Thermochimica Acta, 57 (1982) 147–154
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

EXCESS ENTHALPIES OF SOME AROMATIC ALDEHYDES IN *n*-HEXANE, *n*-HEPTANE AND BENZENE

ITALO FERINO, BRUNO MARONGIU *, VINCENZO SOLINAS and SERGIO TORRAZZA

Istituto di Chimica Fisica e Industriale, 09100 Cagliari (Italy)

(Received 5 February 1982)

ABSTRACT

Calorimetric measurements of molar excess enthalpies, H^E, at 298.15 K, of mixtures containing aromatic aldehydes of general formula C_6H_5–$(CH_2)_m$–CHO (with $m = 0$, 1 and 2) + *n*-hexane, *n*-heptane or benzene are reported, together with the values of H^E at equimolar composition compared with the corresponding values of H^E for the aromatic ketones in the same solvents. The experimental results clearly indicate that the intermolecular interactions between the carbonyl groups (CHO) are influenced by the intramolecular interactions between the carbonyl and phenyl groups, particularly for the mixtures containing benzaldehyde.

INTRODUCTION

This work is part of a systematic study on the thermodynamic properties of organic mixtures [1–5]. The aromatic aldehydes, of general formula C_6H_5–$(CH_2)_m$–CHO (with $m = 0$, 1 and 2), represent a class of substances which deserve particular attention in order to refine the group contribution model currently used for predicting thermodynamic properties. Another interesting aspect of the study of mixtures containing aromatic aldehydes is related to the intramolecular interactions between the phenyl group (C_6H_5), and the functional group (CHO), called n–π interactions. In fact, when two functional groups are located on the same molecule, as happens for dichloroalkanes [6], aromatic ethers [7] and aromatic chlorides [1], a change in thermodynamic properties with varying distance between the functional groups is observed.

Several works have been published regarding the interactions of the carbonyl group (CO) with systems containing groups which specifically

---

* To whom correspondence should be addressed.

interact with the double C = O bond, such as benzene (or phenyl) [8], hexene [9], and other strongly polarizable groups, or electron-acceptor groups like tetrachloromethane [10].

A search of the literature reveals that thermodynamic studies on aldehydes + alkane or benzene mixtures are rather scarce and are limited to aliphatic aldehydes. The liquid–vapor equilibrium of propionaldehyde + cyclohexane has been carefully investigated at 318.15 K by Matsunaga and Katayama [11]. Liquid–vapour equilibrium data on *n*-valeraldehyde + *n*-heptane at 348.15 K and 368.15 K have also been reported [12], together with the molar excess Gibbs energy, G^E, calculated from the isothermal P–x data using a three-parameter Margules equation. Molar excess enthalpies, H^E, of aliphatic aldehydes + alkanes have been measured calorimetrically by Marongiu et al. [3,4].

No experimental G^E or H^E values could be found in the literature for the aromatic aldehydes, except for the excess enthalpy of benzaldehyde ($m = 0$) + *n*-alkanes mixtures [5]. The purpose of the present work was to determine experimentally the enthalpies of mixing of phenylacetaldehyde ($m = 1$) and phenylpropionaldehyde ($m = 2$) with several *n*-alkanes and benzene, and to compare the results with the H^E of the aromatic ketones + *n*-alkanes or benzene previously determined by Grolier et al. [10] and Urdaneta et al. [13] in order to estimate the magnitude of H^E change which occurs when the hydrogen atom of the CHO group is substituted by a methyl group (CH_3–) to form the corresponding ketones.

EXPERIMENTAL

Materials

Aldehydes are easily oxidized and polymerized. Hence the aromatic aldehydes of pure reagent grade (Fluka AG, Switzerland) were first dried with molecular sieve 3A and then distilled in an atmosphere of dry nitrogen. Purity was higher than 99.5% as determined by GLC using a Chromosorb W80-100 mesh column. *n*-Hexane, *n*-heptane and benzene used were extra pure reagent grade for spectroscopy (C. Erba, Milan) and were used without further purification. In order to avoid oxidation, a dry-box with flowing nitrogen was always used for any kind of manipulation.

Procedure

The enthalpy of mixing was measured using a Tian–Calvet ("CRMT") type calorimeter manually tilted The batch mixing cell and the experimental

TABLE 1

Experimental values of molar excess enthalpy, H^E (at 298.15 K), for some binary mixtures containing aromatic aldehydes

x_1	H^E (J mole^{-1})	x_1	H^E (J mole^{-1})	x_1	H^E (J mole^{-1})
Benzaldehyde(1) + *n*-hexane(2)					
0.0482	449	0.4089	1304	0.8975	582
0.0948	770	0.4974	1243	0.9171	496
0.2074	1203	0.8215	820		
0.2888	1310	0.8444	760		
Phenylacetaldehyde(1) + *n*-hexane(2)					
0.0601	670	0.4478	1430	0.8001	960
0.1323	1140	0.5613	1357	0.9020	561
0.2381	1425	0.6373	1280	0.9459	335
0.3137	1472	0.7692	1046		
Phenylpropionaldehyde(1) + *n*-hexane(2)					
0.1106	500	0.4315	1003	0.7363	670
0.2148	796	0.5513	940	0.9046	295
0.2965	932	0.6078	876		
Benzaldehyde(1) + *n*-heptane(2)					
0.1432	938	0.3956	1403	0.7865	869
0.2184	1195	0.4893	1368	0.8272	750
0.2806	1327	0.6315	1202		
Phenylacetaldehyde(1) + *n*-heptane(2)					
0.1305	1026	0.3821	1505	0.6991	1230
0.1941	1260	0.4892	1490	0.7609	1071
0.3026	1461	0.5862	1414	0.9069	506
Phenylpropionaldehyde(1) + *n*-heptane(2)					
0.0910	470	0.3883	1061	0.7077	840
0.1951	805	0.4870	1066	0.7942	658
0.2761	958	0.6062	985	0.9046	340
Benzaldehyde(1) + benzene(2)					
0.0901	80	0.5121	178	0.7353	115
0.2500	163	0.6023	158	0.8775	50
0.3491	186				
Phenylacetaldehyde(1) + benzene(2)					
0.0912	162	0.3843	257	0.7030	186
0.1427	210	0.4907	246	0.8594	97
0.1976	242				
Phenylpropionaldehyde(1) + benzene(2)					
0.1121	90	0.3895	155	0.7044	105
0.2467	140	0.5752	135	0.9312	30

TABLE 2

Values of the coefficients a_i [eqn. (1)] and standard deviation $\sigma(H^E)$ [eqn (2)] of the experimental molar excess enthalpies, H^E, for aromatic aldehydes, Φ-$(CH_2)_m$-CHO, (1)+ n-alkane(2) or benzene mixtures at 298 15 K

m	Aldehyde	Component(2)	a_0	a_1	a_2	a_3	$\sigma(H^E)$ (J mole $^{-1}$)
A_0	Benzaldehyde	C_6H_{14}	4966	−1587	4149		5.0
		C_7H_{16}	5442	−1656	2053		3.0
		C_6H_6	723	−304			1 8
A_1	Phenylacetaldehyde	C_6H_{14}	5597	−1293	4604	−2250	1.5
		C_7H_{16}	5923	−1075	2865	−1824	2.6
		C_6H_6	973	−332	573	−592	1.4
A_2	Phenylpropionaldehyde	C_6H_{14}	3918	−1244	486	303	3 7
		C_7H_{16}	4246	−733	878	−462	2.2
		C_6H_6	585	−251	161	−43	1.2

procedure are described alsewhere [14]. The calorimeter was calibrated by the Joule effect and calibration was repeated after each experiment. Check measurements on benzene + cyclohexane [15] indicate the precision of our results to be ~2%. All measurements were made at an average temperature of 298.15 ± 0.10 K.

RESULTS

The experimental H^E_{exp} values for the various mole fractions, x_1, of the aldehyde component are reported in Table 1. The results were fitted to the smoothing equation

$$H^E_{sm} = x_1 x_2 \sum_{i=0}^{N-1} a_i (x_1 - x_2)^i \quad (1)$$

where x_1 is the mole fraction of the aldehyde, and x_2 is the mole fraction of the n-alkane or benzene. The values of the a_i coefficients and the standard

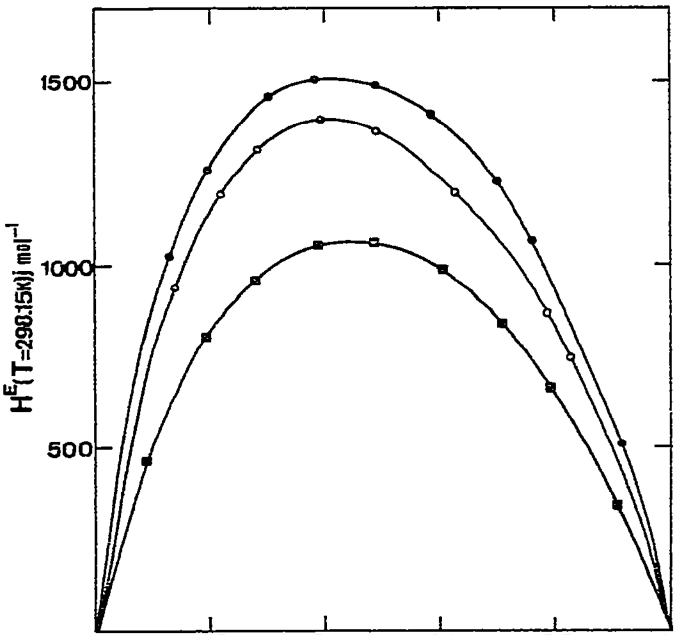

Fig. 1. Excess enthalpy, H^E (at 298.15 K), of aromatic aldehydes(1) + n-heptane(2) mixtures vs. the mole fraction of aldehyde, x_1. Full lines, values calculated by eqn. (1); experimental H^E results. ●, A_1, phenylacetaldehyde; ○, A_0, benzaldehyde, ■, A_2, phenylpropionaldehyde.

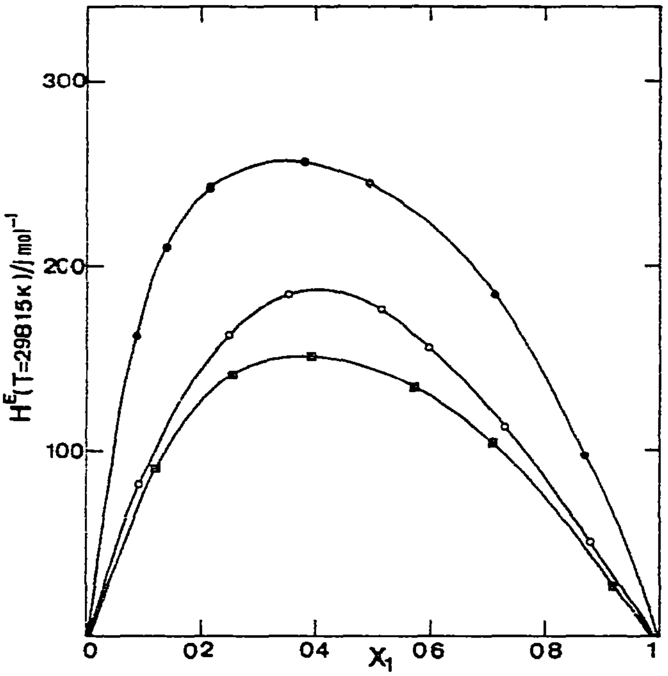

Fig 2 Excess enthalpy, H^E (at 298 15 K), of aromatic aldehydes(1)+benzene(2) mixtures vs the mole fraction of aldehyde, x_1. Full lines, values calculated by eqn. (1), experimental H^E results ●, A_1, phenylacetaldehyde, ○, A_0, benzaldehyde, ▣, A_2, phenylpropionaldehyde.

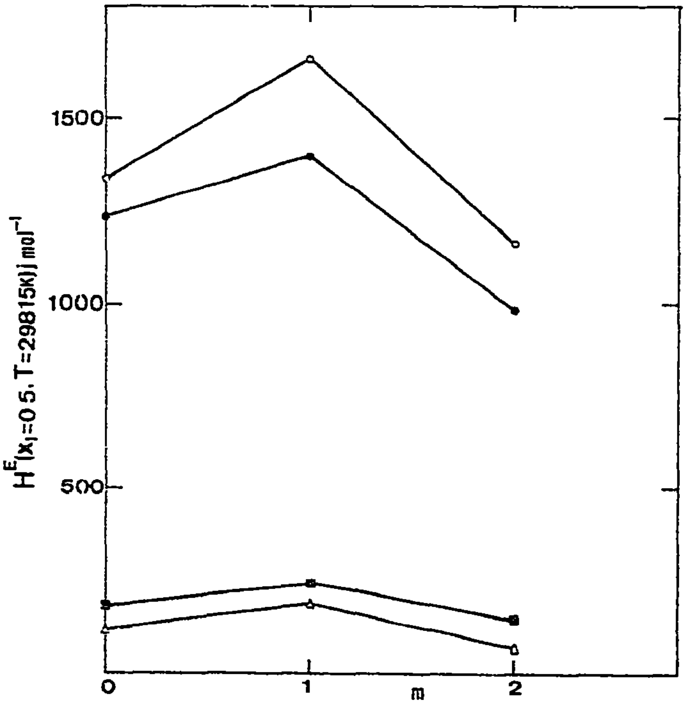

Fig 3 Comparison of the molar excess enthalpy, H^E (at 298 15 K; x_1=0.5), vs m, the number of (–CH_2–) groups in the aromatic aldehydes or ketones in n-hexane (○, ketones; ●, aldehydes) or benzene (△, ketones; ■, aldehydes).

deviation, $\sigma(H^E)$

$$\sigma(H^E) = \left[\Sigma\left(H^E_{sm} - H^E_{exp}\right)^2 / (N - n)\right]^{1/2} \tag{2}$$

(where N is the number of experimental points, and n is the number of a_i coefficients) were determined by least-squares analysis and are reported in Table 2. The equimolar H^E values of aldehydes + n-hexane or benzene mixtures are represented in Fig. 3.

DISCUSSION

The experimental H^E values for the aldehydes with n-heptane and benzene have been plotted as mole fractions, together with the calculated curves, obtained from eqn. (1). Figure 1 is the plot when n-heptane is used as solvent, Fig. 2 refers to mixtures with benzene, and Fig. 3 reports the equimolar H^E values of aldehydes or ketones + n-hexane or benzene mixtures [10].

It can be seen that, as observed when dealing with mixtures of a polar substance with an aliphatic hydrocarbon, the mixing process is endothermic. The positive, rather large, H^E values obtained clearly indicate that the CHO·····CHO and $\pi\cdots\cdots\pi$ interactions are much stronger than the CHO···solvent and $\pi\cdots\cdots$solvent, while the existence of oriented interactions in the aldehydes is pointed out by the fact that the maximum of the H^E vs. mole fraction curve is shifted towards the zone of low concentrations of the polar substance.

Furthermore, it can be noted that the sequence

H^E(phenylacetaldehyde) > H^E(benzaldehyde) > H^E(phenylpropionaldehyde)

is obeyed in the entire mole fraction range. As could have been expected, the H^E value for phenylpropionaldehyde is lower than the corresponding value for phenylacetaldehyde, due to the fact that the longer the aliphatic drain of the polar component, the weaker are the molecular interactions between the polar groups, which is the well-known "diluting effect" of the aliphatic chain. On this basis, however, the central position of the H^E value for benzaldehyde in the above sequence cannot be explained, since a much higher value of the molar excess enthalpy for benzaldehyde with respect to phenylacetaldehyde must have been expected.

The experimentally observed situation is then to be explained by supposing that the interaction between the phenyl group of a molecule and the adjacent carbonyl group of the same molecule weakens the intermolecular-type interactions. Such behaviour of two adjacent groups, one of which is aromatic, has been observed in aromatic ketones [10], aromatic ethers [7], and chlorinated aromatic hydrocarbons [1]. As regards the mixtures in benzene (see Fig. 2) it seems reasonable to affirm that the dipole–dipole interactions between two carbonyl groups are still predominant, but the considerable lowering of the H^E maximum value, which is 1 kJ mole^{-1} in magnitude, is an indication of the occurrence of strong interactions between the π electrons of benzene and the π electrons of the phenyl group.

Finally, the comparison between H^E values for aromatic aldehydes and aromatic ketones [10], represented in Fig. 3, shows that the interactions between CO groups appear to become stronger when the hydrogen atom is replaced by the methyl group. Nevertheless, the ketone–ketone interactions in benzenic solution seem to be counterbalanced by the ketone–benzene interactions, which are stronger than the aldehyde–benzene interactions. Another paper will be presented by the authors concerning the treatment of these measurements on a quantitative basis, with the aid of a statistical thermodynamic model.

REFERENCES

1 J.-P.E. Grolier, K. Sosnkowska-Kehiaian and H.V. Kehiaian, J. Chim. Phys., 70 (1973) 80.
2 H.V. Kehiaian, J.-P.E. Grolier and G.C. Benson, J. Chim. Phys., 75 (1978) 1031.
3 B. Marongiu and H.V. Kehiaian, Int. DATA Ser., Ser. A, Sel. Data Mixtures, 1974, pp. 98–102.
4 B. Marongiu, H. Bros, M. Coten and H.V. Kehiaian, J. Chim. Phys., 72 (1975) 375
5 B. Marongiu, I. Ferino and S. Torrazza, Int. DATA Ser., Ser. A, Sel. Data Mixtures, 1979, pp. 64–66.
6 C. Polo, C. Gutierrez-Losa, M.R. Kechavarz and H.V. Kehiaian, Ber. Bunsenges. Phys. Chem., 84 (1980) 525.
7 H.V. Kehiaian, K. Sosnkowska-Kehiaian and R. Hryniewicz, J. Chim. Phys., 68 (1971) 922.
8 K. Tamura, S. Murakami and R. Fujishiro, J. Chem. Thermodyn., 11 (1975) 851.
9 H. Renon and J.M. Prausnitz, Ind. Eng. Chem., Process Des. Dev., 7 (1968) 220.
10 J.-P.E. Grolier, O. Kiyohara and G.C. Benson, J. Chem. Thermodyn., 9 (1977) 697.
11 I. Matsunaga and T. Katayama, J. Chem. Eng. Jpn., 6 (1973) 397.
12 R.R. Tarakad and W.A. Scheller, J. Chem. Eng. Data, 24 (1979) 119.
13 O. Urdaneta, S. Hammom, Y.P. Handa and G.C. Benson, J. Chem. Thermodyn., 11 (1979) 851.
14 D. Bares, M. Soulie and J. Metzger, J. Chim. Phys., 70 (1973) 1531.
15 K.N. Marsh, Int. DATA Ser., Ser. A, Sel. Data Mixtures, 1973, p. 2.