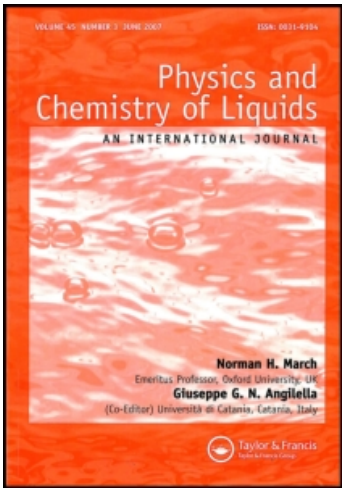

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EXCESS THERMODYNAMIC PROPERTIES OF BINARY LIQUID MIXTURES CONTAINING *N*,*N*-DIMETHYLACETAMIDE WITH SOME ALKAN-1-OLS (C_1–C_6) AT 298.15 K

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Excess molar enthalpies, H_m^E of *N*,*N*-dimethylacetamide + methanol, + ethanol, + propan-1-ol, + butan-1-ol, + pentan-1-ol, and + hexane-1-ol have been determined at 298.15 K and atmospheric pressure using a Parr 1455 solution calorimeter. While the excess molar enthalpies are negative for methanol and ethanol mixtures, those for propan-1-ol, butan-1-o1, pentane-1-ol, and hexan-1-ol mixtures are positive over the entire range of composition of *N*,*N*-dimethylacetamide. The H_m^E at around $x \approx 0.5$ follow the order: methanol < ethanol < propan-1-ol < butan-1-ol < pentan-1-ol < hexan-1-ol. The results are explained in terms of the self-association exhibited by the alkan-1-ols and the formation of aggregates between unlike molecules through O...HO hydrogen bonding. The experimental results for mixtures are well represented by the Redlich – Kister equation.

Keywords: Excess molar enthalpies; *N*,*N*-dimethylacetamide; Alkanols; Self-association

1. INTRODUCTION

For nonideal solutions the magnitude of their excess molar enthalpies can be quite significant and give a direct measure of molecular

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interactions; hence, H_m^E values can provide information needed to that existing theories of solutions.

The thermodynamic properties of binary mixtures containing polar and self-associated components exhibit significant deviation from ideality, arising not only from difference in size and shape but also from possible hydrogen-bounding interactions between unlike molecules [1–4].

An attempt has been made to measure excess molar enthalpies of mixing, H_m^E for *N*,*N*-dimethylacetamide + 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 influence of associated species of alkan-1-ols by dilution with *N*,*N*-dimethylacetamide.

2. EXPERIMENTAL SECTION

2.1. Materials

The chemicals used in this study, their suppliers, and their purities are listed in Table I. Analytical reagent grade *N*,*N*-dimethylacetamide was purified by the standard method of Perrin and Armarego [5]. The alkan-1-ols were dried and distilled as described elsewhere [6] and stored in a glovebox prior to use. Purity of each compound was ascertained by the constancy of the boiling point and also from the

TABLE I Source, purity grades, densities ρ and refractive indices n_D of the pure components at 293.15 K

Component	*Source*	*Purity*/ (mass%)	ρ (g cm^{-3})		n_D	
			Expt.	*Lit.*	*Expt.*	*Lit.*
N,*N*-Dimethylacetamide	Merk	99%	0.93652	0.9366[a]	1.4359	1.4356
Methanol	Merk	99.8%	0.79123	0.7913	1.3288	1.3284
Ethanol	Merk	99.5%	0.78947	0.7894	1.3610	1.3614
Propan-1-ol	Merk	99.5%	0.80361	0.8037	1.3852	1.3856
Butan-1-ol	Merk	99%	0.80979	0.8097	1.3990	1.3993
Pentan-1-ol	Fluka	99%	0.81471	0.8148	1.4105	1.4100
Hexan-1-ol	Merk	98.0%	0.81853	0.8186	1.4186	1.4182

[a]Ref. At 298.15 K.

density and refractive index. Densities were measured at 293.15 K using a bicapillary pycnometer with an accuracy of 4 parts in 10^4. 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 measure is of the order of ± 0.0002.

Table I also gives the density and refractive index measurements, which agree with values obtained from the literature [7].

2.2. Apparatus and Procedure

Excess molar enthalpies, H_m^E were determined using a Parr 1455 solution calorimeter. The calorimeter consists of a dewar glass mixing chamber with a rotating sample cell, a thermistor probe and a specially designed temperature measuring bridge, all assembled in a compact cabinet. Temperature changes can be plotted directly using a strip chart recorder and can be read to an accuracy of ± 0.0002 K. 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 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 20 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 till the concentration reaches 50–60 volume percent. By this method small errors in the earlier additions lead to a large error in latter experiments. Because of the limitation of the calorimeter, one is forced to adopt this method to cover the entire concentration range.

Initially, in order to determine the calorimeter equivalent, it was calibrated with 0.5 g of hydroxy methylaminomethane dissolved in 0.1 mol dm^{-3} hydrochloric acid solution which releases 245.52 J g^{-1} at 298.15 K. The performance and reliability of the solution calorimeter was checked by the test mixture cyclohexane + benzene. The excess enthalpies H_m^E agreed within 1% with the reported values [8].

3. RESULTS AND DISCUSSION

The experimental results for the enthalpies of mixing for the binary mixtures of *N*,*N*-dimethylacetamide + methanol, + ethanol, + propan-1-ol, + butan-1-ol, + pentan-1-ol, and hexan-1-ol at 298.15 K are listed in Table II, together with the deviation $\delta(H_m^E)$

TABLE II Excess molar enthalpies H_m^E and deviations δ (H_m^E) for the binary mixtures of *N*,*N*-dimethylacetamide + alkan-1-ols at 298.15 K

X	H_m^E/ (J mol^{-1})	$\delta(H_m^E)$ (J mol^{-1})	X	H_m^E/ (J mol^{-1})	$\delta(H_m^E)$ (J mol^{-1})
x $CH_3CON(CH_3)_2 + (1-x)CH_3OH$					
0.0783	− 249.2	− 0.6	0.5245	− 819.8	− 5.8
0.1585	− 439.7	3.5	0.5982	− 774.9	− 19.9
0.2358	− 593.2	− 2.8	0.6780	− 687.3	1.2
0.3161	− 709.4	− 2.1	0.7584	− 560.3	0.2
0.3961	− 784.9	− 0.8	0.8434	− 390.3	− 1.0
0.4745	− 808.9	8.0	0.9195	− 211.2	0.3
x $CH_3CON(CH_3)_2 + (1-x)C_2H_5OH$					
0.0959	− 220.0	− 0.5	0.4984	− 399.8	1.6
0.1964	− 333.9	2.5	0.5994	− 360.8	2.1
0.2950	− 393.2	− 1.4	0.6997	− 299.3	0.1
0.3935	− 414.8	− 3.1	0.8018	− 215.9	− 1.5
0.3967	− 412.0	− 0.2	0.9006	− 116.5	0.3
x $CH_3CON(CH_3)_2 + (1-x)C_3H_7OH$					
0.0980	137.6	− 0.3	0.5023	194.4	2.2
0.1975	218.0	1.5	0.6024	155.3	1.3
0.2983	239.5	− 1.0	0.7002	118.6	0.6
0.4019	224.1	− 1.5	0.8014	80.1	− 1.3
0.5004	191.2	− 1.7	0.8982	43.9	0.3
x $CH_3CON(CH_3)_2 + (1-x)C_4H_9OH$					
0.1026	190.2	0.0	0.5064	354.5	− 1.4
0.2011	307.4	0.3	0.5967	320.1	− 0.2
0.3010	365.1	− 0.3	0.6952	266.3	− 1.7
0.4008	375.8	− 1.4	0.7972	199.8	1.1
0.4941	363.5	3.8	0.8965	112.2	− 0.1
x $CH_3CON(CH_3)_2 + (1-x)C_5H_{11}OH$					
0.0946	217.8	− 0.3	0.5980	478.9	4.5
0.1939	387.7	1.6	0.6976	401.6	− 3.8
0.2945	485.2	− 1.3	0.7986	308.7	0.8
0.3953	523.8	− 1.8	0.8974	179.1	0.0
0.4967	517.5	0.1			
x $CH_3CON(CH_3)_2 + (1-x)C_6H_{13}OH$					
0.0999	257.2	0.0	0.6077	613.0	− 2.1
0.2012	454.6	− 0.2	0.5993	620.1	0.9
0.3009	578.1	0.5	0.7023	547.9	1.8
0.4020	638.5	− 0.1	0.8002	427.9	− 0.8
0.5037	648.4	− 0.1	0.9012	246.2	0.1

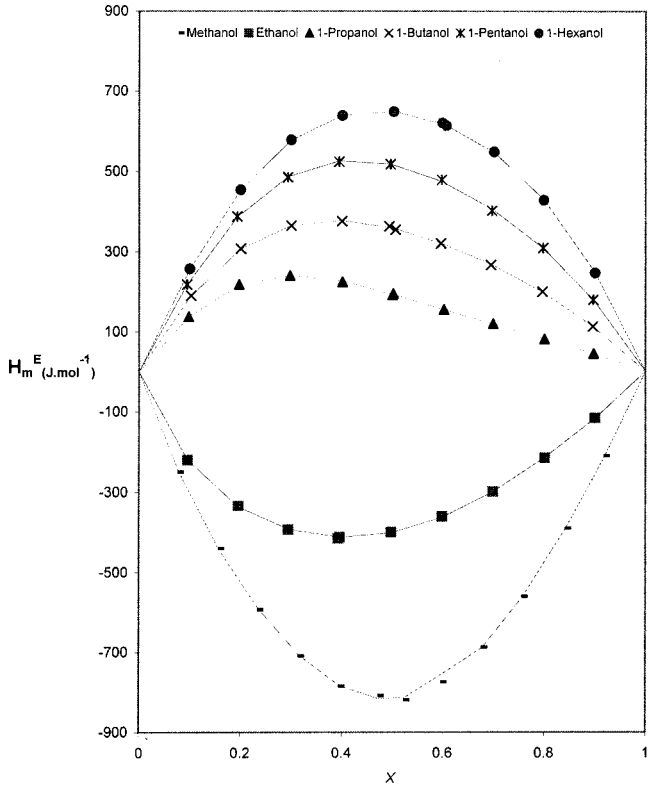

FIGURE 1 Excess molar enthalpies of $\{xN,N$-dimethylacetamide $+(1-x)$*alkan*-1-*ols*$\}$ at 298.15 K. Continuous curves calculated from coefficients of Eq. (1) given in Table III.

and shown graphically in Fig. 1. Each set of results was fitted using a Redlich–Kister equation of the type.

$$H_m^E = x(1-x)\sum_{r=1} A_r(2x-1)^{r-1} \tag{1}$$

where x is the mole fraction of N,N-dimethylacetamide. The coefficients A_r were calculated by a least-square analysis. They are presented in Table III together with the standard deviation $\sigma(H_m^E)$

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

TABLE III Values of adjustable coefficients A_r in Eq. (1) and Standard deviation, $\sigma(H_m^E)$ in Eq. (2) for *N*,*N*-dimethylacetamide + alkan-1-ols at 298.15 K

System	A_1	A_2	A_3	A_4	A_5	$\sigma(H_m^E)$/ (J mol^{-1})
x $CH_3CON(CH_3)_2$ + $(1-x)CH_3OH$	−3270.99	125.55	519.79	313.00	−490.45	9.98
x $CH_3CON(CH_3)_2$ + $(1-x)C_2H_5OH$	−1604.28	497.22	−218.68	401.51	−402.71	6.05
x $CH_3CON(CH_3)_2$ + $(1-x)C_3H_7OH$	772.37	−747.44	552.14	112.35	−266.76	5.27
x $CH_3CON(CH_3)_2$ + $(1-x)C_4H_9OH$	1431.81	−614.27	463.67	121.24	−215.12	4.61
x $CH_3CON(CH_3)_2$ + $(1-x)C_5H_{11}OH$	2065.62	−563.42	421.31	296.32	−216.85	7.18
x $CH_3CON(CH_3)_2$ + $(1-x)C_6H_{13}OH$	2595.64	−206.90	584.63	232.35	−386.14	2.94

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

$$\zeta = \sum \delta^2(H_m^E) \tag{3}$$

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

The excess molar enthalpies for methanol and ethanol mixtures with *N*,*N*-dimethylacetamide are exothermic while those for propan-1-ol, butan-1-ol, pentan-1-ol, and hexan-1-ol systems showed endothermic over the entire range of composition of *N*,*N*-dimethylacetamide. For these six binary mixtures, the equimolar excess molar enthalpies increases in the order:

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

4. CONCLUSIONS

Since alkan-1-ols are strongly associated through hydrogen bonding, dilution with a polar solvent like *N*,*N*-dimethylacetamide results changes in thermodynamic function which may be due to: (i) the break-up of hydrogen bonds with diluent; and (ii) the formation of new species acting as an adduct between the alkan-1-ols and *N*,*N*-dimethylacetamide. The observed negative excess enthalpies of mixing

indicates that the dissociation of the associated species of the alkan-1-ols on dilution with *N*,*N*-dimethylacetamide is the dominating force. A packing effect in the liquid state between chain-like molecules of alkan-1-ols (C_1–C_6) is mainly responsible for the endothermic behavior [9].

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