Excess Molar Enthalpies for Binary Mixtures Containing Ethylbenzene or (2-Chloroethyl)benzene + Five Methyl Alkyl Ketones

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Excess molar enthalpies of the 10 binary systems containing ethylbenzene or (2-chloroethyl)benzene + 2-propanone, + 2-butanone, + 2-pentanone, + 2-octanone and + 2-undecanone have been determined using an LKB flow microcalorimeter. The experimental data were correlated by means of the Redlich-Kister equation.

Introduction

We report here new experimental data for excess enthalpies of 10 binary mixtures having ethylbenzene or (2-chloroethyl)-benzene as the common component (component 1). The noncommon components were a series of five methyl alkyl ketones, namely, 2-propanone, 2-butanone, 2-pentanone, 2-octanone, or 2-undecanone. The present work is part of our extensive program for evaluating the chemical thermodynamic properties of organic systems in which a series of ketones are studied in mixtures with benzene derivatives or naphthalene derivatives with the aim of correlating the experimental data and understanding the effect of ketone chain length on excess enthalpies of the mixtures. Our previous calorimetric works dealt with toluene, *p*-xylene, or pseudocumene + ketones (*1*), methylnaphthalene + ketones (*2*), and chloronaphthalene + ketones (*3*). As far as we know, no excess enthalpies have been reported in the literature for the binary mixtures considered here.

Materials

Ethylbenzene and (2-chloroethyl)benzene obtained from Aldrich Chemical Co. were of purity higher than 99% and were used as supplied. Methyl alkyl ketones are the same as those used in ref 4, and their purifications are described there. All products were stored in dark bottles over molecular sieves (Union Carbide Type 4A, $^1/_{16}$-in. pellets) before use to remove eventual trace amounts of water.

Apparatus and Procedure

Density ρ values of pure liquids, necessary to define flow rates and hence mole fractions in calorimetric measurements (*5*), were determined at 298.15 K with an Anton Paar DMA 60/602 digital precision density meter. The densities of ethylbenzene and (2-chloroethyl)benzene are 0.862 65 (lit. 0.862 53 (*6*)) and 1.068 51 (lit. 1.069 (*7*)) while those of ketones are reported previously (*4*).

Temperature was measured with an Anton Paar digital thermometer (DT-100-25) within 0.005 K: the instrument was calibrated with dry air and bidistilled water, and measurements were made with a sensitivity up to 1×10^{-6} g cm^{-3} with a selected period of 10 000 oscillation cycles. The apparatus and the operating procedure are described in ref 8.

Excess molar enthalpies, H^E, were measured at 298.15 ± 0.01 K (IPTS-68) with an LKB flow microcalorimeter (LKB-2107, LKB Bromma, Sweden) in a manner described elsewere (*9*). Two identical automatic burets, ABU (ABU-Radiometer, Copenhagen, Denmark), were employed to pump liquids

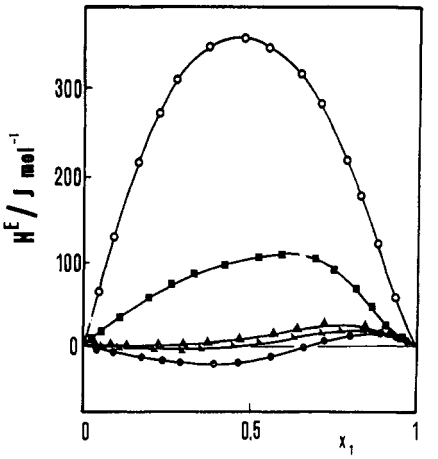

Figure 1. Excess molar enthalpies at 298.15 K for the binary mixtures of ethylbenzene (1) + 2-propane (2) (○), + 2-butanone (2) (■), + 2-pentanone (2) (▲), + 2-octanone (2) (●), and + 2-undecanone (2) (▲).

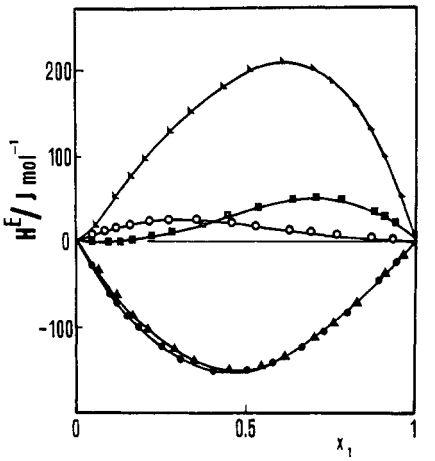

Figure 2. Excess molar enthalpies at 298.15 K for the binary mixtures of (2-chloroethyl)benzene (1) + 2-propanone (2) (○), + 2-butanone (2) (■), + 2-pentanone (2) (▲), + 2-octanone (2) (●), and + 2-undecanone (2) (▲).

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Table I. Experimental Molar Excess Enthalpies H^E for Binary Mixtures of Ethylbenzene or (2-Chloroethyl)benzene + Methyl Alkyl Ketones at 298.15 K

x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
Ethylbenzene (1) + 2-Propanone (2)									
0.0477	63.3	0.2311	269.6	0.4742	356.2	0.7063	281.7	0.8782	120.0
0.0911	123.9	0.2861	307.8	0.5459	346.9	0.7829	218.2	0.9352	57.5
0.1669	212.1	0.3755	345.1	0.6433	316.3	0.8279	176.4		
Ethylbenzene (1) + 2-Butanone (2)									
0.0296	7.5	0.1964	56.5	0.4231	93.4	0.6875	102.6	0.8544	43.9
0.0576	14.6	0.2683	70.4	0.5238	102.1	0.7458	89.0	0.8980	22.0
0.1089	31.7	0.3284	82.1	0.5946	107.6	0.8148	63.0	0.9462	2.3
Ethylbenzene (1) + 2-Pentanone (2)									
0.0351	−1.0	0.2255	−2.8	0.4662	7.2	0.7238	21.5	0.9545	3.8
0.0678	−1.8	0.3039	−1.4	0.5672	14.5	0.8397	16.4		
0.1271	−2.7	0.3680	0.9	0.6359	20.0	0.9129	8.7		
Ethylbenzene (1) + 2-Octanone (2)									
0.0506	−4.5	0.2423	−20.4	0.4603	−20.7	0.7190	4.2	0.9110	12.0
0.0963	−8.6	0.2989	−22.3	0.5613	−12.7	0.7933	10.6	0.9388	9.9
0.1757	−15.8	0.3901	−23.3	0.6574	−2.3	0.8847	13.3		
Ethylbenzene (1) + 2-Undecanone (2)									
0.0655	−2.2	0.2963	−4.8	0.5289	3.4	0.7711	15.8	0.9529	8.6
0.1230	−3.6	0.3596	−3.3	0.6275	9.0	0.8348	16.5		
0.2192	−5.1	0.4571	0.1	0.7164	13.7	0.9100	13.7		
(2-Chloroethyl)benzene (1) + 2-Propanone (2)									
0.0447	6.8	0.1576	18.6	0.3594	22.1	0.6274	11.1	0.8707	2.7
0.0855	12.3	0.2191	21.5	0.4570	19.2	0.6918	8.8	0.9309	0.9
0.1229	15.9	0.2722	22.6	0.5288	16.3	0.7710	5.9		
(2-Chloroethyl)benzene (1) + 2-Butanone (2)									
0.0540	−31.1	0.2550	−122.4	0.5066	−152.0	0.7325	−106.1	0.9426	−23.8
0.1024	−57.0	0.3133	−136.2	0.5779	−143.8	0.8042	−81.8		
0.1858	−95.8	0.4064	−153.7	0.6725	−126.0	0.8915	−43.7		
(2-Chloroethyl)benzene (1) + 2-Pentanone (2)									
0.06360	−39.1	0.2137	−103.7	0.4491	−151.8	0.7098	−114.2	0.9073	−39.8
0.1196	−66.7	0.2896	−127.1	0.5502	−146.1	0.7653	−96.9	0.9514	−22.6
0.1691	−89.2	0.3521	−138.3	0.6198	−135.6	0.8303	−72.9		
(2-Chloroethyl)benzene (1) + 2-Octanone (2)									
0.0474	−1.1	0.1660	1.5	0.3739	18.6	0.6417	45.5	0.8775	33.5
0.0995	−0.9	0.2296	5.4	0.4432	26.6	0.7049	46.9	0.9053	27.6
0.1299	−0.1	0.2847	10.7	0.5442	37.6	0.7818	44.9	0.9348	20.2
(2-Chloroethyl)benzene (1) + 2-Undecanone (2)									
0.0615	27.0	0.2076	93.9	0.4401	178.4	0.7022	197.3	0.8630	129.4
0.1158	50.9	0.2818	126.4	0.5118	196.0	0.7587	186.0	0.9042	96.7
0.1642	74.0	0.3439	148.7	0.6112	205.3	0.8251	151.2	0.9497	53.5

Table II. Coefficients a_k of Redlich–Kister Fits, Equation 1, to Measured Data and Standard Deviations σ, Equation 2, for the Liquid Binary Mixtures Containing Ethylbenzene (1) or (2-Chloroethyl)benzene (1) + Methyl Alkyl Ketones (2)

mixture	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)$/(J mol^{-1})
ethylbenzene (1)						
+2-propanone (2)	1417.6	−153.0	170.4	−173.2	−610.0	1.2
+2-butanone (2)	404.9	214.8	206.4	−429.2	−636.8	1.0
+2-pentanone (2)	38.3	153.8	69.1	−106.7	−96.2	0.1
+2-octanone (2)	−71.6	149.7	142.3			0.2
+2-undecanone (2)	7.9	98.4	70.9	35.7	19.9	0.1
(2-chloroethyl)benzene (1)						
+2-propanone (2)	69.7	−84.4	25.8			0.2
+2-butanone (2)	−614.7	101.6	112.6			1.2
+2-pentanone (2)	−596.8	82.2	52.0			1.4
+2-octanone (2)	132.3	208.0	37.5			0.4
+2-undecanone (2)	777.8	390.6	47.6			1.7

through the mixing cell of the calorimeter. Further details on the apparatus and experimental procedure are given in ref 5. The performance of the calorimeter was checked by measuring H^E for the cyclohexane + hexane mixture at 298.15 K, and these agreed to within the experimental limits with the corresponding literature values (*10*) (less than 0.5% over the central range of concentration).

Results and Discussion

Experimental excess molar enthalpies H^E for the 10 binary mixtures as a function of mole fraction x_1 (Table I and Figures 1 and 2) were fitted to the Redlich–Kister equation

$$H^E/(\text{J mol}^{-1}) = x_1x_2\sum_{k\geq 0} a_k(x_1 - x_2)^k \qquad (1)$$

The adjustable parameters a_k were evaluated by fitting H^E/x_1x_2 to eq 1 by the method of least squares. The standard deviation $\sigma(H)$ is defined by

$$\sigma(H^E) = (\phi_{min}/(N - N_p))^{0.5} \qquad (2)$$

where $\phi = \sum_{j=1}^{n}\eta_j^2$ is the objective function, $\eta_j = H^E/x_1x_2 - \sum_{k\geq 0}a_k(x_1 - x_2)^k$, ϕ_{min} is the minimized objective function, N

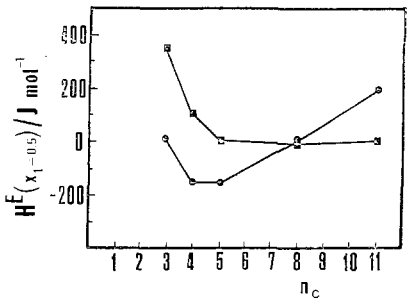

Figure 3. Values of H^E (x_1 = 0.5) at 298.15 K for the binary mixtures of methyl alkyl ketones + ethylbenzene (■) or (2-chloroethyl)benzene (●) as a function of the number n_c of C atoms in the ketone.

is the number of calorimetric experimental points, and N_p is the number of adjustable parameters (Table II).

Excess enthalpies H^E at x_1 = 0.5 have been reported in Figure 3 for all investigated systems.

As can be seen from Figure 1, an increase in the number of C atoms n_C in the ketones in mixtures with ethylbenzene leads to decreasing values of H^E from n = 2 to n_C = 8 and slightly increasing to n_C = 11.

Mixtures of the same ketones with (2-chloroethyl)benzene, Figure 2, show decreasing values of H^E when passing from n_C = 2 to n_C = 4 or 5 and a rapid increase of H^E for n_C = 8 and 11.

Similar trends were observed for mixtures containing toluene, *p*-xylene, pseudocumene (*1*), 1-methylnaphthalene (*2*), 1-chloronaphthalene (*3*), or halothane (*11*) with the same ketones and can be interpreted in terms of group contributions (*11*).

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