Journal of Thermal Analysis and Calorimetry, Vol. 91 (2008) 1, 37–46

EXCESS ENTHALPIES OF CHLOROALKYLBENZENE+*n*-HEPTANE OR +CYCLOHEXANE MIXTURES
DISQUAC analysis

B. Marongiu[*], *Alessandra Piras, Silvia Porcedda and Enrica Tuveri*

Dipartimento di Scienze Chimiche, Università di Cagliari, Cittadella Universitaria di Monserrato, 09042 Cagliari, Italy

A flow microcalorimeter has been used to determine excess enthalpies, H^E, at 298.15 K for binary mixtures of chloroalkylbenzenes (1)+*n*-heptane or cyclohexane (2). All systems are characterized by positive values of H^Es. These data along with the data available in the literature on H^E, molar excess Gibbs energies, G^E, and liquid-vapour equilibria (LVE) are treated in the framework of DISQUAC. Using a set of adjusted contact interchange energies parameters, structure dependent, the model provides a fairly consistent description of the thermodynamic properties as a function of concentration. The occurrence of the 'hetero-proximity effect' between C_6H_5– and –Cl groups is suggested by the variation of the interchange parameters.

Keywords: *chloroalkylbenzenes, data, DISQUAC model, excess enthalpy*

Introduction

DISQUAC [1, 2] model is a physical model based on the rigid lattice theory developed by Guggenheim [3] for liquid mixtures. The main features of the DISQUAC are (a) the partition function is factorized in two terms, in such a way that the excess function are calculated as the sum of two contributions: a dispersive term which represents the contribution from dispersive forces, and a quasichemical term which arises from the anisotropy of the field forces created by the solution molecules; in the case of G^E, the combinatorial entropy is represented by the Flory– Huggins equation [4]; (b) the interactions parameters are assumed to be structure dependent; (c) mixtures are studied systematically in order of increasing complexity of molecular structure and intermolecular interactions.

Under this basic assumption we have studied the ability of DISQUAC to represent a complete set of thermodynamic properties: vapour liquid equilibria (VLE), liquid-liquid equilibria (LLE), solid-liquid equilibria (SLE), excess molar Gibbs energies (G^E), excess molar enthalpies (H^E), as well as the related partial molar excess quantities at infinite dilution. We have studied several systems, and among them: polychloroalkanes [5], polyethers [6], thioalkanes [7], and alkynes [8] with organic solvents such as alkanes, cyclohexane, benzene or CCl_4: i.e. with inert or unassociated but active components (particularly, non-polar but polarizable molecules).

Table 1 Molar excess Gibbs energies G^E (T; x_1=0.5) of chloroalkylbenzenes (1)+*n*-alkane (2) mixtures at various temperatures T and equimolar composition: comparison of direct experimental results (exp.)[a] with values calculated (calc.) using the coefficients $C^{\mathrm{dis}}_{\mathrm{uv,l}}$ and $C^{\mathrm{quac}}_{\mathrm{uv,l}}$ from Tables 8, 9

Component (2)	T/K	G^E (T; x_1=0.5)/J mol^{-1} calc.	exp.	Source of experimental data
		chlorobenzene		
n-heptane	323.15	407	412	[13]
	338.15	392	430	[13]
		benzylchloride		
n-octane	352.93	707	850	[13]
	363.15	675	820	[13]

[a] Calculation (this work) by reduction of the original P–x data with the 2- or 3-parameter Redlich–Kister equation, vapour phase non-ideality corrected in terms of the second virial coefficient

---

[*] Author for correspondence: maronb@unica.it

1388–6150/$20.00
© 2008 Akadémiai Kiadó, Budapest

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

One of the basic assumptions in group contribution theories, independently of the particular method used, is that each group is situated in a well-defined intramolecular environment. A change in the nearest environment of a given group usually produces a perturbation of the force field around the group and, consequently, a modification of the interaction energies. For example the steric effect exerted by the chain length of the adjacent alkyl group (R–) in aliphatic aldehydes [9], (–CHO group), ketones [10], (CO group) or tertiary amines [11], (–N<group), is one among the many intramolecular factors which alter the values of the interchange energy parameters.

In polyfunctional molecules the proximity of two identical or different groups in a given molecule usually has a quite strong influence on the inter-

Table 2 Molar excess enthalpies H^{E} (T; x_1=0.5) of chloroalkylbenzenes (1)+n-alkane or cyclohexane (2) mixtures at various temperatures T and equimolar composition: comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficients $C^{\mathrm{dis}}_{\mathrm{uv,l}}$ and $C^{\mathrm{quac}}_{\mathrm{uv,l}}$ from Tables 8, 9

Component (2)	T/K	$H^{E}(T; x_1=0.5)$/J mol^{-1}		Source of experimental data
		calc.	exp.	
chlorobenzene				
n-heptane	288.15	685	627	[15]
		685	625	[13]
	293.15	691	692	[16]
	298.15	697	643	[17]
		697	697	[18]
		697	672	[19]
		697	697	This work
	303.15	703	681	[16]
	308.15	708	608	[15]
		708	606	[14]
	318.15	719	610	[17]
n-nonane	298.15	776	712	[19]
n-tetradecane		891	755	[19]
cyclohexane	293.15	751	666	[20]
		751	700	[16]
	298.15	752	680	[21]
		752	701	[22]
		752	752	This work
	303.15	752	902	[23]
	308.65	753	660	[24]
	313.15	753	894	[23]
	318.15	754	639	[24]
	328.15	755	620	[24]
benzylchloride				
n-heptane	298.15	1548	1552	[18]
		1548	1548	This work
cyclohexane	298.15	1325	1325	This work
1-chloro-2-phenylethane				
n-heptane	298.15	1429	1451	[18]
		1429	1429	This work
cyclohexane	298.15	1169	1169	This work
1-chloro-3-phenylpropane				
n-heptane	298.15	1108	1082	This work
cyclohexane	298.15	1004	1004	This work

change coefficients. This ‘proximity effect’ has previously been demonstred for molecules containing the following pairs of identical group (‘homo-proximity’): –O–··–O– [6], –S–··–S– [7] and >N–··–N< [12]. These examples have been confined to symmetrical molecules containing two identical groups X, $X(CH_2)_nX$. The variable *n* affects only the (X, CH_2)-contact energies. The study of asymmetrical molecules containing two different groups X and Y, $X(CH_2)_nY$, will be much more difficult, the variable *n* affecting the energies of three contact simultaneously: (X,CH_2), (Y,CH_2) and (X,Y).

As expected our preliminary calculations showed that the interaction parameters of mixtures of chloroalkylbenzenes with alkane and cyclohexane are affected by the nature and the structure of the neighboring groups. We had the choice between estimating ‘average’ interaction parameters, with the risk of obtaining poor results in extreme cases, or studying carefully the structure dependence of the parameters. Based on previous experience (see for example, [5]) we expected that DISQUAC would permit the finding of parameters which vary regularly with the molecular structure of the compounds. Thus we chose the second method.

The purpose of this paper is to study, in terms of DISQUAC, low-pressure fluid phase equilibria and related thermodynamic excess functions of binary liquid mixtures of *n*-alkanes and cyclohexane with chloroalkylbenzenes of general formula:

$$C_6H_5–(CH_2)_n–Cl\ (n = 0, 1, 2, 3,…..)$$

The input data are the molar excess Gibbs energies, G^E, and the molar excess enthalpies, H^E, obtained from liquid-vapor equilibrium and calorimetric measurements respectively.

Thermodynamic data are rather scarce for the mixture under study. For several systems no data are available, for other only a single source of data exists. The sources of available experimental data and some characteristic values are collected in Tables 1, 2. The G^E data concerning the mixtures under investigation are limited to chlorobenzene and benzylchloride [13]. The direct experimental isothermal *x–y* data have been reduced to obtain the molar excess Gibbs energies, G^E, using the two or three parameters Redlich–Kister equation. Vapour phase imperfection was accounted in terms of the second virial coefficient estimated by the Hayden and O’Connell [14] method. Likewise, H^Es data are abundant only for chlorobenzene in different solvents [13, 15–24]. Excess enthalpies for chlorobenzene+ cyclohexane are known at several temperatures but the reported values are in strong disagreement, especially at the higher values of *T* [23, 24].

Experimental

Materials

Chemicals were commercial products from Aldrich or Fluka. They were used without further purification and their purities, as checked by gas chromatographic analysis, were ≥99%.

The purities declared by the factories as well as the molar mass and the liquid densities we measured at 298.15 K along with literature ones are collected in Table 3.

Instrumentation

Heats of mixing were determined by means of a flow micro-calorimeter (model 2277, LKB-producer AB, Bromma, Sweden). The apparatus and the experimental procedure are described in detail elsewhere [25]. Fully automatic burets (ABU80, Radiometer, Copenhagen) were used to pump the liquid into the LKB unit. The molar flow rate m_i (mol s^{-1}), of component *i* flowing into the mixing cell is given by:

$$m_i = \phi_i\rho_i/M_i \qquad (1)$$

where ϕ_i is the volumetric flow rate, ρ_i the density and M_i the molar mass. The necessary densities were determined with a vibrating tube densimeter (Anton Paar, model DMA 58) with a reproducibility of $1\cdot10^{-5}$ g cm^{-3}.

Table 3 Supplier, molar masses, purities and densities at 298.15 K of chloroalkylbenzenes, *n*-heptane and cyclohexane

Compound	Supplier	M/g mol^{-1}	Purity/%	ρ_{exp}/g cm^{-3}	ρ_{lit}/g cm^{-3}
Chlorobenzene	Aldrich	112.56	99.9	1.10117	1.1009[a]
Benzylchloride	Aldrich	129.59	99.0	1.09482	1.1004[b]
1-chloro-2-phenylethane	Aldrich	140.61	99.0	1.06691	–
1-chloro-3-phenylpropane	Aldrich	154.64	99.0	1.04184	–
n-heptane	Fluka	100.21	99.5	0.67956	0.67946[a]
Cyclohexane	Aldrich	84.16	99.9	0.77386	0.77389[a]

[a][29], [b][30], value at 293.15 K

The molar excess enthalpies have been evaluated from the formula

$$H^{\mathrm{E}} = I^2R(E/E_{\mathrm{c}})/m_{\mathrm{i}} \qquad (2)$$

where I and R are the electrical current and resistance in the electrical calibration experiment, E and E_{c} are the voltage readings for measurement and electrical calibration, respectively, and m is the molar flow rate of the mixture. All enthalpy measurements were carried out at 298.15 K. The accuracy of the LKB bath temperature is 0.1 K. The reliability of the apparatus and procedure adopted were checked by

Table 4 Experimental values of the molar excess enthalpies, H^{E} of binary mixtures of chloroalkylbenzenes (1)+*n*-heptane or cyclohexane (2), at 298.15 K

x_1	H^{E}/J mol^{-1}	x_1	H^{E}/J mol^{-1}	x_1	H^{E}/J mol^{-1}
chlorobenzene+*n*-heptane					
0.1073	282	0.3511	624	0.6839	607
0.1261	324	0.4190	672	0.7937	464
0.1938	440	0.4903	706	0.8523	362
0.2651	536	0.5906	688	0.9203	212
chlorobenzene+cyclohexane					
0.0962	305	0.3472	715	0.7614	538
0.1506	426	0.4438	742	0.8646	337
0.2101	544	0.5155	740		
0.2618	632	0.6803	658		
benzylchloride+*n*-heptane					
0.2375	1139	0.4830	1554	0.8692	684
0.3838	1485	0.5547	1515	0.9088	504
0.4537	1542	0.7686	1072		
benzylchloride+cyclohexane					
0.1030	639	0.3799	1321	0.6476	1149
0.1868	944	0.4788	1348	0.7861	823
0.2563	1130	0.5795	1246	0.8802	497
1-chloro-2-phenylethane+*n*-heptane					
0.1227	658	0.5281	1436	0.8995	514
0.2187	1044	0.6266	1295	0.9180	389
0.3588	1347	0.7490	1029		
0.4272	1414	0.8174	839		
1-chloro-2-phenylethane+cyclohexane					
0.1710	868	0.5239	1179	0.8320	565
0.2921	1080	0.5531	1156	0.8684	445
0.3549	1136	0.6227	1035	0.8919	340
0.4521	1179	0.7675	672		
1-chloro-3-phenylpropane+*n*-heptane					
0.0904	454.8	0.3984	1098	0.7488	755
0.1105	535.3	0.4984	1074	0.7990	650
0.1990	820.6	0.5984	973	0.8882	383
0.3319	1062.5	0.6652	928		
1-chloro-3-phenylpropane+cyclohexane					
0.1089	530.3	0.4230	1008	0.7457	685
0.1549	675.9	0.4943	1009	0.8147	534
0.1964	787.1	0.5237	1000	0.8543	435
0.2682	904.2	0.5945	930		
0.3283	990.0	0.6874	794		

Table 5 Values of the coefficients, a_i, standard deviations, σ (H^E), of molar excess enthalpies, H^E at 298.15 K, for chloroalkylbenzenes (1)+*n*-heptane or cyclohexane (2) mixtures

Component (2)	a_0/	a_1/	a_2/	a_3/	$\sigma(H^E)$/
	J mol^{-1}				
			chlorobenzene		
n-heptane	2788.6	175.0	145.1	–384.4	7
cyclohexane	3008.4	–291.1	342.9	–	11
			benzylchloride		
n-heptane	6192.5	–420.0	–136.2	570.9	3
cyclohexane	5300.2	–970.2	653.2	–507.3	14
			1-chloro-2-phenylethane		
n-heptane	5715.8	–476.1	221.8	–	18
cyclohexane	4676.3	–1399.6	523.2	–	35
			1-chloro-3-phenylpropane		
n-heptane	4328.3	–981.1	666.0	–	14
cyclohexane	4014.6	–958.0	659.9	–563.5	8

performing H^E measurements on the test system benzene+cyclohexane. Our results concerning this system differed by <2% from reliable literature data [26] over the entire composition range.

Results and discussion

The experimental H^E data are collected in Table 4. The H^E values were fitted to the smoothing Redlich–Kister equation:

$$H^E = x_1 x_2 \sum_{i=0}^{p-1} a_i (x_1 - x_2)^i \qquad (3)$$

were x_1 is the mole fraction of chloroalkylbenzenes and p is the number of coefficients. The values of the coefficients a_i and the standard deviation of the fit, σ (H^E), obtained by a least squares treatment, are given in Table 5.

All mixtures containing alkylbenzenes+*n*-heptane exhibit positive values of H^E. At equimolar composition, values are in the range 1548–698 J mol^{-1}. The same compounds in cyclohexane show a similar behaviour but the range of variation of H^Es at x_1=0.5 is smaller 1325–752 J mol^{-1}.

Our experimental results generally agree with data from other authors (Table 2) with the exception of the values relative to the chlorobenzene+cyclohexane system. Our value at equimolar composition (752 J mol^{-1}) is significantly higher than the corresponding values found by Amaya [21] and Tanaka [22], 680 and 701 J mol^{-1}, respectively.

Theory

Chloroalkylbenzenes+*n*-alkane or +cyclohexane systems under study are regarded as possessing three (in alkane) or four (in cyclohexane) types of contact surfaces: type a, aliphatic (CH_3, CH_2 groups, which are assumed to exert the same force field); type b, aromatic (C_6H_6 and C_6H_5 groups); type c, cyclo-aliphatic (cy-CH_2 groups), type d, chlorine (Cl group).

The equations used to calculate G^E and H^E are the same as in other applications [5] and need not be repeated here.

The temperature dependence of the interaction parameters has been expressed in terms of the dispersive or quasi-chemical interchange coefficients $C^{\text{dis}}_{\text{uv,l}}$ and $C^{\text{quac}}_{\text{uv,l}}$ where u,v=a,b,c,d and l=1 (Gibbs energy) or l=2 (enthalpy). Heat capacity coefficients, l=3, have not been considered.

Assessment of geometrical parameters

The relative geometrical parameters r_i, q_i, and α_{vi} were calculated from the relative group parameters, the volumes r_G and surfaces q_G, taking arbitrarily the volume V_{CH_4} and surface A_{CH_4} of methane as unity. Thus $r_G = V_G/V_{CH_4}$ and $q_G = A_G/A_{CH_4}$. In general, for linear molecules, the V_G and A_G values calculated by Bondi [27] have been adopted (Table 6). Table 7 lists the geometrical parameters of all compounds reported in this paper.

Estimation of interaction parameters

The groups investigated in the present work are no polar (contacts a and c), polarizable (contact b) or

Table 6 Relative group increments for molecular volumes, $r_G=V_G/V_{CH_4}$, and areas, $q_G=A_G/A_{CH_4}$, calculated by Bondi's method [27], ($V_{CH_4}=17.12\cdot10^{-6}$ m^3 mol^{-1}; $A_{CH_4}=2.90\cdot10^5$ m^2 mol^{-1})

Group	r_G	q_G
$–CH_3$	0.79848	0.73103
$–CH_2–$	0.59755	0.46552
$C_6H_5–$	2.67757	1.83793
cy-$CH_2–$	0.58645	0.43277
–Cl	0.67874	0.62069

weakly polar (contact d). DISQUAC should be well adapted to study mixtures formed by these groups.

It is sometimes difficult to assign unambiguously interchange coefficients to individual systems. The coefficients can be varied, indeed, within certain limits, without affecting significantly the agreement with experiment. However, considering a larger number of systems, we were able to identify a number of general and physically reasonable 'rules' which we applied consistently in determining the values of the interchange coefficients. In the application of the DISQUAC model, we make the physically reasonable assumption that the parameters may vary with the molecular structure. The assumption improves the predictions, especially in the case of branched or cyclic molecules and for the first members of homologous series. A basic requirement is that the variation is regular and that similar classes follow the same rules. The final selection of parameters is achieved by plotting the, usually few, adjusted values on smooth curves and estimating the other values by interpolation or extrapolation. In other group-contribution methods, the interaction parameters, reported as constant, are in reality values which depend on the number and nature of the systems considered in the averaging. Moreover, the values listed in Tables 1, 2 were calculated with zero heat capacity coefficients. This has little effect on G^E calculated but not on H^E (calculated). The temperature dependence of our calculated H^E values results therefore from the Boltzmann factor only.

In this section we formulate the rules and list the selected values of the coefficients. In the following sections we discuss the physical meaning of the observed rules and compare the calculated data with experiment.

The contacts under examination are treated by using the model in the zeroth approximation (DIS) with the exception of the (a,d) and (c,d) contacts that needed the adoption of a quasichemical contribution. Values of the interchange parameters determined in the first section have been adopted in the second one.

Chloroalkylbenzenes+*n*-alkanes

These systems are characterized by three types of contact: (a,b), (a,d) and (b,d). The rules we found as follows:

- (1a) the dispersive coefficients, $C^{\text{dis}}_{\text{ab},1}$, of the (a,b)-contact decrease with the *n*, the number of alkyl groups $CH_2–$ adjacent to the phenyl ($C_6H_5–$) group attaining asymptotically $C^{\text{dis}}_{\text{ab},1}$ the value for alkane+benzene mixtures [5] when *n*≥3 (Table 8 and Fig. 1).
- (1b) the dispersive coefficients, $C^{\text{dis}}_{\text{ad},1}$ of the (a,d)-contact determined independently on the basis of 1-chloroalkane+alkane mixtures [5] can be used and are constant for all the chloroalkyl-

Table 7 Relative volumes, r_i, relative total surfaces, q_i, and molecular surface fractions, α_v, (v=a, b, c, d) of chloroalkylbenzenes, heptane and cyclohexane calculated from the group increments r_G and q_G given in Table 6

Compound	r_i	q_i	α_a	α_b	α_c	α_d
chlorobenzene	3.3563	2.4586	0.0000	0.7475	0.0000	0.2525
benzylchloride	3.9539	2.9241	0.2500	0.6285	0.0000	0.1215
1-chloro-2-phenylethane	4.5514	3.3897	0.3526	0.5422	0.0000	0.1052
1-chloro-3-phenylpropane	5.1490	3.8552	0.3622	0.4767	0.0000	0.1611
n-heptane	4.5847	3.7891	1.0000	0.0000	0.0000	0.0000
cyclohexane	3.5187	2.5966	0.0000	0.0000	1.0000	0.0000

Table 8 Dispersive interchange coefficients for the contacts (a,b), (a,c), (a,d) (b,c) (b,d) and (c,d) determined from mixtures of chloroalkylbenzenes+*n*-alkane or cyclohexane

n	$C^{\text{dis}}_{\text{ab},1}$	$C^{\text{dis}}_{\text{ab},2}$	$C^{\text{dis}}_{\text{ac},1}$	$C^{\text{dis}}_{\text{ac},2}$	$C^{\text{dis}}_{\text{ad},1}$	$C^{\text{dis}}_{\text{ad},2}$	$C^{\text{dis}}_{\text{bc},1}$	$C^{\text{dis}}_{\text{bc},2}$	$C^{\text{dis}}_{\text{bd},1}$	$C^{\text{dis}}_{\text{bd},2}$	$C^{\text{dis}}_{\text{cd},1}$	$C^{\text{dis}}_{\text{cd},2}$
0	0.644	1.400	0.030	0.120	0.093	0.180	0.245	0.562	3.370	6.708	2.695	4.492
1	0.460	1.000	0.030	0.120	0.093	0.180	0.245	0.562	1.701	2.379	0.944	1.574
2	0.350	0.762	0.030	0.120	0.093	0.180	0.245	0.562	0.650	1.000	0.396	0.661
≥3	0.260	0.562	0.030	0.120	0.093	0.180	0.245	0.562	0.500	0.825	0.194	0.323

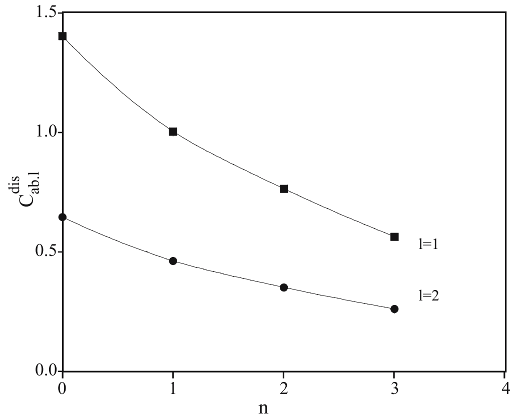

Fig. 1 Change of the coefficients, $C^{dis}_{ab,l}$, with the number *n* of $-CH_2$ groups in chloroalkylbenzenes of general formula $C_6H_5-(CH_2)_n-Cl$ (*n*=0,1,2,3)

benzenes (0.093 for *l*=1 and 0.180 for *l*=2) (Table 8).

- (1c) the quasichemical coefficients, $C^{quac}_{ad,l}$ of the (a,d)-contact increase with the 'distance' *n* between the phenyl (C_6H_5-) and chlorine (Cl–) groups attaining asymptotically the $C^{quac}_{ad,l}$ value for 1-chloroalkane+alkane mixtures [5] when *n*≥3 (Table 9 and Fig. 2).
- (1d) the dispersive coefficients, $C^{dis}_{bd,l}$ of the (b,d)-contact decrease with the *n*, the number of alkyl groups CH_2- between the phenyl (C_6H_5-) and chlorine (Cl–) groups attaining asymptotically the $C^{dis}_{bd,l}$ value for 1-chloroalkane+benzene mixtures [28] when *n*≥3 (Table 8 and Fig. 3).

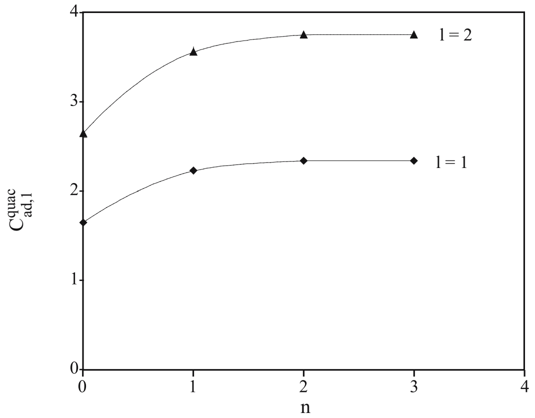

Fig. 2 Change of the coefficients, $C^{quac}_{ad,l}$, with the number *n* of $-CH_2$ groups in chloroalkylbenzenes of general formula $C_6H_5-(CH_2)_n-Cl$ (*n*=0,1,2,3)

Table 9 Quasichemical interchange coefficients for the contacts (a,d) and (c,d) determined from mixtures of chloroalkylbenzenes+*n*-alkane or cyclohexane

n	$C^{quac}_{ad,1}$	$C^{quac}_{ad,2}$	$C^{quac}_{cd,1}$	$C^{quac}_{cd,2}$
0	1.650	2.650	0.400	0.800
1	2.230	3.560	2.230	3.560
2	2.340	3.750	2.340	3.750
≥3	2.340	3.750	2.340	3.750

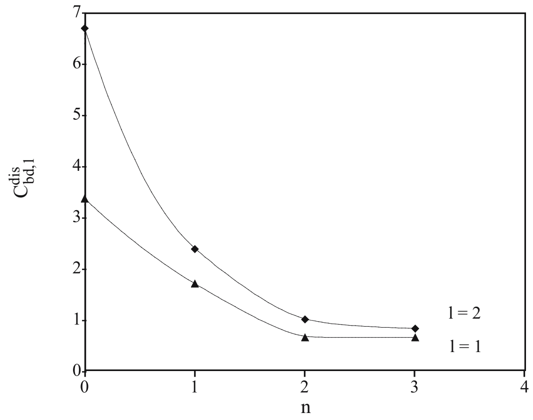

Fig. 3 Change of the coefficients, $C^{dis}_{bd,l}$, with the number *n* of $-CH_2$ groups in chloroalkylbenzenes of general formula $C_6H_5-(CH_2)_n-Cl$ (*n*=0,1,2,3)

Chloroalkylbenzenes+cyclohexane

These systems are characterized by six types of contact: (a,b), (a,c), (a,d), (b,c), (b,d) and (c,d). The rules we found as follows:

- (2a) see above, rule (1a) that can be applied except, of course, for chlorobenzene (*n*=0), which $C^{dis}_{ab,l}=C^{dis}_{ab,2}=0$ being absent the aliphatic surface.
- (2b) see above, rule (1b)
- (2c) see above, rule (1c)
- (2d) see above, rule (1d)
- (2e) the dispersive coefficients, $C^{dis}_{ac,l}$ of the non-polar (a,c)-contact, derived from the properties of alkane+cyclohexane mixtures [5] can be used and are constant for all the chloroalkylbenzenes (0.030 for *l*=1 and 0.120 for *l*=2), except, of course, for chlorobenzene (*n*=0), which $C^{dis}_{ac,l}=C^{dis}_{ac,2}=0$ being absent the aliphatic surface, a) (Table 8).
- (2f) the dispersive coefficients, $C^{dis}_{bc,l}$ of the non-polar (b,c)-contact, derived from the properties of benzene+cyclohexane mixtures [4] can be used and are constant for all the chloroalkylbenzenes (0.245 for *l*=1 and 0.562 for *l*=2) (Table 8).
- (2g) the quasi-chemical coefficients, $C^{quac}_{cd,l}$ of the polar (c,d)-contact equal the quasi-chemical coefficients of the polar (a,d)-contact, i.e. $C^{quac}_{cd,l}=C^{quac}_{ad,l}$ except for the chlorobenzene (*n*=0) which are slightly smaller with cyclohexane (0.400 for *l*=1 and 0.800 for *l*=2), (Table 9 and Fig. 4).
- (2h) the dispersive coefficients, $C^{dis}_{cd,l}$ of the (c,d)-contact decrease with increase in the chain length *n* of the alkyl groups CH_2- adjacent the chlorine (Cl–) group, (Table 8 and Fig. 5).

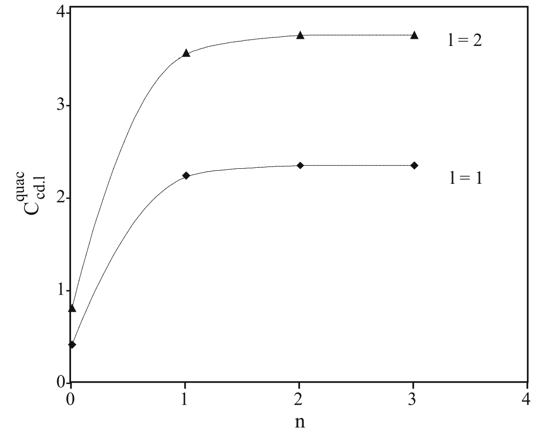

Fig. 4 Change of the coefficients, $C^{quac}_{cd,1}$, with the number *n* of $–CH_2$ groups in chloroalkylbenzenes of general formula $C_6H_5–(CH_2)_n–Cl$ (*n*=0,1,2,3)

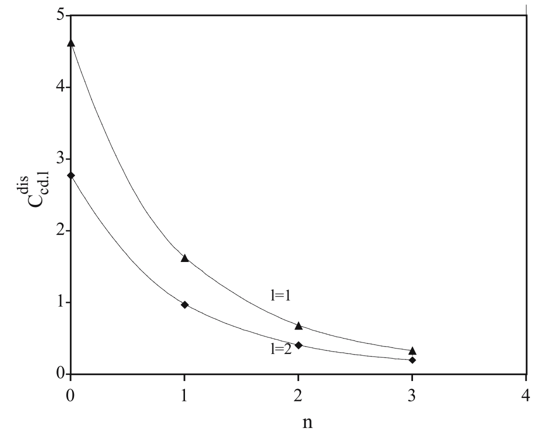

Fig. 5 Change of the coefficients, $C^{dis}_{cd,1}$, with the number *n* of $–CH_2$ groups in chloroalkylbenzenes of general formula $C_6H_5–(CH_2)_n–Cl$ (*n*=0,1,2,3)

Using the set of parameters dispersive and quasi-chemical reported in Tables 8, 9 a good agreement with experiment is obtained for the excess Gibbs energies of chlorobenzene+*n*-heptane at the lower *T*, 323.15 K (Fig. 6). As the temperature increases the discrepancy became bigger (Table 1). The agreement between DISQUAC predictions and experimental data for the excess enthalpies, at 298.15 K, of chloroalkylbenzenes+*n*-heptane (Fig. 7) or +cyclohexane (Fig. 8) are good. Also in this case the dependence of H^E from *T* is not well reproduced (the range of variation is too short) even if the contradictory data at the higher temperatures do not permit to quantify this defect.

In fact, the temperature dependence of H^E all the quantities listed in Table 2 were calculated with zero heat capacity of interchange coefficients, $C_{uv,3}$, dispersive and quasi-chemical. Accordingly, the dispersive contribution to the excess capacity (calculated) is zero and the quasi-chemical contribution results from the Boltzmann factor only.

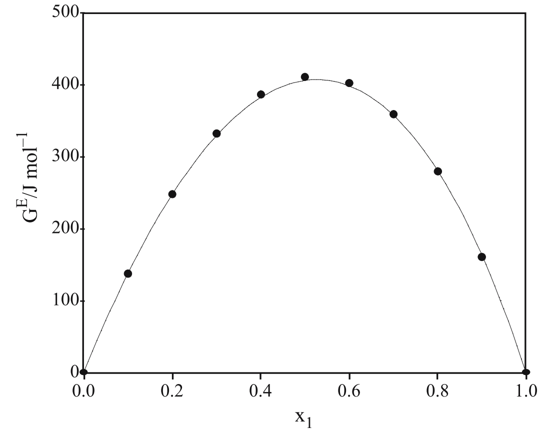

Fig. 6 Comparison of theory with experiments for the molar excess Gibbs energy, G^E, at 323.15 K for chlorobenzene (1)+*n*-heptane (2). Full lines, predicted values; points, experimental results: ● – [18]

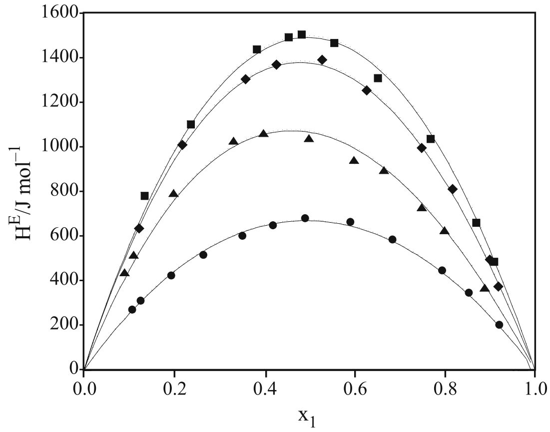

Fig. 7 Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for chloroalkylbenzenes of general formula $C_6H_5–(CH_2)_n–Cl$ (*n*=0,1,2,3) (1)+*n*-heptane (2) mixtures *vs.* x_1, the mole fraction of component (1): full lines, predicted values; points, experimental results (this work): ● – *n*=0; ■ – n=1, ◆ – *n*=2, ▲– *n*=3

It is generally admitted that the interchange energy parameters, g_{uv}, in lattice-type models are temperature dependent, i.e. they must be regarded as free energies. There is a priori no reason that g_{uv} should be a linear function of *T*. The difficulty of using $C_{uv,3}$ in the framework of group-contribution models results from the more complex physical significance of this parameter, and $C_{uv,3}$ adjusted for a particular system, reflects not only the true thermal coefficient of the interchange energy, but also many other inter- and intramolecular effects that are not explicitly accounted for in the model.

Inspection of the coefficients listed in Tables 8, 9 permits us to formulate several general rules. A priori

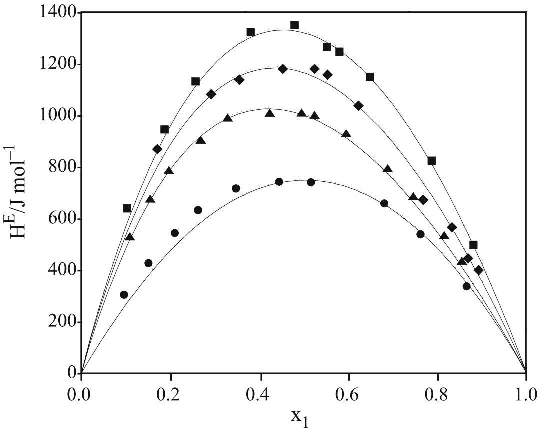

Fig. 8 Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for chloroalkylbenzenes of general formula C_6H_5–$(CH_2)_n$–Cl (n=0,1,2,3) (1)+cyclohexane (2) mixtures *vs.* x_1, the mole fraction of component (1): full lines, predicts values; points, experimental results (this work): ● – n=0; ■ – n=1, ◆ – n=2, ▲– n=3

the hetero-proximity effect modifies the interchange coefficients of all types of contacts, but it is impossible to estimate the variations of each coefficient separately. Assuming, quite arbitrarily, that the dispersive coefficients corresponding to the aliphatic-cyclohexane (a,c), benzene-cyclohexane (b,c) and aliphatic-chlorine (a,d)-contact remain constant, we found that the dispersive coefficients corresponding to the aliphatic-benzene (a,b), benzene-chlorine (b,d) and cyclohexane-chlorine (c,d)-contact decrease for the first members, especially when the functional group contain π-electrons (contact b) or is weakly polar (contact d), due, in our opinion, to an inductive effect on the inter- and intramolecular interactions. A good representation of the symmetry of the experimental H^E curves was obtained using a non negligible quasi-chemical contribute for the polar contacts, aliphatic-chlorine (a,d) and cyclohexane-chlorine (c,d). The quasi-chemical interchange coefficients, $C^{\text{quac}}_{\text{ad},l}$ and $C^{\text{quac}}_{\text{cd},l}$, increase with n and approach the values for 1-chloroalkane+alkane or +cyclohexane when $n \geq 3$ (disappearance of the hetero-proximity effect).

Intramolecular effects are by far the most important factors upon which the applicability of group contribution methods depends. They also condition the definition of groups. The group interaction energy parameters have constant values, independent of the components, only if the given groups are in a given intramolecular environment. The most common environment is formed by aliphatic hydrocarbon chain segments, i.e. CH_2 and CH_3 groups. The proximity of two or more, identical or different groups, in a molecule, changes drastically the interchange energy parameters. If a group is sterically hindered by other groups or is imbedded in a cycle, then the parameters also change, though usually to a lesser extend.

No remedy can be found for these and other intramolecular effects by changing the statistical model or by using empirical group contribution models. One solution is to define new, larger, groups including several simple groups. This does not only increase the number of parameters but, more important, the new groups may become too complex to be described by a simple interaction potential, and thus we may reach the upper limit of applicability of statistical models. In our opinion, the proximity effect is strictly intramolecular and no group-contribution model, however sophisticated, can improve the agreement with experimental data without adjusting the interaction energies. As one of the most serious causes of (apparent) failure of group contribution methods, the proximity effect deserves careful and systematic investigation, using both thermodynamic and extra-thermodynamic techniques. The curves shown in Figs 1–5 may serve for extrapolations and are typical of many functional groups.

In our opinion, the main advantage of using DISQUAC is, apart from the more accurate representation of all the experimentally available low-pressure phase equilibrium and related data, the better physical significance of the parameters, than in any other group contribution method. Despite the relatively large number of interchange coefficients (Tables 8, 9), many are derived from previous adjustments on other systems and most show a regular trend conform to what one qualitatively anticipate based on molecular considerations. This confers on DISQUAC rather unique predictive capabilities, provided it is used within the limits of validity of the underlying statistical theory, the rigid quasi-chemical pseudo-lattice model.

Conclusions

This work, following the previous on chloroalkanes [5], polyethers [6], alkanals, [9], alkanones [10], illustrate the advantage of applying group-contribution models in a more ‘flexible’ manner, i.e. with structure-dependent interaction parameters. This may appear as a derogation from the classical group-contribution concept. However, it reflects a physical reality, since there is no a priori reason that the force field of an atom or group of atoms should be completely independent of the intramolecular environment. The observed regular change in the parameters with molecular structure is a decisive importance from a practical point of view, since it permits useful predictions to be made based on a relatively limited number of experimental data. The interest of the method increases with the number of classes of systems examined. One find, indeed, that the rules governing the structure dependence of the parameters are quite similar for many classes. However, in traditional group-contribution methods, the 'average' interaction parameters are often only apparently constant. In reality, they depend on the number and nature of systems actually considered in the averaging. Moreover, in extreme cases, certain member of homologous series must be either ignored or treated as separate groups, with specific parameters.

It would be quite useful, and perhaps possible, to develop structure dependent parameter tables for other group-contribution models, e.g. for modified UNIFAC. It remain to investigate whether the structure/parameters relationships are comparable with those that we obtained with DISQUAC.

List of symbols

C	interchange coefficient
G	molar Gibbs energy
g	interchange energy parameter
H	molar enthalpy
q	relative molecular area
r	relative molecular volume
u, v	any contact surfaces
x	mole fraction
a	molecular surface fraction
Subscripts	
a, b, c, d	type of contact surface (group) a, CH_2; b, C_6H_6; c, C_6H_{12}; d, Cl
calc	calculated quantity
exp	experimental quantity
i	type of molecule (component)
l	order of interchange coefficient: l=1, Gibbs energy; l=3, heat capacity
Superscripts	
dis	dispersive
E	excess property
quac	quasi-chemical

Acknowledgements

We are grateful to Dr. H. V. Kehiaian for his highly valued and helpful suggestions and comments.

References

1 H. V. Kehiaian, Fluid Phase Equilib., 13 (1983) 243.
2 H. V. Kehiaian, Pure Appl. Chem., 57 (1985) 15.
3 E. A. Guggenheim, Mixtures. Oxford University Press, London 1952.
4 H. V. Kehiaian, J.-P. E. Grolier and G. C. Benson, J. Chim. Phys., 75 (1978) 1031.
5 H. V. Kehiaian and B. Marongiu, Fluid Phase Equilib., 40 (1988) 23.
6 H. V. Kehiaian, M. R. Tinè, L. Lepori, E. Matteoli and B. Marongiu, Fluid Phase Equilib., 46 (1989) 131.
7 B. Marongiu, G. Marras, B. Pittau and S. Porcedda, Fluid Phase Equilib., 97 (1994) 127.
8 D. Falconieri, B. Marongiu, A. Piras and S. Porcedda, Thermochim. Acta, 418 (2004) 85.
9 I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H. V. Kehiaian, Fluid Phase Equilib., 12 (1983) 125.
10 H. V. Kehiaian, S. Porcedda, B. Marongiu, L. Lepori and E. Matteoli, Fluid Phase Equilib., 63 (1991) 23.
11 I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H. V. Kehiaian, Fluid Phase Equilib., 9 (1982) 49.
12 I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H. V. Kehiaian, Fluid Phase Equilib., 11 (1983) 1.
13 H. I. Paul, J. Krug and H. Knapp, Fluid Phase Equilib., 39 (1988) 307.
14 G. Hayden and J. P. O'Connell, Ind. Eng. Chem. Process Des. Dev., 14 (1975) 209.
15 J. Krug, Thesis Berlin (1985).
16 B. S. Harsted and E. S. Thomsen, J. Chem. Thermodyn., 7 (1975) 369.
17 T. M. Letcher and J. W. Bayles, J. Chem. Eng. Data, 16 (1971) 266.
18 J.-P. E. Grolier, K. Sosnkowska-Kehiaian and H. V. Kehiaian, J. Chim. Phys. – Chim. Biol., 70 (1975) 367.
19 E. Wilhem, A. Inglese, J.-P. E. Grolier and H. V. Kehiaian, Ber. Bunsenges. Phys. Chem., 82 (1978) 384.
20 K. Merkel, Nova Acta Leopoldina, 9 (1940) 243.
21 K. Amaya, Bull. Chem. Soc. Jpn., 34 (1961) 1271.
22 R. Tanaka, S. Murakami and R. Fujishiro, J. Chem. Thermodyn., 6 (1974) 209.
23 A. V. Anantaraman, S. N. Bhattacharyya and S. R. Palit, Trans. Faraday Soc., 59 (1963) 1101.
24 A. V. Anantaraman, S. N. Bhattacharyya and S. R. Palit, Trans. Faraday Soc., 57 (1961) 40.
25 P. Monk, and I. Wadsö, Acta Chem. Scand., 22 (1968) 1842.
26 K. N. Marsh, Int. DATA Ser., Sel. Data Mixtures, Ser. A (1973) 75.
27 A. Bondi, Physical Properties of Molecular Crystals, Liquids and Gases. Wiley, New York, 1968.
28 I. Garcia Vicente, N. Garcia-Lisbona, I. Velasco and S. Otin, Fluid Phase Equilib., 49 (1989) 251.
29 J. A. Riddick, W. B. Bunger and T. K. Sakano, Organic Solvents – Physical Properties and Methods of Purification. Wiley, New York, 1968.
30 The Merk Index, (12th Edition), 1996.

OnlineFirst: September 17, 2007

DOI: 10.1007/s10973-007-8337-8