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EXCESS MOLAR ENTHALPIES AND EXCESS MOLAR VOLUMES OF BINARY MIXTURES OF BENZENE AND ALKANOLS WITH QUINOLINE

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Abstract

Molar excess enthalpies H_m^E have been determined over the whole composition range for mixtures of benzene, methanol, ethanol, 1-propanol, 2-propanol and 1-butanol with quinoline at 298.15 K using a Thermometric flow calorimeter. The results reflect a strong H-bond association between an alkanol and quinoline which decreases with increasing length of the alkanol chain. The small H_m^E for (benzene+quinoline) reflects the similarity of the two molecules.

Keywords: alkanols, benzene, excess molar enthalpies, excess molar volumes, quinoline

Introduction

Quinoline is a polar, self-associated, nonvolatile compound with a high boiling point of 510 K. It is an interesting compound because it has the right properties to act as an entrainer for separating aromatic and aliphatic mixtures and, possibly, to be used as a co-solvent for separating alkanols from water [1]. In an attempt to understand the interactions between quinoline and an alkanol, it was decided to measure their enthalpies of mixing. No alkanes were included in this work because of their insolubility in quinoline. The molar excess enthalpies H_m^E were measured at 298.15 K over the whole composition range for (benzene+quinoline) and (an alkanol+quinoline) mixtures, where the alkanols were methanol, ethanol, 1-propanol, 2-propanol and 1-butanol. The results are discussed in terms of hydrogen bonding.

The molar excess enthalpies of mixing H_m^E for (benzene+quinoline) mixtures have been measured at 303.15 K by Kaira *et al.* [2]. No H_m^E values for (an alkanol+quinoline) mixtures were found in the literature.

Experimental

A Thermometric flow microcalorimeter 2277 was used to determine the molar enthalpies of mixing. All the measurements were made at constant temperature (298.15±0.01 K). The calibration and experimental determinations have been described elsewhere [3, 4]. The performance of the calorimeter was checked by measur-

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Table 1 Excess enthalpy H_m^E data for binary mixtures of benzene, methanol, ethanol, 1-propanol, 2-propanol and 1-butanol with quinoline at 298.15 K

x	H_m^E/ J mol^{-1}	Δ/ J mol^{-1}	x	H_m^E / J mol^{-1}	Δ/ J mol^{-1}	x	H_m^E/ J mol^{-1}	Δ/ J mol^{-1}
				$xC_6H_6+(1–x)C_9H_{11}N$				
0.1056	15.0	0.0	0.4099	35.2	1.0	0.8759	31.2	1.9
0.1436	19.0	0.2	0.4884	36.3	0.3	0.9106	25.4	1.0
0.2066	24.0	0.1	0.6024	37.8	0.4	0.9347	20.8	1.1
0.2954	28.8	–0.7	0.6739	36.6	– 0.9	0.9417	16.4	–1.8
0.3214	30.6	–0.1	0.7401	36.2	– 0.7	0.9650	8.9	–3.4
0.3770	32.6	–0.5						
				$CH_3OH+(1–x)C_9H_{11}N$				
0.0475	–91.5	–0.4	0.4310	–532.3	–8.1	0.8439	–196.8	6.1
0.0711	–139.9	–2.4	0.5142	–557.4	–4.7	0.8904	–137.4	–2.6
0.1282	–241.2	–0.1	0.6057	–544.8	4.3	0.9330	–83.7	–2.6
0.2196	–374.0	3.4	0.7012	–495.7	–6.5	0.9640		
0.2924	–454.7	1.8	0.7850					
				$C_2H_5OH+(1–x)C_9H_{11}N$				
0.0879	–55.1	–3.0	0.5468	–219.5	–0.3	0.8598	–158.6	–6.3
0.1813	–102.4	3.3	0.6318	–221.0	1.9	0.8980	–123.3	–1.7
0.2200	–124.7	0.7	0.7451	–207.0	0.2	0.9311	–44.7	8.3
0.3266	–171.5	–1.8	0.8084	–180.3	2.8	0.9617		
0.4319	–200.9	–0.9						
				$C_3H_7OH+(1–x)C_9H_{11}N$				
0.0580	–22.9	–0.05	0.3840	–92.2	0.2	0.8447	–61.7	0.4
0.0869	–32.8	0.2	0.4791	–96.3	–0.5	0.8914	–50.6	–0.9
0.1522	–52.8	0.3	0.6392	–90.0	–0.1	0.9277	–36.9	0.0
0.2318	–73.6	–1.3	0.7337	–80.3	0.4	0.9580	–22.9	0.7
0.3172	–84.9	1.1	0.7909	–72.7	–0.1			
				$CH_3CH(OH)CH_3+(1–x)C_9H_{11}N$				
0.0407	25.7	0.0	0.3344	123.1	0.8	0.8708	85.3	–2.2
0.0669	37.8	–1.9	0.4190	130.1	–2.2	0.9097	70.2	–0.3
0.1158	62.0	0.0	0.4959	136.8	1.1	0.9328	58.4	1.0
0.1480	77.2	2.7	0.6096	132.2	0.2	0.9730	29.8	2.6
0.1930	88.1	–1.3	0.7207	121.1	0.1			
0.2331	100.9	0.0	0.7690	114.2	0.6			
				$C_4H_9OH+(1–x)C_9H_{11}N$				
0.0600	2.1	0.0	0.4802	–11.6	–0.2	0.8498	–11.3	0.3
0.1342	1.9	0.5	0.5942	–14.7	–0.1	0.8908	–9.2	0.0
0.1882	–0.8	–0.7	0.7046	–15.6	0.00	0.9155	–7.7	–0.3
0.3833	–7.3	0.4						

ing H_m^E over the whole composition range for the test mixture (cyclohexane+hexane). The maximum difference between our results and the interpolated results of McLure and Rodriguez [5] was less than 1.5%.

The solvent quinoline was supplied by Saarchem and was first dried by the addition of potassium iodide, followed by distillation. This procedure was repeated on a daily basis before each mixing experiment. Benzene was supplied by Holpro and had a purity greater than 99.9 mol%. Methanol and ethanol were dried with calcium hydride. 1-Propanol, 2-propanol and 1-butanol were dried with anhydrous potassium carbonate. Using the Karl Fischer titration technique, the percentage of water in the alkanols was found to be less than 0.1 mol%. GC analysis indicated that the quinoline and each of the alkanols had a purity in excess of 99.5 mol%.

Results

Results for H_m^E are given in Table 1, together with the corresponding deviations, Δ. The deviations were calculated from the smoothing equation:

$$\Delta = H_m^E - x(1-x)\sum_{r=0}^{r=3} A_r (1-2x)^r \quad (1)$$

where x is the mol fraction of the first mentioned species. The coefficients A_r are given in Table 2.

Table 2 Values at 298.15 K of coefficients A_r in J mol^{-1} for Eq. (1)

Mixture	A_r			
	A_0	A_1	A_2	A_3
x1–C_6H_6+(1–x)$C_9H_{14}N$ +(1–x)$C_9H_{14}N$	144	–33	81	66
x1–CH_3OH +(1–x)$C_9H_{14}N$	–2243	2249	–304	–404
x1–C_2H_5OH +(1–x)$C_9H_{14}N$	–852	312	–306	167
x1–C_3H_7OH +(1–x)$C_9H_{14}N$	–383	–15	–104	127
x1–$CH_3CH(OH)CH_3$ +(1_x)$C_9H_{14}N$	542	–12	138	–197
x1–C_4H_9OH +(1–x)$C_9H_{14}N$	–48	63	–3	15

Discussion

Quinoline is partly self-associated [2, 6] . Kaira *et al.* [2] suggested that the interaction between quinoline and benzene is probably due to weak hydrogen bonding. Murrell and Gil [7] suggested a parallel-plane interaction between benzene and pyridine through hydrogen bonding. Schaefer and Sneider [8] reported, from NMR studies, that the benzene and quinoline lie in parallel planes and that the N of quinoline lies above the H of the benzene. For the (benzene+quinoline) mixture the H_m^E is small and positive. This reflects the fact that the enthalpy of the breakdown of the self-association of the quinoline molecules [2] is almost compensated by the enthalpy of the dissociation of benzene molecules and the dissociation of the quinoline molecules.

For the (alkanol+quinoline) mixtures, there are two contributions to the excess molar enthalpy H_m^E: (a) a positive part due to the dissociation of the associated quinoline [2] and the dissociation of the H-bonded alkanols and (b) a negative part due to the H-bonded association of the alkanol proton with the N lone pair electrons of quinoline. The H_m^E values for (methanol or ethanol or 1-propanol+quinoline) mixtures are negative, for (2-propanol+quinoline) mixtures they are positive, and for (1-butanol+quinoline) are sinusoidal.

The H_m^E value (x=0.5) for the (methanol+quinoline) mixture is –560 J mol^{-1} and reflects the fact that the enthalpy involved in the H-bonding between the methanol and quinoline is greater than the dissociation enthalpies of the methanol and the quinoline [2]. The H-bond effect decreases with the decreasing accessibility of the H atom of the alkanol molecule, in the order methanol (–560), ethanol (–215), 1-propanol (–95), 1-butanol (–12) and 2-propanol (135 J mol^{-1}), with the H_m^E (x=0.5) values in parentheses.

It is possible that the H-bonding of the alkanol to the quinoline is also influenced by the electron donating effect of the methyl groups. This will create the strongest H-bond for methanol and the weakest for 2-propanol and is supported by the enthalpy results. The error in the H_m^E values is estimated to be less than 1.5%.

The very large negative excess volumes of mixing for (methanol or ethanol or 1-propanol or 1-butanol+quinoline) mixtures, ranging from –1.18 to –0.92 cm^3 mol^{-1}, as reported by Dewan *et al.* [9] also reflect a strong association between the alkanol and quinoline.

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