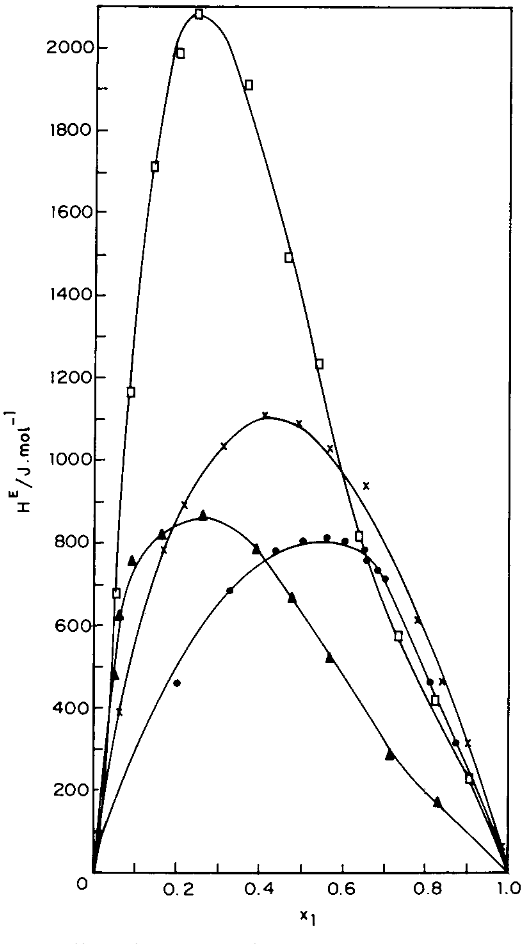

Figure 2. Effect of 5% mass of the salts NaI (▲), Mg(NO$_3$)$_2$ (□), and HgCl$_2$ (●) and salt-free solution (×) on the enthalpy of mixing of methanol (1) + ethyl acetate (2) at 303.15 K. Solid lines indicate calculated value.

It may be presumed that the decrease in the original (salt-free) values of H^E may be due to the reduction in surface tension values of methanol (+ salt), which favors much interaction with ethyl acetate. When the mass of these salts was increased to 10% in methanol and the solution was mixed with ethyl acetate, the enthalpy of mixing values obtained were altogether different from those obtained at lower mass fraction.

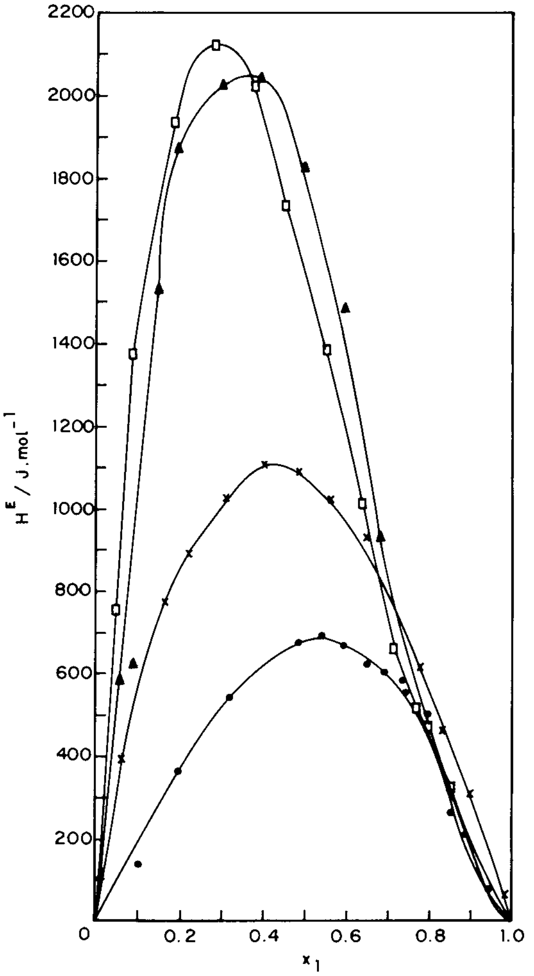

Figure 3. Effect of 10% mass of the salts NaI (▲), $Mg(NO_3)_2$ (□), and $HgCl_2$ (●) and salt-free solution (×) on the enthalpy of mixing of methanol (1) + ethyl acetate (2) at 303.15 K. Solid lines indicate calculated value.

Figure 3 shows the values of H^E of the system with 10% mass values of NaI, $Mg(NO_3)_2$, and $HgCl_2$. The peak values have tremendously increased in the case of the NaI salt while the increase is marginal in the case of $Mg(NO_3)_2$. However, the salt $HgCl_2$ has further reduced the H^E values at higher mass fraction in the binary mixture.

Correlation of the Data

The experimental H^E values were fitted in the following equation

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

by the method of least squares, with each point weighted equally, and the binary parameters h_i have been evaluated and are listed in Table 5 along with the percentage standard deviations. The values of the percentage standard deviation σ are computed from the relation

$$\%\sigma(H^E) = \left[\frac{\sum\left(\dfrac{H^E_{\mathrm{exp}} - H^E_{\mathrm{cal}}}{H^E_{\mathrm{exp}}} \times 100\right)^2}{(N-K)}\right]^{1/2} \qquad (2)$$

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

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

salt		h_0	h_1	h_2	h_3	%σ-(H^E)
salt-free		4377.10	−886.36	261.88	−1442.34	1.8
NaI	5 mass %	2417.54	−1803.50	3056.25	−5945.10	1.8
	10 mass %	7204.44	−7016.20	−476.93	3376.50	1.6
$Mg(NO_3)_2$	5 mass %	5648.67	−9183.18	5580.86	3176.77	1.7
	10 mass %	6174.09	−7792.72	4541.02	−706.03	1.6
$HgCl_2$	5 mass %	3286.41	788.94	−220.74	−1186.20	1.5
	10 mass %	2741.16	800.73	−603.34	−254.52	1.7

Conclusion

From the experimental H^E data we may conclude that, among the three salts studied, the salts NaI and $Mg(NO_3)_2$ contribute the enhancement in the H^E values of the system methanol + ethyl acetate while the salt $HgCl_2$ reduces the salt-free values. The salt NaI contributes to a greater extent to the mixing characteristics of the system than the salt $Mg(NO_3)_2$. It may be of interest to study the mixing of the system in the presence of mixed salts such as NaI + $Mg(NO_3)_2$ with equimolar mass fraction dissolved in methanol.

Literature Cited

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.

Dharmendira Kumar, M.; Rajendran, M. Enthalpy of mixing of methanol + benzene + mercuric chloride at 303.15 K. *J. Chem. Eng. Data* **1999a**, *44*, 248−250.

Dharmendira Kumar, M.; Rajendran, M. Salt effect on enthalpy of mixing of water + methanol at 303.15 K. *Fluid Phase Equilib.* **1999b**, *164*, 217−224.

Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*; Addison-Wesley Longman: Essex, England, 1989.

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

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

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

Long F. A.; McDevit, W. F. Activity coefficients of nonelectrolyte solutes in aqueous salt solutions. *Chem. Rev.* **1952**, *51*, 119−169.

Murti, P. S.; Van Winkle, M. Vapour liquid equilibria and heat of mixing of N-octane−ethyl benzene−cellosolve system. *AIChE. J.* **1957**, *3*, 517−524.

Nowicke, B.; Taniewska-Osinka, S. Enthalpies of solution of *N*-acetylamino acid amides in aqueous solutions of electrolytes at the temperature 298.15 K. *J. Chem. Thermodyn.* **1997**, *29*, 1017−1024.

Rajendran, M.; Renganarayanan, S.; Srinivasan, D. Effect of dissolved inorganic salts on the vapour-liquid equilibria and heat of mixing of methanol ethyl acetate system. *Chem. Eng. Comm.* **1988**, *74*, 179−193.

Rajendran, M.; Renganarayanan, S.; Madhavan, P. R.; Srinivasan, D. Effect of dissolved salts on the heat of mixing of three binary systems. *J. Chem. Eng. Data* **1989a**, *34*, 375−382.

Rajendran, M.; Renganarayanan, S.; Srinivasan, D. Salt effect in phase equilibria: effect of dissolved inorganic salts on the liquid−liquid equilibria of benzene−2-propanol−water system and the vapour liquid equilibria of its constituent binaries. *Fluid Phase Equilib.* **1989b**, *50*, 133−164.

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.

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

Riddick, J. A.; Bunger, W. S.; Sakano, T. K. *Techniques of chemistry*, 3rd ed.; Wiley-Interscience: New York, 1986; Vol. II.

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

Taso, C. C.; Smith, J. M. Heat of mixing of liquids. *Chem. Eng. Prog. Symp. Ser.* **1953**, *49*, 107−117.

Timmermans, J. *Physico-Chemical Constants in Concentrated Solutions*; Interscience: NewYork, 1980.

Received for review March 12, 1999. Accepted September 13, 1999. M.D.K. thanks CSIR for the grant of a Senior Research Fellowship during the tenure of this research work.

JE990074U