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THERMODYNAMICS OF BINARY MIXTURES OF ALKANONE–CHLOROALKANE.
I. HEAT OF MIXING OF n-ALKANONE–1-CHLOROHEXADECANE MIXTURES AT 298.15 K

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ABSTRACT

The molar excess enthalpies H^E have been determined as a function of mole fraction x at atmospheric pressure and 298.15 K for six n-alkanone–1-chlorohexadecane mixtures. The n-alkanones were 2-pentanone, 3-pentanone, 2-heptanone, 4-heptanone, 2-nonanone and 5-nonanone. All the mixtures show positive molar excess enthalpies.

INTRODUCTION

We are interested in the study of the thermodynamic behaviour of alkanone–chloroalkane mixtures. The aim of this study is to characterize the interactions between the carbonyl and chloro groups. For this purpose we have initiated a systematic study of the thermodynamic excess properties (H^E, G^E, V^E, C_p^E) of this kind of mixture. In this paper we report excess enthalpies, H^E of mixtures formed by 2-pentanone(1), 3-pentanone(1), 2-heptanone(1), 4-heptanone(1), 2-nonanone(1) and 5-nonanone(1) with 1-chlorohexadecane(2) at 298.15 K and atmospheric pressure.

EXPERIMENTAL

A standard Calvet type microcalorimeter, equipped with a batch mixing cell with small ($< 2\%$) vapour phase was used. The experimental technique of Paz Andrade et al. [1] was employed to determine the excess enthalpies over the whole mole fraction range (x). The microcalorimeter was calibrated electrically and the calibration was checked by determining the molar excess

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TABLE 1

Physical properties of pure compounds

Compound	Refractive index η(D, 298.15 K)		Density ρ(298.15 K) (kg m^{-3})	
	This study	Literature	This study	Literature
2-Pentanone	1.3882	1.3880	801.6	801.5
3-Pentanone	1.3899	1.39002	809.5	809.45
2-Heptanone	1.4066	1.40655	811.1	811.07
4-Heptanone	1.4046	1.4045	811.4	811.6
2-Nonanone	1.4188	1.4187	817.3	817.2
5-Nonanone	1.4174	1.41796	818.3	817.1
1-Chlorohexadecane	1.4480	1.4505 [a]	861.2	865.2 [a]

[a] 293.15 K.

enthalpy of n-hexane–cyclohexane, benzene–cyclohexane and tetrachloromethane–benzene at 298.15 K over the entire range of mole fraction. Our results differ by less than 1% from those in the literature near $x = 0.5$ [2–4]. It was found that the corrections in H^E and x due to the vapour phase, are smaller than 0.1 J mol^{-1} and 0.0001, respectively. The calorimeter was thermostatted at 298.15 ± 0.005 K.

2-Pentanone (Fluka, purum, > 99 mol.%), 3-pentanone (Fluka, purum, ≃ 99 mol.%), 2-heptanone (Fluka, purum, > 98 mol.%), 4-heptanone (Fluka, purum, ≃ 98 mol.%), 2-nonanone (Fluka, purum, ≃ 97 mol.%), 5-nonanone (Fluka, purum, > 97 mol.%) and 1-chlorohexadecane (Aldrich, ≃ 99 mol.%) were used without further purification. Prior to the actual measurements, all liquids were dried over molecular sieves (Union Carbide Type 4A from Fluka). The results of the measurements of the densities and refractive indices are given in Table 1 and are in good agreement with published values [5–7]. Binary mixtures were prepared by mass. All weighings were corrected for buoyancy effects and the error of the final mole fraction is estimated to be less than 0.0001. Conversion to molar quantities is based on the relative atomic mass table of 1976 issued by IUPAC [8].

RESULTS AND DISCUSSION

Table 2 gives experimental results of H^E as a function of the mole fraction x of alkanone. These data were fitted by unweighted least-squares polynomial regression to the equation

$$H^E(\text{J mol}^{-1}) = x(1-x)\sum_{i=0}^{k} A_i(2x-1)^i \tag{1}$$

The coefficients A_i and the standard deviations $\sigma(H^E)$

$$\sigma(H^E) = \left|\sum\left(H^E_{\text{cal}} - H^E_{\text{exp}}\right)^2/(N-n)\right|^{1/2} \tag{2}$$

TABLE 2

Molar excess enthalpy H^{E} for n-alkanone + 1-chlorohexadecane mixtures at 298.15 K

x	H^{E} (J mol^{-1})	x	H^{E} (J mol^{-1})
2-Pentanone(1)–1-chlorohexadecane(2)			
0.1293	340	0.5383	951
0.2040	521	0.5673	952
0.2419	609	0.6191	944
0.3102	734	0.6516	931
0.3338	772	0.7169	875
0.3753	836	0.7605	811
0.4159	884	0.8071	719
0.4247	890	0.8569	592
0.4638	914	0.9002	467
0.5140	946	0.9536	253
2-Heptanone(1)–1-chlorohexadecane(2)			
0.1207	255	0.5291	647
0.1516	305	0.5565	645
0.1757	353	0.6093	631
0.2198	419	0.6676	610
0.2807	498	0.7172	564
0.3227	536	0.7607	512
0.3589	571	0.8078	455
0.4148	608	0.8547	378
0.4611	630	0.9007	280
0.5109	643		
2-Nonanone(1)–1-chlorohexadecane(2)			
0.1022	136	0.4939	408
0.1409	181	0.5578	410
0.1781	221	0.6103	399
0.2201	262	0.6600	383
0.2558	294	0.7105	354
0.3166	338	0.7518	324
0.3694	371	0.8092	278
0.4007	386	0.8513	229
0.4595	401	0.8997	171
3-Pentanone(1)–1-chlorohexadecane(2)			
0.1050	232	0.4470	804
0.1765	395	0.4993	843
0.1781	394	0.5294	853
0.2003	439	0.5635	851
0.2247	503	0.5988	863
0.2394	537	0.6576	839
0.2469	542	0.7140	790
0.2637	581	0.7545	735
0.3019	647	0.8099	643
0.3368	685	0.8550	548
0.3406	694	0.9021	412
0.4008	762	0.9520	232
0.4070	772		

(continued)

TABLE 2 (continued)

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
4-Heptanone(1)–1-chlorohexadecane(2)			
0.1354	230	0.4993	566
0.1555	260	0.5579	567
0.2160	347	0.5981	569
0.2415	379	0.6744	541
0.2982	437	0.7154	512
0.3282	471	0.7674	458
0.3625	501	0.8085	411
0.4173	532	0.8556	341
0.4616	556	0.9054	236
5-Nonanone(1)–1-chlorohexadecane(2)			
0.1051	149	0.5606	434
0.1768	235	0.6027	429
0.2195	283	0.6168	423
0.2541	318	0.6595	402
0.3249	371	0.7039	375
0.3651	396	0.7543	333
0.4156	417	0.8051	289
0.4675	432	0.8495	240
0.5067	435	0.9051	164

where N is the number of direct experimental values and n the number of coefficients of the polynomial, are summarized in Table 3. For all the mixtures $\sigma(H^E)/H^E(\max) < 0.01$, where $H^E(\max)$ denotes the maximum of the H^E value with respect to x. The direct experimental results and the curves calculated from eqn. (1) are represented graphically in Fig. 1. No literature data exist for comparison.

For all the mixtures studied the molar excess enthalpy is positive over the whole range of mole fraction. For the series of symmetrical n-alkanones and

TABLE 3

Coefficients A_i in eqn. (1) and standard deviation $\sigma(H^E)$ (eqn. (2)) at 298.15 K for n-alkanone(1)–1-chlorohexadecane(2) mixtures

n-Alkanone	A_0	A_1	A_2	A_3	$\sigma(H^E)$ (J mol^{-1})
2-Pentanone	3759.6	876.5	425.5	821.8	5
2-Heptanone	2564.7	354.6	294.6	156.3	3
2-Nonanone	1746.7	132.3	−18.5	99.9	2
3-Pentanone	3367.1	865.1	317.2	777.2	6
4-Heptanone	2266.9	452.1	174.0	141.3	3
5-Nonanone	1634.5	178.5	50.6	110.5	2

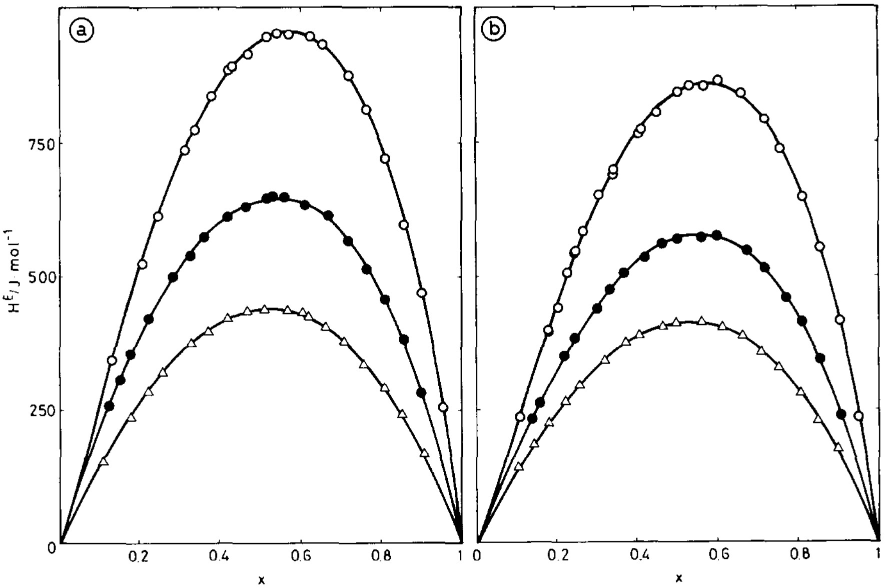

Fig. 1. Molar excess enthalpy H^{E} for n-alkanone(1)–1-chlorohexadecane(2) mixtures vs. x (the mole fraction of component 1): (a), (○) 2-pentanone, (●) 2-heptanone, (△) 2-nonanone; (b), (○) 3-pentanone, (●) 4-heptanone, (△) 5-nonanone. Full curves represent eqn. (1) with the coefficients of Table 3.

for the unsymmetrical n-alkanones the H^{E} maximum decreases as the chain length of the alkanone molecule increases.

For each pair of isomeric n-alkanones the molar excess enthalpy is larger for the unsymmetrical n-alkanone than for the symmetrical n-alkanone. This behaviour can be ascribed to the steric hindrance of the adjacent alkyl groups, since the dipole moments of normal alkanones have nearly the same value [9].

This difference decreases as the chain length of the n-alkanones increases: ΔH^{E}(2-pentanone, 3-pentanone) $\simeq$ 98 J mol^{-1}; ΔH^{E}(2-heptanone, 4-heptanone) $\simeq$ 74 J mol^{-1}; ΔH^{E}(2-nonanone, 5-nonanone) $\simeq$ 28 J mol^{-1} (all H^{E} values were evaluated at $x = 0.5$).

It is interesting to note that this behaviour is very similar to that observed in mixtures of n-alkonones with n-alkanes [10].

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