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EXCESS ENTHALPIES OF BINARY SOLVENT MIXTURES OF METHANOL, ETHANOL AND 1-PROPANOL WITH FORMAMIDE, *N*-METHYLFORMAMIDE AND *N,N*-DIMETHYLFORMAMIDE

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ABSTRACT

The excess molar enthalpies of binary solvent mixtures of methanol, ethanol and 1-propanol with formamide, *N*-methylformamide and *N,N*-dimethylformamide were measured with a flow microcalorimeter at 313.15 K. The excess enthalpies are negative for the methanol–formamide system and positive for the other systems. The partial excess molar enthalpies have also been evaluated. The results are compared with those for mixtures of the same alcohols with *N*-methylacetamide and *N,N*-dimethylacetamide and they are discussed with regard to the associating abilities of the components.

INTRODUCTION

As is generally known, the thermodynamic properties of binary solvent mixtures are sensitive to various association equilibria. Carboxamide–alcohol mixtures make particularly interesting systems for study because substituents have a marked effect on the association behaviour [1–3]. The carbonyl group of carboxamides has considerable proton accepting ability. Unsubstituted and *N*-monosubstituted carboxamides, which have a proton donor group, the NH group, are capable of self-association through formation of N–H ··· O=C hydrogen bonds. Such association is not possible in *N,N*-disubstituted amides, where both NH protons are replaced by alkyl or aryl groups. In addition, because the molecules of carboxamides are dipolar they can self-associate by dipole–dipole interactions [3–5]. The molecules of pure alcohols, in turn, self-associate through O–H ··· O hydrogen bonds. The length and branching of the alkyl chain and the presence of an aromatic group affect the association [1,2].

Our recent work on the thermodynamic properties of binary mixtures of *N*-methylacetamide (NMA) and *N,N*-dimethylacetamide (DMA) with aliphatic and aromatic alcohols [6–9] has provided insight into the role of the NH group in determing the excess enthalpies of the mixtures. To gain a better insight into the effect of the N-substitution, we continue now with

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TABLE 1

Excess molar enthalpies of the binary mixtures at 313.15 K

x [a]	H_m^E (J mol^{-1})	x [a]	H_m^E (J mol^{-1})	x [a]	H_m^E (J mol^{-1})
Methanol + formamide					
0.0705	134.2	0.4341	325.5	0.8055	171.3
0.0923	167.1	0.4860	316.7	0.8356	144.4
0.1196	202.8	0.5061	313.4	0.8853	104.0
0.1709	257.4	0.5267	303.1	0.9113	84.0
0.2021	277.3	0.5768	283.0	0.9322	58.2
0.2914	320.0	0.6719	251.2		
0.3392	331.3	0.7177	218.4		
Methanol + *N*-methylformamide					
0.0642	86.6	0.3409	264.1	0.6317	208.3
0.1220	148.8	0.4086	268.1	0.7363	169.0
0.1459	169.3	0.4287	265.7	0.7741	142.9
0.2172	215.9	0.4790	261.4	0.8739	80.2
0.2572	238.9	0.5072	258.4	0.9027	64.2
0.3167	259.2	0.5800	236.6		
Methanol + *N*,*N*-dimethylformamide					
0.0496	−9.49	0.3448	−68.0	0.6802	−109.7
0.0957	−16.4	0.3637	−70.6	0.7230	−103.4
0.1152	−19.2	0.4118	−84.8	0.7987	−85.9
0.1744	−30.6	0.4395	−89.9	0.8407	−73.9
0.2087	−36.1	0.5126	−105.5	0.8760	−60.8
0.2827	−54.0	0.5664	−110.8	0.9138	−44.6
Ethanol + formamide					
0.0984	323	0.4248	678	0.7853	385
0.1276	399	0.4414	676	0.8563	288
0.1791	487	0.5246	646	0.8797	237
0.2287	564	0.5958	597	0.9085	184
0.2671	611	0.6623	530	0.9366	135
0.3718	673	0.7466	448		
Ethanol + *N*-methylformamide					
0.0685	188	0.3325	575	0.7116	461
0.0898	234	0.4267	605	0.8007	338
0.1164	296	0.4784	602	0.8314	295
0.1666	386	0.5191	599	0.9089	169
0.1973	431	0.5694	565	0.9303	124
0.2853	548	0.6652	500		
Ethanol + *N*,*N*-dimethylformamide					
0.0699	184	0.4309	520	0.7537	275
0.1322	306	0.4512	504	0.7897	229
0.1577	345	0.5019	487	0.8509	182
0.2331	443	0.5301	472	0.8837	133
0.2750	472	0.6021	413	0.9105	112
0.3618	518	0.6527	375		

TABLE 1 (continued)

x [a]	H_m^E (J mol^{-1})	x [a]	H_m^E (J mol^{-1})	x [a]	H_m^E (J mol^{-1})
1-Propanol + formamide					
0.0854	393	0.3362	856	0.7904	551
0.1225	512	0.4310	913	0.8240	468
0.1577	608	0.4859	899	0.8841	336
0.2183	731	0.5855	829	0.9034	277
0.2751	804	0.6536	779	0.9498	150
0.3181	849	0.7151	669		
1-Propanol + *N*-methylformamide					
0.0861	256	0.3893	723	0.7177	550
0.1121	320	0.4604	724	0.7595	482
0.1443	400	0.4879	730	0.8372	353
0.2038	515	0.5400	722	0.8632	291
0.2393	573	0.5600	710	0.9273	165
0.3381	697	0.6286	737		
1-Propanol + *N*,*N*-dimethylformamide					
0.0878	320	0.4250	769	0.7966	379
0.1138	398	0.4922	751	0.8278	310
0.1631	522	0.5128	738	0.8796	231
0.1933	582	0.5908	662	0.9067	177
0.2801	704	0.6595	575	0.9286	144
0.3269	737	0.7063	497		

[a] Mole fraction of the amide.

mixtures of formamides. In the present work we have measured the excess molar enthalpies and evaluated the partial excess molar enthalpies for binary mixtures of methanol, ethanol and 1-propanol with formamide (F), *N*-methylformamide (NMF) and *N*,*N*-dimethylformamide (DMF). The measurements were carried out at 313.15 K, the same temperature as in our earlier studies. This temperature was chosen because some of the amides studied in our project have relatively high melting temperatures or are highly viscous at lower temperatures.

EXPERIMENTAL

The alcohols were the same as before [6]. Formamide (a puriss p.a. product of Fluka A.G.) and *N*-methylformamide (a purum product of Fluka A.G.) were distilled under reduced pressure before use. *N*,*N*-Dimethylformamide (a spectroscopic grade product of Fluka A.G.) was used without further purification. The reagents were stored over molecular sieves.

The excess enthalpies were determined with a flow microcalorimeter as described earlier [6].

RESULTS AND DISCUSSION

The excess molar enthalpies for the binary mixtures are reported in Table 1, and are presented graphically as functions of x, the mole fraction of the amide, in Figs. 1–3. To aid comparison of the properties of the mixtures of the formamides with those of NMA and DMA, the $H_m^E(x)$ curves for the mixtures of methanol, ethanol and 1-propanol with NMA and DMA are included in the figures.

To each set of experimental values was fitted the equation

$$H_m^E = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i \tag{1}$$

where H_m^E is in units of J mol^{-1}. Coefficients A_i of the fitting equations together with the standard deviations $\sigma(H_m^E)$ of the fits are reported in Table 2. Coefficients A_i were further used in the evaluation of the partial excess molar enthalpies for the alcohols (H_1^E) and the amides (H_2^E) from the equations

$$H_1^E = H_m^E - x\left(\frac{\partial H_m^E}{\partial x}\right)_{p,T} \tag{2}$$

$$H_2^E = H_m^E + (1-x)\left(\frac{\partial H_m^E}{\partial x}\right)_{p,T}$$

The curves of H_1^E and H_2^E as functions of x for the formamides are plotted in Fig. 4. The curves for the mixtures of NMA and DMA have been presented in ref. 7.

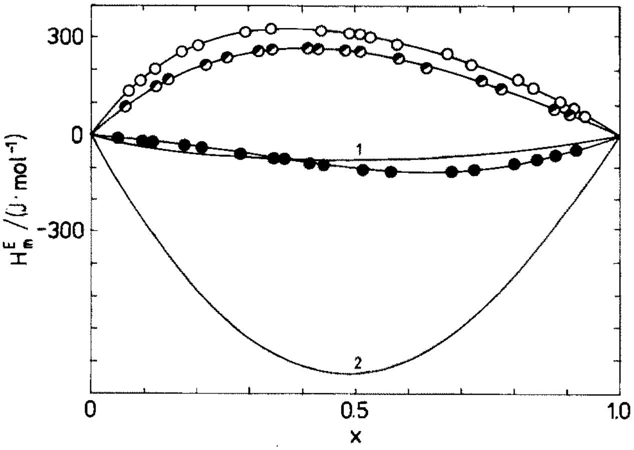

Fig. 1. Excess molar enthalpies, H_m^E, for the mixtures of methanol with the amides vs. the mole fraction, x, of the amide: ○, formamide; ◐, N-methylformamide; ●, N,N-dimethylformamide; curve 1, N-methylacetamide; curve 2, N,N-dimethylacetamide.

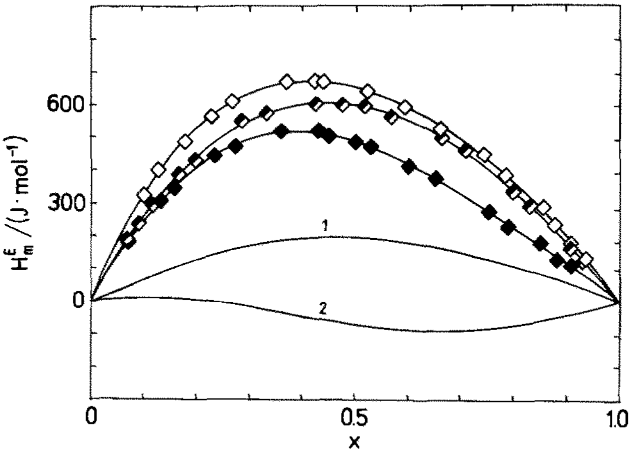

Fig. 2. Excess molar enthalpies, H_m^E, for the mixtures of ethanol with the amides vs. the mole fraction, x, of the amide: ◇, formamide; ◈, N-methylformamide; ◆, N,N-dimethylformamide; curve 1, N-methylacetamide; curve 2, N,N-dimethylacetamide.

As the figures show, the excess enthalpies are negative for the methanol–DMF system and positive for the other systems studied. The values range between -115 and 915 J mol^{-1}. With respect to the alcohols, the values of H_m^E, H_1^E and H_2^E increase in the order methanol < ethanol < 1-propanol. For each alcohol the values are greater for its mixtures with F than with the other amides. The methanol–NMF system displays considerably greater excess enthalpies than the methanol–DMF system, the ethanol–NMF system displays somewhat greater values than the ethanol–DMF system, and the values for the 1-propanol–NMF system are near to those of the

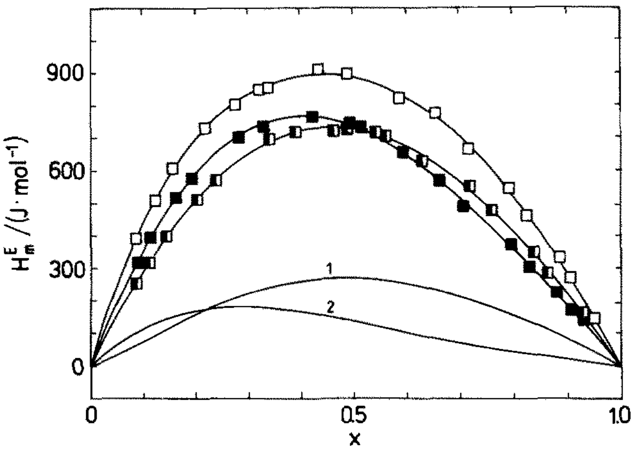

Fig. 3. Excess molar enthalpies, H_m^E, for the mixtures of 1-propanol with the amides vs. the mole fraction, x, of the amide: □, formamide; ◧, N-methylformamide; ■, N,N-dimethylformamide; curve 1, N-methylacetamide; curve 2, N,N-dimethylacetamide.

TABLE 2

Coefficient of eqn. (1) and the standard deviations

	A_0	A_1	A_2	A_3	A_4	$\sigma(H_m^E)$ (J mol^{-1})
Methanol						
+ formamide	1247.4	519.15	512.22	119.29	−199.69	3
+ *N*-methylformamide	1030.6	420.34	56.04	1.418		2
+ *N*,*N*-dimethylformamide	−405.04	325.07	60.488	−152.81		1
Ethanol						
+ formamide	2625.6	846.02	487.45	−21.51		5
+ *N*-methylformamide	2397.4	507.72	248.58	42.01	−283.09	4
+ *N*,*N*-dimethylformamide	1945.6	1032.8	100.80	−270.30		5
1-Propanol						
+ formamide	3572.4	687.06	457.65	590.84	512.13	7
+ *N*-methylformamide	2919.6	520.50	-82.42	−75.84		7
+ *N*,*N*-dimethylformamide	2969.0	1251.6	−195.11	−153.61	563.17	6

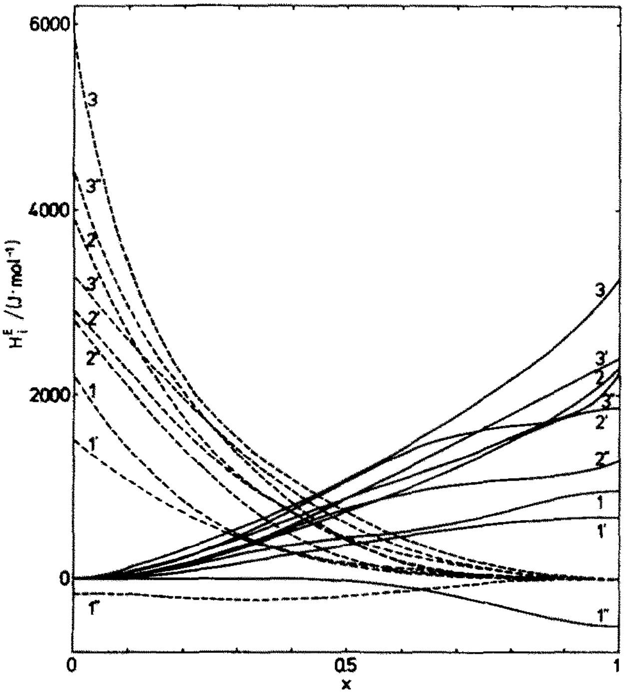

Fig. 4. Partial excess molar enthalpies for the mixtures of methanol (1,1′,1″), ethanol (2,2′,2″) and 1-propanol (3,3′,3″) with formamide (1,2,3), *N*-methylformamide (1′,2′,3′) and *N*,*N*-dimethylformamide (1′,2″,3″): (———) alcohols H_1^E, (- - - - -) amides H_2^E.

1-propanol–DMF system. The excess enthalpies are appreciably greater for DMF than for DMA and for NMF than for NMA. The difference is slightly smaller for the *N*-monosubstituted amides than for the N,N-disubstituted amides. Our results for the mixtures of DMF can be compared with those published recently by Chao et al. [10]. For methanol our values at 313.15 K are nearly the same as their values at 298.15 K. For ethanol and 1-propanol our values are somewhat smaller than theirs.

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 require 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 pair forms 1 : 1 complexes only at low concentrations; at higher concentrations formation of different higher complexes is very likely as well.

When DMF and an alcohol are mixed, the main changes that occur in the association equilibria are evidently the rupture of the hydrogen bonds between the alcohol molecules and the dipolar interactions between the amide molecules and the formation of O–H ··· O=C hydrogen bonds between the alcohol and the amide molecules. An estimate of the magnitude of the first contribution is obtained from the excess enthalpies of the alcohol–n-hexane mixtures. The maximum values in the $H_m^E(x)$ curves are about 760, 830 and 910 J mol^{-1} at 318.15 K for methanol, ethanol and 1-propanol, respectively [11]. To our knowledge, excess enthalpies for DMF–inert solvent mixtures are not available. The slightly negative values for the methanol–DMF mixtures indicate that the opposing contributions are nearly equal but with the effect of the heteroassociation slightly prevailing. Since ethanol and 1-propanol possess less proton donating ability than methanol, the effect of the heteroassociation is expected to be smaller in their mixtures than in the mixtures of methanol [1,2,12–14]. As anticipated, the results for the mixtures of DMF with ethanol and 1-propanol indicate that the contribution due to the heteroassociation is not sufficient to outweigh the positive contributions due to the break-up of interactions between like molecules.

In the mixtures of F and NMF with the alcohols two kinds of heteroassociation may occur, the formation of O–H ··· O=C hydrogen bonds as in the mixtures of DMF, and the formation of N–H ··· O hydrogen bonds. The effect of the first association is expected to be somewhat smaller for NMF and F than for DMF [1,2]. The effect of the second association is expected to be slightly smaller for methanol than for ethanol and 1-propanol [15,16]. F possesses two NH protons, and one molecule of F might form two N–H ··· O hydrogen bonds with the molecules of the alcohols. However, the formation of the second bond is expected to be less favourable than the formation of the first. According to Spencer et al. [17] F forms two N–H hydrogen bonds with DMF but only one with water. The hydrogen bond enthalpy for one N–H · · · O bond is smaller for F than for NMF [17,18]. It seems very likely that the self-association of F is analogous to its association with DMF, i.e. is in agreement with models where also self-associated structures involving both amino protons are present [4,18]. N-Monosubstituted amides like NMF self-associate by forming N–H · · · O=C bonded chains [3]. The heteroassociation of F with the alcohols, we think, resembles its association with water, i.e. mainly one N–H · · · O bond is formed. This leads us to expect that mixing of F or NMF with an alcohol gives rise to considerable positive contributions due to break-up of the self-associated structures of F or NMF and that, especially in the methanol–F system, these contributions may outweigh those due to the N–H · · · O hydrogen bonding. In agreement with these expectations the excess enthalpies for the methanol–F and methanol–NMF systems are positive and considerably greater than those for the methanol–DMF system. In the mixtures of ethanol and 1-propanol the different contributions due to the presence of the NH protons in the molecules of the amides are more nearly equal than in the mixtures of methanol.The fact that the excess enthalpies are considerably greater for the mixtures of the formamides than for the corresponding mixtures of the acetamides is evidently in large part due to the greater proton accepting ability of DMA than of DMF and of NMA than of NMF [1,2,17,19]. Furthermore, in the present mixtures the presence of the NH proton in the molecules of the amides has a greater net effect for NMA than for NMF, and hence the difference between NMF and NMA is smaller than the difference between DMF and DMA. Finally, mention may be made of the role of the formyl proton of the formamides. Self-association through hydrogen bonding of the formyl proton of DMF has been considered possible but there is no conclusive evidence for this association [3,10,20]. Break-up of such associated structures would lead to an additional positive contribution to the mixtures of DMF.

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