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EXCESS ENTHALPIES OF SOME BINARY MIXTURES: A CONTRIBUTION TO THE STUDY OF THE Cl–O SPECIFIC INTERACTION

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ABSTRACT

A Tian–Calvet-type calorimeter has been used to determine molar excess enthalpies H^E as a function of concentration at atmospheric pressure and 298.15 K for some binary liquid mixtures of tetrachloromethane with linear mono- or polyoxaalkanes: 3-oxapentane, 4-oxaheptane, 5-oxanonane, 6-oxaundecane, 7-oxatridecane, 2-oxahexane, 3-oxaheptane, 2,4-dioxapentane, 3,5-dioxaheptane, 2,5-dioxahexane, 3,6-dioxaoctane and 2,5,8,11-tetraoxadodecane. The exothermic heats of mixing provide strong evidence for the specific interaction between the components of the mixtures. Comparison of the excess enthalpies of acetals with the corresponding values for ethers or polyethers containing $-O-(CH_2)_2-O-$ groups reveals a significant decrease in the interactions between the $-O-CH_2-O-$ groups of acetals.

The experimental H^E results are interpreted in terms of oxygen/chloro interchange enthalpies by using equations derived from the group surface interaction version of Guggenheim's lattice theory in the zeroth approximation.

INTRODUCTION

This work is part of a systematic study of the thermodynamic properties of liquid organic mixtures, T.O.M. Project [1–3], undertaken with the purpose of developing accurate group contribution models to be used to predict the thermodynamic excess functions, molar excess Gibbs energy G^E and molar excess enthalpy H^E and to study the Cl–O interaction systems.

As an oxygen-containing compound, we have used mono- and polyoxaalkanes of the general formula

$$CH_3(CH_2)_{m-1}-O-[(CH_2)_u-O-]_{v-1}-(CH_2)_{n-1}-CH_3$$

Three classes deserve special attention: (a) $CH_3(CH_2)_{m-1}-O-(CH_2)_{n-1}-$

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CH_3 (the oxaalkanes); (b) $CH_3(CH_2)_{m-1}$–O–CH_2–O–$(CH_2)_{n-1}CH_3$ (the acetals); and (c) CH_3–O–$(CH_2CH_2$–O–$)_{v-1}CH_3$ (the polyoxaalkanes).

Class (a) allows the study of the steric effect of alkyl groups, class (b), the proximity effect of two –O– groups and class (c), the effect of an increasing number of oxyethylene groups on the model parameters. Thus the influence of the surroundings on the donor capacity of oxygen, or the acceptor capacity of chlorine, and the effect of two or four oxygen atoms in the same molecule can both be studied.

The formation of an electron donor–acceptor complex of tetrachloromethane with 3-oxapentane as indicated by solid–liquid phase equilibrium studies [4,5] provides an instance where interaction of CCl_4 with lone-pair donors is involved. The dielectic constant measurements [6] also confirm the existence of such complexes in the liquid state.

The thermodynamic study of oxaalkanes + tetrachloromethane originally began with the rather restricted purpose of estimating the magnitude of the "non-specific" contributions to the oxaalkane + chloroform mixtures.

Dioxane was the first oxaalkane studied, by McKinnon and Williamson [7]. Their results supported to some extent the validity of McGlashan and Rastogi's treatment [8] in terms of the model of ideal associated mixtures. A more surprising result was, however, the negative sign of the enthalpy of mixing because this provided thermochemical evidence for complex formation between dioxane and tetrachloromethane due to a specific O–Cl interaction [7].

The purpose of this work was to provide additional experimental H^E data for mixtures of oxaalkanes with tetrachloromethane. A literature search revealed little data on polyoxaalkanes or acetals with CCl_4. The H^E of oxaalkanes were previously determined by several authors [9–13]. We repeated these measurements in order to apply our treatment to a homogeneous set of results.

The experimental H^E values are compared with the predictions of a group contribution model in the random-mixing approximation [14].

In a previous work [2], we showed that the enthalpies of mixing of oxaalkane, polyoxaalkanes and acetals + hydrocarbons can be correlated with a limited number of parameters, in terms of molecular interactions using the random-mixing approximation.

EXPERIMENTAL

Materials

The liquids used, Fluka 99.5 mol% pure, were subjected to GLC analysis and no purification was attempted.

Calorimetric measurements

The excess enthalpies H^E were measured with a Tian–Calvet CRMT-type calorimeter which was manually tilted. The batch-mixing cell and the experimental procedure are described elsewhere [15]. The calorimeter was calibrated by the Joule effect and the calibration was repeated after each experiment. The precision of our H^E measurements was generally better

TABLE 1

Experimental values of the excess enthalpy H^E at 298.15 K for binary mixtures of oxaalkanes of general formula $CH_3(CH_2)_{m-1}$–O–$(CH_2)_{n-1}$ CH_3 (1) + tetrachloromethane, CCl_4 (2)

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
$C_2H_5OC_2H_5$					
0.0511	−105	0.4954	−492	0.7535	−338
0.1490	−244	0.5516	−482	0.8600	−230
0.2607	−365	0.6413	−433	0.9248	−148
0.3822	−460				
$C_3H_7OC_3H_7$					
0.0989	−102	0.4108	−273	0.7115	−225
0.2012	−185	0.5026	−278	0.8200	−166
0.2970	−238	0.5911	−267	0.9033	−100
$C_4H_9OC_4H_9$					
0.0683	−73	0.4289	−257	0.6984	−220
0.1231	−120	0.4995	−262	0.8046	−158
0.2158	−181	0.6023	−252	0.8955	−88
0.3648	−242				
$C_5H_{11}OC_5H_{11}$					
0.0800	−72	0.4024	−183	0.6951	−145
0.1801	−131	0.5012	−183	0.7903	−112
0.2846	−166	0.6000	−170	0.9021	−58
$C_6H_{13}OC_6H_{13}$					
0.1447	−76	0.4967	−136	0.7866	−86
0.3020	−123	0.5986	−126	0.8937	−48
0.3997	−135	0.6989	−108		
$CH_3OC_4H_9$					
0.0957	−145	0.4909	−371	0.7500	−262
0.2061	−252	0.5714	−362	0.8039	−214
0.3008	−315	0.6608	−325	0.8930	−120
0.3977	−356				
$C_2H_5OC_4H_9$					
0.1016	−157	0.4014	−358	0.7017	−265
0.1982	−262	0.5031	−353	0.7991	−191
0.2927	−327	0.6011	−322	0.8906	−108

TABLE 2

Experimental values of the excess enthalpy H^{E} at 298.15 K for binary mixtures of acetals of general formula $CH_3(CH_2)_{m-1}\text{-O-}(CH_2)\text{-O-}(CH_2)_{n-1}CH_3$ (1) + tetrachloromethane, CCl_4, (2)

x_1	H^{E} (J mol^{-1})	x_1	H^{E} (J mol^{-1})	x_1	H^{E} (J mol^{-1})
$CH_3OCH_2OCH_3$					
0.1095	−125	0.4203	−348	0.7317	−304
0.2150	−227	0.5471	−364	0.7996	−255
0.3282	−307	0.6512	−342	0.9114	−136
$C_2H_5\ OCH_2OC_2H_5$					
0.1006	−187	0.4095	−438	0.7100	−385
0.1987	−308	0.4966	−457	0.8052	−281
0.3036	−389	0.6047	−445	0.8969	−145

than 1%, as can be seen from the standard deviation values reported in Table 4 below. The reliability of the apparatus and procedure adopted were checked by performing H^{E} measurements on the test system, benzene + cyclohexane. Our results differed by less than 2% from literature data [16] over the entire composition range.

All measurements were carried out made at an average temperature of 298.15 ± 0.10 K. The experimental values H^{E}, reported in Tables 1–3, were

TABLE 3

Experimental values of the excess enthalpy H^{E} at 298.15 K for binary mixtures of polyoxaalkanes of general formula $CH_3(CH_2)_{m-1}\text{-O-}(CH_2CH_2\text{-O})_{v}\text{-}(CH_2)_{n-1}CH_3(1)$ + tetrachloromethane, CCl_4, (2)

x_1	H^{E} (J mol^{-1})	x_1	H^{E} (J mol^{-1})	x_1	H^{E} (J mol^{-1})
$CH_3O\text{-}(CH_2)_2OCH_3$					
0.0804	−134	0.4383	−441	0.7988	−300
0.1352	−212	0.6011	−432	0.9063	−164
0.2120	−302	0.6942	−387	0.9505	−92
0.2897	−370				
$C_2H_5O\text{-}(CH_2)_2OC_2H_5$					
0.0971	−205	0.4000	−518	0.6986	−435
0.2100	−376	0.5078	−526	0.8077	−322
0.2950	−461	0.6214	−487	0.9312	−136
$CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OCH_3$					
0.0900	−312	0.3991	−707	0.7022	−540
0.2085	−552	0.5096	−698	0.8081	−379
0.3111	−666	0.6024	−645	0.8817	−242

TABLE 4

Values of the coefficients a_i, eqn. (1), and standard deviations $\sigma(H^E)$, eqn. (2), at 298.15 K for binary mixtures of oxaalkanes, acetals or polyoxaalkanes (1) + CCl_4 (2)

Oxaalkane	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)$
3-Oxapentane	−1966	117	785	−195	−1351	0.60
4-Oxaheptane	−1113	70	−52	−113		0.73
5-Oxanonane	−1050	−26	12	226	28	0.43
6-Oxaundecane	−729	138	−121	78		0.57
7-Oxatridecane	−543	93	−37	−36		0.47
2-Oxahexane	−1485	23	155	372	−178	0.34
2-Oxaheptane	−1415	375	−39	21	76	0.45
2,4-Dioxapentane	−1452	−162	−32	−136		0.41
3,5-Dioxaheptane	−1827	−155	−264	739	444	0.41
2,5-Dioxahexane	−1792	−22	−122	−73		0.30
3,6-Doxaoctane	−2109	203	−176	−95		0.51
2,5,8,11-Tetraoxadodecane	−2806	603	−337	502		0.48

fitted to the smoothing equation

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

where x_1 is the mole fraction of the oxaalkane, acetal or polyoxaalkane and x_2 is that of tetrachloromethane. Values of the standard deviations $\sigma(H^E)$ are given by

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

where N is the number of experimental points and n is the number of coefficients a_i. The values for the coefficients a_i and the standard deviations $\sigma(H^E)$ determined by least-squares analysis, are reported in Table 4.

DISCUSSION

The exothermic enthalpies of mixing provide strong evidence that in mixtures of an oxaalkane or acetal or polyoxaalkane with an acceptor molecule such as tetrachloromethane, a specific attractive interaction occurs between unlike molecules in the liquid state. The curves of H^E against x_1 for an oxaalkane, acetal or polyoxaalkane + CCl_4 are negative and almost symmetrical about $x_1 = 0.5$ suggesting that the interaction is mainly of a 1 : 1 type.

It is difficult to comment on the nature of the interaction in the present case. However, it appears that electron donor–acceptor interaction may be present. The oxygen atom in oxaalkanes has two lone-pair electrons which can be used for donation.

CCl_4 may acts as a σ-type acceptor and oxaalkane as an n-type donor.

Analysis in terms of a pseudo-lattice group contribution model

The substitution of a $-CH_2-$ group in *n*-alkane with an $-O-$ group influences the intermolecular forces as a result of two oppositely acting effects, one, weakening, due to smaller dispersion forces exerted by the $-O-$ groups, compared to the $-CH_2-$ groups, and the other, strengthening, due to electrostatic interactions between the C–O bond dipoles [17]. Because the latter effect is relatively weak, the amount of order in the liquid phase is rather small. Thus, oxaalkane + tetrachloromethane mixtures could be described fairly well by pseudo-lattice group contribution model in the zeroth (random mixing) approximation [1,14].

Three kinds of contact surfaces were distinguished on the molecules investigated in this work: a, aliphatic (CH_3 and CH_2); d, tetrachloromethane (CCl_4); and e, oxygen (O). The total relative contact surface, q_i, of a molecule of type i (oxaalkane, acetal or tetrachloromethane) and the oxygen surface fraction, α_{si}, on a molecule of type 1 (oxaalkane or acetal) were calculated from the relative group surfaces [18,19]: $q_{CH_3} = 0.73103$, $q_{CH_2} = 0.46552$, $q_O = 0.20690$, and $q_{CCl_4} = 2.5104$.

According to the model, H^E is given by

$$H^E/RT = \frac{q_1 q_2 x_1 x_2}{q_1 x_1 + q_2 x_2} h_{12}/RT \tag{3}$$

where h_{12} is the overall molar interaction enthalpy, a parameter which depends on the molecular structure of the components, but not on the composition.

For oxaalkane or acetal + tetrachloromethane mixtures, h_{12}/RT is given by [2]

$$h_{12}/RT = C_{ae,2}\alpha_{1e}^2 - (C_{ad,2} + C_{ae,2} - C_{de,2})\alpha_{1e} + C_{ad,2} \tag{4}$$

where $C_{st,2}$ is the enthalpy of interchange between contact surfaces of type s and t (s, t = a, d or e).

For oxaalkane or acetal + *n*-alkane mixtures

$$h_{12}/RT = C_{ae,2}\alpha_{1e}^2 \tag{5}$$

and for tetrachloromethane + *n*-alkane mixtures

$$h_{12}/RT = C_{ad,2} \tag{6}$$

According to the group contribution model, the $C_{st,2}$ coefficients should depend on the type of contact surfaces (or groups) only and should be independent of the type molecules. This is usually not exactly the case, in

TABLE 5

Comparison of molar vaporization enthalpies for dioxaalkane isomers

No.	Compound	ΔH_v (298.15 K)×10^3 (J mol^{-1}) [a]
(A)	CH_3-O-$(CH_2)_2$-O$(CH_2)_3CH_3$	43.65 [21]
(B)	CH_3CH_2-O-$(CH_2)_2$-O-CH_2CH_3	43.20 [21]
(C)	CH_3-O-$(CH_2)_2$-OCH_2CH_3	39.63 [21]
(D)	CH_3CH_2-O-CH_2-O-CH_2CH_3	35.65 [22]

[a] References in square brackets.

part because of the inadequacy of the underlying theoretical model and in part because of additional inter- or intramolecular effects.

Using eqns. (3) and (4), the H^E values in the whole composition range for all the mixtures investigated were calculated using the previously reported average value for the interchange coefficient of the a,e contact, $C_{ae,2} = 29.0$ for mono- and polyoxaalkanes [2] and = 17.5 for acetals [2], and for the a,d contact, $C_{ad,2} = 0.18$ [20] and an additional set of average values for the interchange coefficient of the d,e contact, $C_{de,2} = 21.3$ for mono- and polyoxaalkanes and = 12.10 for acetals. The proximity of the oxygen atoms in the acetalic group -O-CH_2-O- results in a substantial decrease in the interchange coefficients.

When passing from mono- or polyoxaalkanes to acetals, a decrease in the value of the interchange coefficient (of about 40%) is observed for both the aliphatic/oxygen contact and the tetrachloromethane/oxygen contact. This indicates that the energy of the interaction between the acetalic oxygen and the alkanes or CCl_4 is lower than the corresponding interaction energy originated by the "isolated" oxygen of oxaalkane.

A comparison of the molar vaporization enthalpies ΔH_v for dioxaalkane isomers (Table 5) shows that the cohesion energy of acetals is weaker than that of ethers. **A** and **B** isomers bearing "equidistant" oxygen atoms have practically identical vaporization energy values [21] while this is not the case for **C** and **D** isomers, where the closer position of the ethero atoms decreases the ΔH_v value by about 4×10^3 J mol^{-1}.

We calculated H^E $(x_1 = 0.5)$ for all the investigated mixtures (Tables 1–3); they differ from H^E_{exp} by less than 130 J mol^{-1}. At first sight, the 20% descrepancy may be regarded as too large, but it should be borne in mind that in three-surface-type systems the thermodynamic excess functions for oxaalkane + solvent systems will be given by the sum of three contributions resulting from the interchange coefficients of a,d, a,e and e,d contacts. These contributions not all being of the same sign, a slight variation in the interchange coefficients results in a large relative deviation of the calculated thermodynamic properties [23].

In other homologous series of compounds, e.g. the tertiary amines [23,24], the interchange coefficients decrease with increasing chain length of the

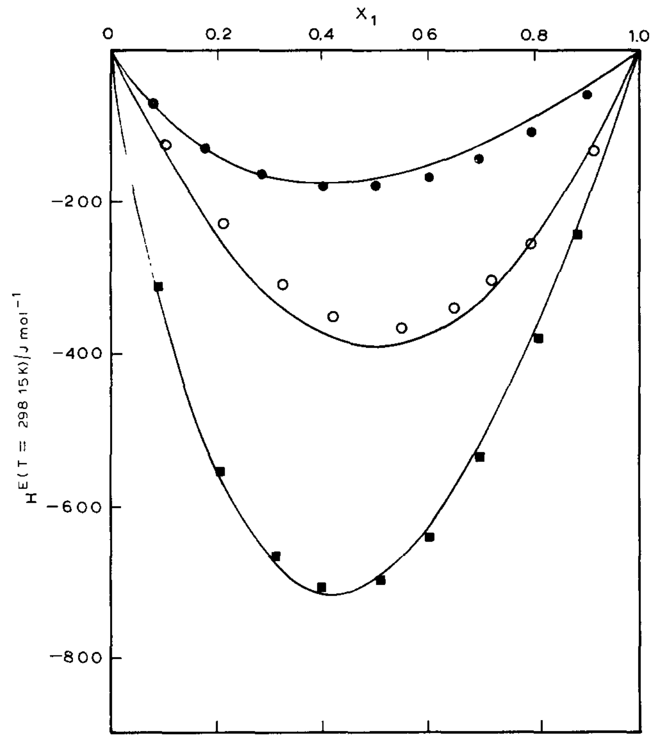

Fig. 1. Comparison of theory with experiment for the molar excess enthalpies H^E at 298.15 K of oxaalkane, acetal or polyoxaalkane (1)+CCl_4 (2) mixtures versus x_1, the mole fraction of oxaalkane. Full lines, predicted values; points, experimental results: ●, 6-oxaundecane; ○, 2,4-dioxapentane; ■, 2,5,8,11-tetraoxadodecane.

alkyl group because of the steric hindrance of adjacent alkyl groups. In the symmetrical oxaalkanes, the coefficients remain practically constant about the average value selected, probably because of the opposing steric and inductive effects of the alkyl group adjacent to the O atom.

Equation (3) successfully reproduced the composition dependence of the H^E curves. However, a careful examination reveals that the H^E_{exp} curves are slightly more asymmetric than the H^E_{calc} curves (Fig. 1), indicating that the mixtures are not entirely random.

A detailed interpretation of these results in terms of DISQUAC, an extended quasi-chemical group contribution model [1,20] will be presented separately.

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