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Application of the DISQUAC group contribution model to binary liquid organic mixtures containing alkanals [1]

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Abstract

The DISQUAC group contribution model for correlating and predicting the thermodynamic properties of liquid mixtures (phase diagrams and basic excess functions) is applied to some binary mixtures containing *n*-alkanals + cyclohexane, + benzene, + tetrachloromethane, and + 1-chloroalkanes.

A fairly good description of the thermodynamic properties of mixing is obtained when the model is used with the group interaction parameters determined in the paper.

INTRODUCTION

Study of the thermodynamics of liquid mixtures is of great practical and theoretical interest. It provides a better understanding of the relationships between the thermodynamic properties and the structural and interactional characteristics of molecules, as well as analytical relations between the thermodynamic functions and composition of multicomponent liquid mixture essential for separation process design. Group contribution methods provide an efficient tool for predicting thermodynamic properties. Several key systems containing a specific pair of structural groups can be systematically studied to build up a consistent set of group parameters with which to estimate the properties of any other system containing the same structural groups. The success of a group contribution method depends on the characteristics of the molecules investigated and the quality of the underlying solution model.

We have recently used DISQUAC [1], an extended quasi-chemical pseudolattice model, to examine the thermodynamic properties of mixing of

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mono- and polychloroalkane + *n*-alkane or + cyclohexane [2], linear or cyclic oxaalkane + *n*-alkane or + cyclohexane [3,4], alkanal + *n*-alkane [5], and linear or cyclic alkanone + *n*-alkane or + cycloalkane [6] mixtures. This paper extends our investigation to mixtures containing alkanals with other solvents.

Vapour–liquid equilibria for a series of alkanal + cyclohexane or + tetrachloromethane mixtures were first determined [7] in the absence of experimental data in the literature. The DISQUAC model is now applied to both these results and the available literature data (G^E and H^E) for linear alkanals + cyclohexane, + benzene, + tetrachloromethane, and + 1-chloroalkanes. The interchange coefficients obtained are compared with those of other open-chain molecules containing different functional groups and discussed in terms of their intramolecular effects, mainly steric and inductive.

THEORY

The contact surfaces in the mixtures considered here are indicated by the following letters: a, alkane ($-CH_3$, $-CH_2$); k, carbonyl (CO); b, benzene (C_6H_6); c, cyclohexane (C_6H_{12}); d, chlorine (–Cl).

The interactional terms in the thermodynamic properties under consideration, G^E and H^E, are given by the DISQUAC model [1] as the sum of the dispersive contribution, $G_{\rm int}^{\rm E,dis}$ or $H^{\rm E,dis}$, and the quasichemical contribution, $G_{\rm int}^{\rm E,quac}$ or $H^{\rm E,quac}$; thus

$$G^{\rm E} = G_{\rm comb}^{\rm E} + G_{\rm int}^{\rm E,dis} + G_{\rm int}^{\rm E,quac} \qquad (1)$$

$$H^{\rm E} = H^{\rm E,dis} + H^{\rm E,quac} \qquad (2)$$

where, for a binary system, $G_{\rm comb}^{\rm E}/RT = x_1 \ln(\phi_1/x_1) + x_2 \ln(\phi_2/x_2)$ is the Flory–Huggins combinatorial term, $\phi_i = r_i x_i/(r_1 x_1 + r_2 x_2)$ is the volume fraction, x_i is the mole fraction, and r_i is the total relative molecular volume of the component i ($i = 1, 2$)

The $G_{\rm int}^{\rm E,dis}$ and $H^{\rm E,dis}$ terms are given by

$$G_{\rm int}^{\rm E,dis} = (q_1 x_1 + q_2 x_2)\xi_1 \xi_2 g_{12}^{\rm dis} \qquad (3)$$

and

$$H^{\rm E,dis} = (q_1 x_1 + q_2 x_2)\xi_1 \xi_2 h_{12}^{\rm dis} \qquad (4)$$

where

$$g_{12}^{\rm dis} = -\tfrac{1}{2} \sum_{\rm s} \sum_{\rm t} (\alpha_{\rm s1} - \alpha_{\rm s2})(\alpha_{\rm t1} - \alpha_{\rm t2}) g_{\rm st}^{\rm dis} \qquad (5)$$

and

$$h_{12}^{\rm dis} = -\tfrac{1}{2} \sum_{\rm s} \sum_{\rm t} (\alpha_{\rm s1} - \alpha_{\rm s2})(\alpha_{\rm t1} - \alpha_{\rm t2}) h_{\rm st}^{\rm dis} \qquad (6)$$

g_{st}^{dis} and h_{st}^{dis} are the dispersive interchange parameters (Gibbs energy and enthalpy respectively) of the (s, t) contact, α_{si} is the molecular surface fraction of the surface of type s = a, b, c, d, k on a molecule of type i, q_i is the total relative molecular area of a molecule of type i, and $\xi_i = q_i x_i/(q_1 x_1 + q_2 x_2)$ is the surface fraction of component i in the mixture ($i = 1, 2$). For a binary system, $G_{int}^{E,quac}$ and $H^{E,quac}$ are given by the quasichemical equations

$$G_{int}^{E,quac} = x_1 \mu_{int,1}^{E,quac} + x_2 \mu_{int,2}^{E,quac} \tag{7}$$

where

$$\mu_{int,i}^{E,quac} = z q_i \sum_{s} \alpha_{si} \ln(X_s \alpha_{si}/X_{si} \alpha_s) \qquad i = 1, 2 \tag{8}$$

and

$$H^{E,quac} = \tfrac{1}{2}(q_1 x_1 + q_2 x_2) \sum_{s} \sum_{t} \left[X_s X_t - (\xi_1 X_{s1} X_{t1} + \xi_2 X_{s2} X_{t2})\right] \eta_{st} h_{st}^{quac} \tag{9}$$

where

$$\eta_{st} = \exp(-g_{st}^{quac}/zRT)$$

g_{st}^{quac} and h_{st}^{quac} are the quasichemical interchange parameters (Gibbs energy and enthalpy respectively) of the (s, t) contact, and z is the "lattice coordination number".

The quantities X_s and X_t are obtained by solving the system of λ equations (λ is the number of contact surfaces)

$$X_s\left(X_s + \sum_{t} X_t \eta_{st}\right) = \alpha_s \qquad \text{s, t} = \text{a, b, c, d, k} \tag{10}$$

X_{si} and X_{ti} ($i = 1, 2$) are the solutions of eqn. (10) for $x_i = 1$ (pure component i). Equations (3) and (4) are obtained from the quasichemical eqns. (7) and (9) as $z \to \infty$ [8], and represent the so-called random mixing (or zero) approximation of the model.

The temperature dependence of the dispersive or quasichemical g_{st} parameters has been expressed by a three constants equation of the type

$$g_{st}(T)/RT = C_{st,1} + C_{st,2}\left[(T^0/T) - 1\right] + C_{st,3}\left[\ln(T^0/T) - (T^0/T) + 1\right] \tag{11}$$

where $T^0 = 298.15$ K is the scaling temperature. Accordingly

$$h_{st}/RT = C_{st,2}(T^0/T) - C_{st,3}\left[(T^0/T) - 1\right] \tag{12}$$

$C_{st,1} = g_{st}(T^0)/RT^0$, $C_{st,2} = h_{st}(T^0)/RT^0$ and $C_{st,3}$ are called interchange energy coefficients. Heat capacity coefficients, $C_{st,3}$, have not been considered in this work.

TABLE 1

Volumes r_i, total surfaces q_i, and molecular surface fractions α_{si} for heterogeneous molecules [a]

Molecule	r_i	q_i	α_{ki}	α_{ai}
Linear alkanal				
CH_3-CHO	1.6828	1.5483	0.3563	0.6437
CH_3CH_2-CHO	2.2804	2.0138	0.2740	0.7260
$CH_3(CH_2)_2$-CHO	2.8779	2.4793	0.2225	0.7775
$CH_3(CH_2)_3$-CHO	3.4755	2.9448	0.1874	0.8126
	r_i	q_i	α_{di}	α_{ai}
Linear chloroalkane				
CH_3CH_2-CH_2Cl	2.6723	2.2828	0.2719	0.7281
$CH_3(CH_2)_2$-CH_2Cl	3.2699	2.7483	0.2258	0.7742
$CH_3(CH_2)_3$-CH_2Cl	3.8674	3.2138	0.8069	0.1931
$CH_3(CH_2)_4$-CH_2Cl	4.4650	3.6793	0.8313	0.1687

[a] For cyclohexane $r_i = 3.5187$, $q_i = 2.5966$, $\alpha_{ci} = 1.0000$; for benzene $r_i = 2.8248$, $q_i = 2.0724$, $\alpha_{bi} = 1.0000$; for tetrachloromethane $r_i = 3.0543$, $q_i = 2.5104$, $\alpha_{di} = 1.0000$.

One of the advantages of DISQUAC is its use of a single coordination number z in calculating the quasichemical term. It can thus be applied to mixtures containing groups of different polarities. The degree of non-randomness is expressed by the relative amounts of quasichemical to dispersive terms. The "reference" value chosen for the coordination number is $z = 4$ [9].

The relative molecular volumes r_i, the surfaces q_i and the surface fractions α_{si} of all the molecules have been calculated on the basis of the group volumes V_G and surfaces A_G recommended by Bondi [10], taking the volume V_{CH_4} and the surface A_{CH_4} of methane arbitrarily as unity [8]. Table 1 lists the geometrical parameters of all the substances referred to in this paper.

ESTIMATION OF THE INTERACTION PARAMETERS

The contact surfaces of the molecules examined can be placed in three classes of pairs of surfaces for the sake of clarity: (a) non-polar–non-polar, (b) polar–non-polar, (c) polar–polar/polarizable.

The interaction parameters for some of these contacts have already been determined independently. In this section, we summarize the results already obtained, and list and discuss the coefficients determined in this work and the criteria used for their estimation.

In the assignment of these coefficients the results obtained with other classes of systems were also taken into consideration, and it was assumed that the interchange parameters vary regularly with the molecular structure. Analysis of many systems enables the ambiguity present to some extent in such assignment to be reduced by identifying some general rules correlating the parameter variations to changes in the molecular structure.

Non-polar–non-polar surface contacts

The interchange coefficients for the (a, b), (a, c) and (a, d) contacts (where d is a chlorine type surface in tetrachloromethane) have been obtained independently from the excess functions of *n*-alkane + benzene, + cyclohexane or + tetrachloromethane mixtures. Average values for these parameters have been proposed by Kehiaian et al. [8] and revised, for the (a, d) contact, by Kehiaian and Marongiu [2]. The random-mixing approximation reproduces the shapes of the experimental curves quite well, i.e. we can assume that G^E and H^E are given only by the dispersive terms with $C_{as,l}^{quac} = 0$ (s = b, c, d; $l = 1, 2$) in accord with the non-polar nature of the groups. Closer examination [11] has shown that, while the Gibbs interchange coefficients for these systems are almost constant, the enthalpy coefficients increase with the chain length of the *n*-alkane (Patterson effect) owing to conformational changes or changes in molecular order occurring when *n*-alkanes are mixed with a globular molecule such as cyclohexane, or benzene or tetrachloromethane [12].

Since the molecules we consider in this work have a short *n*-alkyl chain (no more than four carbon atoms), constant values for both $C_{as,l}^{dis}$ coefficients, namely $C_{ab,1}^{dis} = 0.256$; $C_{ab,2}^{dis} = 0.562$; $C_{ad,1}^{dis} = 0.093$; $C_{ad,2}^{dis} = 0.18$ were taken from refs. 8 and 2 to calculate the (a, b) and (a, d) contacts respectively, and the interchange coefficients $C_{ac,l}^{dis}$ for the (a, c) contact were ignored.

Polar–non-polar surface contacts

Chloroalkane + n-*alkane or* + *cyclohexane*

The polar aliphatic–chlorine (a, d) contact and cyclohexane–chlorine (c, d) contact give both a dispersive and a quasichemical contribution. We have previously assumed that the dispersive coefficients $C_{ad,l}^{dis}$ and $C_{cd,l}^{dis}$ for the chloroalkanes are the same as for the non-polar CCl_4 + *n*-alkanes or + cyclohexane mixtures respectively [2]. The quasichemical coefficients are the same for the (a, d) and (c, d) contacts and decrease regularly as the number of Cl atoms in the chloroalkane increases. For 1-chloroalkanes we take from ref. 2 $C_{sd,1}^{quac} = 2.34$ and $C_{sd,2}^{quac} = 3.75$ (s = a, c). In CCl_4 the quasichemical coefficients, of course, are equal to zero.

Alkanals + n-*alkane or* + *cyclohexane*

The quasichemical and dispersive interchange parameters for the polar–non-polar (a, k) contact have been determined in a previous work [5] by using the experimental G^E and H^E data for alkanals + *n*-alkane mixtures.

TABLE 2

Molar excess Gibbs energies G^E and enthalpies H^E of n-alkanal + cyclohexane, + benzene, + tetrachloromethane or + 1-chloroalkane mixtures at various temperatures (T) and equimolar composition ($x_1 = 0.5$): comparison of direct experimental results (Exp.) with values calculated (Calc.) using the coefficients $C_{st,l}^{dis}$ and $C_{st,l}^{quac}$ from Tables 3–5

Solvent	n [a]	Alkanal	T (K)	G^E (J mol^{-1})		H^E (J mol^{-1})	
				Exp.	Calc.	Exp.	Calc.
Cyclohexane		CH_3-CHO	293.15	1205 [b]	1161		
			298.15			1674 [c]	1670
		CH_3CH_2-CHO	298.15			1340 [c]	1360
			318.15	886 [d]	926		
		$CH_3(CH_2)_2$-CHO	298.15	755 [b]	768	1123 [c]	1140
		$CH_3(CH_2)_3$-CHO	298.15	626 [b]	621	1019 [c]	990
Benzene		CH_3-CHO	298.15			232 [e]	241
		CH_3CH_2-CHO	298.15			54 [e]	52
			313.15	162 [f]	163		
		$CH_3(CH_2)_2$-CHO	298.15			−52 [e]	−37
		$CH_3(CH_2)_3$-CHO	313.15	17 [f]	16		
			298.15			−82 [e]	−82
Tetrachloromethane		CH_3-CHO	293.15	383 [b]	382		
			298.15			321 [e]	323
		CH_3CH_2-CHO	298.15			114 [e]	119
		$CH_3(CH_2)_2$-CHO	298.15			2 [e]	16
		$CH_3(CH_2)_3$-CHO	298.15	285 [b]	286	−56 [e]	−62
1-Chloroalkane	3	CH_3-CHO	298.15			766 [g]	800
	4		298.15			856 [g]	871
	5		298.15			946 [g]	948
	6		298.15			1044 [g]	1027
	3	CH_3CH_2-CHO	298.15			592 [g]	604
	4		298.15			645 [g]	656
	5		298.15			724 [g]	718
	6		298.15			797 [g]	785
	3	$CH_3(CH_2)_2$-CHO	298.15			491 [g]	489
	4		298.15			528 [g]	519
	5		298.15			582 [g]	562
	6		298.15			632 [g]	612
	3	$CH_3(CH_2)_3$-CHO	298.15			430 [g]	419
	4		298.15			445 [g]	431
	5		298.15			481 [g]	461
	6		298.15			520 [g]	500

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[a] Number of carbon atoms in the chain of 1-chloroalkanes ($CH_3(CH_2)_{n-1}$-Cl).

[b] Ref. 7.

[c] Ref. 13.

[d] Ref. 14.

[e] Ref. 15.

[f] Ref. 16.

[g] Ref. 17.

TABLE 3

Dispersive $C^{\mathrm{dis}}_{\mathrm{sk},l}$ and quasichemical $C^{\mathrm{quac}}_{\mathrm{sk},l}$ interchange parameters for (s, k) contact: a (aliphathic); c (cyclohexane); k (CO) in linear alkanals H–CO–$(\mathrm{CH}_2)_{m-2}\mathrm{CH}_3$

m	$C^{\mathrm{dis}}_{\mathrm{ak},1}$	$C^{\mathrm{dis}}_{\mathrm{ak},2}$	$C^{\mathrm{dis}}_{\mathrm{ck},1}$	$C^{\mathrm{dis}}_{\mathrm{ck},2}$	$C^{\mathrm{quac}}_{\mathrm{sk},1}$	$C^{\mathrm{quac}}_{\mathrm{sk},2}$
2	1.4	2.8	1.75	3.40	6.20	8.40
3	1.5	3.0	1.80	3.55	6.10	8.20
4	1.5	3.0	1.80	3.55	5.60	7.60
$\geqslant 5$	1.5	3.0	1.80	3.55	5.20	7.36

Alkanals were regarded as consisting of two types of contact surfaces: a (aliphatic) and k (carbonyl). The H atom of the formyl group was also treated as an alkanic group, so that the characteristic group in alkanals, the carbonyl, is the same as in alkanones. This assumption permits direct comparison of the parameters of alkanals and alkanones. Lengthening of the chain in linear alkanals results in a slight increase of the dispersive and a decrease of the quasichemical coefficients.

This paper extends the treatment to n-alkanal + cyclohexane mixtures. The parameters previously determined for the (a, k) contact were used, and those for the (a, c) contact were ignored because the molecules considered have a short n-alkyl chain ($m \leqslant 5$, m being the number of carbon atoms in the n-alkanal). Assuming that the quasichemical coefficients for the (c, k) contact are the same as for the (a, k) contact, $C^{\mathrm{quac}}_{\mathrm{ak},l} = C^{\mathrm{quac}}_{\mathrm{ck},l}$, and using the G^{E} and H^{E} values in Table 2, we determined the dispersive coefficients $C^{\mathrm{dis}}_{\mathrm{ck},l}$. They are reported in Table 3 and compared with the $C^{\mathrm{dis}}_{\mathrm{ak},l}$ already obtained [5]. The dispersive $C^{\mathrm{dis}}_{\mathrm{ck},l}$ are larger than the $C^{\mathrm{dis}}_{\mathrm{ak},l}$ and both increase slightly from ethanal to propanal and remain

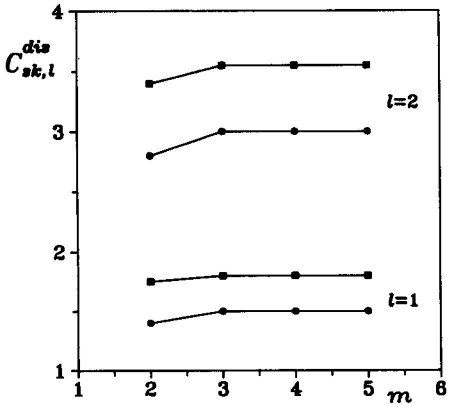

Fig. 1. Dispersive interchange coefficients $C^{\mathrm{dis}}_{\mathrm{sk},l}$ ($l = 1$, Gibbs energy; $l = 2$, enthalpy), for (s, k) contact (s = a or c: a, alkane; c, cyclohexane; k, CO) plotted against m, the number of carbon atoms in alkanal: (●) $C^{\mathrm{dis}}_{\mathrm{ak},l}$, (■) $C^{\mathrm{dis}}_{\mathrm{ck},l}$.

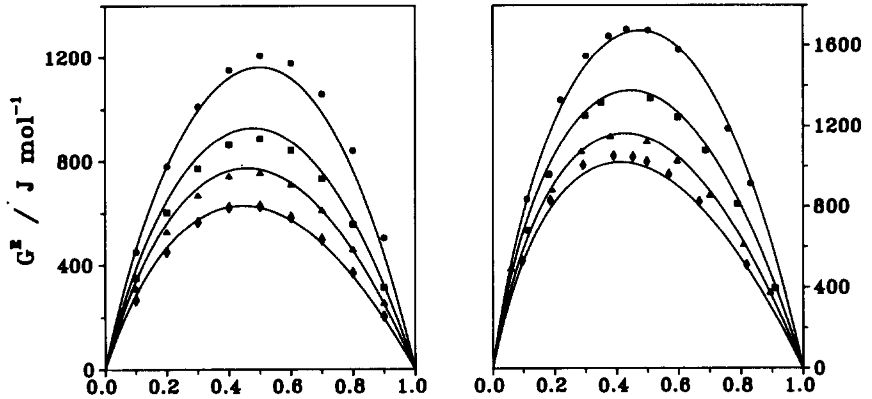

Fig. 2. Comparison of theory with experiment for the molar excess Gibbs energy G^E and the molar excess enthalpy H^E versus x_1 for alkanal + cyclohexane mixtures. Full lines, predicted values; points, experimental results. G^E: (●) ethanal ($T = 293.15$ K, ref. 7), (■) propanal ($T = 318.15$ K, ref. 14) (▲) butanal ($T = 298.15$ K, ref. 7), (◆) pentanal ($T = 298.15$ K, ref. 7). H^E ($T = 298.15$ K, ref. 13): (●) ethanal, (■) propanal, (▲) butanal, (◆) pentanal.

constant for higher *n*-alkanals (see Fig. 1). By contrast, the quasichemical coefficients decrease from ethanal to propanal and remain constant for higher *n*-alkanals (see also Fig. 4 in ref. 5). This behaviour is similar to that reported for *n*-alkanone + *n*-alkane or + cyclohexane mixtures [6]. Table 2 and Fig. 2 show the good agreement between the experimental and calculated G^E and H^E values.

Polar–polar or polarizable surface contacts

Alkanals + benzene

Previously determined values for the (a, b) and (a, k) contacts and the experimental G^E and H^E values available (Table 2), were used to estimate the dispersive and quasichemical coefficients for the (b, k) contact. As can be seen in Table 4, $C_{bk,l}^{dis}$ markedly decreases as the length of the *n*-alkyl chain increases, while $C_{bk,l}^{quac}$ slightly increases (see Fig. 3A). The experimental and calculated G^E and H^E data are compared in Table 2 and in

TABLE 4

Dispersive $C_{bk,l}^{dis}$ and quasichemical $C_{bk,l}^{quac}$ interchange parameters for (b, k) contact: b (benzene); k (CO) in linear alkanals H–CO–$(CH_2)_{m-2}CH_3$

m	$C_{bk,1}^{dis}$	$C_{bk,2}^{dis}$	$C_{bk,1}^{quac}$	$C_{bk,2}^{quac}$
2	1.40	1.02	3.06	2.82
3	0.87	0.66	3.20	2.90
4	0.37	0.30	3.32	2.96
⩾ 5	0.11	0.03	3.40	3.00

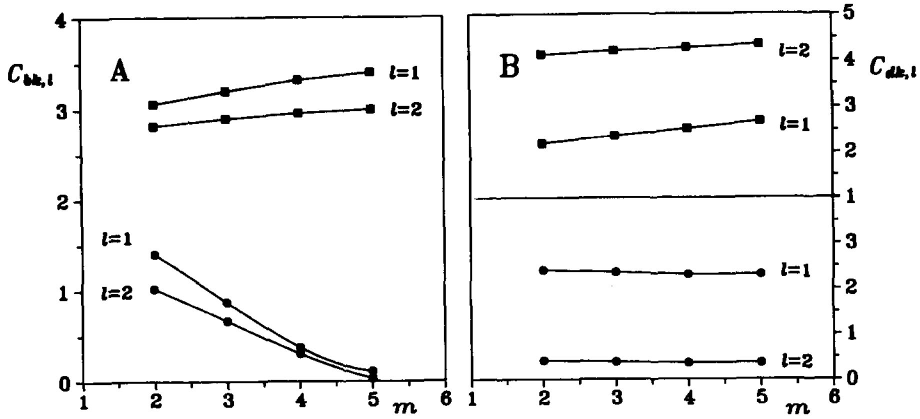

Fig. 3. (A) Dispersive and quasichemical interchange coefficients, $C_{bk,l}$ ($l=1$, Gibbs energy; $l=2$, enthalpy), for (b, k) contact: b, benzene; k, CO plotted against m, the number of carbon atoms in alkanal: (●) $C^{dis}_{bk,l}$, (■) $C^{quac}_{bk,l}$. (B) As above, for (d, k) contact: d, Cl in tetrachloromethane.

Fig. 4. The agreement may be regarded as satisfactory and the model closely reproduces the s-shaped H^E curves.

Alkanals + chloroalkanes or + tetrachloromethane

Since the (a, d) and (a, k) contact parameters are known [2,5], it remained to determine the chlorine–alkanal (d, k) contact parameters. These represent the properties of alkanal + chloroalkane or + tetrachloromethane mixtures.

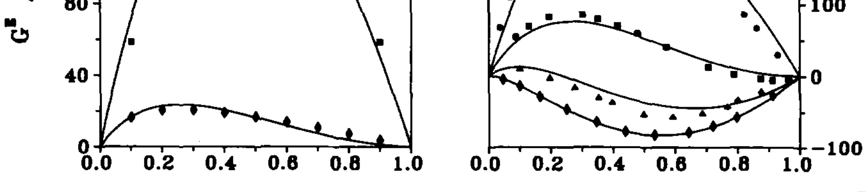

Fig. 4. Comparison of theory with experiment for the molar excess Gibbs energy G^E and the molar excess enthalpy H^E versus x_1 for alkanal + benzene mixtures. Full lines, predicted values; points, experimental results. G^E ($T = 313.15$ K, ref. 16); (■) propanal, (♦) pentanal. H^E ($T = 298.15$ K, ref. 15): (●) ethanal, (■) propanal, (▲) butanal, (♦) pentanal.

TABLE 5

Dispersive $C_{\mathrm{dk},l}^{\mathrm{dis}}$ and quasichemical $C_{\mathrm{dk},l}^{\mathrm{quac}}$ interchange parameters for (d, k) contact: d (Cl); k (CO) in linear alkanals H–CO–$(\mathrm{CH_2})_{m-2}\mathrm{CH_3}$ + 1-chloroalkane and + tetrachloromethane mixtures

m	1-Chloroalkane				Tetrachloromethane			
	$C_{\mathrm{dk},1}^{\mathrm{dis}}$	$C_{\mathrm{dk},2}^{\mathrm{dis}}$	$C_{\mathrm{dk},1}^{\mathrm{quac}}$	$C_{\mathrm{dk},2}^{\mathrm{quac}}$	$C_{\mathrm{dk},1}^{\mathrm{dis}}$	$C_{\mathrm{dk},2}^{\mathrm{dis}}$	$C_{\mathrm{dk},1}^{\mathrm{quac}}$	$C_{\mathrm{dk},2}^{\mathrm{quac}}$
2	3.60	4.80	0.2	0.4	2.40	0.41	2.19	4.13
3	3.30	4.30	0.3	0.6	2.35	0.38	2.36	4.21
4	3.30	4.30	0.3	0.6	2.30	0.36	2.52	4.28
$\geqslant 5$	3.30	4.30	0.3	0.6	2.30	0.36	2.68	4.35

The parameters were adjusted to represent the equimolar G^{E} and H^{E} values (Table 2). Unfortunately no G^{E} data exist for alkanal + 1-chloroalkanes mixtures. The $C_{\mathrm{dk},1}$ coefficients listed in Table 5 are thus estimated values and should be used with caution. A single set of interchange parameters will represent the properties of alkanal + 1-chloroalkane mixtures, independently of the number of carbon atoms in the *n*-alkyl chain of the 1-chloroalkane. The polar–polarizable surface contact (d, k) in *n*-alkanal + tetrachloromethane mixtures, however, is different from the polar–polar (d, k) contact in *n*-alkanal + 1-*n*-chloroalkane mixtures, and must be treated with a different set of interchange parameters. Both sets of $C_{\mathrm{dk},l}$ parameters are listed in Table 5. Figure 3B shows the change of both $C_{\mathrm{dk},l}^{\mathrm{dis}}$ and $C_{\mathrm{dk},l}^{\mathrm{quac}}$ in *n*-alkanal + tetrachloromethane mixtures with *m*, the number of carbon atoms in the *n*-alkanal. The good agreement between the experimental and calculated G^{E} and H^{E} values is illustrated in Table 2 and Fig. 5.

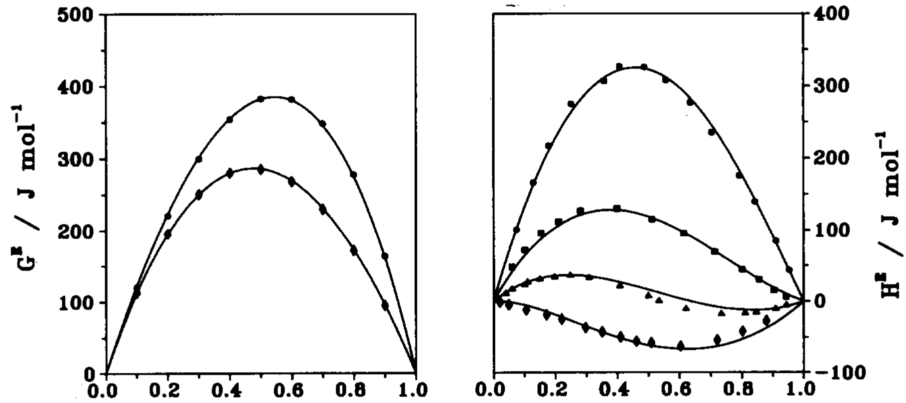

Fig. 5. Comparison of theory with experiment for the molar excess Gibbs energy G^{E} and the molar excess enthalpy H^{E} versus x_1 for alkanal + tetrachloromethane mixtures. Full lines, predicted values; points, experimental results. G^{E}: (●) ethanal ($T = 293.15$ K, ref. 7), (◆) pentanal ($T = 298.15$ K, ref. 7). H^{E} ($T = 298.15$ K, ref. 15): (●) ethanal, (■) propanal, (▲) butanal, (◆) pentanal.

DISCUSSION

Five general rules can be established in the light of our results.

The dispersive coefficients $C^{\mathrm{dis}}_{\mathrm{aX},l}$ or $C^{\mathrm{dis}}_{\mathrm{cX},l}$ (X = Cl, CO) remain almost constant or even increase for the very first members of an homologous series R–X when the chain length of the *n*-alkyl group R increases, especially when X contains π electrons, due, in our opinion, to an inductive effect. Moreover, if we compare the interchange coefficients of alkanals (this work and ref. 5) and alkanones [6] we observe that linear alkanals have much smaller $C^{\mathrm{dis}}_{\mathrm{sk},l}$ than 2-alkanones. In other words, in carbonyl compounds, replacement of R = H (alkanals) with R = CH_3 or higher *n*-alkyls (alkanones) increases the dispersive contribution, in terms of DISQUAC, due to enhancement of the dispersive interaction between the carbonyl groups by the inductive effect of the alkyl group. The ionization potential in the series H–CO–H (10.88 eV), CH_3–CO–CH_3 (9.89 eV), CH_3–CO–CH_2–CH_3 (9.74 eV) [18,19] also indicates that alkylation of methanal increases electron mobility, hence the dispersive forces.

(2) $C^{\mathrm{dis}}_{\mathrm{sX},l}$ values depend on the nature of the alkane and are slightly larger for the (c, X) than the (a, X) contact. In our calculation, this may be partly attributed to the dispersive aliphatic–cycloaliphatic interactions, since the parameters for the (a, c) contact were ignored.

(3) The quasichemical coefficients $C^{\mathrm{quac}}_{\mathrm{sX},l}$ are independent of the nature of the alkane: we found $C^{\mathrm{quac}}_{\mathrm{cX},l} = C^{\mathrm{quac}}_{\mathrm{aX},l}$ for all classes of substances examined. They markedly decrease as the length of the *n*-alkyl chain adjacent to the polar X group increases. This decrease is attributed to the decrease in the electrostatic dipole–dipole interactions between the polar X groups, due to the steric effect of the *n*-alkyl groups.

(4) $C^{\mathrm{dis}}_{\mathrm{bX},l}$ and $C^{\mathrm{dis}}_{\mathrm{dX},l}$ for the benzene/polar group and the chlorine/polar group contacts respectively, decrease as the length of the *n*-alkyl chain adjacent to the polar X group increases. Indeed, the inductive effect of the alkyl group increases the 1–2 type interactions between the polar X group of the type 1 molecule and the polar (Cl) or polarizable (CCl_4, C_6H_6) surface of the type 2 molecule.

(5) $C^{\mathrm{quac}}_{\mathrm{bX},l}$ and $C^{\mathrm{quac}}_{\mathrm{dX},l}$ increase as the length of the *n*-alkyl chain adjacent to the polar X group increases. This is attributed to the steric effect, which reduces the electrostatic 1–2 type interactions.

The influence of the inductive and steric effect of an alkyl group adjacent to a polar X group on the dispersive and the quasichemical interchange parameters $C_{\mathrm{sX},l}$, can be more easily explained if we consider that the interchange energies $\Delta\varepsilon_{\mathrm{sX}}$ are related to the interaction energies $\varepsilon_{\mathrm{sX}}$ [8]

$$\Delta\varepsilon_{\mathrm{sX}} = \varepsilon_{\mathrm{sX}} - \frac{\varepsilon_{\mathrm{ss}} + \varepsilon_{\mathrm{XX}}}{2} = \frac{|\varepsilon_{\mathrm{ss}}| + |\varepsilon_{\mathrm{XX}}|}{2} - |\varepsilon_{\mathrm{sX}}|$$

the ε values being negative.

In polar–non-polar systems (s = a, c), where interactions are mainly of the 1–1 type, the inductive effect exerted by an alkyl group adjacent to the polar X group increases the dispersive interaction energies $|\varepsilon_{XX}|$ and consequently increases $\Delta\varepsilon_{sX}$ (this, in turn, causes an increase in $C^{dis}_{sX,l}$). In polar–polar or polarizable systems it increases the dispersive interaction energies $|\varepsilon_{sX}|$ (s is the polar or polarizable surface contact) and consequently decreases $\Delta\varepsilon_{sX}$ and $C^{dis}_{sX,l}$. The steric effect acts mainly on the quasichemical parameters. In polar–non-polar systems, it decreases the electrostatic dipole–dipole interaction energies $|\varepsilon_{XX}|$ and consequently decreases $\Delta\varepsilon_{sX}$ and $C^{quac}_{sX,l}$ (s = a, c), while in polar–polar or polarizable systems decreases the electrostatic energies $|\varepsilon_{sX}|$ and consequently increases $\Delta\varepsilon_{sX}$ and C^{quac}_{sX}.

Taken as a whole, these results illustrate the advantages of using a flexible group contribution model whose parameters depend on the molecular structure. DISQUAC provides, in fact, a good description of the thermodynamic properties for a large variety of mixtures containing either polar or non-polar groups, and the trend of its group contribution parameters agrees with what one would expect from the physical structure of the molecules.

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