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Excess Enthalpies of Ternary Mixtures of Ethanol + Water + Sodium Chloride or Zinc Chloride at 298.15 K

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Enthalpies of mixing, measured at 298.15 K in a flow microcalorimeter, are reported for the addition of ethanol to some aqueous solutions of sodium chloride and of zinc chloride in the range 1−2 *m*. Excess molar enthalpies of the corresponding ternary mixtures C_2H_5OH (1) + H_2O (2) + NaCl (3) or $ZnCl_2$ (3) are estimated from the results.

Introduction

The thermodynamic properties of mixtures comprised of an electrolyte and an aqueous organic solvent are of interest in a variety of industrial applications. Although there have been many studies of electrolytes in aqueous solution, there is relatively little information available for electrolytes in water + organic mixed solvents. In the present investigation, the changes in enthalpy at 298.15 K were determined for the addition of ethanol to aqueous solutions of sodium chloride and of zinc chloride having various initial molalities.

Experimental Section

BDH absolute "Aristar" ethanol was used in the present work. After drying over molecular sieves type 3A, its density at 298.15 K was 785.14 kg m^{-3}, in reasonable agreement with the literature value of 785.09 kg m^{-3} (*TRC Thermodynamic Tables*, 1988). The sodium chloride was an ACS Certified reagent from the Fisher Scientific Co. The zinc chloride was an Analyzed Reagent from the J.T. Baker Chemical Co. Prior to their use, both salts were dried in an oven at 420 K. Deionized distilled water was used in preparing the aqueous solutions.

The excess molar enthalpies, H^E_m, were determined in an LKB flow microcalorimeter (model 10700-1) at 298.15 K, maintained within ±0.002 K. Details of the equipment and its operation have been described previously (Tanaka *et al.*, 1975; Kimura *et al.*, 1983). Test measurements for ethanol + water at 298.15 K indicated that results for the present type of mixtures were more reproducible when a reduced flow rate (2.5 × 10^{-3} cm^3 s^{-1}) was used. This was adopted for all of the measurements.

In studying the ternary systems C_2H_5OH (1) + H_2O (2) + NaCl (3) or $ZnCl_2$ (3), the excess molar enthalpies, $H^E_{m,1+23}$, were measured for several pseudobinary systems

Table 1. Experimental Excess Molar Enthalpies $H^E_{m,1+23}$ at 298.15 K for the Addition of Ethanol to an Aqueous Sodium Chloride Solution Having Molality *m* To Form C_2H_5OH (1) + H_2O (2) + NaCl (3) and Values of $H^E_{m,123}$ Calculated from Eq 1 Using $H^E_{m,23}$ from Clarke and Glew (1985)

x_1	$H^E_{m,1+23}$/(J mol^{-1})	$H^E_{m,123}$/(J mol^{-1})	x_1	$H^E_{m,1+23}$/(J mol^{-1})	$H^E_{m,123}$/(J mol^{-1})	x_1	$H^E_{m,1+23}$/(J mol^{-1})	$H^E_{m,123}$/(J mol^{-1})
				m = 0.0, $H^E_{m,23}$/(J mol^{-1}) = 0.0				
0.0500	−439.9	−439.9	0.3996	−525.7	−525.7	0.7002	−266.6	−266.6
0.1000	−691.8	−691.8	0.4498	−464.4	−464.4	0.7500	−237.7	−237.7
0.1499	−767.5	−767.5	0.5004	−410.6	−410.6	0.8000	−211.9	−211.9
0.1997	−744.6	−744.6	0.5498	−361.0	−361.0	0.8499	−180.7	−180.7
0.2502	−704.9	−704.9	0.5997	−317.6	−317.6	0.9000	−140.3	−140.3
0.3001	−643.3	−643.3	0.6500	−295.5	−295.5	0.9500	−78.8	−78.8
0.3482	−579.4	−579.4	0.7002	−267.0	−267.0			
				m = 1.0002, $H^E_{m,23}$/(J mol^{-1}) = 66.7				
0.0500	−382.1	−318.7	0.4001	−434.8	−394.7	0.6999	−234.2	−214.2
0.1000	−586.7	−526.7	0.4503	−389.3	−352.6	0.7501	−214.5	−197.8
0.1498	−642.2	−585.5	0.5076	−343.2	−310.4	0.8000	−196.5	−183.1
0.2001	−622.2	−568.8	0.5499	−314.9	−284.8	0.8498	−175.0	−165.0
0.2502	−587.1	−537.1	0.6004	−282.6	−255.9	0.8998	−134.6	−127.9
0.3001	−539.0	−492.3	0.6498	−256.7	−233.4	0.9495	−80.3	−77.0
0.3502	−488.3	−444.9						
				m = 1.4985, $H^E_{m,23}$/(J mol^{-1}) = 90.2				
0.0500	−357.6	−271.9	0.3000	−483.8	−420.6	0.4999	−306.1	−261.0
0.1000	−537.8	−456.5	0.3502	−434.2	−375.6	0.5004	−304.7	−259.6
0.1499	−575.5	−498.7	0.4001	−389.1	−335.0	0.5499	−273.0	−232.4
0.1997	−562.0	−489.8	0.4504	−344.4	−294.8	0.5998	−243.1	−207.0
0.2502	−525.0	−457.3						
				m = 1.9967, $H^E_{m,23}$/(J mol^{-1}) = 108.5				
0.0500	−335.3	−232.2	0.2498	−478.5	−397.1	0.4487	−319.9	−260.1
0.0999	−486.1	−388.4	0.2998	−440.1	−364.1	0.4996	−286.5	−232.2
0.1499	−517.2	−425.0	0.3498	−399.6	−329.1	0.5001	−290.3	−236.1
0.1999	−505.0	−418.2	0.4001	−360.0	−295.0	0.5499	−260.3	−211.5

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Table 2. Experimental Excess Molar Enthalpies $H^E_{m,1+23}$ at 298.15 K for the Addition of Ethanol to an Aqueous Zinc Chloride Solution Having molality *m* To Form C_2H_5OH (1) + H_2O (2) + $ZnCl_2$ (3) and Values of $H^E_{m,123}$ Calculated from Eq 1 Using $H^E_{m,23}$ from Rossini *et al.* (1952)

x_1	$H^E_{m,1+23}/(J\ mol^{-1})$	$H^E_{m,123}/(J\ mol^{-1})$	x_1	$H^E_{m,1+23}/(J\ mol^{-1})$	$H^E_{m,123}/(J\ mol^{-1})$	x_1	$H^E_{m,1+23}/(J\ mol^{-1})$	$H^E_{m,123}/(J\ mol^{-1})$
$m = 0.9984$, $H^E_{m,23}/(J\ mol^{-1}) = -991.6$								
0.0499	−323.1	−1265.2	0.4003	−335.8	−930.5	0.7003	−175.9	−473.0
0.1000	−490.7	−1383.2	0.4491	−294.0	−840.3	0.7499	−160.7	−408.7
0.1502	−528.6	−1371.3	0.4997	−257.5	−753.6	0.8008	−146.6	−344.1
0.2005	−511.5	−1304.3	0.5498	−231.2	−677.7	0.8497	−131.2	−280.2
0.2505	−478.5	−1221.8	0.6012	−202.5	−598.0	0.9000	−110.9	−210.1
0.3002	−431.7	−1125.7	0.6504	−184.8	−531.4	0.9498	−70.9	−120.7
0.3499	−383.0	−1027.6						
$m = 1.5004$, $H^E_{m,23}/(J\ mol^{-1}) = -1375.7$								
0.0500	−277.8	−1584.7	0.4504	−277.0	−1033.1	0.7502	−159.9	−503.6
0.0999	−424.2	−1662.5	0.5004	−245.2	−932.5	0.7999	−150.2	−425.4
0.1502	−471.6	−1640.7	0.5498	−221.0	−840.4	0.8000	−149.6	−424.8
0.2002	−463.7	−1564.1	0.6002	−198.4	−748.4	0.8500	−134.1	−340.5
0.2503	−435.9	−1467.3	0.6500	−182.5	−664.0	0.8501	−133.6	−339.8
0.3000	−398.7	−1361.7	0.6999	−170.1	−582.9	0.9001	−101.8	−239.2
0.3500	−355.9	−1250.2	0.7001	−169.4	−582.0	0.9500	−55.8	−124.6
0.3999	−314.0	−1139.6	0.7501	−160.4	−504.2			
$m = 1.9904$, $H^E_{m,23}/(J\ mol^{-1}) = -1714.7$								
0.0500	−255.5	−1884.5	0.4003	−309.8	−1338.1	0.6997	−174.8	−689.7
0.1043	−402.4	−1938.2	0.4506	−274.7	−1216.8	0.7501	−162.5	−591.1
0.1500	−437.0	−1894.6	0.5006	−242.9	−1099.3	0.8003	−144.6	−487.0
0.2000	−437.4	−1809.2	0.5495	−222.2	−994.6	0.8504	−123.7	−380.3
0.2508	−415.2	−1699.8	0.5500	−220.4	−992.0	0.9001	−101.3	−272.7
0.3004	−384.9	−1584.5	0.5996	−197.0	−883.5	0.9500	−66.6	−152.4
0.3498	−351.6	−1466.6	0.6499	−179.7	−780.0			

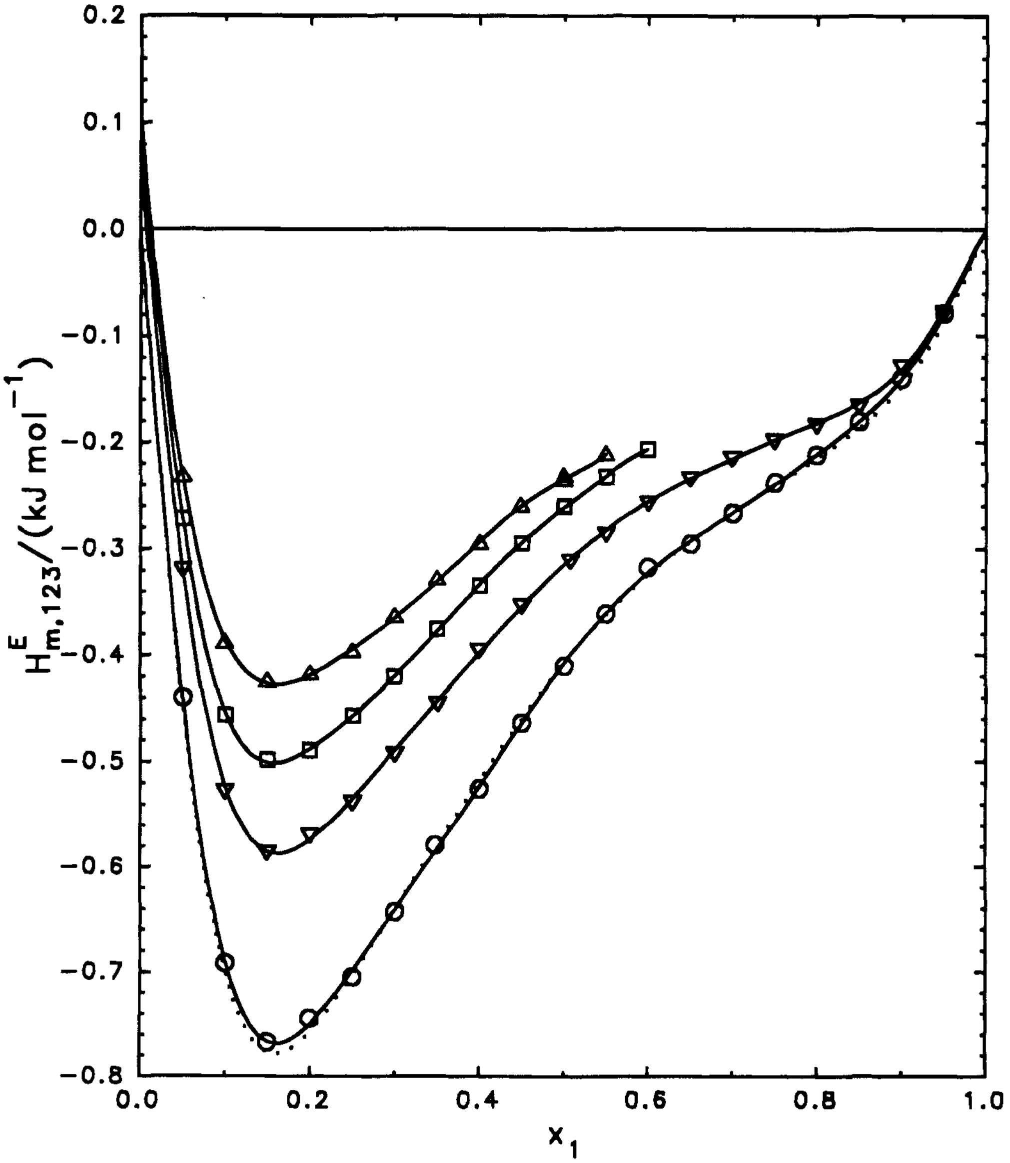

Figure 1. Excess molar enthalpies, $H^E_{m,123}$, of the system C_2H_5OH (1) + H_2O (2) + NaCl (3) at 298.15 K for molalities, *m*, plotted against the mole fraction, x_1, of ethanol: (○) $m = 0$; (▽) $m = 1.0002$; (□) $m = 1.4985$; (△) $m = 1.9967$; (—) calculated from eqs 1 and 2 using the coefficients given in Table 3; (···) $m = 0$ (Costigan *et al.*, 1980).

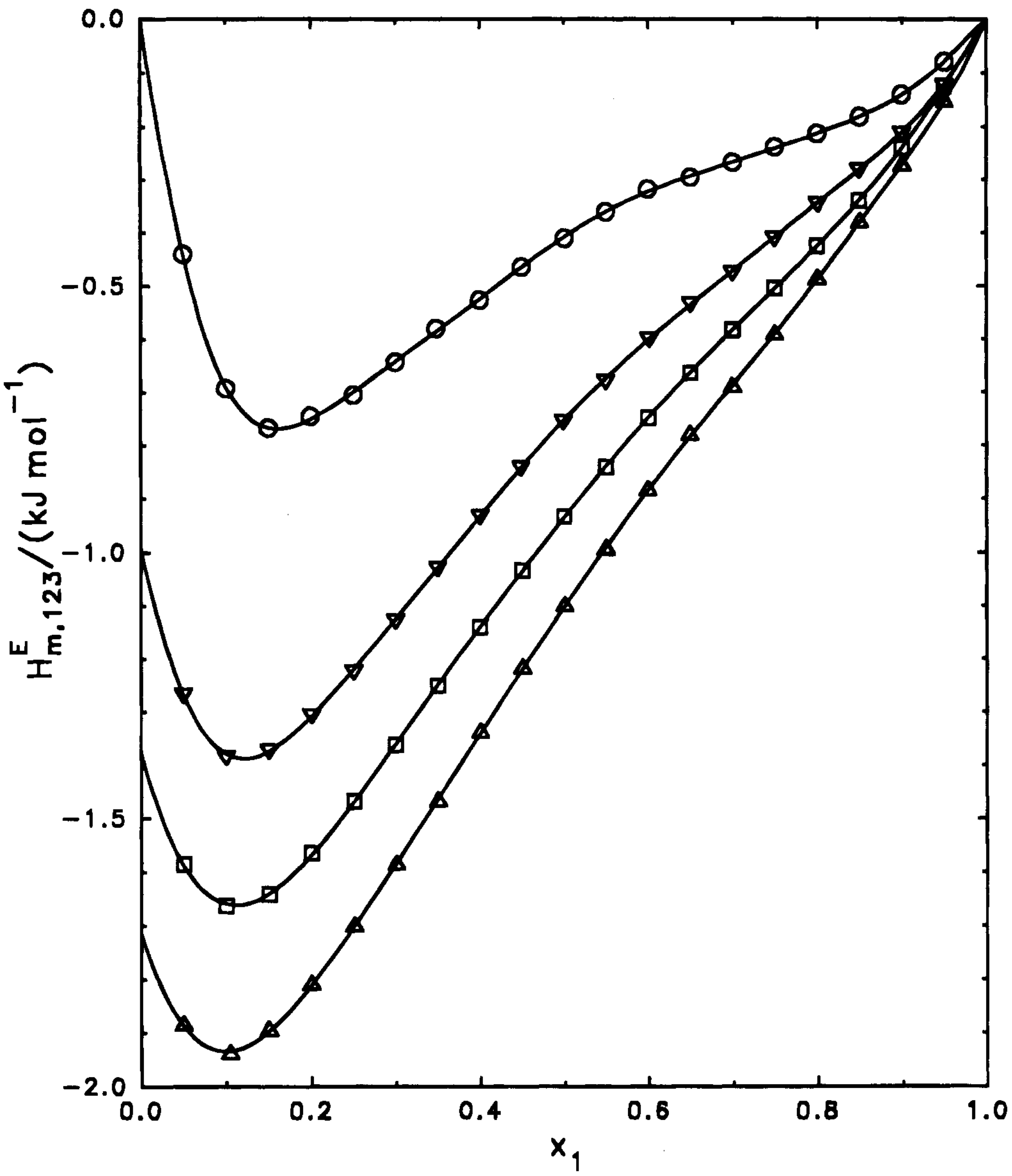

Figure 2. Excess molar enthalpies, $H^E_{m,123}$, of the system C_2H_5OH (1) + H_2O (2) + $ZnCl_2$ (3) at 298.15 K for molalities, m, plotted against the mole fraction, x_1, of ethanol: (○) $m = 0$; (▽) $m = 0.9984$; (□) $m = 1.5004$; (△) $m = 1.9904$; (—) calculated from eqs 1 and 2 using the coefficients given in Table 3.

Table 3. Coefficients, h_j, and Standard Deviations, s, for the Representation by Eq 2 of $H^E_{m,1+23}$ at 298.15 K for C_2H_5OH (1) + H_2O (2) + NaCl (3) or $ZnCl_2$ (3) Obtained from the Addition of Ethanol to an Aqueous Salt Solution with Molality m

	H_2O	H_2O + NaCl			H_2O + $ZnCl_2$		
	$m = 0.0$	$m = 1.0002$	$m = 1.4985$ $x_1 = <0.55$	$m = 1.9967$ $x_1 = <0.60$	$m = 0.9984$	$m = 1.5004$	$m = 1.9904$
h_1	−1633.21	−1393.35	−1225.62	−1154.16	−1026.91	−987.80	−980.30
h_2	−2101.16	−1593.99	−1397.59	−1051.52	−1361.69	−1168.39	−1198.37
h_3	−3307.94	−2737.79	−1771.21	−2068.58	−2633.15	−1900.50	−2040.08
h_4	444.57	−593.01	−5598.14	−12995.21	−452.15	−969.92	281.17
h_5	1817.59	1143.08	−6305.53	48925.03	1550.36	−2354.57	−602.50
h_6	−8960.41	−4341.09	68793.56	−72809.50	−3954.03	−1030.03	−4463.77
h_7	−12542.87	−10071.57	−129567.30	32103.44	−8251.62	998.52	−741.72
h_8	6364.92	2522.03	68641.73		2523.11		3149.38
h_9	10018.36	7797.29			5487.04		
s	3.8	3.3	2.2	2.6	3.0	1.8	3.0

in which component 1 (ethanol) was added to solutions of components 2 (water) and 3 (sodium chloride or zinc chloride) having fixed molality $m = 55.5084x_3/x_2$. For this purpose, aqueous solutions with $m \approx 1$, 1.5, and 2 were prepared by weighing. Over the central mole fraction range, the errors of $H^E_{m,1+23}$ and the mole fractions of the final ternary mixtures are estimated to be less than 0.5% and 5×10^{-4}, respectively.

Results and Discussion

The experimental values of x_1 and $H^E_{m,1+23}$ for the sodium chloride system are summaried in Table 1, along with the results of the test measurements for the mixing of ethanol and water. The latter correspond to the case $m = 0$. The results for the zinc chloride system are listed in Table 2. In the case of the sodium chloride results for $m \approx 1.5$ and 2, it was not possible to cover the full range of

x_1, due to solubility changes which upset the flow through the calorimeter for ethanol mole fractions greater than ~0.55.

Also included in Tables 1 and 2 are values of the excess molar enthalpies, $H^E_{m,123}$, of the ternary mixtures. These were calculated from the relation

$$H^E_{m,123} = H^E_{m,1+23} + (1 - x_1)H^E_{m,23} \tag{1}$$

where $H^E_{m,23}$ is the excess molar enthalpy of the particular aqueous solution. Values of $H^E_{m,23}$ for water + sodium chloride were calculated from the equation given by Clarke and Glew (1985); those for water + zinc chloride were estimated from the data tabulated by Rossini *et al.*, (1952).

The smoothing function

$$H^E_{m,1+23}/(\mathrm{J\ mol^{-1}}) = x_1(1 - x_1)\sum_{j=1}^{m} h_j(1 - 2x_1)^{j-1} \tag{2}$$

was fitted to each set of results in Tables 1 and 2, by the method of least squares with all points assigned equal weight. The values of the coefficients, h_j, obtained from the analyses are listed in Table 3, along with the standard deviation, s, for each representation. Plots of the $H^E_{m,123}$ given in Tables 1 and 2, along with curves calculated from eqs 1 and 2 using the coefficients in Table 3, are shown in Figures 1 and 2.

The results for ethanol + water are shown in both figures for comparison with the other results. Also included in Figure 1 is a curve for ethanol + water calculated from the smoothing function reported by Costigan *et al.* (1980). The mean absolute relative deviation of the results listed for $m = 0$ in Table 1 from this curve is 1.6%.

The values of $H^E_{m,1+23}$ for both of the present systems are negative and of fairly similar magnitudes over the investigated range of molalities. However, the contributions of the $H^E_{m,23}$ term in eq 1 lead to quite different values of $H^E_{m,123}$ for the two systems. In the case of sodium chloride, these contributions are positive and result in relatively small upward displacements of the curves in Figure 1 as m is increased. For zinc chloride, the values of $H^E_{m,23}$ are negative and of larger magnitude, as illustrated by the increasing downward displacements of the curves in Figure 2.

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