

# Excess Molar Enthalpies of Binary Mixtures Containing *N,N*-Dimethylformamide + Six 2-Alkanols (C<sub>3</sub>–C<sub>8</sub>) at 300.15 K

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Excess molar enthalpies,  $H_m^E$ , of *N,N*-dimethylformamide + 2-propanol, + 2-butanol, + 2-pentanol, + 2-hexanol, + 2-heptanol, and + 2-octanol have been determined at 300.15 K and atmospheric pressure using an isothermal microcalorimeter.  $H_m^E$  values are positive over the entire range of composition of *N,N*-dimethylformamide and increase in the order 2-propanol < 2-butanol < 2-pentanol < 2-hexanol < 2-heptanol < 2-octanol. Maximum values of  $H_m^E$  vary from 500 J·mol<sup>-1</sup> up to 900 J·mol<sup>-1</sup>. The results are explained in terms of the strong self-association exhibited by the 2-alkanols and the cross-association of the O···HO specific interaction. The Redlich–Kister equation, fitted to the experimental results, provides a satisfactory mathematical representation of  $H_m^E$  in all mixtures.

## Introduction

The present work forms part of a program involved in the study of the thermodynamic behavior of some binary mixtures in which specific interactions between unlike molecules can occur (Iloukhani, 1997; Iloukhani and Parsa, 1998; Iloukhani and Ghorbani, 1998; Iloukhani et al., 1999). We have determined the experimental excess molar enthalpies,  $H_m^E$ , of *N,N*-dimethylformamide (DMF) + six 2-alkanols, namely, 2-propanol, 2-butanol, 2-pentanol, 2-hexanol, 2-heptanol, and 2-octanol at 300.15 K.

Experimental values have been fitted to the Redlich–Kister (1948) equation to determine the binary coefficients and standard deviation. A qualitative discussion of the results is given. To our knowledge, mixtures of DMF with 2-alkanols have not been previously studied.

## Experimental Section

**Materials.** Characterization data for DMF and the 2-alkanols are listed in Table 1. *N,N*-Dimethylformamide was purified by the standard method described by Perrin and Armarego (1970). All 2-alkanols used were purified by distillation using a 10 m fractionation column. The purified compounds were stored in brown glass bottles and fractionally distilled immediately before use. The purity of each compound was ascertained by the constancy of the boiling point and also from the density and refractive index, which agreed, as shown in Table 1, with the literature values (Riddick and Bunger, 1970; Weast, 1990). The densities were measured at 293.15 K using a bicapillary pycnometer with an uncertainty of 5 parts in 10<sup>5</sup>. Refractive indices were measured at 293.15 K with an Abbé refractometer. Water was circulated to the refractometer from a constant-temperature bath at 293.15 K. The uncertainty of the refractive index measured is on the order of ±0.0002.

**Apparatus and Procedure.** Excess molar enthalpies,  $H_m^E$ , were determined using an isothermal microcalorimeter (Thermal Activity Monitor, TAM, model 2277, Thermometric, Sweden). It was equipped with four channels, allowing for the rate of heat output. Each channel of the calorimeter was independently electronically calibrated

**Table 1. Sources, Purity Grades, Densities,  $\rho$ , and Refractive Indices,  $n_D$ , of Pure Components and Comparison with Literature Values at 293.15 K**

component	source	purity		$\rho/\text{g}\cdot\text{cm}^{-3}$		$n_D$	
		mass %		exp	lit.	exp	lit.
DMF	Merck	99.8		0.948 62	0.94873 <sup>a</sup>	1.430 29	1.43047 <sup>a</sup>
2-propanol	Merck	99.7		0.785 61	0.78545 <sup>a</sup>	1.377 31	1.37720 <sup>a</sup>
2-butanol	Merck	99.5		0.807 01	0.8069 <sup>a</sup>	1.397 31	1.3972 <sup>a</sup>
2-pentanol	Merck	>98		0.809 53	0.8094 <sup>a</sup>	1.406 59	1.4064 <sup>a</sup>
2-hexanol	Merck	>98		0.816 84	0.8167 <sup>b</sup>	1.414 56	1.4144 <sup>b</sup>
2-heptanol	Merck	>99		0.817 24	0.8171 <sup>a</sup>	1.421 25	1.4210 <sup>b</sup>
2-octanol	Merck	>98		0.819 11	0.8193 <sup>b</sup>	1.420 19	1.4203 <sup>b</sup>

<sup>a</sup> Riddick and Bunger, 1970. <sup>b</sup> Weast, 1990.

with a precision of ±0.2%. Each channel is a twin heat-conduction calorimeter, where the heat-flow sensor is a semiconductor thermopile (multijunction thermocouple plates) positioned between the vessel made from stainless steel. The insertion vessel was also made from stainless steel. The rate of heat output from the sample cell with respect to the reference cell, displayed digitally, was recorded with an accuracy of 0.1  $\mu\text{W}$  by a DIGITAM 3 computer program.

The microcalorimetric experiments were performed at a fixed temperature of (300.15 ± 0.01 K). The uncertainty in mole fraction is estimated to be ±1 × 10<sup>-4</sup> and was determined from weighing the pure components and pump reservoir. These uncertainties were also based on the assumption that the pump could deliver steady flow to at least the same uncertainty as ±1 × 10<sup>-4</sup> mole fraction. The average uncertainty in  $H_m^E$  was estimated to be 1%.

Before measurement, the calorimeter was checked using the test mixture cyclohexane + hexane, for which literature values are well-known (Gmehling, 1993), and agreement between ours and literature data was better than 0.6% over the central range of mole fraction of cyclohexane.

## Results and Discussion

The measured excess molar enthalpies,  $H_m^E$ , of *N,N*-dimethylformamide + 2-propanol, + 2-butanol, + 2-pentanol, + 2-hexanol, + 2-heptanol, and + 2-octanol at 300.15

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**Table 2. Excess Molar Enthalpies,  $H_m^E$  ( $J \cdot mol^{-1}$ ), for Binary Mixtures of *N,N*-Dimethylformamide + 2-Alkanols at 300.15 K**

$x$	$H_m^E$	$\delta H_m^E$	$x$	$H_m^E$	$\delta H_m^E$	$x$	$H_m^E$	$\delta H_m^E$
xDMF + (1 - x)2-Propanol								
0.0537	51.1	-0.2	0.4246	432.5	-6.7	0.7129	338.8	-7.2
0.1455	141.6	0.8	0.4599	463.6	-0.24	0.7766	265.1	0.7
0.2211	220.8	1.5	0.4911	488.1	10	0.8528	185.8	4.9
0.2846	294.6	3.5	0.5721	493.4	17.6	0.9455	95.3	-0.7
0.3381	348.6	-4.2	0.6124	458.4	5.8			
0.3844	394.2	-8.2	0.6589	392.8	-17.3			
xDMF + (1 - x)2-Butanol								
0.0638	78.7	0.6	0.4697	522.3	-8.7	0.7488	467.9	5.2
0.1697	180.7	-6.8	0.5054	559.4	-4.0	0.8067	372.9	-0.2
0.2541	278.3	8.1	0.5366	588.7	4.8	0.8743	263.4	1.7
0.3229	356.9	-7.5	0.6161	604.5	13.2	0.9542	124.5	0.3
0.3801	422.7	0.0	0.6548	567.4	-2.9			
0.4284	476.4	-7.8	0.6986	521.5	-7.3			
xDMF + (1 - x)2-Pentanol								
0.0748	90.7	0.2	0.5123	601.9	5.7	0.7795	532.5	0.8
0.1951	206.8	1.7	0.5480	644.9	-4.1	0.8319	471.4	-12.7
0.2878	309.3	-5.3	0.5787	674.0	-15.2	0.8912	345.8	5.5
0.3613	396.1	1.3	0.6556	654.9	0.4	0.9612	158.9	-0.4
0.4211	480.7	3.8	0.6923	624.0	6.7			
0.4706	552.5	3.2	0.7333	581.9	8.3			
xDMF + (1 - x)2-Hexanol								
0.0857	98.2	-0.1	0.5491	677.2	-0.3	0.8039	607.5	11.6
0.2194	246.2	1.3	0.5842	720.3	3.1	0.8516	495.4	2.5
0.3190	372.2	-2.6	0.6143	745.7	3.3	0.9053	364.7	4.3
0.3960	470.2	-0.8	0.6872	751.2	1.4	0.9663	185.1	0.4
0.4574	555.3	2.8	0.7228	716.1	10.3			
0.5075	621.0	1.1	0.7612	670.5	3.8			
xDMF + (1 - x)2-Heptanol								
0.0952	135.9	0.0	0.5777	732.7	-0.4	0.8215	635.4	-7.7
0.2399	290.2	0.7	0.6122	778.5	-0.8	0.8657	507.7	-7.9
0.3448	414.9	-1.7	0.6414	806.0	-5.3	0.9148	386.0	5.1
0.4242	519.5	-1.9	0.6666	820.7	-9.3	0.9699	205.1	-0.4
0.4864	608.5	4.7	0.7455	816.7	11.7			
0.5365	678.2	4.0	0.7817	752.1	9.6			
xDMF + (1 - x)2-Octanol								
0.1055	153.8	0.1	0.6052	799.1	7.6	0.8377	715.3	9.4
0.2613	323.5	-1.9	0.6389	843.3	2.9	0.8784	564.5	0.0
0.3709	475.3	10.7	0.6672	875.9	-1.8	0.9233	415.5	-2.9
0.4522	576.5	-15.7	0.7353	904.8	-7.1	0.9731	228.3	0.3
0.5149	669.1	-2.9	0.7665	874.7	-9.4			
0.5647	742.7	8.0	0.8005	820.2	3.1			

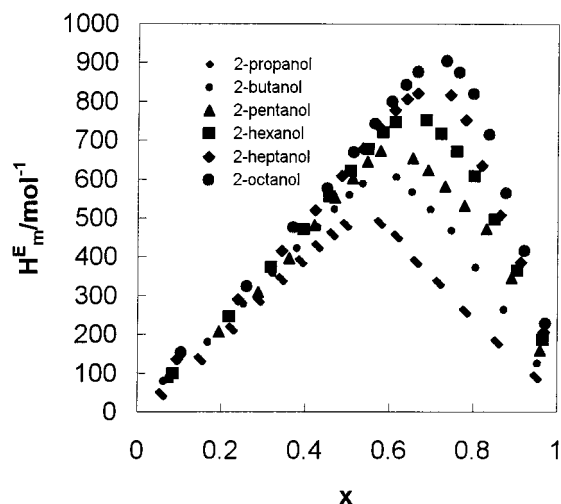
K are listed in Table 2, together with the deviations,  $\delta(H_m^E)$ , and are shown graphically in Figure 1. The results were fitted to the Redlich–Kister (R–K) polynomial

$$H_m^E/(J \cdot mol^{-1}) = x(1 - x) \sum A_i (1 - 2x)^{i-1} \quad (1)$$

where  $x$  is the mole fraction of DMF and  $A_i$  are the coefficients for the binary mixtures. They are presented in Table 3 together with the standard deviation  $\sigma(H_m^E)$ ,

**Table 3. Values of the Adjustable Coefficients,  $A_i$ , in Eq 1 and the Standard Deviation,  $\sigma(H_m^E)$ , in Eq 2 for *N,N*-Dimethylformamide + Alkanols at 300 K**

$A_i, \sigma$	DMF +					
	2-propanol	2-butanol	2-pentanol	2-hexanol	2-heptanol	2-octanol
$A_1$	1922.8	2236.9	2373.8	2447.2	2490.2	2615.2
$A_2$	-511.4	-1648.7	-2377.7	-2785.3	-2770.6	-2444.9
$A_3$	-2388.4	-1623.7	-1222.0	2011.0	3328.1	2018.9
$A_4$	1514.7	3072.4	4602.3	3163.3	-2802.2	-11137.6
$A_5$	2237.8	1718.7	2654.2	-7406.2	-7925.6	4376.2
$A_6$	-1855.3	-2553.6	-7586.5	-2761.9	17134.4	44504.5
$A_7$			-689.8	7737.5	6700.9	-8506.7
$A_8$			3922.6		-16689.2	-42533.5
$\sigma$	9.8	7.8	9.0	6.0	8.2	9.7

**Figure 1. Excess molar enthalpies for the binary mixtures of (x)-*N,N*-dimethylformamide + (1 - x)2-alkanols at 300.15 K.**

which is evaluated from the equation

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

where  $n$  is the number of the experimental points and  $p$  is the number of adjustable parameters  $A_i$ .  $\varphi$  is the objective function defined as

$$\varphi = \sum \delta^2(H_m^E) \quad (3)$$

where

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

The  $H_m^E$  values for the binary mixture are positive for all the systems. The maxima vary from 500  $J \cdot mol^{-1}$  up to 900  $J \cdot mol^{-1}$  and increase in the order 2-propanol to 2-octanol. These positive values suggest that the structure-breaking effect of the components is dominant in the mixtures and associations of pure 2-alkanols, owing to strong hydrogen bonding between molecules.

The complex molecular interactions in these systems make difficult even a qualitative interpretation of the results. In fact, in addition to the H-bond association between DMF molecules, the H-bond association of 2-alkanols with the DMF considerably affects the properties of the mixtures with endothermic as well as exothermic contributions.

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