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EXCESS ENTHALPIES OF BINARY MIXTURES OF ACETOPHENONE WITH BENZENE AND SUBSTITUTED BENZENES

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ABSTRACT

Excess molar enthalpies of binary mixtures of acetophenone with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, chlorobenzene, bromobenzene and nitrobenzene have been measured at 298.15 K over the entire range of composition with a solution calorimeter. The excess enthalpies are positive in all the systems over the entire mole fraction range. Comments on the effect of intramolecular interactions on intermolecular interactions are made on the basis of the results.

INTRODUCTION

The existence of dipole–induced-dipole interactions between the carbonyl group of a cycloalkanone or aliphatic ketone and the benzene ring of aromatic hydrocarbons has been investigated extensively [1–3]. In contrast to aliphatic and alicyclic ketones, it appears that few attempts have been made to study the interactions in mixtures containing aromatic ketones. Grolier et al. [4] reported excess enthalpy (H^E) data for mixtures containing aromatic ketones. Benson and coworkers [5] interpreted H^E data for mixtures of aromatic ketones with *n*-alkanes in terms of inter- and intramolecular interactions present in the pure ketone. Excess volumes of mixing of acetophenone with cyclohexane and aromatic hydrocarbons were reported by Mahl et al. [6]. It would be interesting to study the molecular interactions in mixtures containing acetophenone as a common component, since in acetophenone intramolecular interactions exist between the carbonyl group and the π-electrons of the phenyl ring. We report here experimental data on excess enthalpy for mixtures of acetophenone with benzene, toluene,

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TABLE 1

Mole fraction of acetophenone x and excess enthalpy H^E for mixtures of acetophenone with benzene and substituted benzenes at 298.15 K

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
Acetophenone + benzene			
0.0240	22.0	0.4116	140.1
0.0698	56.9	0.5717	122.1
0.1247	88.4	0.6804	100.0
0.1738	109.6	0.7815	75.1
0.2722	134.6	0.8633	49.4
0.3196	139.3	0.9169	31.8
Acetophenone + toluene			
0.0394	33.6	0.4702	143.3
0.0790	63.0	0.5913	125.8
0.1157	83.6	0.6962	101.8
0.1624	105.4	0.7874	75.6
0.2883	139.8	0.8931	42.0
0.3820	146.6	0.9432	22.9
Acetophenone + *o*-xylene			
0.0705	65.0	0.4823	174.3
0.1155	96.6	0.5828	158.9
0.1722	127.5	0.6784	135.9
0.2710	161.8	0.7394	116.7
0.3317	172.6	0.8299	82.5
0.4297	176.4	0.9236	39.9
Acetophenone + *m*-xylene			
0.0762	86.7	0.5260	215.9
0.1231	124.9	0.5775	205.3
0.2177	183.1	0.6852	173.4
0.3330	215.7	0.7855	129.7
0.4218	222.8	0.8814	78.9
0.4758	221.8	0.9282	50.6
Acetophenone + *p*-xylene			
0.0573	72.0	0.5240	247.1
0.1269	138.8	0.5808	238.2
0.2578	218.9	0.6878	205.8
0.3135	233.1	0.7431	184.3
0.4237	249.9	0.8213	142.5
0.4767	248.9	0.9296	64.6
Acetophenone + chlorobenzene			
0.0794	19.0	0.5708	33.0
0.1406	29.2	0.6300	29.0
0.2026	36.0	0.6721	25.6
0.3330	41.4	0.7261	22.0
0.3835	40.9	0.8109	15.2
0.4352	39.6	0.8949	8.4

TABLE 1 (continued)

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
Acetophenone + bromobenzene			
0.0294	20.0	0.4423	64.3
0.0699	42.3	0.5523	50.3
0.1248	61.9	0.6218	41.6
0.1831	74.3	0.7053	33.2
0.2514	79.0	0.8201	24.1
0.3800	69.9	0.9115	14.8
Acetophenone + nitrobenzene			
0.0831	6.4	0.6956	24.3
0.1716	12.7	0.7423	22.7
0.2388	17.0	0.7837	20.4
0.3380	22.2	0.8375	16.8
0.4291	25.6	0.8855	12.5
0.5839	27.4	0.9353	7.6

o-xylene, *m*-xylene, *p*-xylene, chlorobenzene, bromobenzene and nitrobenzene. The data throw light on the effect of different substituents into the benzene ring on excess enthalpy.

EXPERIMENTAL

Acetophenone (BDH) was dried over anhydrous potassium carbonate and distilled, retaining the middle fraction. Benzene, toluene, xylenes, chlorobenzene and bromobenzene (BDH) were purified as described earlier [7,8]. Nitrobenzene (BDH) was dried over anhydrous calcium chloride for 2 days and the sample was fractionally distilled. The purity of the chemicals was checked by comparing their measured densities and boiling points with literature values [9]. Excess enthalpies were measured using a Parr 1451 solution calorimeter. Details of the calorimeter and the experimental procedure were described elsewhere [10].

RESULTS

The experimental results for H^E at 298.15 K are given in Table 1. The data are fitted by the method of least squares to the equation

$$H^E = x(1-x)\sum_{i=0}^{i=2} A_i(1-2x)^i \qquad (1)$$

where x is the mole fraction of acetophenone and H^E is in J mol^{-1}. The coefficients A_i, along with the percentage standard deviation, $\%\sigma(H^E)$, are

TABLE 2

Values of coefficients A_i in eqn. (1) determined by least squares analysis, and percentage standard deviation $\%\sigma(H^{\mathrm{E}})$ in mixtures of acetophenone with benzene and substituted benzenes at 298.15 K

System	A_0	A_1	A_2	$\%\sigma(H^{\mathrm{E}})$ (J mol^{-1})
Acetophenone + benzene	527.7	−263.1	164.6	1.2
Acetophenone + toluene	557.9	−249.4	120.4	0.9
Acetophenone + *o*-xylene	687.7	−240.4	122.9	0.8
Acetophenone + *m*-xylene	873.7	−270.0	159.3	0.9
Acetophenone + *p*-xylene	996.1	−184.9	215.5	0.8
Acetophenone + chlorobenzene	148.0	−102.5	37.1	0.8
Acetophenone + bromobenzene	224.7	−263.5	260.8	1.1
Acetophenone + nitrobenzene	107.8	24.6	−4.9	0.8

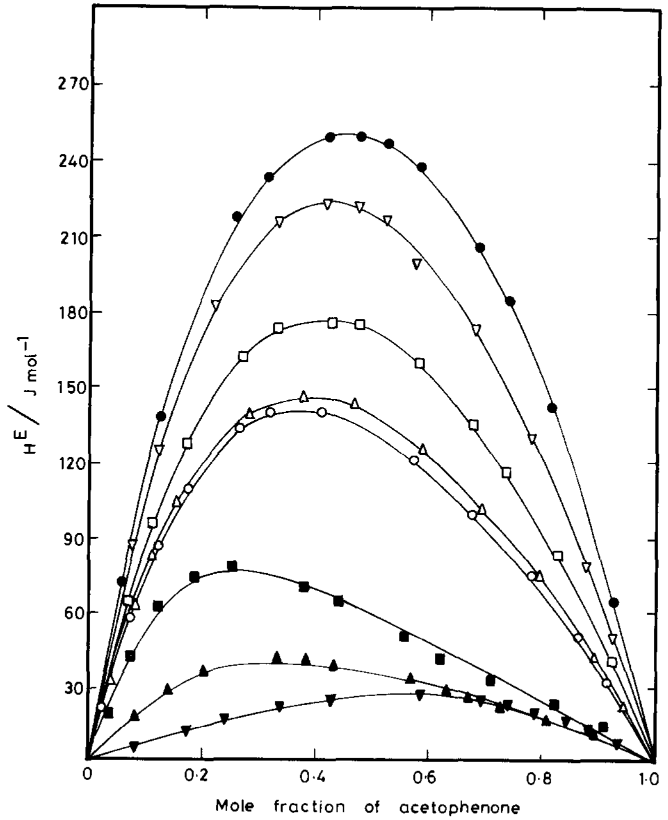

Fig. 1. Excess enthalpies H^{E} at 298.15 K of acetophenone + benzene (○), + toluene (△), + *o*-xylene (□), + *m*-xylene (▽), + *p*-xylene (●), + chlorobenzene (▲), + bromobenzene (■) and + nitrobenzene (▼).

included in Table 2. The variation of excess enthalpy with content of acetophenone is graphically represented in Fig. 1.

DISCUSSION

The excess enthalpies are positive over the entire range of composition in all the systems. Our values of H^E for the system acetophenone + benzene are slightly more positive than those reported by Grolier et al. [4]. Excess enthalpy data are influenced by (i) loss of dipolar association, owing to differences in size and shape of unlike molecules and (ii) dipole–induced-dipole and π–π' interactions between the π-electrons of the phenyl ring of the ketone and the π'-electrons of the benzene ring. The former effect leads to positive excess enthalpies, whereas the latter effect results in negative values. The experimental results suggest that the positive contributions are still predominant, but there is a decrease of about 1 kJ mol^{-1} in the maximum H^E compared with that of the system acetophenone + cyclohexane [4]. This decrease in H^E may be attributed to the π–π' interaction.

Values of H^E in mixtures of acetophenone with substituted benzenes decrease in the order *p*-xylene > *m*-xylene > *o*-xylene > toluene > benzene > bromobenzene > chlorobenzene > nitrobenzene. This order suggests that H^E decreases with decrease in π'-electron density on the benzene ring from *p*-xylene to nitrobenzene.

Further, the effect of intramolecular interactions on the intermolecular interactions may be visualized by comparing the equimolar H^E values between the mixtures of aliphatic, alicyclic and aromatic ketones as common components with aromatic hydrocarbons as non-common components. For example, diethyl ketone and cyclohexanone mix with benzene and toluene exothermically [1,2], whereas acetophenone mixes endothermically, indicating that the interaction between acetophenone and benzene or toluene is weak compared with that of diethyl ketone or cyclohexanone with benzene or toluene. This may be attributed to intramolecular interactions between the ketoxy group and the phenyl group, which weakens the intermolecular interactions.

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REFERENCES

1 K. Tamura, S. Murakami and R. Fujishiro, J. Chem. Thermodyn., 7 (1975) 1089.
2 K. Tamura, S. Murakami and R. Fujishiro, J. Chem. Thermodyn., 13 (1981) 47.

3 B.S. Mahl and H. Kaur, Thermochim. Acta, 112 (1987) 351.
4 J.P.E. Grolier, O. Kiyohara and G.C. Benson, J. Chem. Thermodyn., 9 (1977) 697.
5 O. Urdaneta, S. Haman, Y.P. Handa and G.C. Benson, J. Chem. Thermodyn., 11 (1979) 851.
6 B.S. Mahl, H. Kaur, H. Singh and J.R. Kurma, Thermochim. Acta, 99 (1986) 291.
7 A. Krishnaiah, M. Sreenivasulu and P.R. Naidu, Can. J. Chem., 57 (1979) 1915.
8 K. Ramanjaneyulu, A. Krishnaiah and M. Ramakrishna, Fluid Phase Equilib., 40 (1988) 311.
9 J.A. Riddick and W.B. Bunger, Organic Solvents, Vol. II, Wiley–Interscience, New York, 3rd edn., 1970.
10 A. Krishnaiah, K.N. Surendranath and M. Ramakrishna, Proc. Indian Acad. Sci., 100 (1988) 323.