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Excess Molar Enthalpies of *N,N*-Dimethylformamide + Alkan-1-ols (C_1-C_6) at 298.15 K

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Excess molar enthalpies, H_m^E, for the binary systems *N,N*-dimethylformamide + methanol, + ethanol, + propan-1-ol, + butan-1-ol, + pentan-1-ol, and + hexane-1-ol have been measured at 298.15 K and atmospheric pressure with a Parr 1455 solution calorimeter. While the excess molar enthalpies are negative for the methanol mixture, those for ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, and hexan-1-ol mixtures are positive over the entire range of composition of *N,N*-dimethylformamide. The H_m^E values at around $x \approx 0.5$ follow the order methanol < ethanol < propan-1-ol < butan-1-ol < pentan-1-ol < hexan-1-ol. The experimental results are explained on the basis of possible hydrogen-bonding between unlike molecules. The experimental data have been correlated using Redlich−Kister polynomials, and parameters from least-squares analysis have been reported.

Introduction

Estimation of the molecular interaction of binary mixtures and information to test existing theories of solution may be related to the magnitude of excess thermodynamic properties such as excess molar enthalpies. The thermodynamic properties of binary mixtures containing polar and self-associated components exhibit significant deviation from ideality, arising not only from the difference in size and shape but also from possible hydrogen-bonding interactions between unlike molecules.[1−6]

Excess molar enthalpies, H_m^E, have been measured for *N,N*-dimethylformamide + methanol, + ethanol, + propan-1-ol, + butan-1-ol, + pentan-1-ol, and + hexan-1-ol at 298.15 K. The purpose of this investigation is to study the interactions between alkan-1-ols and *N,N*-dimethylformamide.

A survey of the literature has shown that no excess enthalpy measurement for a mixture of *N,N*-dimethylformamide + alkan-1-ols (C_1-C_6) exists.

Experimental Section

Materials. The material used in this study, suppliers, and purities are listed in Table 1. *N,N*-Dimethylformamide, showing a stated purity of 99.8%, was used as received. All alkan-1-ols were purified by the standard method.[7]

The purities of all the liquid samples were ascertained by the constancy of the density and refractive index. Densities were measured at 293.15 K using a bicapillary pycnometer with an accuracy of 5 parts in 10^5. Refractive indexes were measured at 293.15 K with an Abbe refractometer. Water was circulated to the refractometer from a constant-temperature bath at 293.15 K. The accuracy of the refractive index measurement is on the order of ±0.0002.

Table 1 also gives the density and refractive index measurements, which agree with values obtained from the literature.[8,9]

Apparatus and Procedure. Mixtures were prepared by weighing the liquids in ground stoppered weighing bottles, taking due precaution to minimize the evaporation losses. All the weighings were performed on an electronic balance (AB 204-N Mettler) accurate to 0.1 mg. The uncertainty in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$.

The excess molar enthalpies, H_m^E, were determined using a Parr 1455 solution calorimeter. The measurements were carried out in an isolated room at 298 K and atmospheric pressure.The calorimeter consists of a silvered glass dewar, a mixing chamber with a rotating sample cell, a thermistor probe, and a built-in, microprocessor-based thermometer for precise temperature measurements. Digital readings are shown on an LED display and fed to outputs for a printer or computer, which are all assembled in a compact cabinet. The two-piece cell serves as both the sample holder and agitator. It is closed with a detachable Teflon disk. The liquid sample can be added to the cell from a pipet inserted through the top stem. Excellent thermal insulation is provided by the fully silvered dewar glass which serves as the mixing chamber. The enthalpy of mixing experiments were conducted in the calorimeter by considering 100 cm^3 of one component as solvent and a maximum of 25 cm^3 of other component as solute. In the subsequent runs 100 cm^3 of the previous solution was taken as the solvent and the pure solute was add to it. These experiments were continued until the concentration reached 50 to 60 vol %. By this method small errors in the earlier addition lead to a large error in latter experiments. The temperature measurement can be read to an accuracy of ±0.0002 K. Because of the limitation of the calorimeter, one is forced to adopt this method to cover the entire concentration range.

Initially, to determine the calorimeter equivalent, it was calibrated with 0.5 g of hydroxymethylaminomethane dissolved in a 0.1 $mol \cdot dm^{-3}$ hydrochloric acid solution which releases 245.52 $J \cdot g^{-1}$ at 298.15 K. The performance and reliability of the solution calorimeter were checked by the test mixture cyclohexane + benzene. The excess enthalpies, H_m^E, agreed within 1% with the reported values.[10]

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Table 1. Sources, Purity Grades, Densities, ρ, and Refractive Indices, n_D, of the Pure Components at 293.15 K

			ρ/g·cm^{-3}		n_D	
component	source	purity/(mass%)	expt	lit.[a]	expt	lit.[a]
N,*N*-dimethylformamide	Merck	99.8	0.943 90	0.943 97[b]	1.4282	1.42817[b]
methanol	Merk	99.5	0.791 23	0.7913	1.3288	1.3284
ethanol	Merk	99.8	0.789 47	0.7894	1.3612	1.3614
propan-1-ol	Merk	99.5	0.803 61	0.8037	1.3852	1.3856
butan-1-ol	Merk	99	0.809 79	0.8097	1.3990	1.3993
pentan-1-ol	Fluka	99	0.814 71	0.8148	1.4105	1.4100
hexan-1-ol	Merk	98	0.818 53	0.8186	1.4186	1.4182

[a] Dean, 1973. [b] Riddick et al., 1986.

Table 2. Excess Molar Enthalpies, H_m^E, and Deviations, $\delta(H_m^E)$, for the Binary Mixtures of *N*,*N*-Dimethylformamide + Alkan-1-ols at 298.15 K

x_1	H_m^E J·mol^{-1}	$\delta(H_m^E)$ J·mol^{-1}	x_1	H_m^E J·mol^{-1}	$\delta(H_m^E)$ J·mol^{-1}
		N,*N*-Dimethylformamide (1) + Methanol (2)			
0.0805	−22.8	−0.5	0.5252	−129.1	6
0.1617	−43.5	1.8	0.6065	−135.2	2.7
0.2409	−68.7	0.3	0.6866	−130.3	0.1
0.3237	−95	−1.4	0.7654	−114	−0.9
0.4031	−115.4	−1	0.8420	−87.8	−1.1
0.4827	−136.3	−6.4	0.9229	−47.8	0.4
		N,*N*-Dimethylformamide (1) + Ethanol (2)			
0.0987	33.8	−0.6	0.6029	257.2	4.4
0.1974	104.3	2.5	0.7017	221	−0.15
0.2959	171.6	0.25	0.8027	160.1	−2.3
0.3954	219.7	−5.9	0.9011	86.1	0.5
0.4983	256.2	1.2			
		N,*N*-Dimethylformamide (1) + Propan-1-ol (2)			
0.0976	399.6	−0.2	0.5037	829.7	−1.5
0.1994	669.4	1.2	0.6012	745.9	2.6
0.3072	819.0	−0.4	0.7012	605.0	−0.7
0.4032	859.7	−2	0.8006	430.6	−0.7
0.4981	836.2	1.5	0.8995	229	0.2
		N,*N*-Dimethylformamide (1) + Butan-1-ol (2)			
0.0965	445.6	−0.4	0.6019	937.5	0.2
0.1977	771.6	2	0.6055	933.9	1.3
0.2997	963.5	−1.4	0.7034	777.6	1.1
0.4006	1043.4	−2.2	0.8018	565.3	−1.9
0.5018	1031.5	0.7	0.9002	311.5	0.4
		N,*N*-Dimethylformamide (1) + Pentan-1-ol (2)			
0.1001	520.4	−0.2	0.6001	1111	−0.2
0.2014	885.7	1.4	0.699	927.3	−5.1
0.3007	1106.8	−2.3	0.8021	683.6	3.1
0.4011	1214.4	−1.7	0.9018	378	−0.4
0.5005	1217.4	5.3			
		N,*N*-Dimethylformamide (1) + Hexan-1-ol (2)			
0.0975	537.7	−0.1	0.6047	1271.6	3.8
0.2044	956.3	0.4	0.6990	1098.6	−2.4
0.3051	1208.2	0.7	0.7018	1092.8	−1.9
0.4066	1333.2	−2.9	0.7968	843.2	1.4
0.5055	1352.9	1	0.9029	457.9	−0.1

Results and Discussion

The experimental results for the enthalpies of mixing for the binary mixtures of *N*,*N*-dimethylformamide + methanol, + ethanol, + propan-1-ol, + butan-1-ol, + pentan-1-ol, and + hexan-1-ol at 298.15 K are listed in Table 2, together with the deviation $\delta(H_m^E)$, and are shown graphically in Figure 1. Each set of results was fitted using a Redlich−Kister equation of the type

$$H_m^E/\text{J·mol}^{-1} = x(1 - x)\sum_{r=1}^{n} A_r(2x - 1)^{r-1} \qquad (1)$$

where x is the mole fraction of *N*,*N*-dimethylformamide.

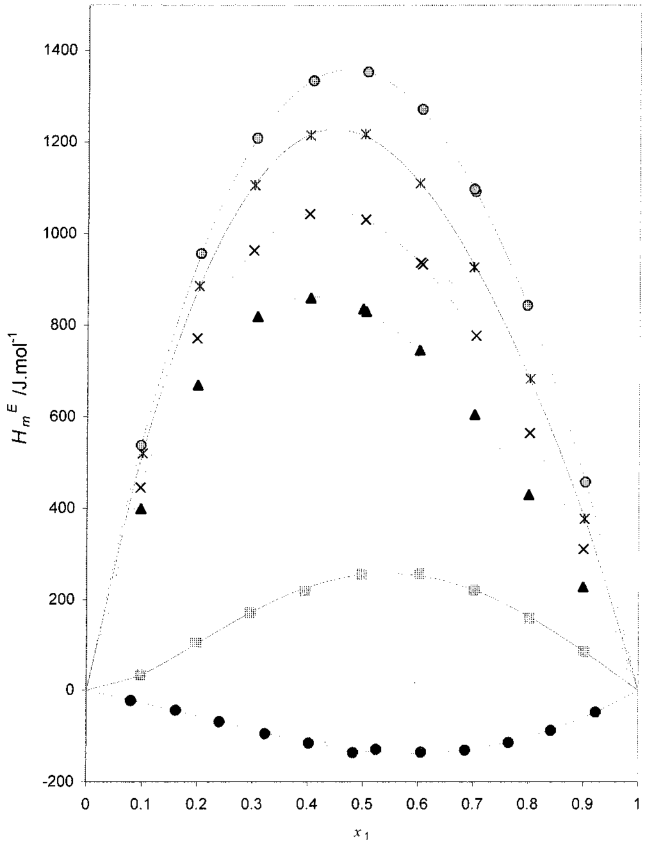

Figure 1. Excess molar enthalpies of *N*,*N*-dimethylformamide (1) + alkan-1-ols (2) at 298.15 K. Solid curves are calculated with eq 1: ●, methanol; shaded box, ethanol; ▲, propan-1-ol; ×, butan-1-ol; × with a line through it, pentan-1-ol; shaded circle, hexan-1-ol.

The cofficients A_r were calculated by a least-squares analysis. They are presented in Table 3 together with the standard deviation $\sigma(H_m^E)$

$$\sigma(H_m^E) = |\zeta/(n - p)|^{0.5} \qquad (2)$$

where n is the number of experimental points and p is the number of adjustable parameters A_r. ζ is the objective function, defined as

$$\zeta = \sum \delta^2(H_m^E) \qquad (3)$$

where $\delta(H_m^E) = H_{m,exp}^E - H_{m,cal.}^E$.

The excess molar enthalpies for the methanol mixture with *N*,*N*-dimethylformamide are exothermic while those for the mixtures with ethan-1-ol, propan-1-ol, butan-1-ol, pentan-1-ol, and hexan-1-ol were endothermic over the

Table 3. Adjustable Parameters, A_r (Eq 1), and Standard Deviations, $\sigma(H_m^E)$ (Eq 2), of *N*,*N*-Dimethylformamide + Alkan-1-ols at 298.15 K[a]

A_1	A_2	A_3	A_4	A_5	$\sigma(H_m^E)$
N,*N*-Dimethylformamide (1) + Methanol (2)					
−529.2	−254.2	124.6	43.9	−95.6	8.5
N,*N*-Dimethylformamide (1) + Ethanol (2)					
1020.8	261.2	−472.0	149.7	−105.4	8.9
N,*N*-Dimethylformamide (1) + Propan-1-ol (2)					
3334.3	−1213.0	300.1	−60.2	9.9	4.9
N,*N*-Dimethylformamide (1) + Butan-1-ol (2)					
4127.2	−1105.6	205.4	120.5	62.1	5.2
N,*N*-Dimethylformamide (1) + Pentan-1-ol (2)					
4849.3	−1095.1	−66.6	237.2	537.3	9.8
N,*N*-Dimethylformamide (1) + Hexan-1-ol (2)					
5414.9	−602.2	313.1	76.8	118.4	6.6

[a] Units: J·mol^{-1}.

entire range of composition of *N*,*N*-dimethylformamide. For these six binary mixtures, the equimolar excess molar enthalpies increased in the order

$$\text{methanol} < \text{ethanol} < \text{propan-1-ol} < \text{butan-1-ol} < \text{pentan-1-ol} < \text{hexan-1-ol}$$

Since alkan-1-ols are strongly associated through hydrogen-bonding, dilution with a polar solvent like *N*,*N*-dimethylformamide results in a thermodynamic function which may be due to (i) the breakup of hydrogen bonds with diluent and (ii) the formation of a new species acting as an adduct between the alkan-1-ols and *N*,*N*-dimethylformamide. The observed negative excess enthalpies of mixing indicate that the association of the dissociated species of the methanol on dilution with *N*,*N*-dimethylformamide is the dominating force. According to our results for the systems studied, the positive excess enthalpies may be influenced by the dissociation of self-associated alkan-1-ols by *N*,*N*-dimethylformamide and the reduction in the dipole−dipole interaction between like molecules. On the other hand, the endothermic behavior definitely is due to the destruction of associated alkan-1-ol molecules.

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