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Salt Effect on the Enthalpy of Mixing of 1,4-Dioxane + Acetic Acid at 303.15 K

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The effect of five dissolved salts (sodium chloride, calcium chloride, zinc chloride, cadmium chloride, and ammonium chloride) on the enthalpy of mixing of the binary system 1,4-dioxane + acetic acid has been investigated at 303.15 K in an isothermal displacement calorimeter with vapor space. A decreasing trend in excess enthalpy for the salts NH_4Cl and NaCl but an increasing trend for the salts $CaCl_2$, $ZnCl_2$, and $CdCl_2$ with increasing salt concentration was observed. The Redlich−Kister equation has been used to fit the experimental enthalpy of mixing data, and the binary parameters have been estimated.

Introduction

In recent years, there has been considerable increase in the experimental investigation of the excess thermodynamic properties of liquid mixtures. Excess thermodynamic functions 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 an extractive agent to modify the relative volatility of the binary mixtures. Furter and Cook[1] and Jaques and Furter[2] 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.[3] Furter[4] has reported that the salt effect is believed to be a complex function of salt and solvent interaction among all the components of the system. An equation has been derived by Sada et al.[5] indicating the changes in the chemical potentials of the solvent components when a salt is added to a mixed solvent. Meranda and Furter[6] have observed the gradual shift in the azeotropic composition in certain azeptropic 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 binary mixtures in the presence of dissolved inorganic salts has been reported.[7−14] In this investigation, the effect of five dissolved salts (sodium chloride, calcium chloride, zinc chloride, cadmium chloride, and ammonium chloride) on the enthalpy of mixing of the binary 1,4-dioxane + acetic acid system has been studied. The experiments were performed at 303.15 K.

Experimental Section

Chemicals Used. Solvents and salts used were of analytical reagent grade. The solvents were further purified by fractional distillation, and the salts were dried. The purities of the solvents were checked by comparing measured densities and boiling points with those reported in the literature.[15,16] Densities were measured using a bicapillary pycnometer, and boiling points were measured using an ebulliometer giving an accuracy of ±0.2 K. The measured values are given in Table 1, along with the literature values.

Table 1. Physical Properties of the Solvents Used

solvent	T_b/K this work	T_b/K lit.[15]	ρ/(g cm^{-3}) this work	ρ/(g cm^{-3}) lit.[15]
1,4-dioxane	374.2	374.0	1.0334	1.0337
acetic acid	390.6	390.9	1.0491	1.0492

Experimental Apparatus. The calorimeter used in the present investigation is of the same type as that employed by Tsao and Smith[17] and Murti and Van Winkle.[18] The description of the apparatus and microprocessor design details has been given in our earlier paper.[8] 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 binary system water + methanol at 303.15 K. The data obtained in the present work compared well within 2% with the literature[18] (Figure 1). The standard experimental procedure followed is described in our earlier paper.[8] The salt was first dissolved in the component in which it is freely soluble. The weight percentages of salt reported in this work are 5%, 10%, and 15% [mass of salt/(mass of salt + mass of solvent)], and these concentrations are the initial concentration of the salt in the component before mixing with the other solvent and w is the salt concentration (in weight percent) after addition of the second component.

Results and Discussion

Acetic acid is a polar protic solvent, and 1,4-dioxane is a nonpolar aprotic solvent. The miscibility of the two solvents can be ascribed to a hydrogen bonding interaction between them. The enthalpy of mixing is negative, indicating strong intermolecular forces. Tables 2−5 give the enthalpy of mixing of 1,4-dioxane + acetic acid in the presence of the salts NaCl, $CaCl_2$, $ZnCl_2$, $CdCl_2$, and NH_4Cl. The system is exothermic. When the salts ammonium chloride and sodium chloride are added, the area of heterogeneity decreases with increase in salt concentration. The effect is more pronounced from 0.3 to 0.8 mole fraction of 1,4-dioxane. For the salts $CaCl_2$, $ZnCl_2$, and $CdCl_2$, the exo-

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Table 2. Enthalpy of Mixing Data for the System 1,4-Dioxane (1) + Acetic Acid (2) at 303.15 K for the Salt NaCl

no salt			5% NaCl				10% NaCl			
x_1	H^E_{exp}/(J mol^{-1})	H^E_{cal}/(J mol^{-1})	x_1	w^a	H^E_{exp}/(J mol^{-1})	H^E_{cal}/(J mol^{-1})	x_1	w	H^E_{exp}/(J mol^{-1})	H^E_{cal}/(J mol^{-1})
0.102	−44.1	−45.8	0.104	3.90	−42.2	−42.5	0.104	7.50	−39.2	−39.1
0.224	−108.6	−107.5	0.223	2.90	−101.1	−100.3	0.221	5.00	−92.7	−92.1
0.349	−156.5	−153.8	0.346	2.10	−143.2	−144.2	0.350	4.10	−134.0	−136.1
0.450	−169.3	−172.7	0.452	1.50	−162.7	−162.3	0.443	3.10	−154.2	−152.4
0.539	−175.6	−176.6	0.537	1.10	−164.9	−164.9	0.538	2.20	−156.5	−155.9
0.621	−171.6	−171.2	0.620	0.75	−160.1	−159.1	0.625	1.50	−147.2	−149.1
0.712	−160.3	−156.4	0.714	0.46	−142.1	−144.4	0.711	0.94	−137.3	−134.4
0.786	−134.3	−136.6	0.789	0.27	−127.6	−125.7	0.786	0.53	−111.2	−115.0
0.861	−106.5	−106.3	0.862	0.13	−98.7	−98.6	0.862	0.26	−89.6	−87.3
0.891	−89.3	−90.1	0.894	0.06	−81.6	−82.6	0.892	0.13	−73.2	−73.2
0.976	−25.6	−25.1	0.976	0.07	−24.5	−23.7	0.975	0.01	−20.2	−20.8

[a] w = salt concentration in weight percent.

Table 3. Enthalpy of Mixing Data for the System 1,4-Dioxane (1) + Acetic Acid (2) at 303.15 K for the Salt $CaCl_2$[a]

5% $CaCl_2$				10% $CaCl_2$				15% $CaCl_2$			
x_1	w^a	H^E_{exp}/(J mol^{-1})	H^E_{cal}/(J mol^{-1})	x_1	w	H^E_{exp}/(J mol^{-1})	H^E_{cal}/(J mol^{-1})	x_1	w	H^E_{exp}/(J mol^{-1})	H^E_{cal}/(J mol^{-1})
0.105	3.90	−52.1	−52.1	0.103	7.50	−85.1	−85.2	0.105	11.0	−78.5	−77.2
0.225	2.90	−110.4	−110.4	0.224	5.90	−143.4	−142.4	0.223	8.40	−156.5	−156.3
0.347	2.10	−173.6	−173.6	0.346	4.20	−197.5	−200.5	0.315	6.20	−226.3	−231.0
0.447	1.60	−208.2	−208.2	0.445	3.10	−253.4	−250.3	0.446	4.50	−283.7	−279.4
0.532	1.10	−236.4	−236.4	0.534	2.20	−286.1	−285.6	0.534	3.30	−305.1	−303.4
0.622	0.75	−233.1	−233.1	0.624	1.50	−296.2	−298.1	0.621	2.20	−301.5	−303.8
0.714	0.46	−214.6	−214.6	0.715	0.91	−273.2	−275.2	0.716	1.40	−273.1gt	−272.1
0.789	0.27	−176.1	−176.1	0.781	0.52	−237.5	−232.9	0.786	0.81	−223.4	−226.4
0.862	0.13	−120.1	−120.1	0.864	0.25	−149.2	−152.8	0.865	0.38	−155.5	−154.1
0.894	0.06	−89.3	−89.3	0.891	0.13	−123.6	−122.2	0.892	0.19	−126.2	−125.3
0.975	0.01	−21.2	−21.2	0.977	0.02	−23.6	−23.4	0.974	0.02	−31.5	−30.6

[a] w = salt concentration in weight percent.

Table 4. Enthalpy of Mixing Data for the System 1,4-Dioxane (1) + Acetic Acid (2) at 303.15 K for the Salt $ZnCl_2$ and $CdCl_2$

5% $ZnCl_2$				5% $CdCl_2$				10% $CdCl_2$			
x_1	w^a	H^E_{exp}/(J mol^{-1})	H^E_{cal}/(J mol^{-1})	x_1	w	H^E_{exp}/(J mol^{-1})	H^E_{cal}/(J mol^{-1})	x_1	w	H^E_{exp}/(J mol^{-1})	H^E_{cal}/(J mol^{-1})
0.104	3.90	−56.2	−57.1	0.098	3.90	−39.8	−40.0	0.101	7.60	−46.9	−44.9
0.224	2.90	−111.7	−110.9	0.221	2.90	−92.6	−91.7	0.223	5.70	−123.6	−124.6
0.347	2.10	−160.1	−159.8	0.345	2.00	−146.2	−146.9	0.345	4.10	−209.6	−213.6
0.447	1.60	−191.5	−190.6	0.449	1.50	−185.2	−185.9	0.452	2.90	−281.6	−275.2
0.532	1.10	−199.2	−204.7	0.539	1.10	−203.6	−204.8	0.537	2.10	−298.9	−298.5
0.622	0.75	−208.3	−202.3	0.620	0.76	−209.8	−204.1	0.610	1.40	−289.6	−293.9
0.715	0.46	−176.2	−177.4	0.711	0.46	−176.8	−179.7	0.715	0.81	−245.9	−244.0
0.789	0.27	−139.7	−141.5	0.784	0.27	−139.6	−142.6	0.784	0.45	−185.9	−187.0
0.864	0.13	−94.3	−93.4	0.860	0.12	−94.6	−91.9	0.862	0.18	−109.8	−109.7
0.893	0.06	−73.2	−72.9	0.891	0.07	−69.8	−69.5	0.894	0.07	−78.9	−77.8
0.975	0.03	−15.2	−15.6								

[a] w = salt concentration in weight percent.

Table 5. Excess Enthalpy of the System 1,4-Dioxane (1) + Acetic Acid (2) at 303.15 K for the Salt NH_4Cl

5 mass % NH_4Cl				10 mass % NH_4Cl			
		H^E_{exp}	H^E_{cal}			H^E_{exp}	H^E_{cal}
x_1	w^a	J mol^{-1}	J mol^{-1}	x_1	w	J mol^{-1}	J mol^{-1}
0.104	3.90	−26.5	−26.2	0.101	8.00	−42.6	−42
0.223	2.90	−61.9	−61.8	0.220	6.20	−79.8	−80.6
0.347	2.10	−96.7	−96.8	0.345	4.70	−112.6	−110.9
0.451	1.50	−115.9	−116.5	0.453	2.40	−123.5	−127.1
0.536	1.00	−121.6	−121.8	0.531	1.40	−133.6	−131.2
0.612	0.72	−119.2	−116.6	0.613	0.96	−129.4	−127.2
0.711	0.41	−94.5	−95.6	0.709	0.53	−107.9	−110.8
0.790	0.22	−67.5	−69.4	0.794	0.27	−85.9	−85.8
0.860	0.09	−43.6	−42.7	0.861	0.14	−61.3	−60.2
0.895	0.03	−30.5	−29.5	0.898	0.02	−44.6	−44.6

[a] w = salt concentration in weight percent.

thermicity increases and a much more pronounced effect is seen for 10% and 15% $CdCl_2$ and 10% $CaCl_2$ (by mass). The univalent electrolytes NaCl and NH_4Cl provide less negative enthalpy of mixing than those of the other bivalent salts and the salt free system. In each bivalent salt system, excess enthalpy of mixing increases with increase in salt concentration, illustrating the increase of solvation of ions as the salt concentration increases. As both the negative and positive sites of acetic acid, namely the carbonyl proton, are necessary and involved in solvation of the ions of the salts, the molecule as a whole may not be free and available to associate with 1,4-dioxane when the salt concentration is increased. Among the bivalent salts, $CaCl_2$, $ZnCl_2$, and $CdCl_2$, the changes of the excess enthalpy follow the order $CaCl_2 \cong CdCl_2 > ZnCl_2$; they also follow the order of the ionic radii, $Ca^{2+} = 1.0$ Å $\cong Cd^{2+} = 0.95$ Å $> Zn^{2+} \cong 0.74$ Å. Ca^{2+} and Cd^{2+} ions having large ionic radii can facilitate coordination of solvents with minimum interligand (solvent) repulsive forces. But, around smaller Zn^{2+}, comparatively more interligand forces are expected on its coordination sphere, providing less negative enthalpy of mixing. NaCl and NH_4Cl systems show more negative excess enthalpy with increase in salt concentration, illustrating

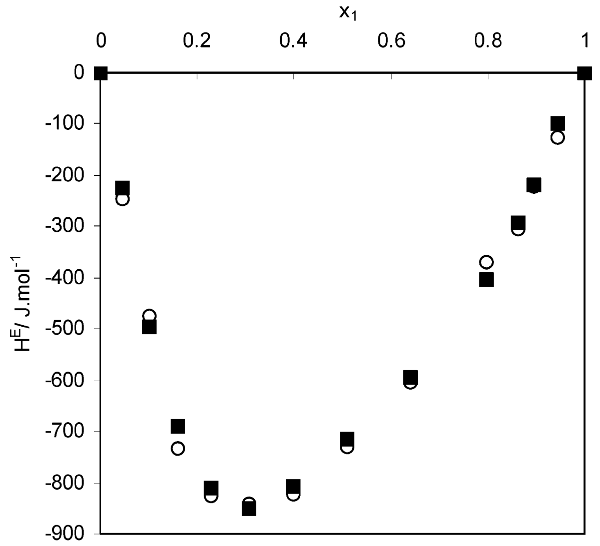

Figure 1. Enthalpy of mixing of water + methanol at 303.15 K: ○, this work; ■, Battler and Rowley.[18]

Table 6. Estimated Parameters of Eq 1 for the System 1,4-Dioxane + Acetic Acid at 303.15 K

salt conc (wt %)	A_0	A_1	A_2	A_3
		NaCl		
5%	−704.9	−69.3	−21.6	−324.7
10%	−623.8	−42.2	−8.8	−353.2
		$CaCl_2$		
5%	−909.2	−474.8	227.1	340.8
10%	−1096.5	−761.5	−18.3	883.2
15%	−1186.6	−497.2	−203	312.7
		$ZnCl_2$		
5%	−804.0	−295.9	188.6	323.4
		$CdCl_2$		
5%	−795.7	−399.9	341.6	500.7
10%	−1167.4	−512.5	812.2	−138.2
		NH_4Cl		
5%	483.9	106.4	−297	−138.2
10%	521.77	87.8	−73.1	−115.2

the existence of strong intermolecular forces in acetic acid compared to solvation of their ions.

Data Correlation. The experimental H^E values were fitted with the following equation

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

by the method of least squares, and the binary parameters have been evaluated and are given in Table 6.

Conclusion

From the experimental H^E data we may conclude that, among the five salts studied, the salts $CaCl_2$, $ZnCl_2$, and $CdCl_2$ show more negative values of enthalpy of mixing for the system 1,4-dioxane + acetic acid while the salts NaCl and NH_4Cl shows more positive values of excess enthalpy with an increase in the salt concentration, illustrating the existence of strong intermolecular forces in acetic acid.

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