Liquid-Phase Excess Enthalpies for the Binary Mixtures of 1-Chloronaphthalene + Dichloroalkanes

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Excess enthalpies H^E of the binary liquid systems 1-chloronaphthalene + five dichloroalkanes were determined at 298.15 K by means of a flow microcalorimeter. The experimental H^E values were correlated with the Redlich–Kister equation. H^E is positive for the short-chain dichloroalkanes, increasing from dichloromethane to 1,2-dichloroethane and then decreasing for 1,2-dichloropropane, to become increasingly negative for 1,4-dichlorobutane, and 1,10-dichlorodecane.

Introduction

In continuation of a long-term study of liquid mixtures containing 1-chloronaphthalene as a common solvent (*1*), we report now the molar excess enthalpies H^E of 1-chloronaphthalene with several dichloroalkanes. The systems covered were chosen to study the influence of chain length and proximity of Cl atoms in the dichloroalkanes on the calorimetric behavior of the mixtures. Five dichloroalkanes were taken into consideration: dichloromethane, 1,2-dichloroethane, 1,2-dichloropropane, 1,4-dichlorobutane, and 1,10-dichlorodecane.

Calorimetric data were obtained at 298.15 ± 0.005 K. No literature values could be found for any one of these mixtures.

Experimental Section

Materials. The sources and stated purities of the chemicals are listed in Table I. 1-Chloronaphthalene was purified as described in ref 1. Dichloromethane was used without further purification; the other chloroalkanes were dried and fractionally distilled in a 60-cm Widmer column. Prior to use, all the compounds were stored in the dark over molecular sieves (Union Carbide, type 4A, $^1/_{16}$-in. pellets).

Density Measurements. Since in the calorimetric measurements flow rates and hence mole fractions are influenced by the density of the liquid components, density values ρ of the pure components were determined with a two-capillary pycnometer (volume, 31.41 mL at 297.45 K) calibrated with distilled mercury (*2*). The densities of 1-chloronaphthalene and 1,2-dichloroethane are reported in earlier papers (*1, 3*). The densities of the other chloroalkanes were measured at different temperatures T under atmospheric pressure and were fitted by the following linear equation

$$\rho/(\text{kg m}^{-3}) = A + B((T/\text{K}) - 273.15) \qquad (1)$$

Coefficients A and B, correlation coefficient R, and sample standard deviation $\sigma(\rho)$ obtained by the least-squares method are given in Table II. There is good agreement between our experimental data and literature values (Table II).

Table I. Source and Purity of the Chemicals

component	vendor	stated purity, %
1-chloronaphthalene	Kodak	99.5+
dichloromethane	Aldrich	99.99
1,2-dichloroethane	Fluka	99.5+
1,2-dichloropropane	Fluka	99+
1,4-dichlorobutane	Aldrich	99+
1,10-dichlorodecane	Aldrich	99+

Calorimetric Measurements. Molar excess enthalpies H^E were measured in an LKB flow microcalorimeter, Model 2107, AB (Bromma, Sweden) as described in ref 4. The microcalorimeter was calibrated electrically before use (*2*), and its performance was checked by determining the H^E at 298.15 K of the test system cyclohexane–hexane over the whole composition range. Our results agree within 0.5% over the central range of composition with literature data (*5*).

Results

The experimental molar enthalpies, H^E_{exp}, of the five binary systems, (Table III and Figure 1) were fitted by least-squares to the Redlich–Kister equation

$$H^E/(\text{J mol}^{-1}) = x_1x_2\sum_{k\geq 0} a_k(x_1 - x_2)^k \qquad (2)$$

where the a_k's are adjustable parameters and x_1 and x_2 are respectively the mole fractions of 1-chloronaphthalene and of the second component. The coefficients a_k and the standard deviations

$$\sigma(H^E) = |\sum(H^E_{\text{exp}} - H^E)^2/(N - n)|^{0.5} \qquad (3)$$

where N is the number of experimental points and n the number of coefficients a_k, are reported in Table IV.

Discussion

As can be seen from Figure 1, the mixtures of 1-chloronaphthalene with the two short-chain dichloroalkanes, dichloromethane and 1,2-dichloroethane, show positive H^E, increasing with the number of C atoms. Instead, the H^E of the higher dichloroalkanes we investigated decreases with an increasing number of C atoms, i.e., with a decrease in the site fraction of Cl atoms on the molecule, reaching large negative values (Figure 1). However, since H^E of 1-chloronaphthalene

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Table II. Densities ρ of Dichloroalkanes as a Function of Temperature T, Coefficients A and B (Equation 1), Standard Deviations $\sigma(\rho)$, and Correlation Coefficients R

	dichloromethane		1,2-dichloropropane		1,4-dichlorobutane		1,10-dichlorodecane	
	T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})
	290.05	1331.3	291.05	1158.6	293.05	1146.3	293.15	995.8
	291.05	1329.4	292.65	1156.6	294.25	1145.1	294.50	994.8
	292.30	1327.3	294.20	1154.5	295.45	1143.6	295.00	994.4
	293.55	1324.8	295.65	1152.5	297.00	1420.0	295.15 (994.1)^c	994.3
	295.40	1321.7	297.10	1150.6	298.15	1140.7 (1140.8)^b	296.40	993.2
	296.90	1319.0	298.15	1149.3 (1149.4)^a	299.25	1139.6	298.15	991.8
	298.15	1316.8 (1316.8)^a	299.65	1147.2	300.60	1138.1	300.35	990.8
	299.40	1314.5	300.50	1146.1	301.95	1136.6	301.90	988.8
	300.85	1311.8	301.65	1144.6	303.25	1135.1	303.55	987.5
	302.55	1308.8	302.70	1143.3	304.70	1133.6	304.85	986.4
	303.85	1306.4	303.65	1141.9	305.95	1132.1		
A	1361.6		1182.5		1168.2		1011.9	
B	−1.7968		−1.3288		−1.1006		−0.8041	
$\sigma(\rho)$/(kg m^{-3})	0.07		0.05		0.05		0.04	
R	0.99997		0.99996		0.99994		0.99992	

^{a}Reference 10. ^{b}Reference 11. ^{c}Reference 12.

Table III. Experimental Liquid-Phase Molar Excess Enthalpies H^E at 298.15 K of 1-Chloronaphthalene (1) + Dichloroalkane (2) Mixtures as a Function of Mole Fraction x_1

dichloromethane		1,2-dichloroethane		1,2-dichloropropane		1,4-dichlorobutane		1,10-dichlorodecane	
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})
0.0378	38.1	0.0462	76.9	0.0565	49.2	0.0635	−18.7	0.0609	−169.5
0.0729	64.7	0.0883	131.7	0.1071	86.7	0.1196	−36.6	0.1148	−311.2
0.1055	84.5	0.1269	174.1	0.1524	112.0	0.1691	−51.3	0.2061	−507.3
0.1333	98.2	0.1623	209.4	0.1934	135.6	0.2135	−63.5	0.2803	−627.7
0.1909	124.6	0.2252	257.4	0.2645	162.6	0.2894	−82.8	0.3418	−706.8
0.2393	139.3	0.2793	289.4	0.3241	177.6	0.3519	−98.2	0.4379	−802.6
0.3206	153.3	0.3676	307.7	0.4184	183.4	0.4489	−126.3	0.5094	−839.0
0.4145	157.7	0.4658	304.0	0.5190	177.7	0.5500	−136.7	0.6090	−832.1
0.4855	158.8	0.5376	287.7	0.5899	165.5	0.6200	−137.2	0.7003	−749.7
0.5960	146.8	0.6346	252.0	0.6834	139.6	0.7097	−128.9	0.7570	−669.6
0.6537	131.6	0.6993	216.5	0.7421	118.8	0.7652	−116.4	0.8238	−540.2
0.7390	101.4	0.7772	170.7	0.8119	89.8	0.8302	−101.3	0.8617	−445.5
0.7906	76.6	0.8230	139.3	0.8520	72.1	0.8670	−79.7	0.9033	−334.7
0.8499	52.5	0.8746	102.7	0.8962	50.6	0.9072	−61.2	0.9257	−255.5
0.9189	25.9	0.9331	60.0	0.9453	27.4	0.9514	−33.2	0.9492	−182.4
								0.9740	−90.6

Table IV. Coefficients a_k and Standard Deviations $\sigma(H^E)$ (Equations 1 and 2)

	a_0	a_1	a_2	a_3	$\sigma(H^E)$/(J mol^{-1})
1-chloronaphthalene (1) +					
dichloromethane	633.1	−153.0	−6.0	−313.0	18
1,2-dichloroethane	1203.9	−468.4	70.1	206.3	2.4
1,2-dichloropropane	725.4	−222.4			1.0
1,4-dichlorobutane	−523.2	−239.8			1.2
1,10-dichlorodecane	−3357.6	−485.8			7.0

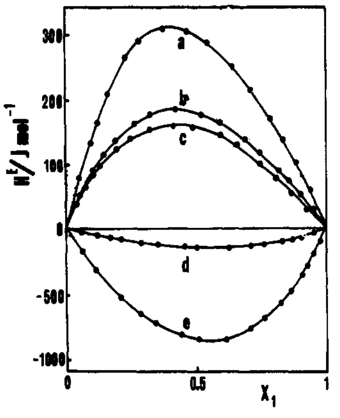

Figure 1. Liquid-phase molar excess enthalpies H^E for the mixtures 1-chloronaphthalene (1) + dichloroalkane (2) at 298.15 K: dichloromethane (c), 1,2-dichloroethane (a), 1,2-dichloropropane (b), 1,4-dichlorobutane (d), and 1,10-dichlorodecane (e). (●) Experimental values; (—) calculated by eq 2 with the parameters a_k of Table IV.

(1) + n-alkanes (2) has fairly large positive values, e.g., 665 J mol^{-1} with hexane at 298.15 K and x_1 = 0.5 (*6*, *7*), we may expect that H^E with still higher dichloroalkanes will go through a minimum and then increase to reach positive values. This trend is easily predicted by simple group contribution considerations (*8*) applied to mixtures of a common solvent with a homologous series of compounds containing a functional group which strongly interacts with the solvent.

The relatively small H^E value of 1-chloronaphthalene + dichloromethane is certainly due to the "proximity effect" of the Cl atoms in dichloromethane (*9*).

Glossary

a_k	parameters in eq 2
A, B	parameters in eq 1
H^E	liquid-phase molar excess enthalpy, J mol^{-1}
R	correlation coefficient, Table II
N	number of experimental points, eq 3
n	number of parameters, eq 3

T	absolute temperature, K
x_i	mole fraction of component i (i = 1, 1-chloronaphthalene, i = 2, dichloroalkanes)

Greek Letters

ρ	density, kg m^{-3}
$\sigma(\rho)$, $\sigma(H^E)$	standard deviations, Tables II and IV

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