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EXCESS ENTHALPIES OF SOME N-ALKANALS WITH BENZENE, TETRACHLOROMETHANE AND N-CHLOROALKANES

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A Tian–Calvet-type calorimeter has been used to determine molar excess enthalpies at 298.15 K as a function of concentration for the following binary mixtures: ethanal, propanal, butanal or pentanal + 1-chloropropane, 1-chlorobutane, 1-chloropentane and 1-chlorohexane.

These data are examined on the basis of a quasi-chemical theory using group-surface interactions.

We recently investigated the thermodynamic properties and molecular interactions of *n*-alkanal $CH_3(CH_2)_{k-2}(CHO$ (F_k) (with $k = 2,3,4,5$) + *n*-alkane mixtures [1]. These mixtures were regarded as possessing two types of groups or surfaces: type *a*, aliphatic (CH_3— or —CH_2— groups) and type *f*, formyl (—CHO group). We applied the quasi chemical group-contribution theory in the surface-interaction version [2] and determined the interchange energy coefficients $C_{af,l}$ ($l = 1,2$).

If the *n*-alkanes are replaced by other solvents, the number of surface types and, consequently, the number of interchange parameters are increased.

For a systematic study the *n*-alkanes should be replaced by other homogeneous, i.e. one-surface type solvents. The most typical, in the order of increasing "activity", are cyclohexane, benzene and tetrachloromethane. Cyclohexane being the most *n*-alkane-like solvent, we devoted the first study to *n*-alkanal + cyclohexane mixtures [3].

The data are examined on the basis of DISQUAC, a very simple extension of the quasi-chemical group contribution theory previously used [1]. We have now decided to extend the investigation to other solvents, such as benzene, tetrachloromethane and *n*-chloroalkanes.

We decided to measure H^E in a systematic way for 24 binary mixtures of *n*-alkanal + benzene (C_6H_6), tetrachloromethane (CCl_4) or *n*-chloroalkane of general formula $CH_3(CH_2)_{n-1}Cl$ ($n = 3,4,5,6$).

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Experimental

Materials

The source, purification and purity control of the aldehydes were the same as described in [1]. The benzene, tetrachloromethane and *n*-chloroalkanes used Fluka AG, 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.

Table 1 Values of the coefficients a_i of Eq. (1) and standard deviation $\sigma(H^E)$, Eq. (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 or $CH_3(CH_2)_{n-1}$—Cl(2) mixtures at 298.15 K (k and n are the number of C atom in the *n*-alkanal and in the chloroalkane respectively

F_k	*n*-alkanal	n	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)$/J·mol
F_2	ethanal	3	3063	489	135	45	—	1.5
		4	3424	750	159	−131	269	2.1
		5	3784	915	441	−56	—	1.2
		6	4174	1043	682	319	−137	1.5
		C_6H_6	926	−568	−6	−125	257	1.7
		CCl_4	1284	−349	−66	73	42	1.7
F_3	propanal	3	2366	197	−201	−196	663	1.8
		4	2579	252	95	−289	412	1.6
		5	2894	239	265	−547	−277	2.3
		6	3188	164	215	92	481	3.9
		C_6H_6	359	−422	145	−34	—	1.1
		CCl_4	457	−294	102	−136	−76	1.1
F_4	butanal	3	1964	−77	−128	32	396	2.2
		4	2112	−193	−48	425	117	4.2
		5	2329	−218	−281	57	291	5.4
		6	2529	249	−550	159	785	3.0
		C_6H_6	−210	−176	265	—	—	1.5
		CCl_4	7	−247	86	13	16	0.7
F_5	pentanal	3	1718	−238	83	−33	−187	1.3
		4	1779	−119	−45	117	—	1.8
		5	1924	12	−115	−99	319	2.3
		6	2078	137	125	−12	−317	1.5
		C_6H_6	−327	−89	87	−42	48	0.7
		CCl_4	−223	−113	63	37	—	0.9

Procedure

Enthalpies of mixing were measured at 298.15±0.10 K using a Tian–Calvet calorimeter tilted manually. The batch mixing cell and the experimental procedure have been described elsewhere [4].

The calorimeter was calibrated by means of the Joule effect, and the calibration was repeated after each experiment. A check measurement for benzene + cyclohexane [5] indicates that the precision of the results is ~1.5%.

The accuracy is probably better than 2%. The direct experimental H^E_{exp} values were fitted to the smoothing equation

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

where x_1 is the mole fraction of *n*-alkanal and x_2 that of benzene or tetrachloromethane or *n*-chloroalkane.

Values of the coefficients a_i and the standard deviations $\sigma(H^E)$, given by

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

(where N is the number of experimental points and n the number of coefficients a_i), were determined by least-squares analysis and are reported in Table 1.

Discussion

As no molar excess Gibbs energy, G^E, data for *n*-alkanal + benzene, tetrachloromethane or *n*-chloroalkane mixtures are available in the literature, it is not possible to examine the excess enthalpy data, H^E, on the basis of a quasi-chemical theory (QUAC) or an extension of this theory (*D*ISQUAC). Therefore, merely a qualitative interpretation of the H^E data for the investigated mixtures is possible at the moment.

n-Alkanal + benzene or tetrachloromethane mixtures

As shown in Figs 1 and 2, the excess enthalpies decrease when the number of alkyl groups *k*, in the *n*-alkanal, increases, assuming negative values for $k \geqslant 4$. This confirms the weakening of the dipole-dipole interactions (CHO—CHO) previously observed with *n*-alkane or cyclohexane as solvent [1, 3], and also demonstrates the existence of specific intermolecular interactions between the polar group (CHO) and the π-electrons of benzene (*n*-π interactions), or between CHO and the polar group (—Cl) of tetrachloromethane.

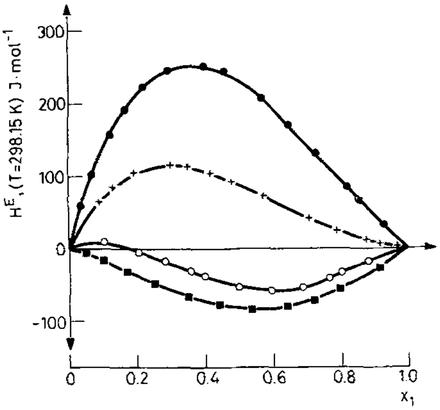

Fig. 1 Molar excess enthalpies, H^E, at 298.15 K, of n-alkanal(1)+benzene(2) mixtures *vs.* x_1, the mole fraction of n-alkanal. Experimental results (F_2, ●, ethanal; F_3, +, propanal; F_4, ○, butanal; F_5, ■, pentanal)

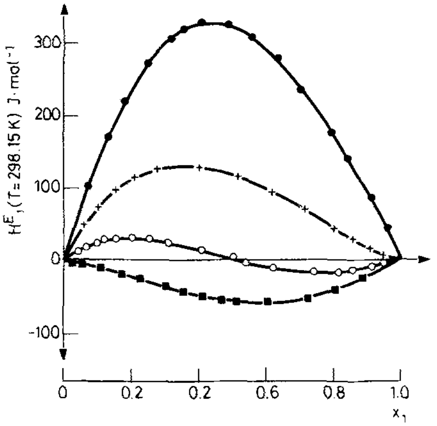

Fig. 2 Molar excess enthalpies, H^E, at 298.15 K, of n-alkanal(1)+tetrachloromethane(2) mixtures *vs.* x_1, the mole fraction of n-alkanal. Experimental results (F_2, ●, ethanal; F_3, +, propanal; F_4, ○, butanal; F_5, ■, pentanal)

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.

As regards pentanal + C_6H_6 or CCl_4 mixtures, the CHO-solvent interactions predominate in the entire concentration range, always giving rise to exothermic mixtures.

n-Alkanal + n-chloroalkane mixtures

The variation of H^E for *n*-alkanal with the chain length *n* of the chloroalkane is quite similar to the variation observed in the case of *n*-alkanals with *n*-alkane [1]. The excess enthalpies increase with increase of the alkyl chain length of the chloroalkane, as shown in Fig. 3.

Preliminary calculation for *n*-alkanal + *n*-chloroalkane systems have been performed on the basis of the DISQUAC model [3]. In agreement with previous

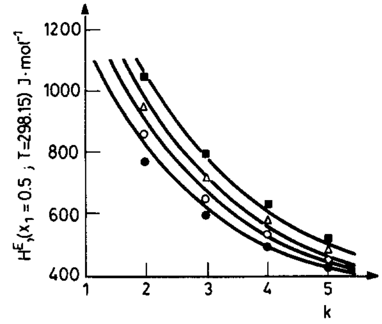

Fig. 3 Molar excess enthalpies, H^E (298.15^r $x_1 = 0.5$) of *n*-alkanal(1) + *n*-chloroalkane mixtures *vs.* *k*, the number of carbon atoms in the *n*-alkanal: full lines, predicted values; points, experimental H^E results (●, + *n*-chloropropane; ○, + *n*-chlorobutane; △, + *n*-chloropentane; ■, + *n*-chlorohexane)

Table 2 Interchange energy coefficients, $C_{st,1}$ (Gibbs energy) and $C_{st,2}$ (enthalpy) for *n*-alkanal(1) + 1-chloroalkane(2) mixtures

l	$C^{DIS}_{cf,l}$	$C^{QUAC}_{ac,l}$	$C^{QUAC}_{af,l}$
1	2.200	2.455	3.900
	3.400	3.850	5.930

results [2, 3], the contact *ac* (aliphatic/chloro) and *af* (aliphatic/carbonyl) was treated quasi-chemically ($z = 4$) with no dispersive contribution. The chloro/carbonyl contact, *cf*, was regarded as dispersive, with no quasi-chemical contribution, because of a probable compensation of the quasi-chemical interactions of the two polar groups, chloro (—Cl) and carbonyl (—CHO).

The geometrical parameters and the interchange coefficients $C_{af,l}$ and $C_{ac,l}$ were the same as defined previously [2, 3]. We adjusted the coefficients $C_{cf,l}$ in the usual manner. All the values are listed in Table 2.

The results, which are necessarily only approximate due to the lack of G^E data for these mixtures, indicate that it is impossible at present to make a general statement on the applicability of the DISQUAC model to polar + non-polar or polar + polar systems. All we can say now is that DISQUAC seems quite suitable for describing polar + cyclohexane systems [3] and polar + polar systems, assuming dispersive ($z_{st} = \infty$) polar-polar contacts.

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Zusammenfassung — Ein Kalorimeter des Tian–Calvet-Typs wurde zur Bestimmung der molaren Überschußenthalpien der im folgenden angeführten binären Gemische bei 298,15 K in Abhängigkeit von der Konzentration verwendet: Ethanal, Propanal, Butanal und Pentanal mit 1-Chlorpropan, 1-Chlorbutan, 1-Chlorpentan bzw. 1-Chlorhexan. Diese Daten wurden an Hand einer quasi-chemischen, Gruppen-Oberflächen-Wechselwirkungen involvierenden Theorie geprüft.

Резюме — Калориметр типа Тиан–Кальвет был использован для определения при 298,15 К молярных избыточных энтальпий в зависимости от концентрации смесей этаналь, пропаналь, бутаналь или пентаналь + 1-хлорпропан, 1-хлорбутан, 1-хлорпентап и 1-хлоргексан. Анализ полученных данных проведен на основе квази-химической теории, используя взаимодействия типа группа — поверхность.