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EXCESS ENTHALPIES OF BINARY SOLVENT MIXTURES OF 2-BUTANONE WITH ALIPHATIC ALCOHOLS

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ABSTRACT

The molar excess enthalpies of binary solvent mixtures of 2-butanone with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol have been measured with a flow microcalorimeter at 313.15 K. The excess enthalpies are positive over the whole composition range for all alcohols studied. The values for the primary alcohols increase with the length of the alkyl chain of the alcohol. The values for the secondary and the tertiary alcohol are slightly greater than those for the primary analogues. The partial molar excess enthalpies have also been evaluated. The results are discussed in terms of intermolecular interactions in the mixtures.

INTRODUCTION

Mixing of associated liquids generally gives rise to diverse intermolecular effects such as changes in molecular association equilibria, which affect the thermodynamic properties of the mixtures. Earlier results for binary solvent mixtures of *N*,*N*-dimethylacetamide (DMA) with aliphatic alcohols have indicated that one of the contributions to both enthalpies of mixing [1,2] and viscosities and volumes of the mixtures [3] is the result of formation of C=O ··· H–O hydrogen bonds between the amide and alcohol molecules. Since the carbonyl group of ketones is a considerably poorer proton acceptor than the carbonyl group of the corresponding carboxamides [4–6], it was interesting to see how this difference was reflected in the properties of ketone–alcohol mixtures. Here the molar excess enthalpies and the partial molar excess enthalpies for binary mixtures of 2-butanone (MEK) with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol are reported at 313.15 K, and compared with those for mixtures of DMA with the same alcohols.

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TABLE 1

Molar excess enthalpies, H_m^E, of binary mixtures of 2-butanone with aliphatic alcohols at 313.15 K

x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})
Methanol					
0.0831	195	0.3109	626	0.6456	761
0.1003	244	0.3798	704	0.6909	728
0.1532	352	0.4739	769	0.7521	672
0.1842	427	0.5280	781	0.8188	556
0.2492	527	0.5501	793	0.8582	459
Ethanol					
0.0605	268	0.3232	976	0.7238	975
0.0875	362	0.3936	1076	0.7628	877
0.1382	535	0.4684	1120	0.8667	589
0.2065	758	0.5644	1139	0.8970	489
0.2452	849	0.6167	1155		
1-Propanol					
0.0761	426	0.2937	1151	0.6732	1184
0.1094	577	0.3794	1297	0.7703	996
0.1430	706	0.4538	1370	0.8045	885
0.1703	788	0.5300	1349	0.8927	572
0.2499	1021	0.6238	1270	0.9176	441
2-Propanol					
0.0778	527	0.2988	1339	0.6785	1383
0.1118	719	0.3852	1484	0.7746	1133
0.1461	855	0.4599	1550	0.8084	1039
0.1738	967	0.5362	1545	0.8951	671
0.2545	1253	0.6296	1457	0.9195	507
1-Butanol					
0.0916	513	0.3414	1345	0.8041	993
0.1306	686	0.4279	1446	0.8343	857
0.1696	857	0.5041	1463	0.9106	524
0.2007	1003	0.5798	1423	0.9317	422
0.2896	1251	0.6699	1302		
0.3372	1349	0.7159	1207		
2-Methyl-2-propanol					
0.0722	371	0.3451	1381	0.8095	995
0.0945	486	0.4366	1491	0.8391	857
0.1347	678	0.5129	1516	0.9134	508
0.1746	845	0.5884	1503	0.9339	414
0.2064	962	0.6776	1378		
0.2967	1266	0.7230	1287		

[a] x is the mole fraction of 2-butanone.

EXPERIMENTAL

The alcohols were the same as in previous studies [1,3]. 2-Butanone (a pro analysis product of E. Merck AG) was purified by distillation. The reagents were stored over molecular sieves.

The excess enthalpies were determined with a flow microcalorimeter (LKB-2107, LKB-Produkter AB) as described earlier [1].

RESULTS AND DISCUSSION

The molar excess enthalpies for the binary mixtures are collected in Table 1, and are also represented graphically as a function of x, the mole fraction of the ketone, in Fig. 1. To each set of experimental values we fitted the equation

$$H_{\mathrm{m}}^{\mathrm{E}}\ (\mathrm{J\ mol^{-1}}) = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i \qquad (1)$$

Coefficients A_i of these fitting equations together with the standard deviations $\sigma(H_{\mathrm{m}}^{\mathrm{E}})$ of the fits are collected in Table 2. Coefficients A_i were further

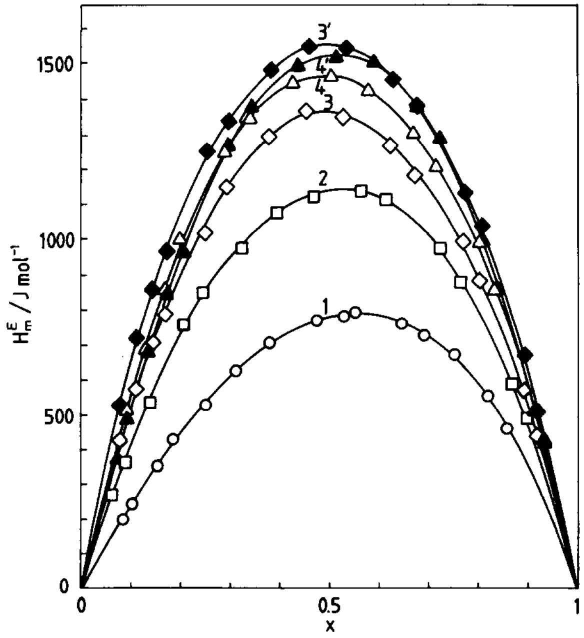

Fig. 1. Molar excess enthalpies, $H_{\mathrm{m}}^{\mathrm{E}}$, for the mixtures of MEK with aliphatic alcohols vs. the mole fraction, x, of MEK: (1) methanol, (2) ethanol, (3) 1-propanol, (3′) 2-propanol, (4) 1-butanol, (4′) 2-methyl-2-propanol.

TABLE 2

Coefficients of eqn. (1) and the standard deviations

2-Butanone +	A_0	A_1	A_2	A_3	A_4	$\sigma(H_m^E)$ (J mol^{-1})
Methanol	3111.4	−646.5	487.9	−219.8	−350.8	5
Ethanol	4552.9	−358.3	758.5	−27.75	−352.6	8
1-Propanol	5459.8	98.43	−77.75	−230.2	1243.8	10
2-Propanol	6208.5	40.88	1079.9	105.8	476.9	11
1-Butanol	5843.1	287.2	1157.2	−831.0	−746.0	9
2-Methyl-2-propanol	6113.9	−317.1	596.8	−303.7	−1039.7	10

used to evaluate the partial molar excess enthalpies for the alcohols (H_1^E) and the ketone (H_2^E) from the equations

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

$$H_2^E = H_m^E + (1 - x)\left(\frac{\partial H_m}{\partial x}\right)_{p,T} \tag{3}$$

Curves of H_1^E and H_2^E as a function of x are plotted in Fig. 2.

The values of H_m^E, H_1^E and H_2^E are positive over the whole composition range for all MEK–alcohol mixtures studied. The maximum is at about $x = 0.5$ in all $H_m^E(x)$ curves, and for the primary alcohols its magnitude increases with the length of the alkyl chain from 790 J mol^{-1} for methanol to 1470 J mol^{-1} for 1-butanol. The values for 2-propanol and 2-methyl-2-propanol are greater than those for the primary alcohols. No experimental values could be found in the literature to compare these results, except those of Kopp and Quitsch [7] for the MEK–2-methyl-2-propanol mixtures at 318.15 K. The present values at 313.15 K are very close to theirs.

The results can be qualitatively explained in terms of changes that occur in intermolecular interactions when the components are mixed. Before looking at these changes, it is useful to recall some properties of the pure components and of their mixtures with a solvent that is generally regarded as inert, e.g. n-alkanes. As is well known, the molecules of pure alcohols are extensively self-associated through hydrogen bonding. For the alcohols studied, the enthalpies of association are − 25 ± 2 kJ mol^{-1} and the fraction of the free OH groups is some few per cent at 318.15 K increasing slightly with the length of the alkyl group of the alcohol [8]. Break-up of the hydrogen bonds produces positive contributions to enthalpies of mixing for mixtures of alcohols. According to Smith and Brown [9,10], the values for alcohol–n-alkane mixtures contain, in addition, a dipole–dipole contribution. As a result of these contributions the alcohol–n-alkane systems exhibit relatively large positive excess enthalpies. For example, the magnitude of the

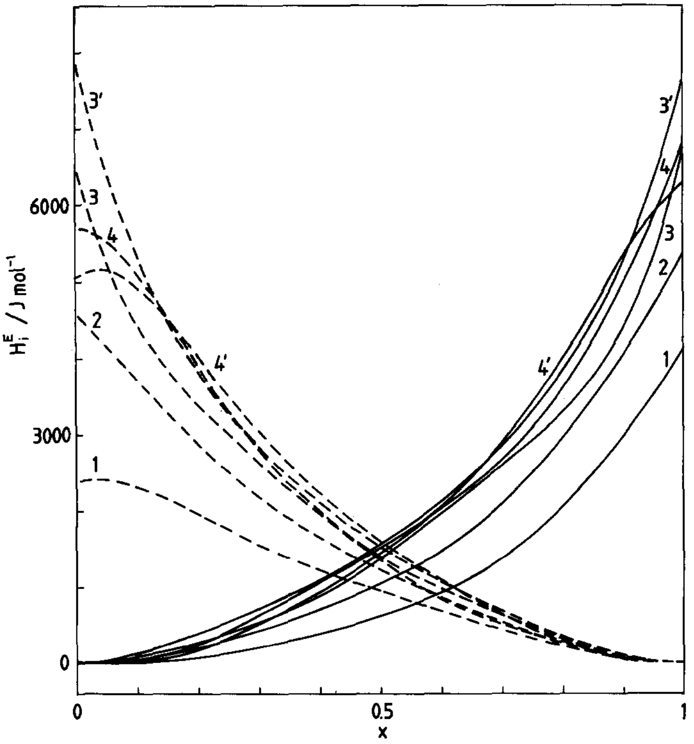

Fig. 2. Partial molar excess enthalpies for the mixtures of MEK with aliphatic alcohols. (———) Alcohols H_1^E, (- - -) MEK H_2^E. Symbols as in Fig. 1.

maximum in the $H_m^E(x)$ curve for the mixtures of methanol, ethanol, 1-propanol, and 1-butanol with n-hexane, at 318.15 K, is about 760, 830, 910, and 850 J mol^{-1}, respectively [11].

The molecules of MEK are dipolar (the dipole moment of MEK is 2.8 D at 298.15 K [12]) and can self-associate by dipole–dipole interactions. Mixing of MEK with alkanes results in large positive excess enthalpies, which arise mainly from breaking of the dipole–dipole interactions between ketone molecules [13–15]. The maximum in the $H_m^E(x)$ curve for the MEK–n-hexane system is about 1260 J mol^{-1} at 298.15 K [13]. Although the values at 313.15 K are not available for this system, we assume that they are close to the values at 298.15 K, since the $H_m^E(x)$ curves at 298.15 and 318.15 K for MEK–cyclohexane mixtures are very similar (the maximum is about 1300 J mol^{-1}) [7].

The large positive values for the mixtures of MEK with all alcohols studied indicate that contributions due to the break-up of alcohol–alcohol and ketone–ketone interactions, discussed above, clearly predominate in these mixtures. However, owing to the proton-accepting ability of the carbonyl group of MEK one would expect to find traces of negative contributions due to C=O · · · H–O hydrogen bonding as well. And indeed, the magnitudes of H_1^E and H_2^E, together with a comparison of the values of H_m^E with those for MEK–hydrocarbon and alcohol–hydrocarbon systems, suggest that at least in the mixtures of the lower alcohols there are some slight contributions due to hetero-association.

The conclusion that the effects of the hetero-association equilibria are very small in the MEK–alcohol mixtures obtains support from a comparison of the present values with those for the mixtures of the same alcohols with the considerably stronger proton acceptor DMA. Although the contributions of dipolar origin are presumably somewhat different for mixtures of MEK and mixtures of DMA, the magnitude of the results is what one would expect on the basis of the proton-accepting abilities of MEK and DMA: i.e. the excess enthalpies are much greater for MEK than for DMA [1]. For example, whereas the values for the MEK–methanol system are noticeably positive ($H_m^E(\max) \approx 790$ J mol^{-1}) those for DMA–methanol system are noticeably negative ($H_m^E(\min) \approx -750$ J mol^{-1}). The difference is somewhat smaller for mixtures of the higher alcohols, where the contributions due to hetero-association are smaller.

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