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STUDIES OF THERMODYNAMIC PROPERTIES OF BINARY MIXTURES CONTAINING AN ALCOHOL

Part XV. Excess molar enthalpies of alkan-1-ol + methyl ethyl ketone and + methyl isobutyl ketone at 298.15 K *

JIAN-PING CHAO and MING DAI

Research Laboratory of Solution Chemistry, Henan Institute of Chemistry, Zhengzhou, Henan 450003 (People's Republic of China)

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ABSTRACT

Molar excess enthalpies, H^E, for methanol, ethanol, propan-1-ol, pentan-1-ol and hexan-1-ol with methyl ethyl ketone or methyl isobutyl ketone were measured as a function of composition at 298.15 K with a Picker flow microcalorimeter. For all the mixtures studied. H^E values are positive over the entire composition range and increase in 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 of alkanol, the dipole–dipole interaction and the alkyl chain length of the ketone.

INTRODUCTION

In our systematic investigation of the excess thermodynamic properties of binary mixtures containing an alcohol, we have previously reported excess molar enthalpies, H^E, of alcohols with organic solvents containing oxygen [1–4] and have studied the molecular interactions between alcohol and cyclohexanone, 1,4-dioxane, tetrahydrofuran, *N*,*N*-dimethylformamide and dimethyl sulphoxide. The results obtained have demonstrated that the geometry of the solvent molecule, the number of oxygen atoms, their relative position and the influence of other atoms of the solvent molecule play important roles in molecular interactions.

We are interested in the influence of the alkyl chain length of some ketones on the interactions. For this purpose, molar excess enthalpies of methanol, ethanol, propan-1-ol, pentan-1-ol and hexan-1-ol + methyl ethyl ketone (MEK) or methyl isobutyl ketone (MIBK) at 298.15 K were measured and are discussed in this paper.

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EXPERIMENTAL

Molar excess enthalpies were measured with a Picker flow microcalorimeter at 298.15 K and under atmospheric pressure. The principle of the apparatus and the experimental procedure have been reported in our previous work [5]. The performance of the calorimeter was checked regularly by determining the excess enthalpies of some thoroughly investigated test mixtures (benzene + tetrachloromethane and benzene + cyclohexane at 298.15 K). The results obtained at $x = 0.5$ agreed to within 1% with those of Grolier [6].

The six alkan-1-ols were the same as those used in the previous work [3]. MEK and MIBK were from Shanghai Chemical Co. (analytical grade). All were treated prior to use by the methods described in Riddick and Bunger [7]. Refractive indices of the purified liquids were in agreement with available literature values.

RESULTS AND DISCUSSION

The experimental excess enthalpies for the alkan-1-ols with MEK or MIBK are given in Table 1. H^E values of butan-1-ol have already been reported [8]. Molar excess enthalpies of these two series are plotted as a function of the alkan-1-ol composition in Figs. 1 and 2.

The experimental data for H^E were fitted to the smoothing equation

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

where x is the mole fraction of alkan-1-ol. The values of parameters A_i evaluated by the method of least squares are given in Table 2 together with the standard deviations

$$s = \left[\frac{\left(H^E_{\mathrm{exp}} - H^E_{\mathrm{calcd}}\right)^2}{n-m}\right]^{1/2} \tag{2}$$

with n data points and m parameters.

Of the quantities measured, only the H^E values of methanol and ethanol + MEK had apparently been measured before [9,10]. Our results are in agreement with those reported by Nagata et al., but are slightly lower at lower values of x. For the other mixtures, no experimental data at 298.15 K could be found in the literature.

As can be seen from Figs. 1 and 2, molar excess enthalpies, H^E, for all mixtures are positive over the entire composition range at 298.15 K. The dependence of H^E on x for each of the mixtures studied is nearly symmetrical about $x = 0.5$. The excess molar enthalpies measured in this paper are

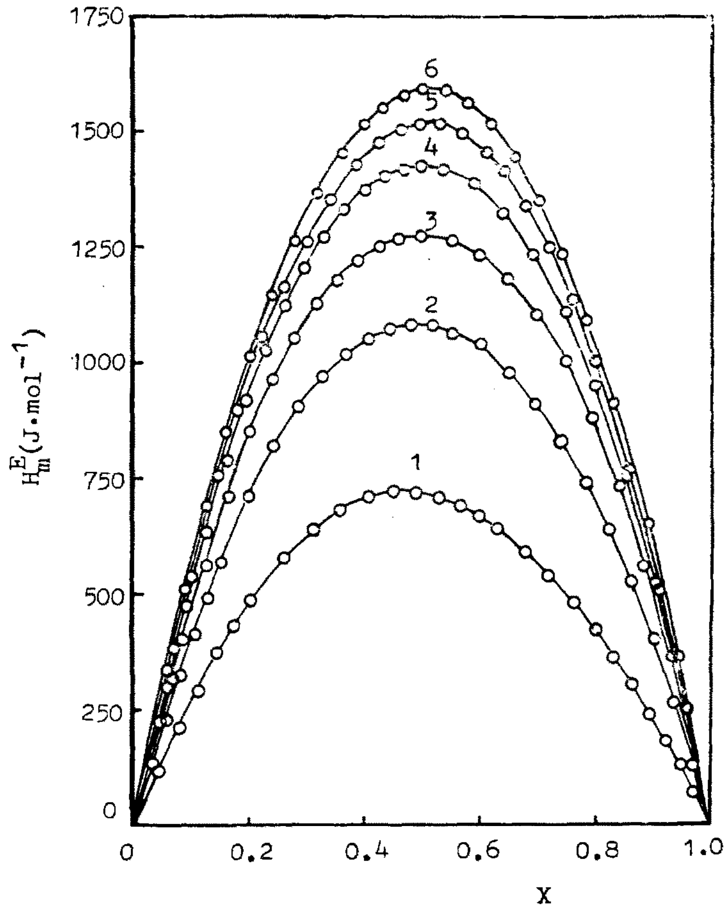

Fig. 1. Excess molar enthalpies of $xC_nH_{2n+1}OH+(1-x)CH_3COC_2H_5$ at 298.15 K: o, experimental data; ———, results calculated from eqn. (1) with coefficients from Table 2; 1, methanol; 2, ethanol; 3, propan-1-ol; 4, butan-1-ol; 5, pentan-1-ol; 6, hexan-1-ol.

more positive than those of the corresponding alkanol–alkane mixtures [11]. This suggests that the dominant effect in the mixing process is the presumably endothermic dissociation of the hydrogen bonds of the alkanols. As we know, MEK or MIBK does not self-associate through hydrogen bonding due to the lack of a proton donor group in the molecule. However, the ability of a carbonyl group to act as an electron donor in hydrogen-bonded complex formation is unquestioned. Furthermore, in comparison with alkanes of similar structure and molecular weight, the higher boiling point and larger heat of vaporisation (H_v) of MEK or MIBK indicates that there are dipole–dipole interactions between like molecules. Combining the chemical properties of the alkanol and MEK or MIBK, we may conclude that the H^E values of alkanol + MEK or MIBK depend on the result of the two opposite contributions: a positive effect from the rupture of alkanol–alkanol hydro-

TABLE 1

Experimental excess molar enthalpies, H_m^E, for alkan-1-ol + methyl ethyl ketone and alkan-1-ol + methyl isobutyl ketone mixtures at 298.15 K

x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})
$x\mathrm{CH_3OH}+(1-x)\mathrm{CH_3COC_2H_5}$					
0.0484	119.2	0.4082	716.9	0.7601	480.8
0.0789	205.3	0.4541	720.1	0.7966	423.7
0.1113	290.3	0.4918	712.5	0.8301	363.7
0.1433	364.7	0.5295	711.4	0.8605	307.2
0.1742	434.8	0.5667	691.7	0.8924	241.6
0.2039	490.7	0.6009	668.9	0.9205	183.1
0.2603	588.2	0.6333	640.5	0.9470	126.2
0.3139	652.8	0.6788	590.1	0.9717	68.3
0.3621	694.2	0.7209	537.9		
$x\mathrm{C_2H_5OH}+(1-x)\mathrm{CH_3COC_2H_5}$					
0.0311	133.9	0.3286	961.9	0.6955	911.4
0.0564	234.5	0.3689	1013.4	0.7393	830.1
0.0814	321.2	0.4079	1047.2	0.7812	739.5
0.1058	411.3	0.4457	1069.8	0.8218	630.2
0.1300	493.2	0.4823	1080.8	0.8607	515.4
0.1525	569.2	0.5178	1075.5	0.8979	391.9
0.1995	711.2	0.5523	1062.8	0.9341	262.7
0.2440	808.6	0.6021	1029.8	0.9687	127.1
0.2870	894.2	0.6498	980.5		
$x\mathrm{C_3H_7OH}+(1-x)\mathrm{CH_3COC_2H_5}$					
0.0452	226.8	0.3174	1125.2	0.6485	1178.1
0.0655	320.2	0.3542	1180.1	0.6972	1102.1
0.0857	413.5	0.3905	1221.4	0.7450	1004.7
0.1257	579.9	0.4264	1251.5	0.7919	882.1
0.1650	725.3	0.4618	1265.9	0.8381	731.2
0.2037	849.7	0.4967	1272.3	0.8832	556.8
0.2422	955.3	0.5482	1261.5	0.9277	364.4
0.2801	1046.3	0.5988	1231.7		
$x\mathrm{C_5H_{11}OH}+(1-x)\mathrm{CH_3COC_2H_5}$					
0.0681	380.8	0.3867	1424.3	0.6804	1327.1
0.1042	546.9	0.4278	1472.1	0.7184	1237.7
0.1440	730.2	0.4624	1496.1	0.7570	1131.7
0.1813	887.9	0.4976	1512.1	0.7961	998.5
0.2224	1036.5	0.5332	1510.6	0.8558	766.2
0.2609	1160.1	0.5692	1492.5	0.9085	519.8
0.3033	1265.1	0.6058	1451.2	0.9581	255.1
0.3430	1354.8	0.6428	1396.3		
$x\mathrm{C_6H_{13}OH}+(1-x)\mathrm{CH_3COC_2H_5}$					
0.0602	336.1	0.3580	1453.1	0.6575	1439.7
0.0927	509.1	0.3983	1517.2	0.6982	1349.2
0.1288	691.0	0.4329	1555.6	0.7401	1235.6
0.1631	846.2	0.4681	1579.6	0.7828	1095.9
0.2012	1004.6	0.5042	1589.5	0.8268	929.5
0.2372	1140.1	0.5411	1584.8	0.8857	659.2
0.2775	1267.4	0.5791	1560.1	0.9419	354.1
0.3156	1368.4	0.6177	1513.6		

TABLE 1 (continued)

x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})
$x CH_3OH+(1-x)CH_3COCH_2CH(CH_3)CH_3$					
0.0603	164.3	0.3634	578.1	0.7116	484.1
0.1069	270.1	0.4199	600.8	0.7517	438.6
0.1505	353.8	0.4711	607.4	0.7878	389.2
0.1913	424.9	0.5174	603.9	0.8307	324.9
0.2301	470.7	0.5597	590.6	0.8625	270.2
0.2662	507.6	0.5985	570.8	0.9022	197.2
0.3004	533.2	0.6341	548.2	0.9324	140.1
0.3328	560.1	0.6669	524.1	0.9595	85.1
$x C_2H_5OH+(1-x)CH_3COCH_2(CH_3)CH_3$					
0.0428	173.6	0.3354	816.7	0.6785	746.9
0.0771	291.2	0.3830	857.7	0.7213	701.9
0.1101	391.2	0.4278	882.5	0.7738	605.3
0.1417	477.7	0.4699	892.5	0.8216	504.7
0.1723	552.2	0.5096	891.7	0.8655	399.7
0.2019	622.6	0.5471	880.2	0.9058	290.8
0.2304	678.9	0.5826	859.6	0.9430	184.6
0.2847	757.3	0.6324	816.8		
$x C_3H_7OH+(1-x)CH_3COCH_2(CH_3)CH_3$					
0.0343	149.2	0.3739	989.6	0.6924	891.3
0.0622	250.2	0.4148	1022.5	0.7305	826.1
0.0894	349.7	0.4511	1042.7	0.7644	758.0
0.1421	521.2	0.4920	1048.5	0.7995	680.8
0.1924	667.4	0.5285	1042.4	0.8438	565.8
0.2407	781.8	0.5739	1019.3	0.8802	458.3
0.2869	874.3	0.6140	989.1	0.9154	338.5
0.3313	940.8	0.6556	942.9	0.9491	216.2
$x C_5H_{11}OH+(1-x)CH_3COCH_2(CH_3)CH_3$					
0.0289	143.4	0.4175	1180.5	0.6997	1018.7
0.0818	374.8	0.4540	1199.8	0.7333	960.1
0.1301	564.5	0.4903	1208.4	0.7667	880.5
0.1816	743.9	0.5261	1202.9	0.7996	798.7
0.2286	877.5	0.5615	1187.9	0.8420	678.8
0.2671	972.4	0.5966	1161.1	0.8807	543.2
0.3053	1052.8	0.6313	1124.1	0.9220	375.7
0.3431	1111.7	0.6657	1074.9	0.9597	200.1
0.3805	1151.2				
$x C_6H_{13}OH+(1-x)CH_3COCH_2(CH_3)CH_3$					
0.0251	139.2	0.3835	1205.1	0.6691	1126.4
0.0718	364.6	0.4192	1236.8	0.7048	1066.4
0.1149	545.1	0.4550	1254.8	0.7404	986.5
0.1615	724.3	0.4907	1259.1	0.7760	901.9
0.2045	858.6	0.5264	1250.7	0.8223	769.5
0.2403	956.6	0.5621	1231.1	0.8650	624.6
0.2761	1041.8	0.5978	1210.3	0.9112	443.3
0.3119	1109.7	0.6335	1173.8	0.9538	247.2
0.3477	1163.1				

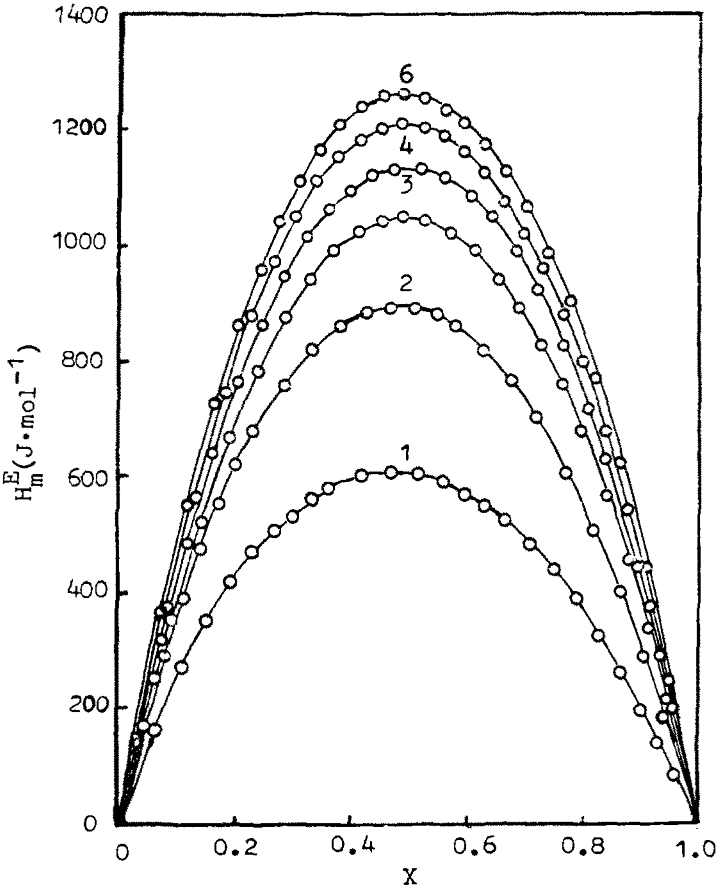

Fig. 2. Excess molar enthalpies of $xC_nH_{2n+1}OH+(1-x)CH_3COCH_2CH(CH_3)CH_3$ at 298.15 K: o, experimental data; ———, calculated results from eqn. (1) with coefficients from Table 2; 1, methanol; 2, ethanol; 3, propan-1-ol; 4, butan-1-ol; 5, pentan-1-ol; 6, hexan-1-ol.

gen bonds and of ketone–ketone dipole interaction, as well as from physical interactions between like molecules; and a negative effect from the formation of $O{-}H\cdots O{=}C\langle$ hydrogen-bonded complexes. The positive experimental results may indicate that the predominant contribution to the mixing process is from the first effect. In other words, the formation of a hydrogen-bonded complex between unlike molecules, absent in alkanol–alkane mixtures, makes the self-associated alkanol more easily dissociated, but the energy released from the formation of the complex is less than that required to elongate or break the hydrogen bond in the alkanol or the dipole–dipole interaction between MEK or MIBK.

Excess molar enthalpies of alkanol + MEK are more positive than those of alkanol + MIBK (Fig. 3). A possible explanation is that the specific interaction between alkanol and MIBK is weaker than that between the corresponding alkanol and MEK. Thus, in comparison with the MIBK

TABLE 2

Coefficients, A_i, of the Redlich–Kister equation and standard deviations, s

	A_0	A_1	A_2	A_3	A_4	s
$(1-x)CH_3COC_2H_5$						
$+xCH_3OH$	2873.0	563.6		−579.2	−501.5	3.5
$+xC_2H_5OH$	4320.1	55.5	134.8		−182.7	3.4
$+xC_3H_7OH$	5097.7	−49.6	757.4	−69.9	−570.9	2.5
$+xC_4H_9OH$	5685.8	19.1	862.4	−164.2	−1099.8	1.7
$+xC_5H_{11}OH$	6051.0	−127.7		−107.6	168.7	3.5
$+xC_6H_{13}OH$	6355.7	−73.0	190.8	−294.9	−480.5	3.0
$(1-x)CH_3COCH_2CH(CH_3)CH_3$						
$+xCH_3OH$	2414.4	231.0	325.7	215.0	−180.9	2.3
$+xC_2H_5OH$	3572.9	234.1	123.5	237.4	203.1	2.3
$+xC_3H_7OH$	4200.4	98.5		−186.0	323.7	2.9
$+xC_4H_9OH$	4524.4	108.3	625.0	−388.8	−361.8	2.8
$+xC_5H_{11}OH$	4827.0	96.4	530.7	−243.9	−175.6	4.2
$+xC_6H_{13}OH$	5045.1	105.0	486.2	−153.8	224.9	3.5

mixtures, more alkanol–alkanol hydrogen bonds in MEK mixtures are broken at a given mole fraction. It is clear that the larger steric hindrance effect of the isobutyl chain of MIBK on the carbonyl group may be mainly responsible for the lower excess molar enthalpies.

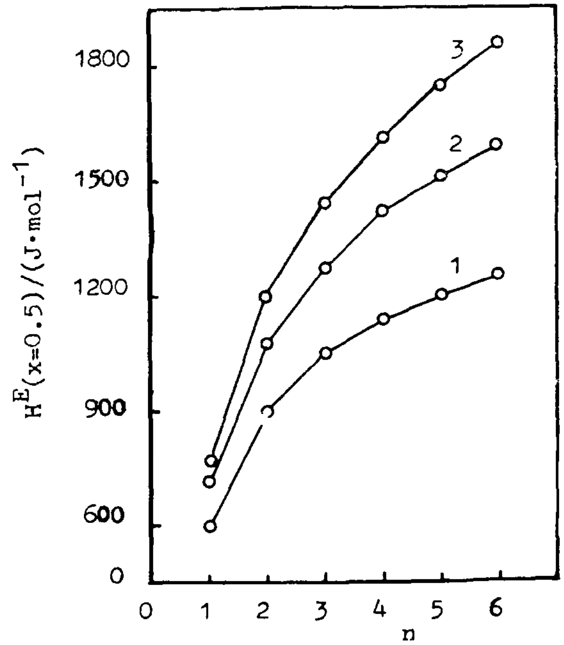

Fig. 3. Excess enthalpies of each of the five alkan-1-ols + 1, methyl isobutyl ketone; 2, methyl ethyl ketone; 3, acetone; n, number of carbon atoms of alkan-1-ol.

To further examine the steric hindrance effect of the alkyl chain of the ketones and alkanols on excess enthalpies, a plot of H^E at 298.15 K for each of the six alkanols with acetone [12] at $x = 0.5$ against the number of carbon atoms in the alkanol molecule is also shown in Fig. 3. Excess molar enthalpies of all three series increase in the order: methanol < ethanol < propan-1-ol < butan-1-ol < pentan-1-ol < hexan-1-ol, but the differences in H^E values between neighbouring alkanols decrease in the same order. This indicates that the various specific interactions become weaker with increasing alkyl chain length of the alkanol and, in accordance with our previous work [13], the reduction of interaction between unlike molecules may be essential. As was expected, excess molar enthalpies of mixtures of alkanol with acetone are more positive than those of the corresponding MEK or MIBK mixtures. It is clear that the ability of acetone to act as a proton donor in the mixing process is stronger than that of MEK or MIBK. The difference in the steric hindrance effect is more significant in the mixtures containing larger alkanols.

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