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Excess molar enthalpies of N,N-dimethylformamide with ketones at 298.15 K

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Abstract

Excess molar enthalpies (H^E) at 298.15 K of N,N-dimethylformamide with a series of ketones: methyl ethyl ketone (MEK), methyl propyl ketone (MIPK), diethyl ketone (DEK), methyl isobutyl ketone (MIBK), cyclopentanone (CP) and cyclohexanone (CH) have been measured by using a Parr 1451 solution calorimeter, as a function of mole fraction of the N,N-dimethylformamide. The experimental H^E values are positive for all binary mixtures over the entire range of composition. The excess enthalpies of the above mentioned binary systems, were used to discuss interactions between the ketonic (>CO) and DMF molecules. The results are interpreted to gain insight into the changes in molecular association equilibria and structural effects in these systems. When the compounds are mixed, the changes that occur in association equilibria are evidently rupture of the hydrogen bonds in pure compounds and the formation of OH... CO hydrogen bonds between the compounds. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Excess molar enthalpies; N,N-dimethylformamide; Ketones; Binary mixtures; Molecular interactions

1. Introduction

Thermodynamic properties of non-electrolytic solutions have proven to be a very useful tool in elucidating the structural interactions among the components. Many long term-studies of many research-workers [1–6], both experimentalists and theoreticians, have shown the important and fundamental role of the molecular details of the solvent species to determine the specific interactions which are responsible for the thermodynamic and the transport properties in non-electrolyte solutions. As is generally known, the thermodynamic properties of liquid mixtures are sensitive to various association equilibria. Unsubstituted and N-monosubstituted carboxamides, which have a proton donor group, the NH group, are capable of self-association through formation of NH... OC hydrogen bonds. Such association is not possible in N,N-disubstituted amides (DMF), where both NH protons are replaced by alkyl group. N,N-disubstituted amides occurs extensively in aprotic donor solvents, such as N,N-dimethylformamide, despite the fact that these aprotic donor solvents have stronger electron-pair donating ability than water. Infact, the reaction is generally endothermic with an unusually large and positive entropy at the initial stage of complexation. The thermodynamic behaviour is related to the car-

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bonyl group of the ketones upon their complexation. The carbonyl group of ketones is a considerably proton acceptor, it was interesting to see how this difference was reflected in the properties of DMF-ketones mixtures. To investigate these effects, a series of measurements [7,8] of the binary mixtures of polar fluids of DMF with ketones are in progress. The excess enthalpies for the mixtures of N,N-dimethylformamide with substituted benzenes [9], with 1-alkanols [10], with four butanols [11], with methanol, ethanol and 1-propanol [12], with tetrahydrofuran and cyclohexane [13] and with ammonium methanoate in water [14] are already reported in the literature. However, no effort appears to have been made to collect the excess enthalpies for the mixtures of N,N-dimethylformamide with ketones and there is no evidence for a specific interactions between DMF' with ketones. Molar excess enthalpies of DMF with ketones are also of interest from thermodynamic and structural points of view. As part of our research programme to explore the interactions between DMF with ketones [15–19], we report here the measurements of excess molar enthalpies on mixtures of N,N-dimethylformamide with methyl ethyl ketone, methyl propyl ketone, diethyl ketone, methyl isobutyl ketone, cyclopentanone and cyclohexanone at 298.15 K.

2. Experimental

2.1. Materials

N,N-dimethylformamide (Fluka, initial purity >99%) was purified by the method described by Umebayashi et al [20]. Methyl ethyl ketone (BDH Ltd., initial purity >98%), methyl propyl ketone (Aldrich, initial purity >99%), diethyl ketone (Fluka initial purity >99%), methyl isobutyl ketone (BDH Ltd., initial purity >98%), cyclopentanone (Fluka, initial purity >99%) and cyclohexanone (Aldrich initial purity >99%) were initially dried over 4A molecular sieves for several days and purified by fractional distillation. The purity of the chemical products was verified by measuring the densities, which were in good agreement with literature values [21,22] as can be seen in Table 1. The purities of the samples were further confirmed by GLC single sharp peaks.

2.2. Measurements

A new Parr 1451 solution calorimeter was used in the measurements of H^E of liquid mixtures. The detailed procedures and apparatus used have been described in our earlier publications [9,23,24]. In the measurement of excess enthalpies, known weight of 100 ml of Component A is taken into the Dewar vessel and 20 ml of Component B is weighed in a sealed glass rotating cell. Both the components are kept in thermal contact with each other in the Dewar mixing champer at 298.15 K. After attaining the thermal equilibrium (about 30′) Component B in the rotating cell is mixed with Component A in the Dewar vessel by pushing the glass rod. The temperature change accompanying the mixing process is sensed by the thermistor and recorded on the strip chart recorder. These experiments were continued till the concentrations reach 50–60%. This procedure was repeated by taking Component A as Component B and Component B as Component A. The reliability of

Table 1
Experimental and literature densities at 303.15 K of pure components

Liquid	Experimental Density g^{-1} cm^{-3}	Literature [21,22]
N,N-dimethylformamide	0.941 18	0.941 20
Methyl ethyl ketone	0.794 50	0.795 52
Methyl propyl ketone	0.796 53	0.796 60
Diethyl ketone	0.804 58	0.804 61
Methyl isobutyl ketone	0.796 07[a]	0.796 10[a]
Cyclopentanone	0.939 01	0.939 02
Cyclohexanone	0.937 58	0.937 57

[a] At 298.15 K.

the apparatus and the method was established by measuring H^E values of standard systems, i.e., benzene with carbontetrachloride and chlorobenzene with toluene, throughout the concentration range at 298.15 K. Results were in good agreement with the reported date in the literature [25,26]. The uncertainty in the measured H^E values are ±1%.

3. Results and discussion

Table 2
Experimental excess molar enthalpies of N,N-dimethylformamide (x_1) + ketones (x_2) at 298.15 K

x_1	H^E J^{-1} mol^{-1}	x_1	H^E J^{-1} mol^{-1}
N,N-dimethylformamide + methyl ethyl ketone			
0.1258	57.5	0.4972	145.6
0.1497	70.5	0.5462	141.4
0.1957	89.6	0.5997	139.2
0.2446	104.9	0.6503	127.9
0.2956	114.3	0.7662	93.9
0.3447	121.7	0.8222	72.2
0.3971	123.8	0.8702	56.8
0.4478	123.6	0.9022	43.8
N,N-dimethylformamide + methyl ethyl ketone			
0.0455	29.8	0.5513	222.0
0.1061	68.9	0.5997	214.9
0.1517	95.5	0.6487	202.1
0.2057	122.5	0.6987	183.9
0.2505	141.5	0.7524	161.6
0.3027	154.4	0.7982	138.6
0.3480	164.1	0.8554	103.6
0.3993	176.1	0.9000	72.9
0.4503	193.8	0.9553	34.4
0.5022	205.2		
N,N-dimethylformamide + methyl ethyl ketone			
0.0492	44.6	0.5512	262.2
0.1065	93.2	0.6012	270.9
0.1510	125.3	0.6485	253.7
0.2055	163.2	0.6985	229.7
0.2507	186.4	0.7520	196.5
0.3038	206.4	0.7982	167.6
0.3469	221.3	0.8526	129.7
0.3974	230.7	0.8998	92.9
0.4505	234.5	0.9552	43.5
0.5014	255.6		
N,N-dimethylformamide + methyl ethyl ketone			
0.0590	77.7	0.5522	374.5
0.1075	134.4	0.6015	375.9
0.1468	174.0	0.6551	362.9
0.1977	215.7	0.7037	333.1
0.2570	257.6	0.7553	294.3
0.3022	283.1	0.7989	254.8
0.3481	306.1	0.8586	189.2
0.4028	320.9	0.9053	132.9
0.4467	330.0	0.9533	69.3
0.4975	360.6		
N,N-dimethylformamide + cyclohexanone			
0.0474	20.0	0.5538	114.9
0.1025	33.4	0.6041	105.6
0.1482	46.6	0.6521	96.0
0.2025	60.0	0.6982	84.6
0.2464	68.9	0.7415	71.5
0.3020	76.2	0.8016	54.9
0.3536	80.9	0.8466	42.1
0.4050	87.8	0.9000	27.2
0.4947	108.7	0.9462	14.6
N,N-dimethylformamide + cyclohexanone			
0.0562	93.4	0.5517	422.9
0.1025	155.4	0.6003	405.6
0.1572	216.6	0.6484	379.4
0.2050	259.3	0.6952	344.6
0.2523	306.1	0.7475	300.8
0.3011	338.6	0.7989	249.8
0.3587	363.6	0.8499	197.2
0.3974	376.6	0.8988	140.7
0.4517	381.9	0.9426	83.3
0.5029	415.2		

Experimental excess molar enthalpies at 298.15 K of the binary mixtures of N,N-dimethylformamide with ketones are reported in Table 2 and are graphically presented in Fig. 1 in the form of H^E versus the mole fraction (x_1) of DMF. The experimental H^E values may be represented by

$$H^E = x_1 x_2 \sum_i h_1 (x_1 - x_2)^i \tag{1}$$

where x_1 and x_2 are mole fraction of N,N-dimethylformamide and ketones. The h_1 binary parameters have been evaluated by the method of least squares and are listed in Table 3 along with the percentage standard deviation. The values of the percentage standard deviation are computed from the relation:

$$\%\,\sigma\,(H^E) = \left[\frac{\sum \left(((H^E_{\mathrm{exp}} - H^E_{\mathrm{cal}})/(H^E_{\mathrm{exp}})) \times 100 \right)^2}{n-p} \right]^{1/2} \tag{2}$$

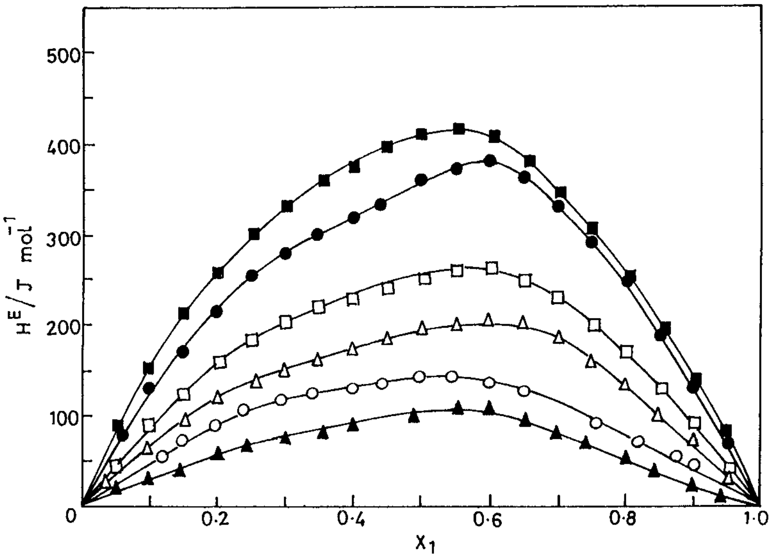


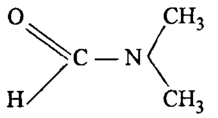
Fig. 1. Excess enthalpies (H^E) for DMF with MEK (○), MPK(△)DEK (□), MIBK (●) CP (▲) and CH (■) at 298.15 K.

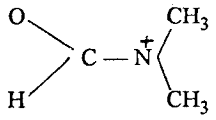
Table 3
Estimated parameters of Eq. (1) and percentage of standard deviation, %σ (H^E) for the mixtures of N,N-dimethylformamide with ketones at 298.15 K

N,N-dimethylformamide	h_0	h_1	h_2	h_3	h_4	h_5	%σ(H^E)
	J mol^{-1}						
+ methyl ethyl ketone	549.2	166.1	65.3	−1112.4	−253.7	1383.5	2.0
+ methyl propyl ketone	810.2	313.3	170.2	−829.4	−116	648.9	1.8
+ diethyl ketone	1028.6	299.1	147.3	−957.5	−902.4	792.4	2.6
+ methyl isobutyl ketone	1449.8	625.5	132.3	−1691.0	−141.7	1297.0	2.7
+ cyclopentanone	426.6	135.4	−315.8	−497.0	290.5	292.3	1.9
+ cyclohcxanonc	1638.5	216.3	−255.7	−942.8	344.5	672.2	2.1

where n and p are number of results and parameters, respectively. The data included in Table 2 shows that the H^E values are positive (endothermic) in the mixtures of DMF with ketones at 298.15 K over the whole range of composition. The positive H^E values observed in our results suggest that loss of dipolar association by the addition of one component to the other and the difference in size and shape of the component molecules. The maximum positive H^E values are observed around 0.5–0.55 mole fraction of N,N-dimethylformamide for these binary systems.

The solvency power of N,N-dimethylformamide can be ascribed to the molecule, high dielectric constant, the electron donor properties and the ability to form complexes. According to the study on the thermodynamic properties, Chu et al [27] and Singh et al [28] assumed DMF to have the resonance structure;





The negative pole in DMF is on an oxygen atom that juts out from the rest of the molecule. Through unshared pairs of electrons on these negatively charged, well exposed atoms are solvated very strongly. The positive pole on the other hand, is buried within the molecule. In DMF the presence of two electron – repelling – CH_3 groups make the lone pair at nitrogen still more perceptible towards donation. Thus, it may be argued that in DMF it is actually the donation of nitrogen – electron pairs. Meanwhile, owing to the proton – accepting ability of the carbonyl (>CO) group the ketones is a considerably poorer proton acceptor. The molecules of ketones are dipolar and can be self-associated by dipole–dipole interactions.

In general, the excess enthalpies of mixtures like the present one, where both components have considerable association properties, are sums of so many different contributions that only a qualitative interpretation of the results is possible. A quantitative interpretation would requires all association equilibria – both their equilibrium constants and enthalpies of association – to be taken into account. Moreover, different associates prevail at different concentration ratios of proton donor and proton acceptor. For example, a strongly associating pairs forms 1 : 1 complexes only at low concentrations; at higher concentrations formation of different higher complexes is very likely as well. When DMF and ketones are mixed, the main changes that occur in association equilibria are evidently the rupture of the C=O. . .H–C hydrogen bonded chain between DMF molecules, and mainly arise from the breaking of strong self association interactions and dipole–dipole interactions between ketone molecules. Break-up of such associated structures would lead to a positive contribution to the mixtures of DMF. Therefore, on the basis of the actual experimental evidence, we can suggest that the addition of ketones to DMF certainly is responsible hydrogen bonding network breaking, different molecular arrangements of components should be responsible for the appearance of different complex adducts with different stoichiometric composition and thermostabilities. The algebraic values of H^E for the systems of DMF with ketones fall in the order:

Cyclohexanone > methyl isobutyl ketone > diethyl ketone > methyl propyl ketone > methyl ethyl ketone > cyclopentanone.

The fact that for a given positive excess enthalpies increases as in aliphatic chain length of the ketone increases can be explained in terms of the effect of chain length on the polarity of the CO group, dipole moments [29] show that the longer the chain of the ketone, the less the polarity of CO, and hence, the weaker the corresponding dipole–dipole interaction. Moreover, increasing the ketone chain length reduces the concentration of CO groups, which must like wise weaker their interactions. Both effects make it likely that the DMF-ketone interactions become relatively more important as the ketone chain length increases. The large positive values for the mixtures of DMIF with cyclohexanone (at $x_1 = 0.55$, 423 J mol^{-1}) indicate that contributions due to the break-up of DMF-ketone interactions, discussed above, clearly predominate in the mixture, and indeed the magnitudes of H^E values of these systems that at least in mixtures of the lower chain length of ketones there are some slight contributions due to hetero-association. The lower positive values (at $x_1 = 0.55$, 115 J $mo1^{-1}$) for cyclopentanone mixture compared with cyclohexanone mixture serves as evidence that cyclopentanone interact with DMF more strongly than cyclohexanone. We might expect moderate steric hindrance in cyclohexanone; that is, larger groups are tend to resist crowing more than smaller groups. The positive H^E values of aliphatic ketones with DMF can be explained by considering the structural implications of the four ketones. The inductive effect of the substituted, ethyl, propyl or isobutyl group on one side of carbonyl group results in an enhanced H^E values.

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