Excess Molar Enthalpies of *N*,*N*-Dimethylformamide with Chloroethanes and Acetates at 298.15 K

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The excess molar enthalpies (H^E) at 298.15 K of *N*,*N*-dimethylformamide (DMF) with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, ethyl acetate, and butyl acetate have been measured, using a Parr 1451 solution calorimeter, over the whole mole fraction range. The values of H^E are negative for the mixtures of *N*,*N*-dimethylformamide with 1,2-dichloroethane and 1,1,2,2-tetrachloroethane, and an inversion of sign from positive to negative is observed in the mixture *N*,*N*-dimethylformamide with 1,1,1-trichloroethane. The H^E values are positive over the whole mole fraction range for *N*,*N*-dimethylformamide with ethyl acetate and butyl acetate. The H^E data are interpreted on the basis of possible intermolecular interactions between unlike molecules.

Introduction

In recent years there has been considerable advancement in the experimental investigation of the excess thermodynamic properties of liquid mixtures. The heat of mixing of two components is of importance in design calculations involving chemical separation and fluid flow and is a measure of their molecular interactions. A literature survey reveals many of the thermodynamic properties of liquid mixtures, a primary source of fundamental data for the solution of practical problems about heat and mass transfer in real systems, for process development, and for engineering design. However, inspite of these great and concerted research efforts by many experimentalists and theoreticians (Francesconi and Comelli, 1994; Hofman and Casanova, 1996; Mollmann and Gmehling, 1997; Domanska and Gonzalez, 1997), it must be deduced that a lot of work has to be done to reach the final objective represented by a more general predictive ability. We are engaged in a research program on the thermodynamic properties of organic solvents, employing some selected binary and ternary mixtures (Venkatesulu et al., 1994, 1997; Venkatesu and Rao, 1998; Goud et al., 1999). The excess enthalpies for the mixtures of *N*,*N*-dimethylformamide with substituted benzenes (Ramadevi et al., 1996a), with 1-alkanols (Chao et al., 1989), with four butanols (Chao et al., 1991), with methanol, ethanol, and 1-propanol (Pikkarainen, 1991), with tetrahydrofuran and cyclohexane (Conti, 1994), and with ketones (Venkatesu et al., 1999) are already reported in the literature. However, no excess enthalpies for the mixtures of *N*,*N*-dimethylformamide with chloroethanes and acetates appear to have been measured, and there is no evidence for specific interactions between these mixtures. The molar excess enthalpies of DMF with chloroethanes and acetates are of interest from thermodynamic and structural points of view. As a part of our research program to explore the interactions of liquid mixtures, we report here the measurements of the excess molar enthalpies of *N*,*N*-dimethylformamide with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, ethyl acetate, and butyl acetate at 298.15 K.

Table 1. Experimental and Literature Densities at 303.15 K of Pure Components

liquid	density/g cm^{-3} expl.	density/g cm^{-3} lit.
N,*N*-dimethylformamide	0.941 18	0.941 20[a]
1,2-dichloroethane	1.238 45	1.238 47[b]
1,1,1-trichloroethane	1.320 93	1.320 96[b]
1,1,2,2-tetrachloethane	1.578 58	1.578 60[b]
ethyl acetate	0.888 45	0.888 47[c]
butyl acetate	0.871 28	0.871 29[c]

[a] Rao and Reddy (1995). [b] Reddy et al., 1984. [c] Rao (1990).

Experimental Section

Chemicals. *N*,*N*-Dimethylformamide (Fluka) was purified by the method described by Ramadevi et al. (1996) and Rao and Reddy (1985). 1,2-Dichloroethane (Fluka), 1,1,1-trichloroethane (Aldrich), and 1,1,2,2-tetrachloroethane (Fluka) were purified by the method described by Reddy et al. (1984). Ethyl acetate (BDH) and butyl acetate (BDH) were further purified by standard procedures described by Rao (1990). The purity of the chemical products was verified by measuring the densities, determined with a bicapillary-type pycnometer of 12 cm^3 capacity, which offers an accuracy of 2 parts in 10^5, which were in good agreement with literature values, as can be seen in Table 1. The purities of the samples were further confirmed by GLC single sharp peaks.

Procedure. A Parr 1451 solution calorimeter was used in the measurements of H^E. The detailed procedures and apparatus used have been described (Ramadevi et al., 1996b; Venkatesulu et al., 1994, 1997). In the measurement of excess enthalpies, known masses of 100 mL of component A are 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 chamber at 298.15 K. After thermal equilibrium is attained (about 30 min), component B in the rotating cell is mixed with component A in the Dewar

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Table 2. Experimental Excess Enthalpies of *N,N*-Dimethylformamide (1) with Chloroethanes or Acetates (2) at 298.15 K

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
N,N-Dimethylformamide (1) + 1,2-Dichloroethane (2)					
0.0982	−228	0.4127	−663	0.6535	−575
0.1794	−391	0.4682	−674	0.7024	−535
0.2457	−504	0.5130	−669	0.7587	−475
0.2998	−586	0.5385	−641	0.8258	−383
0.3484	−628	0.5904	−619	0.9048	−240
N,N-Dimethylformamide (1) + 1,1,1-Trichloroethane (2)					
0.0539	12	0.2987	52	0.6449	−33
0.1047	19	0.4010	61	0.6968	−40
0.1547	25	0.4547	51	0.7995	−50
0.2008	29	0.4956	30	0.8523	−48
0.2454	39	0.5969	−14	0.8969	−39
N,N-Dimethylformamide (1) + 1,1,2,2-Tetrachloroethane (2)					
0.0725	−1042	0.5709	−3855	0.7611	−2553
0.1802	−2395	0.6093	−3698	0.8108	−2116
0.2664	−3194	0.6471	−3533	0.8486	−1748
0.3389	−3663	0.6540	−3268	0.8902	−1308
0.3972	−3895	0.6846	−3288	0.9582	−531
0.4669	−4016	0.7039	−2995	0.9791	−267
0.5219	−3979				
N,N-Dimethylformamide (1) + Ethyl Acetate (2)					
0.0927	60	0.4047	167	0.7005	153
0.1650	105	0.4561	168	0.7795	116
0.2010	120	0.4963	168	0.8394	89
0.2756	144	0.5495	193	0.9066	52
0.3468	159	0.6351	173		
N,N-Dimethylformamide (1) + Butyl Acetate (2)					
0.1002	170	0.4908	407	0.7442	314
0.1656	250	0.5546	397	0.7849	279
0.2821	351	0.6044	389	0.8298	234
0.3674	391	0.6464	379	0.8792	175
0.4344	407	0.6911	355	0.9350	98

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. Those experiments were continued till the concentration reached 50−60%. This procedure was repeated by interchanging the two components. The reliability of the apparatus and the method was established by measuring H^E values of standard systems, that is, benzene + carbon tetrachloride and chlorobenzene + toluene, throughout the concentration range at 298.15 K. Results were in good agreement with the reported data in the literature (Nicolaides and Eckert, 1978; Tanaka and Benson, 1976). The uncertainty in the measured H^E values is ±1%.

Results and Discussion

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

$$H^E = x_1x_2\sum_i h_i(x_1 - x_2)^i \tag{1}$$

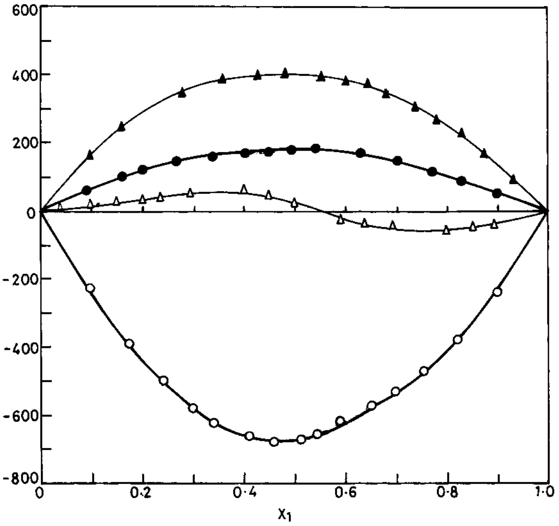

Figure 1. Excess molar entalpies for *N,N*-dimethylformamide + 1,2-dichloroethane (○), + 1,1,1-trichloroethane (△), + ethyl acetate (●), and + butyl acetate (▲) at 298.15 K.

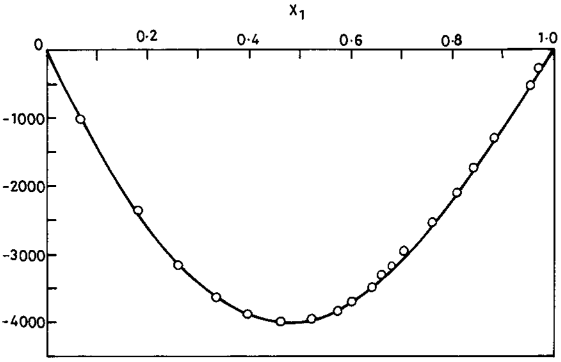

Figure 2. Excess molar enthalpies for *N,N*-dimethylformamide + 1,1,2,2-tetrachloroethane (○) at 298.15 K.

where x_1 and x_2 are the mole fractions of components 1 and 2, respectively. 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

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

where n and p are the number of results and parameters, respectively.

The excess enthalpy values are negative (exothermic) in the system of *N,N*-dimethylformamide with 1,2-dichloroethane and 1,1,2,2-tetrachloroethane over the entire composition range at 298.15 K. The observed negative excess enthalpies suggest that the specific interactions between unlike molecules are stronger than the interactions between like molecules. An inversion of H^E from positive to negative is observed for the system *N,N*-dimethylforma-

Table 3. Estimated Parameters of Eq 1 and Percentage of Standard Deviation, 100σ(H^E), for the Mixtures of *N,N*-Dimethylformamide with Chloroethanes and Acetates

	h_0/J mol^{-1}	h_1/J mol^{-1}	h_2/J mol^{-1}	h_3/J mol^{-1}	100σ(H^E)/J mol^{-1}
1,2-dichloroethane	−2655.20	385.9	26.4	−825.8	1.2
1,1,1-trichloroethane	118.8	−757.0	−651.6	1289.3	4.1
1,1,2,2-tetrachloroethane	−15944.4	2541.0	2204.2	−1741.2	1.8
ethyl acetate	710.9	183.1	97.2	−1086.5	6.1
butyl acetate	1641.5	−37.3	208.1	−208.7	1.0

mide with 1,1,1-trichloroethane at 298.15 K. The interaction between unlike molecules in the system may be ascribed to dispersion forces and dipolar interactions, considering the nature of the chemical species in the system. H^E values are positive (endothermic) in the mixtures of *N*,*N*-dimethylformamide with ethyl acetate and butyl acetate over the whole range of composition. The positive H^E values suggest that the property in these mixtures is determined by the loss of dipolar association by the addition of one component to the other and the difference in size and shape of the component molecules.

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