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Excess molar enthalpies of *N*,*N*-dimethylacetamide with substituted benzenes at 298.15 K

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Abstract

Excess molar enthalpies (H^E) of binary mixtures of *N*,*N*-dimethylacetamide with ethylbenzene, chlorobenzene, bromobenzene, nitrobenzene, aniline and acetophenone have been measured with a Parr 1451 calorimeter at 298.15 K, over the entire range of composition. The experimental values of H^E are positive in the mixture of *N*,*N*-dimethylacetamide with ethylbenzene. The other experimental values of H^E are negative. The results are discussed with regard to the associating abilities of the components.

Keywords: Excess molar enthalpies; Dipolar interactions; *N*,*N*-dimethylacetamide; Calorimeter

1. Introduction

The excess enthalpies of non-electrolyte solutions are importance in design calculations involving chemical separations. 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 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 (DMA), where both NH protons are replaced by alkyl group. *N*,*N*-disubstituted amides occurs extensively in aprotic donor solvents, such as *N*,*N*-dimethylacetamide, despite the fact that these aprotic donor solvents have stronger electron pair donating ability than water. We report here experimental excess enthalpy data for binary mixtures containing *N*,*N*-dimethylacetamide; with ethylbenzene, chlorobenzene, bromobenzene, nitrobenzene, aniline and acetophenone at 298.15 K. The purpose of study was to investigate the effects of substituted benzene group on the interactions between like and unlike molecules by measuring the excess enthalpies of the mixtures.

2. Experimental

In the present investigation, all the chemicals used were of analytical grade and purchased from

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

Liquid	Purification	Experimental density ($g\,cm^{-3}$)	Literature [7,8]
N,*N*-dimethylacetamide	[9]	0.93240	0.93243
Ethylbenzene	[11]	0.85766	0.85770
Chlorobenzene	[10]	1.09547	1.09550
Bromobenzene	[10]	1.48147	1.48150
Nitrobenzene	[10]	1.19338	1.19341
Aniline	[10]	1.01314	1.01317
Acetophenone	[10]	1.01942	1.01947

commercial sources. The purity of chemicals was verified by measuring densities, which were in good agreement with literature values [7,8] as can be seen in Table 1. The purities of samples were further confirmed by GLC single sharp peaks. A Parr 1451 solution calorimeter was used in the measurements of H^E of liquid mixtures. It consists of Dewar mixing chamber with rotating sample cell, a thermistor probe and specially designed temperature bridge. The two-piece cell, which served both as sample holder and agitator consisted of a cell closed with a detachable Teflon disc. Liquid samples were added to the cell from a pipette inserted through the top stem. At the start of the experiment, one of the components is held in a sealed glass-rotating cell in thermal contact with the other liquid but not combined with it. The mixing process can be effected by pressing a push rod, which drops the contents of the cell into the surrounding liquid. Whenever two liquids combined temperature changes will be sensed immediately by the thermistor bridge, which can be plotted directly degrees using an accessory strip chart recorder and were read to an accuracy of 0.001 K.

In the measurement of excess enthalpies, known weight of 100 ml of Component A is taken into the Dewar Vessel 20 ml Component B is weighed in a sealed glass-rotating cell. Both the components are kept in thermal contact with each other in Dewar mixing chamber at 298.15 K. Sufficient time is allowed (about 30 min) for the system to attain thermal equilibrium. Due care is taken for any heating effects due to evaporation (volatile components) or condensation (heavy components) which are independent of mixing. These experiments were continued until the concentrations reached 50–60%. The procedure was repeated

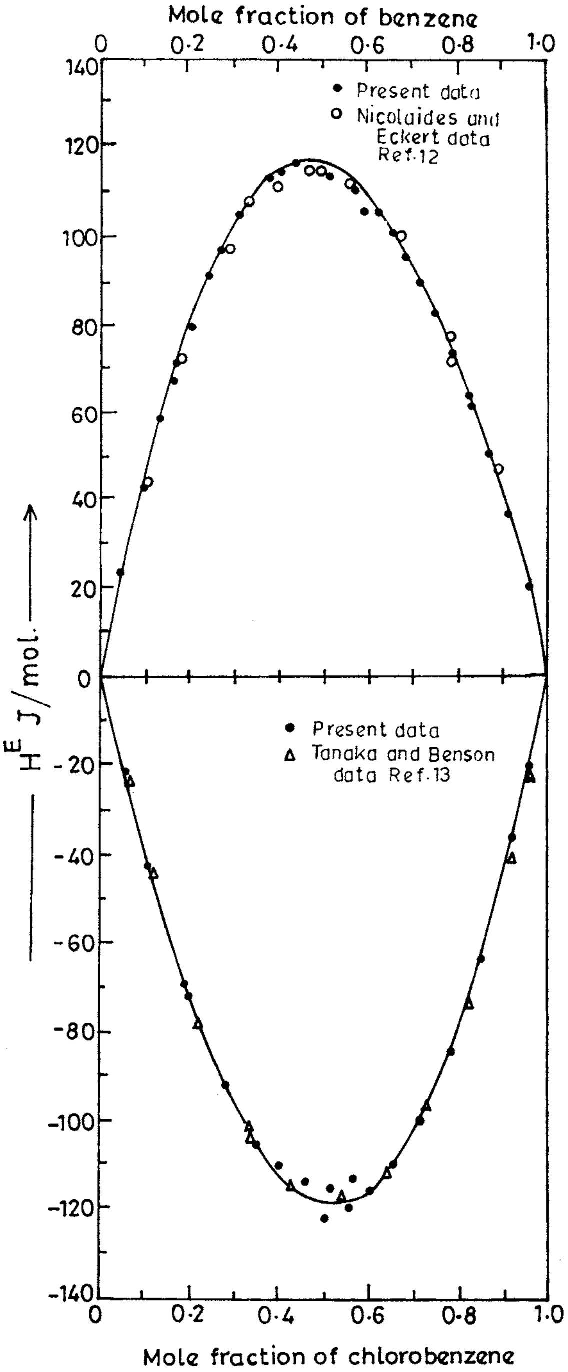

Fig. 1. Excess enthalpies (H^E) as a function of mole fraction (x_1) for benzene + carbontetrachloride (○), chlorobenzene + toluene (△) at 298.15 K.

Table 2
Experimental excess molar enthalpies of *N*,*N*-dimethylacetamide (x_1) + substituted benzenes (x_2) at 298.15 K

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
N,*N*-dimethylacetamide + ethylbenzene			
0.0685	11.5	0.5743	23.1
0.1421	19.5	0.6168	22.8
0.2207	24.9	0.6634	22.0
0.2924	26.9	0.7113	20.6
0.3601	27.8	0.7623	18.4
0.4218	28.1	0.8123	15.5
0.4776	27.8	0.8638	11.8
0.4797	26.7	0.9138	7.1
0.5301	25.1	0.9580	3.2
0.5721	22.9		
N,*N*-dimethylacetamide + chlorobenzene			
0.0612	−14.3	0.5302	−51.3
0.1244	−24.6	0.5757	−51.2
0.1880	−32.9	0.6238	−50.4
0.2510	−39.4	0.6750	−48.8
0.3131	−43.2	0.7295	−45.0
0.3719	−46.1	0.7856	−39.5
0.4251	−48.1	0.8438	−32.3
0.4745	−49.1	0.9002	−23.0
0.5221	−48.8	0.9250	−12.2
N,*N*-dimethylacetamide + bromobenzene			
0.0612	−11.9	0.5731	−43.3
0.1253	−21.8	0.5797	−41.1
0.1928	−29.6	0.6277	−39.8
0.2581	−36.1	0.6792	−37.3
0.3213	−41.2	0.7345	−34.0
0.3798	−43.9	0.7913	−29.6
0.4338	−45.3	0.8480	−24.0
0.4838	−45.6	0.9039	−17.2
0.5308	−44.9	0.9554	−9.2
0.5343	−41.3		
N,*N*-dimethylacetamide + nitrobenzene			
0.0592	−10.6	0.5337	−32.5
0.1253	−19.2	0.5780	−33.2
0.1881	−26.6	0.6239	−33.0
0.2512	−31.5	0.6753	−31.8
0.3118	−33.7	0.7293	−29.3
0.3695	−34.7	0.7856	−24.7
0.4231	−34.9	0.8446	−20.3
0.4722	−34.2	0.9001	−14.8
0.5168	−33.1	0.9550	−8.0
N,*N*-dimethylacetamide + aniline			
0.0590	−65.5	0.5464	−343.7
0.1225	−129.4	0.5960	−337.0
0.1943	−200.7	0.6500	−320.7
0.2680	−267.9	0.7067	−297.2
0.3359	−311.6	0.7657	−256.2
0.4077	−341.6	0.8263	−203.5
0.4598	−332.0	0.8876	−141.3
0.4768	−356.2	0.9477	−65.7
0.5017	−341.9		
N,*N*-dimethylacetamide + acetophenone			
0.0704	−12.2	0.5997	−34.7
0.1426	−21.9	0.6467	−35.4
0.2143	−29.2	0.6975	−34.0
0.2839	−34.3	0.7504	−31.3
0.3509	−37.5	0.8039	−27.2
0.4119	−39.1	0.8566	−21.5
0.4677	−39.9	0.9087	−15.4
0.5179	−40.0	0.9562	−8.2
0.5630	−39.6		

by taking Component A as Component B and Component B as Component A. The experimental method has been checked with known systems of benzene with carbontetrachloride and chlorobenzene with toluene, throughout the concentration range at 298.15 K. The results obtained were in good agreement with literature values [12,13], and graphically shown in Fig. 1. The uncertainty in the measured H^E values are ±1%.

3. Results and discussion

The measured experimental excess molar enthalpies at 298.15 K of the binary mixtures of

Table 3
Estimated parameters of Eq. (1) and percentage of standard deviation, $\%\sigma(H^E)$ for the mixtures of *N*,*N*-dimethylacetamide with substituted benzenes at 298.15 K

	h_0 (J mol^{-1})	h_1 (J mol^{-1})	h_2 (J mol^{-1})	h_3 (J mol^{-1})	$\%\sigma(H^E)$ (J mol^{-1})
N,*N*-dimethylacetamide + ethylbenzene	105.9	−30.5	41.2	31.9	5.3
N,*N*-dimethylacetamide + chlorobenzene	−200.7	−32.3	−71.0	30.6	1.4
N,*N*-dimethylacetamide + bromobenzene	−175.6	26.8	37.4	−39.2	2.5
N,*N*-dimethylacetamide + nitrobenzene	−138.4	25.3	−60.8	−26.3	3.1
N,*N*-dimethylacetamide + aniline	−1406.8	−84.3	171.6	−31.2	2.5
N,*N*-dimethylacetamide + acetophenone	155.0	14.8	−45.5	23.3	4.8

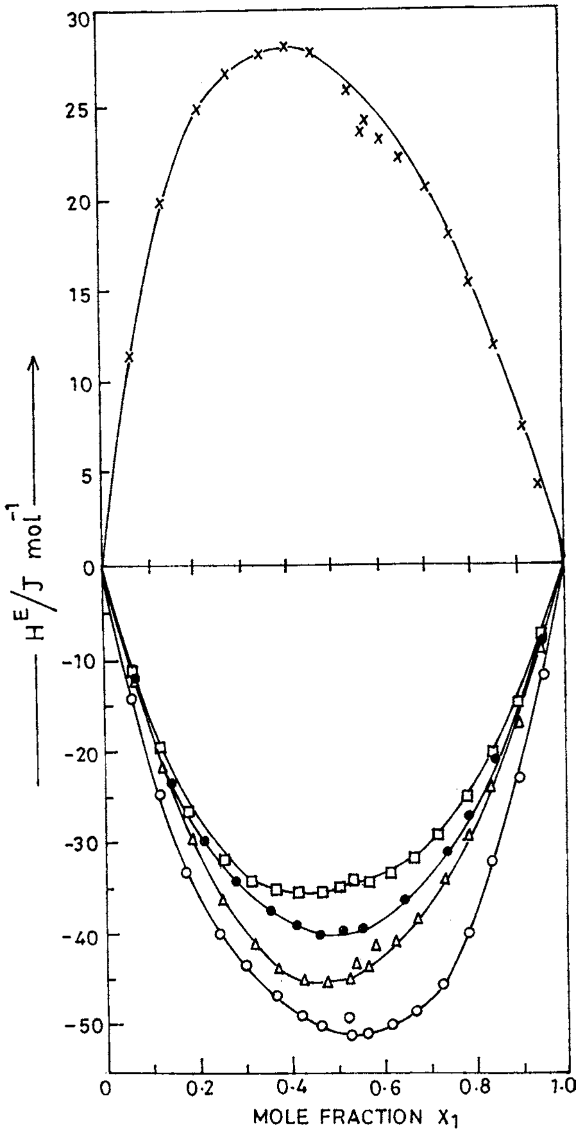

Fig. 2. Excess enthalpies (H^E) as a function of mole fraction (x_1) for *N,N*-dimethylacetamide + chlorobenzene (○); *N,N*-dimethylacetamide + bromobenzene (△); *N,N*-dimethylacetamide + acetophenone (●); *N,N*-dimethylacetamide + nitrobenzene (□); and *N,N*-dimethylacetamide + ethylbenzene (×) at 298.15 K.

N,N-dimethylacetamide with substituted benzenes are reported in Table 2 and graphically presented in Figs. 2 and 3. The experimental values of H^E may be represented by

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

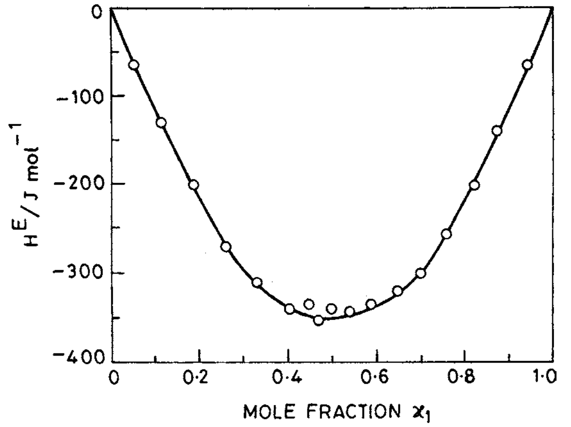

Fig. 3. Excess enthalpies (H^E) as a function of mole fraction (x_1) for *N,N*-dimethylacetamide + aniline (○) at 298.15 K.

where x_1 and x_2 are the mole fractions of *N,N*-dimethylacetamide and substituted benzenes. The h_{i-1} binary parameters have been evaluated by the method of least squares and are listed in Table 3 along with the standard deviation in percentage. The values of standard deviation are computed from the relation:

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

where n and p are the number of results and parameters, respectively. The measured H^E values are positive (endothermic) in mixture of *N,N*-dimethylacetamide with ethylbenzene over the entire range of composition. The maximum positive H^E value is observed for the above system around 0.5 mole fraction. 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 H^E values are negative (exothermic) over the whole range of composition in the mixtures of *N,N*-dimethylacetamide with chlorobenzene, bromobenzene, nitrobenzene, aniline and acetophenone. The maximum negative H^E value is observed around 0.5 mole fraction of *N,N*-dimethylacetamide. The negative H^E observed in our results because of dipole–induced dipole interactions and electron donor–acceptor complex formation. The experimental negative excess enthalpies indicate that the interactions between unlike molecules are stronger in the mixtures of *N*,*N*-dimethylacetamide with chlorobenzene, bromobenzene, nitrobenzene, aniline and acetophenone.

Algebraic value of H^E for the systems of DMA with substituted benzenes fall in the order: ethylbenzene > nitrobenzene > acetophenone > bromobenzene > chlorobenzene > aniline.

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