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Excess Enthalpies of Binary Mixtures Containing Halothane + Methyl Alkyl Ketones

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Molar excess enthalpies H^E of binary liquid systems of halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) + five methyl alkyl ketones (2-alkanones) have been determined with a flow microcalorimeter at 298.15 K and at atmospheric pressure in the entire composition range. The data were correlated by means of the Redlich–Kister expression. All these mixtures are strongly exothermic with a minimum of H^E of ca. −2900 J mol^{-1} at nearly equimolar composition.

Introduction

The increasing interest in studying halothane (2-bromo-2-chloro-1,1,1-trifluoroethane), a substance used as an anaesthetic in surgery, is evidenced by the numerous papers published recently in the literature.

In continuation of our earlier investigations on liquid-phase enthalpy of binary mixtures containing halothane as a common solvent (*1*, *2*), we have undertaken a detailed study of mixtures containing this compound with five aliphatic ketones, namely, 2-propanone, 2-butanone, 2-hexanone, 2-octanone, and 2-undecanone. The purpose of this paper is to correlate the experimental data and to study the calorimetric behavior as a function of the increasing chain length of ketones.

Experimental Section

Purity of Materials. Halothane (Aldrich product; analytical grade 99%, stabilized with 0.01% thymol) was purified as described in ref 1. 2-Propanone and 2-butanone (C. Erba and Aldrich products; analytical grade 99.7% and 99.9%, respectively) were used without further purification. 2-Hexanone, 2-octanone, and 2-undecanone (Aldrich products; analytical grade 99%, 98%, and 99%, respectively) were distilled following the method of Collerson et al. (*3*). All purified compounds were stored in dark bottles over molecular sieves (Union Carbide; type 4A $^1/_{16}$-in. pellets).

Apparatus and Procedure. The densities of the liquids, necessary to evaluate fluxes and hence mole fraction in the calorimetric measurements, were determined in previous papers (*1*, *4–6*) by means of a two-capillary pycnometer (31.41-mL volume at 297.45 K), described elsewhere (*4*).

Table I. Experimental Molar Excess Enthalpies H^E for the Halothane (1) + Aliphatic Ketones (2) Systems as a Function of the Mole Fraction x_1 of Halothane 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})
		Halothane + 2-Propanone			
0.457	−390.1	0.3167	−2092.4	0.7355	−2252.8
0.1039	−739.7	0.4101	−2517.8	0.8066	−1800.0
0.1481	−1054.8	0.5106	−2770.2	0.8476	−1456.2
0.1881	−1317.3	0.5817	−2769.2	0.8930	−1038.9
0.2580	−1759.4	0.6759	−2559.9	0.9435	−547.6
		Halothane + 2-Butanone			
0.0660	−564.2	0.2978	−2194.4	0.7179	−2317.9
0.0959	−801.1	0.3612	−2502.0	0.7723	−1934.6
0.1239	−1014.5	0.4589	−2822.1	0.8358	−1441.4
0.1749	−1411.0	0.5599	−2845.0	0.8715	−1131.0
0.2204	−1724.5	0.6291	−2718.9	0.9105	−778.4
				0.9532	−396.1
		Halothane + 2-Hexanone			
0.0463	−323.6	0.2800	−1993.3	0.7000	−2458.4
0.0886	−616.4	0.3684	−2475.5	0.7778	−1957.6
0.1273	−922.8	0.4375	−2726.7	0.8238	−1610.2
0.1628	−1182.7	0.5384	−2885.5	0.8750	−1153.1
0.2258	−1629.8	0.6363	−2719.7	0.9334	−631.6
		Halothane + 2-Octanone			
0.0580	−417.8	0.3303	−2241.0	0.7474	−2174.0
0.1097	−719.3	0.4252	−2660.3	0.8161	−1690.7
0.1562	−1060.4	0.4966	−2785.4	0.8557	−1381.5
0.1978	−1409.0	0.5967	−2759.2	0.8988	−997.6
0.2700	−1981.1	0.6894	−2492.1	0.9467	−533.8
		Halothane + 2-Undecanone			
0.0750	−358.3	0.3937	−2222.5	0.7957	−1742.9
0.1396	−748.4	0.4934	−2524.7	0.8539	−1322.9
0.1958	−1106.6	0.5650	−2565.5	0.8864	−1047.1
0.2451	−1422.9	0.6608	−2410.0	0.9212	−754.6
0.3275	−1912.4	0.7450	−2038.7	0.9590	−409.8

Table II. Coefficients a_k and Standard Deviations $\sigma(H^E)$ Obtained by Least-Squares Analysis with Equation 1

systems	a_0	a_1	a_2	a_3	$\sigma(H^E)$/(J mol^{-1})
halothane					
+ 2-propanone	−11013	−2950	2551	1809	7.8
+ 2-butanone	−11477	−1480	3091	1893	8.2
+ 2-hexanone	−11448	−2214	3627	1132	8.0
+ 2-octanone	−11181	−2175	2676	576	9.4
+ 2-undecanone	−10099	−3025	3266		6.9

Molar excess enthalpies H^E for the five systems were obtained by using a flow microcalorimeter LKB (Model 2107, Produkter AB, Bromma, Sweden). Full automatic burets ABU (Radiometer, Copenhagen, Denmark) are used to pump the pure liquids into the mixing cell. The apparatus and the procedure used were the same as those described in refs 7 and 8. The microcalorimeter was electrically calibrated before use

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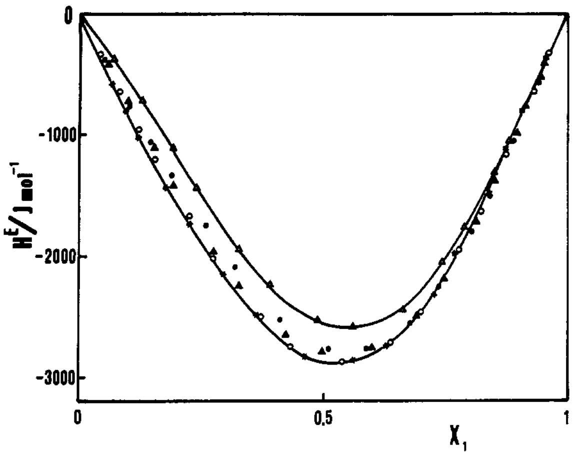

Figure 1. Experimental molar excess enthalpies H^E for halothane (1) + 2-propanone (2) (●), + 2-butanone (2) (✱), + 2-hexanone (2) (○), + 2-octanone (2) (▲), or + 2-undecanone (2) (△) at 298.15 K. The curves were calculated by eq 1 with the parameters of Table II.

and calibration subsequently checked by using the standard cyclohexane + hexane mixture (*9*). The discrepancy between calculated and experimental H^E values was less than 1% in the central range of the mole fraction. All measurements were made at an average temperature of 298.15 ± 0.01 K.

Results and Discussion

The experimental data for the five systems and the results of the least-squares analysis are listed in Tables I and II, respectively, and are presented graphically in Figure 1.

Correlation of the molar excess enthalpies was carried out by the usual Redlich-Kister relation

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

where x_1 denotes the mole fraction of halothane and x_2 that of ketone. Values of coefficients a_k and the standard deviation $\sigma(H^E)$ were evaluated by means of a least-squares method, described in ref 4. As can be seen from Figure 1, all the curves H^E vs x_1 are almost symmetric at x_1 about 0.5 and show large negative values with $H^E(x_1=0.5)$ ranging from -2500 to -2900 J mol^{-1}. A qualitative interpretation of this behavior may be given by considering that the high negative values of H^E are due to the strong H bonding between the positively charged H atom of halothane and the negatively charged O atom of the ketones. Curves referring to all ketones but 2-undecanone are largely overlapped and intersect each other, whereas the one of 2-undecanone is well distinct from the other curves.

Figure 2 represents a plot of $H^E(x=0.5)$ vs the site fraction of the CO group in the 2-alkanones (*10*). The nearly parabolic trend is easily predicted by simple group contribution considerations (*11*) applied to mixtures of a common solvent with a homologous series of compounds containing a functional group that strongly interacts with the solvent. Mixtures of 1-chloronaphthalene with the homologous series of dichloroalkanes behave similarly (*12*).

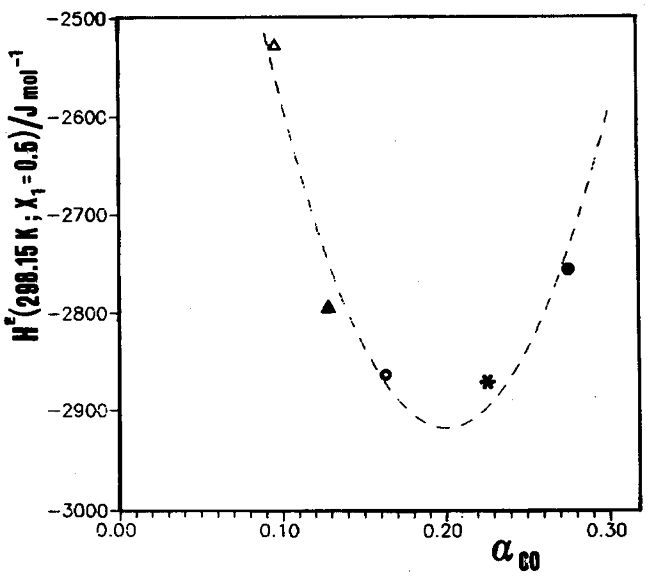

Figure 2. Equimolar excess enthalpies for halothane + 2-alkanones at 298.15 K, H^E (298.15 K;x=0.5), as a function of the site fraction α_{CO} of the CO group in the 2-alkanone (*10*). The same symbols are used as in Figure 1.

Glossary

a_k	parameters in eq 1
H^E	molar excess enthalpy, J mol^{-1}
T	temperature, K
x_1,x_2	mole fraction of halothane and component 2 (ketone), respectively

Registry No. Halothane, 151-67-7; 2-propanone, 67-64-1; 2-butanone, 78-93-3; 2-hexanone, 591-78-6; 2-octanone, 111-13-7; 2-undecanone, 112-12-9.

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