Thermochimica Acta, 95 (1985) 105–110
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS OF BINARY MIXTURES CONTAINING ALDEHYDES. EXCESS ENTHALPIES OF *n*-ALKANALS + BENZENE AND + TETRACHLOROMETHANE MIXTURES

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(Received 4 May 1985)

ABSTRACT

Molar excess enthalpies H^E have been measured as a function of mole fraction at atmospheric pressure and 298.15 K for the binary liquid mixtures of ethanal, propanal, butanal and pentanal + benzene or + tetrachloromethane. The results show that the excess enthalpies decrease with increasing the *n*-alkanal chain length, with negative values for *n*-pentanal.

INTRODUCTION

In previous studies [1–4], we investigated the thermodynamic properties of *n*-alkanal $CH_3(CH_2)_{k-2}$–CHO (F_k) + *n*-alkane mixtures. We applied the quasi-chemical group contribution theory in the form of the surface interaction version [4]. By replacing the *n*-alkane with other solvents, we increase the number of surface-type and, consequently, the number of interchange parameters. For a systematic study one should replace the *n*-alkane with other homogeneous solvents, i.e., those having only one type of surface. The most typical are, in order of increasing "activity": cyclohexane, benzene and tetrachloromethane. Cyclohexane being the most *n*-alkane-like solvent, we have devoted the first study to *n*-alkanal + cyclohexane mixtures [5,6].

A survey of the literature revealed that no calorimetric molar excess enthalpy, H^E, data for *n*-alkanal + benzene or + tetrachloromethane mixtures are available except some preliminary measurements for *n*-butanal + benzene mixtures [1,2]. Hence, we decided to measure H^E in a systematic way for eight binary mixtures of *n*-alkanals + benzene or + tetrachloromethane, $CH_3(CH_2)_{k-2}$–CHO + C_6H_6 or + CCl_4 ($k = 2, 3, 4, 5$).

EXPERIMENTAL

Materials

Aldehydes are easily oxidized and polymerized. Hence, the material (Fluka AG, Switzerland, pure reagent grade) was first dried over a molecular

0040-6031/85/$03.30

sieve (type 3A) and then distilled in a dry nitrogen atmosphere. Purities were higher than 99% as determined by GLC using a Chromosorb W80-100 mesh column. The benzene and tetrachloromethane (Fluka AG, Switzerland, extrapure reagent grade for spectroscopy) were employed without further purification.

In order to avoid oxidation, a dry-box with flowing nitrogen was always used for any kind of manipulation.

Procedure

Enthalpies of mixing were measured at 298.15 ± 0.10 K using a Tian–Calvet type calorimeter tilted manually. The batch mixing cell and the experimental procedure have been described elsewhere [7].

The calorimeter was calibrated by means of the Joule effect and the calibration repeated after each experiment. Check measurement for benzene + cyclohexane [8] indicates that the precision of the results is ~ 1.5%.

RESULTS AND DISCUSSION

The direct experimental $H^{\mathrm{E}}_{\mathrm{exp}}$ values, reported in Tables 1 and 2, were fitted to the smoothing equation

$$H^{\mathrm{E}} = x_1 x_2 \sum_{i=0}^{N-1} a_i (x_1 - x_2)^i \tag{1}$$

where x_1 is the mole fraction of *n*-alkanal and x_2 that of benzene or tetrachloromethane. Values of the coefficients a_i and the standard deviations $\sigma(H^{\mathrm{E}})$ are given by

$$\sigma(H^{\mathrm{E}}) = \left[\sum\left(H^{\mathrm{E}} - H^{\mathrm{E}}_{\mathrm{exp}}\right)^2/(N-n)\right]^{1/2} \tag{2}$$

(where N is the number of experimental points and n the number of coefficients a_i). These were determined by least-squares analyses and are reported in Table 3.

Though a detailed treatment of all our results, mainly in terms of group-contribution theory, will be the subject of a future article, a preliminary qualitative discussion of several features of the present work seems justified.

First, we note the pronounced decrease in H^{E} in each case when changing from cyclohexane to benzene as second component. Second, when comparing the excess enthalpy, say, H^{E} ($T = 298.15$ K; $x_1 = 0.5$), of an *n*-alkanal (F_k) + an active solvent (s, benzene or tetrachloromethane) with that pertaining to its homomorphic alkane (A_k), the increment $\Delta = H^{\mathrm{E}}(\mathrm{F}_k) - H^{\mathrm{E}}(\mathrm{A}_k)$ is always a rather larger negative quantity.

TABLE 1

Experimental molar excess enthalpies, H^E, for $CH_3(CH_2)_{k-2}$-CHO (F_k) (1)+C_6H_6 (2) mixtures at 298.15 K (k is the number of C atoms in the n-alkanal)

	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
F_2 (ethanal)				
	0.0355	67	0.4681	238
	0.0689	109	0.5644	208
	0.1213	150	0.6466	171
	0.1629	190	0.7287	133
	0.2180	221	0.8208	85
	0.2840	244	0.8607	66
	0.3962	252	0.9285	29
	0.4569	243		
F_3 (propanal)				
	0.0867	54	0.5716	40
	0.1285	69	0.7069	12
	0.1930	82	0.7894	2
	0.3017	85	0.8751	−4
	0.3502	79	0.9130	−6
	0.4143	70	0.9645	−4
	0.4791	59		
F_4 (butanal)				
	0.1000	+10	0.5913	−57
	0.1968	−2.7	0.6860	−51.9
	0.2774	−16	0.7664	−42.2
	0.3527	−30	0.7996	−32.8
	0.3965	−36.9	0.8768	−21
	0.4979	−53		
F_5 (pentanal)				
	0.0463	−5	0.5332	−83
	0.1014	−14	0.6430	−79
	0.1645	−29	0.7204	−70
	0.2500	−47	0.7964	−58
	0.3462	−65	0.9122	−27
	0.4393	−78	0.9122	−27

Measurements for mixtures with benzene as second component are $\Delta(k = 5;\ s = C_6H_6) = -985$ J mol^{-1} [9].

Thermodynamic excess properties of compounds containing the carbonyl group + benzene mixtures have been qualitatively discussed in terms of specific n–π interactions [10]. The Δ increments for mixtures with tetrachloromethane are of similar magnitude, that is to say $\Delta(k = 5;\ s = CCl_4) = -372$ J mol^{-1} [11].

Specific interactions of the n–σ type have been postulated for mixtures of tetrachloromethane with a polar compound, i.e., ether; evidence includes compound formation as observed in solid–liquid phase diagrams and dielec-

TABLE 2

Experimental molar excess enthalpies, H^E, for $CH_3(CH_2)_{k-2}$-CHO (F_k) (1)+CCl_4 (2) mixtures at 298.15 K (k is the number of C atoms in the n-alkanal)

	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
F_2 (ethanal)				
	0.0738	101	0.6357	276
	0.1286	166	0.7036	235
	0.1784	217	0.7929	175
	0.2505	275	0.8431	139
	0.3142	262	0.9111	84
	0.3570	307	0.9536	43
	0.4068	327		
	0.4868	326		
	0.5570	308		
F_3 (propanal)				
	0.0593	48	0.5112	115
	0.1013	72	0.6140	95
	0.1536	96	0.7136	69
	0.2102	112	0.8023	44
	0.2810	127	0.8567	30
	0.3985	130	0.9045	15
			0.9437	6
F_4 (butanal)				
	0.0397	12	0.4996	8
	0.0604	18	0.5338	1
	0.1013	24	0.6211	−10
	0.1105	28	0.7347	−17
	0.1500	32	0.8116	−16
	0.1975	35	0.8479	−15
	0.2482	37	0.9098	−10
	0.3088	34	0.9446	−5
	0.4079	22		
F_5 (pentanal)				
	0.0203	−1	0.4098	−50
	0.0497	−5	0.4612	−56
	0.1056	−12	0.5090	−58
	0.1711	−19	0.6033	−63
	0.2200	−25	0.7206	−54
	0.2971	−37	0.8027	−42
	0.3505	−43	0.8800	−27

tric behaviour [12]. As shown in Figs. 1 and 2 the excess enthalpies decrease when the number of alkyl groups of the n-alkanal, k, increases, assuming negative values for $k \geqslant 4$. This confirms the weakening of the dipole–dipole interactions (CHO–CHO) previously observed when using n-alkane or cyclohexane as solvent [4,6], and also confirms the existence of specific

TABLE 3

Values of the coefficients a_i of eqn. (1) and standard deviation, $\sigma(H^E)$, eqn. (2), of the experimental molar excess enthalpies, H^E, for $CH_3(CH_2)_{k-2}$-CHO(F_k) (1)+C_6H_6 or CCl_4 (2) mixtures at 298.15 K (k is the number of C atoms in the n-alkanal)

F_k n-Alkanal	(2)	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)$ (J mol^{-1})
F_2 ethanal	C_6H_6	926	−568	−6	−125	257	1.7
	CCl_4	1284	−349	−66	73	42	1.7
F_3 propanal	C_6H_6	359	−422	145	−34	–	1.1
	CCl_4	457	−294	102	−136	−76	1.1
F_4 butanal	C_6H_6	−210	−176	265	–	–	1.5
	CCl_4	7	−247	86	13	16	0.7
F_5 pentanal	C_6H_6	−327	−89	87	−42	48	0.7
	CCl_4	−223	−113	63	37	–	0.9

intermolecular interactions between the polar group (CHO) and the π-electrons of benzene (n–π) or between CHO and the polar group (–Cl) or tetrachloromethane (n–σ).

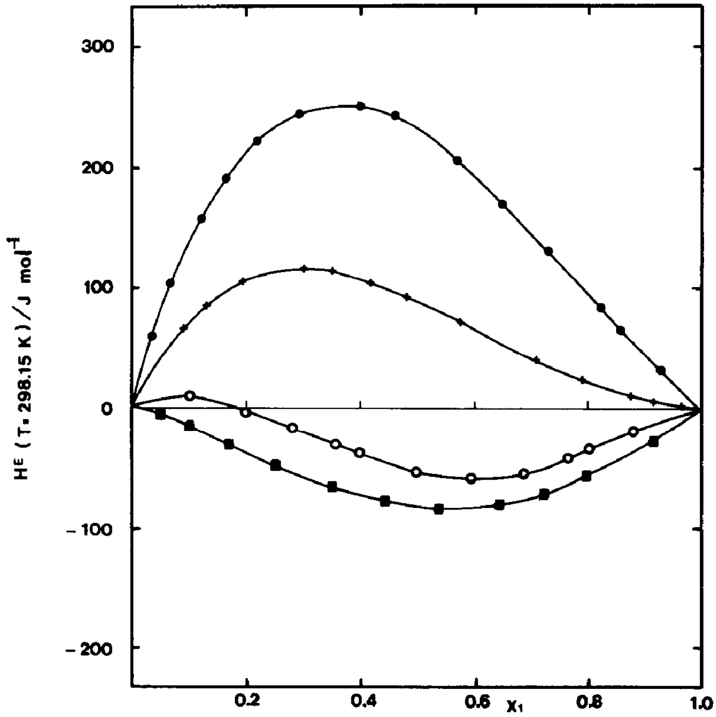

Fig. 1. Molar excess enthalpies, H^E, at 298.15 K, of n-alkanal (1)+benzene (2) mixtures versus x_1, the mole fraction of n-alkanal. Experimental results: F_2, ethanal (●); F_3, propanal (+), F_4, butanal (○); F_5, pentanal (■).

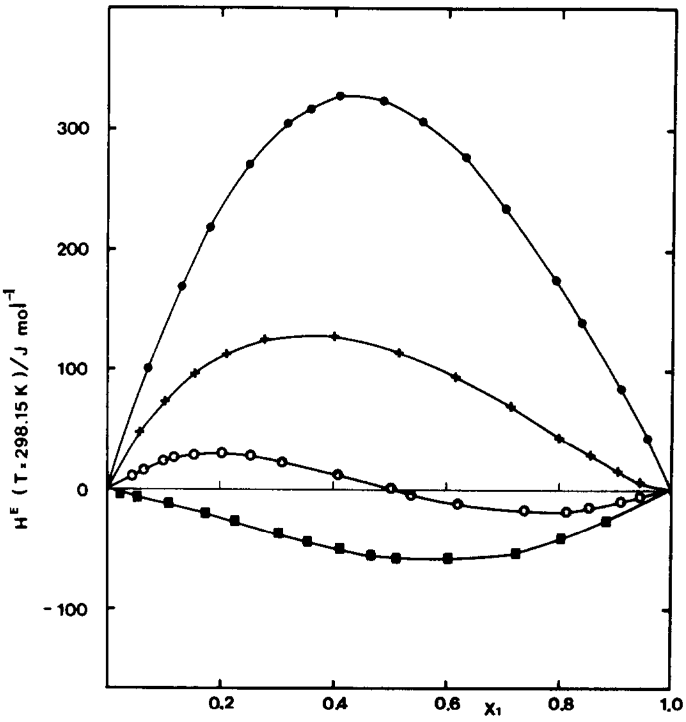

Fig. 2. Molar excess enthalpies, H^E, at 298.15 K, of *n*-alkanal (1)+tetrachloromethane (2) mixtures versus x_1, the mole fraction of *n*-alkanal. Experimental results: F_2, ethanal (●); F_3, propanal (+); F_4, butanal (○); F_5, pentanal (■).

The occurrence of oriented interactions between the alkanal molecules is also confirmed in the case of butanal (F_4) by the S-shaped curve of H^E vs. x_1, which is positive at low alkanal concentrations and negative at high ones.

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