

Effect of Calcium chloride and Cadmium chloride on the enthalpy of mixing of 1,4 Dioxane + Water at 303.15 K

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Abstract

This paper presents the effect of two dissolved inorganic salts, CaCl₂ and CdCl₂ on the enthalpy of mixing of the binary 1,4 dioxane + water system has been investigated at 303.15 K in an isothermal displacement calorimeter with vapour space. A significantly increasing trend in the endothermic excess enthalpy values for the addition of calcium chloride and cadmium chloride were noticed. The experimental values of H^E were fitted into the Redlich –Kister equation, and deviations from the ideal value and binary parameters were calculated. The importance of solute–solvent interactions was demonstrated from the excess enthalpy of mixing in the positive direction with an increase in the salt concentration.

Keywords: Thermodynamics, Excess Enthalpy, Inorganic Salts, 1,4 dioxane, Water.

1. Introduction

Experimental data of excess thermodynamic properties of liquids and liquid mixtures are of great fundamental and practical importance. These properties allow one to draw information on the structure and interactions of mixed solvents. The chemical industries have recognized the importance of the thermodynamic properties in the design calculations involving chemical separations, heat transfer, mass transfer and fluid flow. The physical properties of various binary mixtures are studied for many reasons, the most important of which is to provide some basic information about molecular interactions are present in the liquid state. The excess thermodynamic properties have been used as a qualitative guide to predict the extent of complex formation in binary liquid mixtures. Furter and Cook (1967) and Jacques and Furter (1972) 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 Mc Devit (1952). The salt effect is also believed to be a complex function of salt + solvent interaction and self-interaction among the system components (Furter1976). An equation derived by Sada *et al.* (1975) which indicates the changes in a chemical potential of the solvent components when a salt is added to a solvent mixtures. In most cases, azeotropic mixtures require some special methods to facilitate their separation. There is a need to search for a separating agent other than energy, and this agent might be a salt material for evaporation or an entrainer for extractive distillation. Tomkins *et al.* (1976) studied addition of electrolytes to the liquid mixtures, an appreciable change in the free energy of the liquid component is expected.

Meranda and Furter (1974) have observed the 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. Therefore, it is of greater interest to investigate the effect of dissolved salts on enthalpy of mixing of liquid mixtures which are of commercial importance. Since there is an interrelation between the excess free energy and the excess enthalpy of liquid mixtures, a few researchers (Lim and Smith, 2001; Loehe and Donohue, 1997) have studied the effect of added salts on the excess enthalpy values of liquid mixtures along with notable contributions from our group (Rajendran *et al.*, 1988, 1989, 1991, 1994; Dharmendra Kumar *et al.*, 1994, 1999; Tamilarasan *et al.*, 2008, 2009a, 2009b, 2009c, 2010). In this investigation, the effect of two dissolved inorganic salts, namely calcium chloride and cadmium chloride on the enthalpy of mixing values of 1,4 dioxane + water binary system has been studied experimentally.

2. Experimental Section

2.1 Chemicals Used

Analytical reagent grade 1,4 dioxane and the salts (calcium chloride, cadmium chloride,) used in this investigation were supplied by E-Merck. The solvents were purified by fractional distillation; the physical properties of the solvents (density, ρ , boiling point, T_b) and the salts (melting point, T_m) used in this study were found to be almost identical to the literature values (Timmermanns, 1980) as shown in Table 1. 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.

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
1,4 dioxane	374.20	374.00	1.0334	1.0337
water	100.00	100.00	0.9982	0.9988

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

2.2 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 concentrations by mass [mass of salt/(mass of salt + mass of solvent)] before mixing with the other solvent.

2.3 Experimental Procedure

The experimental procedure adopted in this work is described elaborately in another paper (Rajendran *et al.*, 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 1,4 dioxane + water composition (refer to varying mole % 1,4 dioxane (x_1) values given in Tables 2 and 3) to ensure reproducibility (within $\pm 3\ %$), and the average values are presented. 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.

3. Result and Discussion

The experimental H^E values obtained for the 1,4 dioxane + water system for various concentrations of the two salts used herein are presented in Tables 2-3 and also represented graphically in Figures 2- 3. The salt-free data are also given in the figure for comparison. It is well known that the excess enthalpy of mixing of 1,4 dioxane (non polar) with water (polar) is positive (endothermic) at lower mole fraction of 1,4 dioxane and negative (exothermic) at higher mole fraction of 1, 4 dioxane over the entire composition range studied here, and this explains the weak attraction between the 1,4 dioxane and water molecules through dipole- induced dipole forces and van der Waals forces. The H^E of the salt-free 1,4 dioxane + water system decreases when the mole fraction of 1,4 dioxane (x_1) is increased from 0.129 to 0.653 (Table 2 and Figure 2), indicating that energy is lost in overcoming the intermolecular forces of attraction in water and an increase in the miscibility of the 1,4 dioxane + water system is observed.

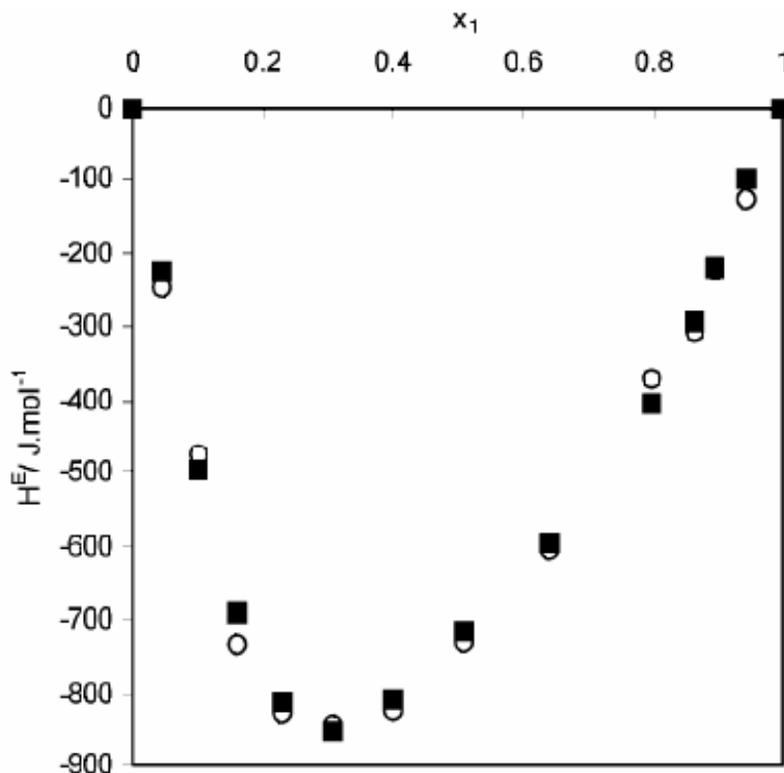


Figure 1. Enthalpy of mixing of water + methanol at 303.15 K:
○, this work; ■, Battler and Rowley.

Table 2 Enthalpy of mixing data for the system 1,4 dioxane + water at 303.15 K for the salts CaCl_2 and CdCl_2

Salt - free			5% CaCl_2				5% CdCl_2			
X_1	H^E	H^E	X_1	X_3	H^E	H^E	X_1	X_3	H^E	H^E
	J.mol^{-1} (Exptl.)	J.mol^{-1} (Calcd.)			J.mol^{-1} (Exptl.)	J.mol^{-1} (Calcd.)			J.mol^{-1} (Exptl.)	J.mol^{-1} (Calcd.)
0.129	411.00	423.29	0.134	2.766×10^{-2}	32.68	33.22	0.124	2.840×10^{-2}	37.80	38.72
0.161	453.02	447.89	0.202	2.041×10^{-2}	140.12	138.01	0.162	2.320×10^{-2}	82.61	82.67
0.249	440.02	428.00	0.247	1.636×10^{-2}	221.44	223.45	0.251	1.591×10^{-2}	216.33	217.55
0.301	381.92	379.02	0.293	1.365×10^{-2}	316.15	311.26	0.302	1.261×10^{-2}	303.92	302.50
0.342	329.49	329.88	0.321	1.092×10^{-2}	356.42	359.20	0.345	1.002×10^{-3}	365.90	371.98
0.396	250.56	253.48	0.396	7.866×10^{-3}	472.44	478.05	0.397	7.750×10^{-3}	442.51	447.69
0.425	202.98	207.69	0.454	5.85×10^{-3}	540.40	538.71	0.426	6.301×10^{-3}	489.63	484.00
0.460	145.05	149.8	0.500	4.527×10^{-3}	566.85	564.82	0.461	5.061×10^{-3}	537.00	520.04
0.520	36.65	37.29	0.545	3.388×10^{-3}	572.01	569.50	0.521	2.880×10^{-3}	567.52	559.53
0.525	-14.39	-14.02	0.641	2.045×10^{-3}	506.21	508.89	0.546	2.052×10^{-4}	582.10	566.67
0.580	-89.38	-88.55	0.684	1.433×10^{-3}	451.82	453.02	0.589	1.460×10^{-4}	546.00	562.22
0.624	-187.12	-189.44	0.733	9.220×10^{-3}	376.19	373.22	0.621	3.950×10^{-4}	515.10	552.60
0.653	-255.69	-256.5	0.799	4.890×10^{-4}	246.22	248.54	0.827	2.320×10^{-5}	366.00	271.40

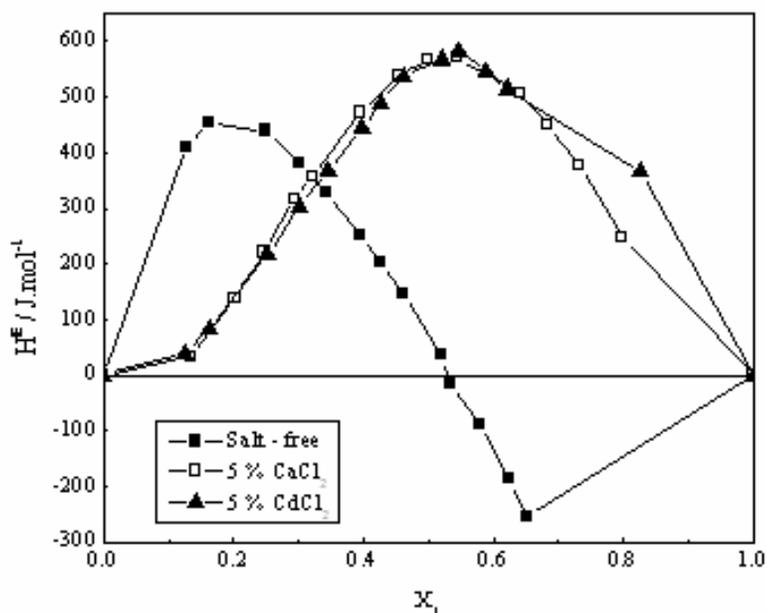


Figure. 2 Effect of addition of 5% mass of salts, CaCl_2 , CdCl_2 and salt-free solution on the enthalpy of mixing (H^E) of 1,4 dioxane + water at 303.15 K against the mole fraction of x_1 .

Figure 2 shows the enthalpy values of the system with 5 % mass of the salts CaCl_2 and CdCl_2 . The addition of 5% CaCl_2 and CdCl_2 salts are increases in the original endothermic excess enthalpy values significantly from 0.134 to 0.545 mole fraction range of 1,4-dioxane. It illustrates the weak association of water with 1,4-dioxane through hydrogen bonding as well as the added salts enhance the solvent-solvent interaction, therefore the miscibility of the solvents increases. The increasing enthalpy indicating a pronounced effect on the system compared to non-salt system. The decrease in the original positive values of the excess enthalpy of mixing is well pronounced when x_1 is between 0.5 and 0.8, and this trend may be due to contribution from the solvation energy of the salts with the intermolecular forces in the solvents remaining unchanged. and the 1,4-dioxane group disfavor for enhanced molecular association, so enthalpy value decreases with increasing the mole fraction of 1,4 dioxane.

The effect of increase in the salt concentration (10% by mass) on the H^E values of the 1,4 dioxane + water system was studied using CaCl_2 , as shown in Tables 3 and Figure 3. The addition of 10% CaCl_2 gave results similar to those obtained for the 5% salt system; however, the addition of 10% salts resulted in an increase in the excess enthalpy of mixing values in the positive direction with change in peak value. This implied that the energy released during salt addition was greater than that for overcoming the intermolecular forces during the solvation of the ions and also it increases the enhanced molecular association through hydrogen bonding between the solvents.

4. 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. 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 (1948) polynomial.

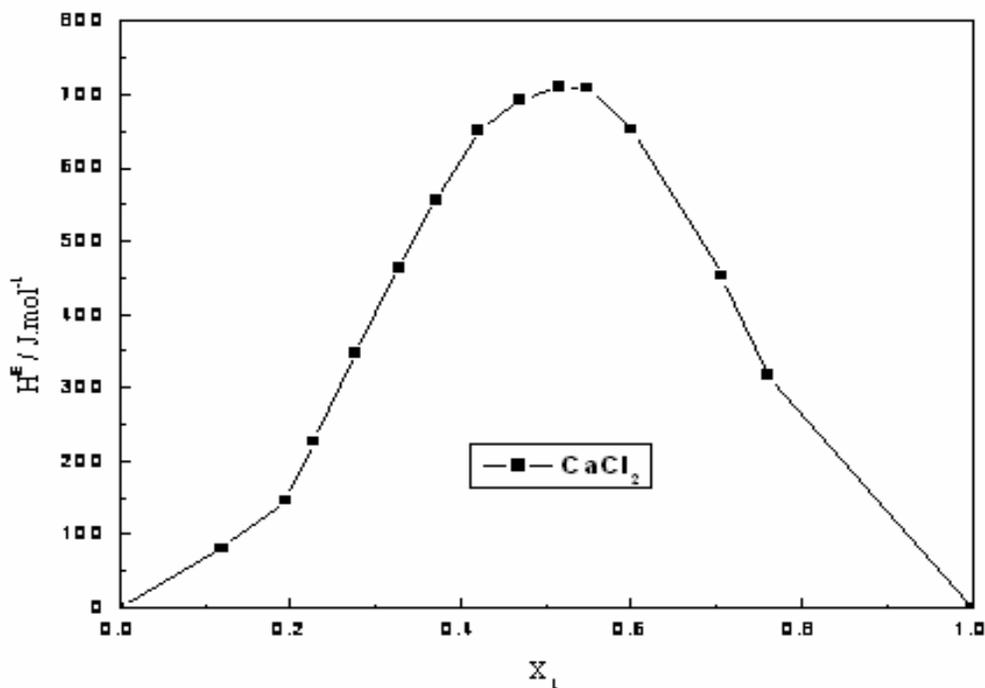
$$H^E / [\text{J} \cdot \text{mol}^{-1}] = x_1 x_2 \sum_{i=0}^j A_i (2x_1 - 1)^i \quad (1)$$

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 4 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 4.

Table 3. Enthalpy of mixing data for the system 1,4 dioxane + water at 303.15 K for the salt CaCl_2

Salt - free			5% CaCl_2				10% CaCl_2			
X_1	H^E	H^E	X_1	X_3	H^E	H^E	X_1	X_3	H^E	H^E
	J.mol ⁻¹ (Exptl.)	J.mol ⁻¹ (Calcd.)			J.mol ⁻¹ (Exptl.)	J.mol ⁻¹ (Calcd.)			J.mol ⁻¹ (Exptl.)	J.mol ⁻¹ (Calcd.)
0.129	411.00	423.29	0.134	2.766×10^{-2}	32.68	33.22	0.120	5.66×10^{-2}	80.30	79.85
0.161	453.02	447.89	0.202	2.041×10^{-2}	140.12	138.01	0.194	4.105×10^{-2}	146.15	146.20
0.249	440.02	428.00	0.247	1.636×10^{-2}	221.44	223.45	0.228	3.425×10^{-2}	226.86	225.10
0.301	381.92	379.02	0.293	1.365×10^{-2}	316.15	311.26	0.277	2.705×10^{-2}	347.05	347.68
0.342	329.49	329.88	0.321	1.092×10^{-2}	356.42	359.2	0.327	2.123×10^{-2}	463.25	466.89
0.396	250.56	253.48	0.396	7.866×10^{-3}	472.44	478.05	0.371	1.680×10^{-2}	556.19	559.04
0.425	202.98	207.69	0.454	5.85×10^{-3}	540.40	538.71	0.421	1.295×10^{-2}	650.00	641.25
0.460	145.05	149.80	0.500	4.527×10^{-3}	566.85	564.82	0.470	9.899×10^{-3}	693.11	694.50
0.520	36.65	37.29	0.545	3.388×10^{-3}	572.01	569.5	0.515	7.465×10^{-3}	710.86	711.38
0.525	-14.39	-14.02	0.641	2.045×10^{-3}	506.21	508.89	0.549	5.719×10^{-3}	708.12	704.00
0.580	-89.38	-88.55	0.684	1.433×10^{-3}	451.82	453.02	0.601	3.958×10^{-3}	652.01	658.00
0.624	-187.12	-189.44	0.733	9.220×10^{-3}	376.19	373.22	0.707	2.082×10^{-3}	453.20	454.55
0.653	-255.69	-256.50	0.799	4.890×10^{-4}	246.22	248.54	0.761	1.202×10^{-3}	317.66	313.69

Figure. 3 Effect of addition of 10% mass of salt, CaCl_2 on the enthalpy of mixing (H^E) of 1,4 dioxane + water at 303.15 K against the mole fraction of x_1 .

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

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 functional groups present in 1,4 dioxane + water system.

Table 4. Estimated parameters of equation 1 and percentage of standard deviation $\% \sigma(H^E)$ of the system 1,4 dioxane + water at 303.15 K

System	Salt concentration	A_0	A_1	A_2	A_3	$\% \sigma H^E$
1,4 dioxane + Water	Salt - free	306.17	-38.24.80	-1621.33	-3727.87	1.72
	5% CaCl_2	2260.12	673.90	-2957.85	-265.78	1.35
	10% CaCl_2	2836.63	535.38	-4705.35	-821.50	1.32
	5% CdCl_2	2196.75	1171.73	-2121.62	-565.78	1.75

5. Conclusion

The experimental H^E study and its statistical analysis show that, among the two salts studied, the salts CaCl_2 and CdCl_2 exhibits more positive values of enthalpy of mixing for the binary mixture indicates the added salts are not reduce intermolecular forces in the solvents, which will increase the molecular association between the solvents. In this case, the solvent-solvent interaction is expected to be less important than solute-solvent interaction. The addition of the 10% CaCl_2 salt in this system further increased the excess enthalpy values, implying that energy released during salt addition was greater than that for overcoming the intermolecular forces during the solvation of the ions and the formation of molecular association through hydrogen bonding. The model represented the experimental data with the required accuracy for the studied system and therefore, this model is suitable to predict the excess enthalpy of mixing in 1,4 dioxane + water binary mixture in the presence of the selected inorganic salts. The study helps in future, for the effective phase separation of industrially important solvents and the design of process equipments. Another contribution to this study is the development of theoretical models capable of interpolating excess enthalpy data for the systems at any concentration of the salts used in this study.

Nomenclature

H^E - Excess enthalpy of mixing.
 T_b - Boiling point
 T_m - Melting point
 Calcd. - Calculated values
 Exptl. - Experimental Values
 ρ - density

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