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A COMPARATIVE STUDY OF THERMODYNAMIC PROPERTIES OF BINARY MIXTURES CONTAINING DIMETHYLSULFOXIDE

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A flow microcalorimeter has been used to determine excess enthalpies (H^E) at 298.15 K for binary mixtures of dimethylsulfoxide (1)+alkylbenzenes (benzene, methylbenzene, ethylbenzene, *n*-propylbenzene and *sec*-propylbenzene, *n*-butylbenzene, *sec*-butylbenzene and *tert*-butylbenzene) or tetrachloromethane, trichloromethane, tetrachloroethane, dichloromethane and monochloroalkanes (1-chloropropane, 1-chlorobutane, 1-chloropentane, 1-chlorohexane) (2). These data with the data available in the literature on the molar excess enthalpies (H^E), molar excess Gibbs energies (G^E), activity coefficients at infinite dilution, γ_i^∞, liquid–vapour equilibria (LVE) and liquid–liquid equilibria (LLE) for dimethylsulfoxide (DMSO)+*n*-alkanes, cyclohexane, benzene or alkylbenzenes (mono-, dialkyl- and trialkyl-) or tetrachloromethane, trichloromethane, dichloromethane and monochloroalkanes are treated in the framework of DISQUAC, an extended quasi-chemical group contribution theory.

The systems are characterized by three types of contact surfaces: sulfoxide (S=O group), aliphatic (CH_3, CH_2, CH groups), cycloaliphatic (c-CH_2 group), aromatic (C_6H_6, C_6H_5 groups) and chlorine (Cl group). 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 model may serve to predict missing data.

Keywords: *data, dimethylsulfoxide, DISQUAC model, excess enthalpy, group contribution*

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 represent the contribution from dispersive forces, and a quasi-chemical 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 interaction 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 systems of polychloroalkanes [5], polyethers [6], alkanones [7], alkanals [8], thioalkanes [9], nitroalkanes [10], alkanenitriles [11], alkenes [12], alkanoates [13] and alkynes [14] with organic solvents such as alkanes, cyclohexane, benzene or CCl_4: i.e. with inert or unassociated but active components (particularly, nonpolar but polarizable molecules).

In the same way Gonzales *et al*. [15] have studied the problem of systems including two self-associated compounds, which then also exhibit cross-association, showing that DISQUAC is indeed a reliable tool to represent such systems. They have focused the attention on binary mixtures containing two alkan-1-ols [16], two linear monocarboxylic acids [17] or alkan-1ols and monocarboxylic acids [17].

However, until now, systems which exhibit strongly negative deviations from Raoult's law, and eventually complex formation between components, have not been considered in the framework of DISQUAC, except for linear alkanones+ trichloromethane [15]. So the aim of the present paper is to study the mixtures of dimethylsulfoxide with several organic solvent (alkanes, cyclohexane, benzene, chloroalkanes, tetrachloroalkane, trichloro- methane or dichloro-methane).

Aside from solubility data on LLE of dimethylsulfoxide in hexane or cyclohexane [18, 19], activity coefficients at infinite dilution, γ_i^∞, in

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n-alkane or cycloalkane, G^E and H^E of mixtures with benzene, trichloromethane, dichloromethane and CCl_4 [20–43] only very few papers have dealt with thermodynamic properties of mixtures with alkylbenzenes or chloroalkanes. In particular the almost complete absence of excess Gibbs energies data represents a major obstacle for an improved understanding of the influence exerted by a SO group upon the overall thermodynamics of binary dimethylsulfoxide systems.

The purpose of this and following papers of this series is to investigate the ability of the first-approximation quasi-chemical theory [5], on which the quasi-chemical term in DISQUAC is reliant, to account for the possible interactions in binary mixtures of the polar group S=O with the π–electron system and/or the active hydrogen and or the polar group of the second component.

The sources of available experimental data and some characteristic values are collected in Tables 4–6. The G^E data for mixtures containing dimethylsulfoxide are scarce and limited to tetrachloro-, trichloro-, dichloro-methane and benzene [20–23]. 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 for in terms of the second virial coefficient estimated by the Hayden and O'Connell [44] method.

Theory

DISQUAC is an extended quasi-chemical group-contribution model based on Guggenheim's lattice theory [1, 2]. In the classic model [3], molecules are assumed to possess one of several types of contacts *u* or *v* and occupy the sites of a lattice with coordination number *z*. The type of lattice and the assignment of contact points are arbitrary and irrelevant in applications to liquid mixtures and can be avoided by using the group-surface interaction version of the theory [4]. In the classical model, the interchange energies of every (*u*,*v*) contact generate no randomness to the extent expressed by *z*, which is the same for all the contacts. For non-polar systems, the random-mixing equations are obtained for $z=\infty$. In mixtures containing a single pair of contact, *z* may be treated as an adjustable parameter. DISQUAC circumvents the difficulty of treating mixtures containing pairs of groups of different polarities by taking into account a dispersive, random, contribution for every contact ($z=\infty$), eventually supplemented by an electrostatic, no random, contribution treated quasi-chemically with a constant $z=4$.

One of the advantages of DISQUAC is the use of a single coordination number *z* in calculating the quasi-chemical term. This permits the model to apply to mixtures containing groups of different polarities. The degree of no randomness is expressed by the relative amounts of quasi-chemical to dispersive terms. If both groups, *u* and *v*, are non-polar, then the contact *(u,v)* is characterized by the dispersive coefficients $C^{\text{dis}}_{\text{uv,l}}$ only, all $C^{\text{quac}}_{\text{uv,l}}=0$. If one group is polar and the other non-polar, then the contact (*u*,*v*) is characterized by both sets of coefficients, $C^{\text{dis}}_{\text{uv,l}}$ and $C^{\text{quac}}_{\text{uv,l}}$. In a binary non polar or polar (component 1)+no polar (component 2) mixture, the shapes of the calculated G^E and H^E curves, adjusted to fixed equimolar values, depend on the relative amounts of quasi-chemical to dispersive terms. The mole fraction $x_1^{\max}$ of the maxima of the dispersive curves $G^{\text{E,dis}}_{\text{int}}$ and $H^{\text{E,dis}}$ *vs.* x_1, are determined by geometrical factors only, $x_1^{\max}=1/(1+\sqrt{q1/q2})$. The quasi-chemical curves, $G^{\text{E,quac}}_{\text{int}}$ and especially $H^{\text{E, quac}}$, have the maxima shifted towards smaller x_1 values, the more, the smaller *z* is. Adding the two terms, one calculates with DISQUAC flatter G^E and H^E *vs.* x_1 curves, than by using the classical quasi-chemical model. This being supported by experiment [2] represents another advantage of DISQUAC.

The 'reference' value chosen for the coordination number is $z=4$, the same as in our previous application of DISQUAC [45, 46]. This choice is to some extent, but not entirely, arbitrary. The *z* value is low enough to treat contacts formed by a fairly strong polar, or even weakly associating, group and a no polar group. Contacts formed by a strongly associating group and a no polar group would require a smaller value of *z* to reproduce the pronounced experimental asymmetry of the excess functions as, e.g., in alcohol+alkane mixtures [47]. These types of mixtures may be well at, if not beyond, the limits of accurate applicability of quasi-chemical models, including DISQUAC, especially in the dilute solution range.

The groups investigated in the present work are non polar (contacts *a* and *c*), and polarizable (contact *b*), weakly polar (contact *d*) and polar (contact *s*). DISQUAC should be well adapted to study mixtures formed by these groups.

Experimental

Materials

All chemicals were commercial products from Aldrich of the best grade quality, with the exception of CCl_4 that was purchased from Fluka. They were used without further purification and their purities, as

Table 1 Supplier, molar masses, purities and densities at 298.15 K of pure dimethylsulfoxide, alkylbenzenes and chloroalkanes

Compound	Supplier	Mm/g mol^{-1}	Purity/%	ρ_{exp}/g cm^{-3}	ρ_{lit}/g cm^{-3}
Dimethylsulfoxide	Aldrich	78.134	99.7	1.0953	1.0954^{R}
Benzene	Aldrich	78.113	99.9	0.8736	0.8736^{R}
Methylbenzene	Aldrich	92.140	99.9	0.8622	0.8622^{R}
Ethylbenzene	Aldrich	106.167	99.0	0.8626	0.8625^{R}
n-Propylbenzene	Aldrich	120.194	98.0	0.8581	0.8578^{R}
iso-Propylbenzene	Aldrich	120.194	99.0	0.8566	0.8574^{R}
n-Butylbenzene	Aldrich	134.221	99.0	0.8559	0.8561^{R}
sec-Butylbenzene	Aldrich	134.221	99.0	0.8580	0.8580^{R}
tert-Butylbenzene	Aldrich	134.221	99.0	0.8623	0.8624^{R}
Tetrachloromethane	Fluka	153.823	99.5	1.5842	1.5844^{R}
1,1,2,2-Tetrachloroethane	Aldrich	169.866	98.0	1.5870	1.5867^{R}
Trichloromethane	Aldrich	119.378	99.8	1.4717	1.4797^{R}
1-Chloropropane	Aldrich	78.451	98.0	0.8843	0.8330^{R}
1-Chlorobutane	Aldrich	92.569	99.5	0.8810	0.8804^{R}
1-Chloropentane	Aldrich	106.594	99.0	0.8766	0.8771^{R}
1-Chlorohexane	Aldrich	120.620	99.0	0.8736	0.8739^{R}

^{R}Riddick Bunker and Sakano [51]

checked by gas cromatographic analysis, were ≥99%, with the exception of *n*-propylbenzene, 1,1,2,2-tetrachloroethane and 1-chloropropane which contained about 2% impurities.

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 1.

Instrumentation

Heats of mixing were determined by means of a flow microcalorimeter (model 2277, LKB-producer AB, Bromma, Sweden). The apparatus and the experimental procedure are described in detail elsewhere [48]. 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:

$$m_i=\Phi_i\rho_i/M_i \tag{1}$$

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}.

The molar excess enthalpies have been evaluated from the formula

$$H^E=I^2R(E/E_c)/m_i \tag{2}$$

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 performing H^E measurements on the test system benzene+cyclohexane. Our results differed by <2% from literature data [49] over the entire composition range.

Results and discussion

The experimental H^E data are collected in Table 2. The H^E values were fitted to the smoothing Redlich–Kister equation:

$$H^E=x_1x_2\sum_{i=0}^{n-1}a_i(x_i-x_2)^i \tag{3}$$

where x_1 is the mole fraction of DMSO and n is the number of coefficients. The values of the coefficients a_i and the standard deviation of the fit, $\sigma(H^E)$, obtained by a least squares treatment, are given in Table 3.

Excess enthalpies for equimolar mixtures, H^E (x_1=0.5), agree with results from other authors for DMSO+benzene and +cyclohexane (Table 4). The negative sign of H^E for mixtures with trichloromethane, 1,1,2,2-tetrachloroethane and dichloromethane can be ascribed to a complexes formation, namely to the strong interaction between DMSO and H of the three chloroalkanes.

Table 2 Experimental values of the molar excess enthalpies, H^E (J mol^{-1}) of binary mixtures of dimethyl sulfoxide (1)+ alkylbenzenes or chloroalkanes (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}
dimethylsulfoxide+benzene					
0.1114	289.7	0.4552	586.9	0.7148	499.4
0.1903	400.3	0.4845	586.5	0.8337	351.0
0.3197	522.3	0.5562	582.7	0.8699	290.6
0.3853	565.7	0.6528	545.5		
dimethylsulfoxide+methylbenzene					
0.1303	474.7	0.4283	820.2	0.7498	634.2
0.1835	570.0	0.4997	828.8	0.7998	541.7
0.2305	649.7	0.5291	817.5	0.8888	343.3
0.2725	703.3	0.5997	793.4	0.9230	249.7
0.3597	782.2	0.6664	746.1		
dimethylsulfoxide+ethylbenzene					
0.1471	630.1	0.3651	972.6	0.6331	948.4
0.1774	707.6	0.4631	1029.5	0.7753	752.4
0.2444	818.2	0.5349	1022.4	0.8734	491.1
0.3013	903.6	0.5799	990.5		
dimethylsulfoxide+*n*-propylbenzene					
0.1406	663.0	0.3956	1097.8	0.7236	1001.6
0.1971	818.7	0.4954	1159.7	0.7970	860.0
0.2691	955.4	0.5669	1153.7	0.8871	568.6
0.3293	1045.1	0.6626	1088.7	0.9128	453.6
dimethylsulfoxide+*iso*-propylbenzene					
0.1644	800.3	0.4958	1205.3	0.8872	572.3
0.2469	987.1	0.5960	1149.0	0.9219	425.8
0.3296	1097.9	0.7239	1016.6	0.9402	336.9
0.4245	1204.2	0.7973	865.6		
dimethylsulfoxide+*n*-butylbenzene					
0.0643	405.2	0.2681	1076.8	0.7456	1019.7
0.0839	519.3	0.3546	1176.5	0.8147	910.6
0.1208	696.5	0.4518	1248.7	0.8683	731.3
0.1548	809.5	0.5236	1264.9	0.8979	651.9
0.2155	979.6	0.5944	1222.3	0.9462	391.3
0.2155	984.9	0.6873	1151.3		
dimethylsulfoxide+*sec*-butylbenzene					
0.1545	829.0	0.3541	1141.2	0.8143	762.9
0.1798	894.3	0.5938	1075.1		
0.2151	987.1	0.7451	851.1		
dimethylsulfoxide+*tert*-butylbenzene					
0.1270	677.7	0.5218	1197.4	0.8972	567.9
0.1539	772.9	0.5926	1173.5	0.9458	346.7
0.2143	944.7	0.7442	990.5		
0.4500	1192.3	0.8136	856.3		
dimethylsulfoxide+1-chloropropane					
0.1107	435.2	0.3837	867.1	0.7135	795.5
0.1893	598.2	0.4536	914.3	0.7685	657.8
0.2374	691.5	0.4829	915.4	0.8328	515.8
0.3183	805.3	0.5546	911.9	0.9257	257.5
0.3183	807.6	0.6241	871.6		
dimethylsulfoxide+1-chlorobutane					
0.1347	579.8	0.4536	999.1	0.7685	752.2
0.1719	690.2	0.5546	1023.4	0.8328	617.3
0.2374	835.1	0.6513	957.6	0.8819	454.3
0.2933	891.0	0.4536	999.1	0.9257	331.4
0.3837	959.4	0.7135	883.3		

Table 2 Continued

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
dimethylsulfoxide+1-chloropentane					
0.1456	670.5	0.4601	1169.0	0.7732	932.2
0.1756	738.4	0.5319	1209.5	0.8197	772.6
0.2212	879.9	0.5319	1212.1	0.8721	561.3
0.2988	1020.8	0.6303	1128.7	0.9317	347.1
0.3899	1147.0	0.7189	1038.5		
dimethylsulfoxide+1-chlorohexane					
0.1615	814.7	0.5909	1244.2	0.8851	682.7
0.1940	910.4	0.6582	1181.7		
0.3250	1189.1	0.7197	1110.4		
0.3910	1258.6	0.8370	852.4		
dimethylsulfoxide+trichloromethane					
0.1021	–1340.2	0.3625	–2917.8	0.7520	–1437.8
0.1244	–1616.2	0.4312	–2925.7	0.8198	–1018.7
0.2213	–2491.2	0.5321	–2571.6	0.8722	–645.7
0.2748	–2772.1	0.6304	–2165.9	0.9192	–501.4
dimethylsulfoxide+tetrachloromethane					
0.1198	264.0	0.4757	214.5	0.7840	65.7
0.1849	284.8	0.5765	154.8	0.9159	27.9
0.2033	283.2	0.7313	82.7		
dimethylsulfoxide+1,1,2,2-tetrachloroethane					
0.1564	–2151.4	0.4257	–3841.9	0.8557	–1567.4
0.1982	–2593.0	0.4971	–3840.2	0.8990	–1125.3
0.2704	–3205.1	0.5972	–3530.5		
0.3308	–3555.8	0.7478	–2558.6		

Table 3 Values of the coefficients, a_i, standard deviations, σ (H^E), of molar excess enthalpies, H^E at 298.15 K, for dimethylsulfoxide (1)+alkylbenzene or chloroalkane (2) mixtures

Component (2)	a_0	a_1	a_2	a_3	σ (H^E)/J mol^{-1}
Benzene	2350.5	70.2	592.7	–435.1	4.6
Methylbenzene	3296.4	–66.8	854.4	–670.3	6.1
Ethylbenzene	4075.5	–267.9	1207.8	–	14
n-Propylbenzene	4610.7	329.5	1713.1	565.8	5.9
iso-Propylbenzene	4789.7	–178.1	1817.8	–	12.2
n-Butylbenzene	4969.2	–140.5	2666.7	481.6	20
sec-Butylbenzene	4503.7	–1061.7	2491.9	406.8	22
tert-Butylbenzene	4794.1	–244.5	2268.7	337.3	6.9
Tetrachloromethane	788.4	–1230.7	935.4	–	14
1,1,2,2-Tetrachloroethane	–15317.0	2924.7	1620.7	–810.9	4.0
Trichlomethane	–10949.0	6982.1	543.2	–2362.6	44
1-Chloropropane	3676.4	231.0	501.6	–1038.3	11
1-Chlorobutane	4070.0	–218.8	1242.5	–	21
1-Chloropentane	4802.8	393.6	1002.9	–903.0	18
1-Chlorohexane	5108.3	–288.0	2202.6	1103.0	5.2

Assessment of geometrical parameters

Every mixtures under study, i.e. dimethylsulfoxide+alkane, or +cyclohexane, or +benzene and alkylbenzenes, or +tetrachloromethane or chloroalkanes are regarded as possessing three 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, cycloaliphatic (c-CH_2 groups), type d, chlorine (Cl group), type s, sulfoxide (S=O group).

Table 4 Molar excess Gibbs energies G^E (T; x_1=0.5) of dimethylsulfoxide (1)+tetrachloromethane or dichloromethane, trichloromethane, benzene (2) mixtures at various temperatures T and equimolar composition: comparison of direct experimental results (exp.)[a] with values calculated (calc.) using the coefficients $C^{\text{dis}}_{\text{uv},l}$ and $C^{\text{quac}}_{\text{uv},l}$ from Tables 9–13

Component (2)	T/K	G^E (T; x_1=0.5)/J mol^{-1}		Source of experimental data
		calc.	exp.	
Tetrachloromethane	293.15	997	998	[20]
	313.15	1054	1051	[20]
Trichloromethane	293.15	–973	–959	[21]
	298.15	–938	–930	[21]
			–914	[22]
	308.15	–892	–875	[22]
	318.15	–870	–817	[21]
	328.15	–870	–737	[22]
			–757	[21]
Dichloromethane	298.15	–331	–331	[22]
			–341	[21]
Benzene	298.15	794	795	[23]
	313.15	808	829	[23]
	328.15	826	829	[23]
	343.15	849	833	[23]

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

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 [50] have been adopted.

Estimation of interaction parameters

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 4–6 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.

Dimethylsulfoxide+*n*-alkanes or cyclohexane

The mixtures of dimethylsulfoxide with *n*-alkane or cyclohexane exhibit a large miscibility gap consequently no G^E and H^E have been measured. Only liquid–liquid equilibrium data (LLE) [18, 19] at γ_i and infinite dilution are reported in the literature [34–42]. DISQUAC provide a good representation of the experimental data using two dispersive and two quasi-chemical coefficients for the (a,s) and (c,s) contacts. The rules we found are as follows:

(1a) the dispersive coefficients of the (a,s) contact, $C^{\text{dis}}_{\text{as},l}$, are the same for the *n*-alkanes and cyclohexane mixtures (6.8 for l=1 and 8.0 for l=2) (Table 11).

(1b) the quasi-chemical coefficients, $C^{\text{quac}}_{\text{as},l}$, of the (a,s) contact are higher than those of the (c,s) contact, $C^{\text{quac}}_{\text{cs},l}$.

Dimethylsulfoxide+benzene or alkylbenzenes or polyalkylbenzenes

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

(2a) The non-polar aliphatic/benzene (a,b) interactions are represented by dispersive parameters and are determined independently on the basis of *n*-alkane+benzene mixtures: $C^{\mathrm{dis}}_{\mathrm{ab},1}$=0.2598 and $C^{\mathrm{dis}}_{\mathrm{ab},2}$=0.5622 [4]

(2b) The (a,s) contact energies, $C^{\mathrm{dis}}_{\mathrm{as},1}$ and $C^{\mathrm{quac}}_{\mathrm{as},1}$ determined independently on the basis of dimethylsulfoxide+*n*-alkane mixtures ((1a) and (1b) rules), can be used.

(2c) The dispersive coefficients of the (b,s) contact, $C^{\mathrm{dis}}_{\mathrm{bs},1}$ of dimethylsulfoxide in alkylbenzenes decrease regularly with increasing the chain length of the alkyl groups adjacent the phenyl group (C_6H_5–) (Table 12). The interchange coefficients, $C_{\mathrm{bs,l}}$, have been expressed in terms of so-called alkyl-group increments, $\sigma^{\mathrm{R}}_{\mathrm{bs},1}$ by the equation:

$$C_{\mathrm{bs},1} = C^{0}_{\mathrm{bs},1}(1 + n^{\mathrm{m}}\sigma^{\mathrm{m}}_{\mathrm{bs},1} + n^{\mathrm{e}}\sigma^{\mathrm{e}}_{\mathrm{bs},1})$$

where $C^{0}_{\mathrm{bs},1}$ are the interchange coefficients of the base compound, benzene, and n^{m}, n^{e} represent the number of carbon atoms in the alkyl group adjacent the phenyl

Table 5 Molar excess enthalpies H^{E} (T; x_1=0.5) of dimethylsulfoxide (1)+benzene or alkylbenzene or chloroalkane (2) mixtures at various temperatures T and equimolar composition: comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficients $C^{\mathrm{dis}}_{\mathrm{uv},1}$ and $C^{\mathrm{quac}}_{\mathrm{uv},1}$ from Tables 9–13

Component (2)	T/K	H^{E} (T; x_1=0.5)/J mol^{-1}		Source of experimental data
		calc.	exp.	
Tetrachloromethane	298.15	181	190	[24]
			193	[25]
			181	[26]
			197	this work
	308.15	161	242	[26]
1,1,1-Trimethylethane	298.15	636	637	[22]
	308.15	613	655	[22]
Trichloromethane	298.15	–2748	–2802	[27]
			–2750	[25]
			–2735	this work
			–2825	[26]
	309.00	–1855	–2780	[26]
1,1,2,2-Tetrachloroethane	298.15	–3832	–3829	this work
Dichloromethane	298.15	–1309	–1247	[22]
	308.15	–1281	–1228	[22]
1-Chloropropane	298.15	920	919	this work
1-Chlorobutane		1032	1018	this work
1-Chloropentane		1189	1201	this work
1-Chlorohexane		1355	1277	this work
Benzene	298.15	587	588	this work
			585	[28]
			589	[29]
			602	[30]
	308.15	515	588	[26]
	320.65	425	628	[23]
Methylbenzene	298.15	833	826	this work
	303.15	821	857	[31]
Ethylbenzene	298.15	984	1018	this work
n-Propylbenzene		1134	1153	this work
iso-Propylbenzene		1132	1197	this work
n-Butylbenzene		1220	1242	this work
sec-Butylbenzene		1280	1126	this work
tert-Butylbenzene		1308	1198	this work
1,4-Dimethylbenzene		1060	1060	[28]
			1132	[32]
	313.15	1060	1087	[33]
1,2,4-Trimethylbenzene	298.15	1279	1180	[28]
1,3,5-Trimethylbenzene			1279	[28]
			1213	[34]

Table 6 Activity coefficients at infinite dilution, $\ln\gamma_1^\infty$, of dimethylsulfoxide (1)+*n*-alkane or cyclohexane or benzene (2) mixtures at various temperatures *T*: comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficients $C_{\mathrm{uv},1}^{\mathrm{dis}}$ and $C_{\mathrm{uv},1}^{\mathrm{quac}}$ from Tables 9–13

Component (2)	*T*/K	$\ln\gamma_1^\infty$		$\ln\gamma_2^\infty$		Source of experimental data
		calc.	exp.	calc.	exp.	
Pentane	298.15			3.64	4.12	[35]
					3.75	[36]
	303.15			3.59	3.89	[37]
	333.15			3.28	3.25	[37]
	353.15			3.09	2.94	[37]
Hexane	298.15			4.17	4.35	[38]
					4.43	[35]
					4.23	[36]
	303.15			4.10	4.38	[39]
					4.17	[40]
					4.28	[37]
	313.15			3.98	4.28	[41]
	333.15			3.74	3.73	[39]
					3.57	[37]
	353.15			3.53	3.23	[37]
Heptane	298.15			4.61	4.80	[35]
					4.68	[36]
	303.15			4.54	4.67	[37]
					4.65	[39]
					4.56	[40]
	313.15			4.40	4.65	[41]
	333.15			4.14	3.87	[37]
					3.98	[39]
	353.15			3.89	3.51	[37]
Octane	298.15			5.15	5.14	[36]
	303.15			5.07	4.98	[40]
				5.05	5.04	[37]
	333.15			4.61	4.16	[37]
	353.15			4.33	3.77	[37]
Nonane	298.15			5.62	5.58	[36]
	303.15			5.53	5.43	[37]
	333.15			5.02	4.43	[37]
	353.15			4.71	4.03	[37]
Decane	303.15			5.99	5.81	[37]
	333.15			5.43	4.68	[37]
	353.15			5.09	4.26	[37]
Octadecane	353.15	3.18	3.40			[42]
Octacosane	353.15	2.83	2.61			[43]
	373.15	2.47	2.36			[43]
	393.15	2.15	2.06			[43]
Triacontane	353.15	2.77	2.64			[42]
Cyclopentane	303.15			3.01	3.36	[39]
Cyclohexane	298.15			3.31	3.57	[36]
					3.70	[35]
	303.15			3.27	3.42	[40]
					3.75	[39]
					3.60	[37]
	313.15			3.20	3.57	[41]
	333.15			3.08	3.08	[39]
					3.03	[37]
	353.15			2.98	2.74	[37]
Benzene	298.15	4.59	4.65	3.92	3.41	[23]
	313.15	4.36	4.73	3.75	3.31	[23]
	328.15	4.18	4.59	3.62	3.19	[23]
	343.15	4.05	4.24	3.52	2.98	[23]

Table 7 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 [50], (V_{CH_4}=17.12·10^{-6} m^3 mol^{-1}; A_{CH_4}=2.90·10^5 m^2 mol^{-1})

Group	r_G	q_G
$-CH_3$	0.79848	0.73103
$-CH_2-$	0.59755	0.46552
CH_2[a]	0.59755	0.59482
$-CH$	0.39603	0.19655
CH[b]	0.39603	0.40000
>C<	0.19451	0.00000
Cl[c]	0.67874	0.62069
Cl[d]	0.71495	0.62759
C_6H_6	2.82480	2.07280
C_6H_5-	2.67757	1.83793
SO	0.90771	0.66897

[a]In CH_2Cl_2; [b]in $-CHCl_3$; [c]in $-CH_2Cl$; [d] in $-CHCl_2-$

group ($\sigma^{m}_{bs,1}$=–0.110; $\sigma^{e}_{bs,1}$=–0.010; ($\sigma^{m}_{bs,2}$=–0.210; $\sigma^{e}_{bs,2}$=–0.024).

(2d) The dispersive coefficients of the (b,s) contact, $C^{dis}_{bs,1}$ of dimethylsulfoxide in polyalkylbenzenes decreases with increasing the number of the CH_3 groups in the phenyl group from methylbenzene to trimethylbenzene according with the equation:

$$C_{bs,1} = C^{0}_{bs,1}(1 - n^{m}\sigma^{m}_{bs,1})$$

where $C^{0}_{bs,1}$ are the interchange coefficients of the base compound, methylbenzene and n^m represent the number of methyl groups in the polyalkybenzene ($\sigma^{m}_{bs,1}$=–0.040, $\sigma^{m}_{bs,2}$=–0.075).

(2e) The quasi-chemical parameters of the (b,s) – contacts are constant ($C^{quac}_{bs,1}$=4.90, $C^{quac}_{bs,2}$=1.8) except for the benzene ($C^{quac}_{bs,1}=C^{quac}_{bs,2}$=0)

Unfortunately, G^E data are available only for benzene (Table 4). Previous investigations of many classes of systems showed that Gibbs energy coefficients change with the structure of components but slower than the enthalpic coefficients and for the approximate representation of VLE in a limited range of temperature it may be sufficient to assume for the same behaviour of $C^{dis}_{bs,2}$ regardless of the alkyl chain length.

Dimethylsulfoxide+polychloroalkanes

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

(3a) The non-polar aliphatic/chlorine (a,d) – contacts are represented by dispersive parameters $C^{dis}_{ad,1}$=0.093 and $C^{dis}_{ad,2}$=0.180 [5].

Table 8 Relative volumes, r_i, relative total surfaces, q_i, and molecular surface fractions, α_v, (v=a, b, d, s) of dimethylsulfoxide, chloroalkanes and alkylbenzenes calculated from the group increments r_G and q_G given in Table 7

Compound	r_i	q_i	α_a	α_s	α_d	α_b
Dimethylsulfoxide	2.5047	2.1310	0.6861	0.3139	0.0000	0.0000
Tetrachloromethane	3.0543	2.5104	0.0000	0.0000	1.0000	0.0000
Trichloromethane	2.5409	2.2828	0.1752	0.0000	0.8248	0.0000
1,1,2,2-Tetrachloroethane	3.6519	2.9035	0.1354	0.0000	0.8646	0.0000
Dichloromethane	2.0275	1.8500	0.3215	0.0000	0.6785	0.0000
Chloropropane	2.6723	2.2828	0.7281	0.0000	0.2719	0.0000
Chlorobutane	3.2699	2.7483	0.7742	0.0000	0.2258	0.0000
Chloropentane	2.8674	3.2138	0.8069	0.0000	0.1931	0.0000
Chlorohexane	4.4650	3.6793	0.8313	0.0000	0.1687	0.0000
Benzene	2.8248	2.0724	0.0000	0.0000	0.0000	1.0000
Methylbenzene	3.4761	2.5689	0.2846	0.0000	0.0000	0.7154
Ethylbenzene	4.0736	3.0344	0.3943	0.0000	0.0000	0.6057
n-Propylbenzene	4.6719	3.5000	0.4749	0.0000	0.0000	0.5251
sec-Propylbenzene	4.6709	3.4965	0.4744	0.0000	0.0000	0.5256
n-Butylbenzene	5.2687	3.9655	0.5365	0.0000	0.0000	0.4635
sec-Butylbenzene	5.2684	3.9620	0.5360	0.0000	0.0000	0.4640
tert-Butylbenzene	5.2676	4.0310	0.5441	0.0000	0.0000	0.4559
Dimethylbenzene	4.1273	3.0655	0.4769	0.0000	0.0000	0.5231
Trimethylbenzene	4.7786	3.5621	0.6157	0.0000	0.0000	0.3843

For cyclohexane r_i=3.5187, q_i=2.5966, α_c=1.0000. For the parameters r_i and q_i (α_a=1.0000) see Kehiaian *et al.* (1978) [4].

Table 9 Dispersive interchange coefficients for the contacts (a,b), (a,c) and (a,d) previously determined from mixtures of *n*-alkane+benzene or +*n*-alkane or +cyclohexane and *n*-alkane+chloroalkane mixtures respectively (Kehiaian and Marongiu, 1988) [5]

u,*v*	$C^{\text{dis}}_{\text{uv},1}$	$C^{\text{dis}}_{\text{uv},2}$
a,b	0.2598	0.5622
a,c	0.0300	0.1200
a,d*	0.0260	0.0500
a,d**	0.0930	0.1800

*for CH_3Cl, CH_2Cl_2, $CHCl_3$; **for CCl_4, $CH_3–(CH_2)_m–Cl$

Table 10 Quasi-chemical interchange coefficients for the contacts (a,d) and (c,d) previously determined from mixtures of chloroalkane+*n*-alkane mixtures (Kehiaian and Marongiu, 1988) [5]

Chloroalkane	$C^{\text{quac}}_{\text{uv},1}$	$C^{\text{quac}}_{\text{uv},2}$
CCl_4	0.0000	0.0000
$CHCl_3$	0.3350	0.6390
CH_2Cl_2	1.1500	2.1100
$CH_3–(CH_2)_m–Cl$	2.3400	3.7500
$CHCl_2CHCl_2$	0.4390	0.7610

(3b) The (a,s) contact energies, $C^{\text{dis}}_{\text{as},1}$ and $C^{\text{quac}}_{\text{as},1}$, determined independently on the basis of dimethylsulfoxide+*n*-alkane mixtures (see above), can be used.

(3c) The dispersive coefficients of the (d,s) contact generally decrease with increasing the number of Cl atoms in the polychloroalkane of general formula $H_xC_yCl_{4-x}$ with the exception of $CHCl_3$, $CHCl_2–CHCl_2$ and CH_2Cl_2 due to existence of specific interactions between the dimethylsulfoxide and $CHCl_3$ or $CHCl_2–CHCl_2$ or CH_2Cl_2.

For mixtures with these compounds the quasi-chemical enthalpy coefficient are negative (Table 13). To take into account the asymmetry of the excess functions of similar mixtures (propanone+$CHCl_3$) Gonzales *et al.* [15] estimate the CH group surface jointly with the interchange coefficients of the (a,d) contact.

(3d) The quasi-chemical coefficients, $C^{\text{quac}}_{\text{ds},1}$, the (d,s) contact generally decrease with increasing the number of Cl atoms in the polychloroalkane of general formula $H_xC_yCl_{4-x}$ with the exception of $CHCl_3$ and CH_2Cl_2 due to existence of specific interactions between the S=O of dimethylsulfoxide and the hydrogen atoms of $CHCl_3$ or CH_2Cl_2.

(3e) The dispersive parameters of the (d,s) contacts for the *n*-chloroalkane are constant with increasing the number of alkyl group adjacent to the Cl group.

(3f) The quasi-chemical parameters of the (d,s) contacts for the *n*-chloroalkane decrease with increasing the number of alkyl group adjacent to the Cl group.

Comparison with experiment and discussion

Using the set of parameters dispersive and quasi-chemical reported in Tables 9–13 a good agreement with experiment is obtained for the liquid–liquid equilibrium (LLE) of the dimethylsulfoxide+*n*-hexane (Fig. 1) and +cyclohexane (Fig. 2); for the excess Gibbs energies of DMSO+tetrachloromethane (Fig. 3) and +benzene (Fig. 4); for the excess enthalpies of DMSO+benzene (Fig. 5), +alkylbenzenes (Fig. 6), +chloroalkanes (Fig. 7) and +trichloromethane (Fig. 8). Only the symmetry of the G^E of the dimethylsulfoxide+trichloroalkane and dichloroalkane is not satisfactory (also Tables 4–6).

In our opinion, the main advantage of using DISQUAC is, apart from the more accurate represen-

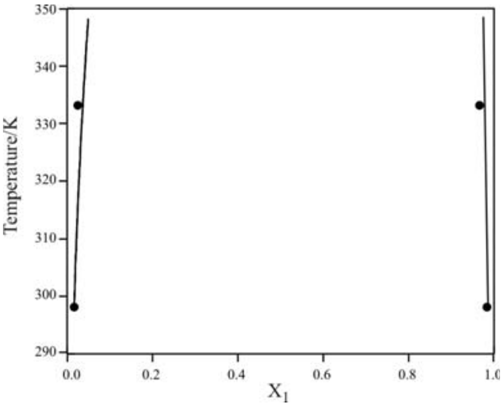

Fig. 1 Comparison of liquid–liquid phase diagrams: temperature *T* for the dimethylsulfoxide (1)+*n*-hexane (2) *vs.* x_1, the mole fraction of DMSO; –– – predicted values, ● – experimental results [18]

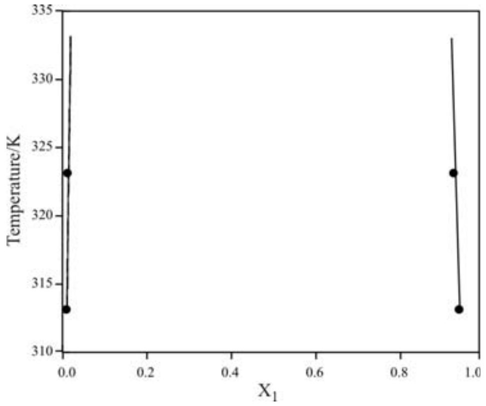

Fig. 2 Comparison of liquid–liquid phase diagrams: temperature *T* for the dimethylsulfoxide (1)+cyclohexane (2) vs. x_1, the mole fraction of DMSO; –– – predicted values, ● – experimental results [19]

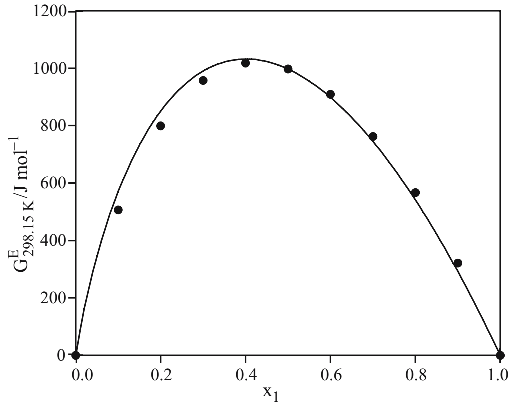

Fig. 3 Comparison of theory with experiments for the molar excess Gibbs energies, G^E, at 293.15 K, for DMSO (1)+CCl_4 (2) mixtures *vs.* x_1, the mole fraction of DMSO; —– predicted values, ● – experimental results [20]

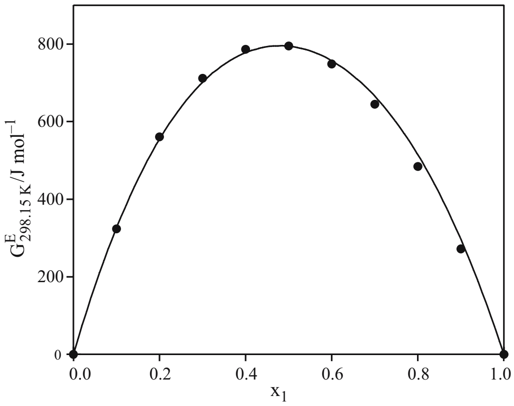

Fig. 4 Comparison of theory with experiments for the molar excess Gibbs energies, G^E, at 293.15 K, for DMSO (1)+C_6H_6 (2) mixtures *vs.* x_1, the mole fraction of DMSO; —– predicted values, ● – experimental results [23]

tation 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 9–13), 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.

Inspection of the coefficients listed in Tables 9–13 permits us to formulate several general rules. The dispersive coefficients remain almost constant or even decrease for the first members, especially when the functional group contain π–electrons, due, in our opinion, to an inductive effect (mixtures

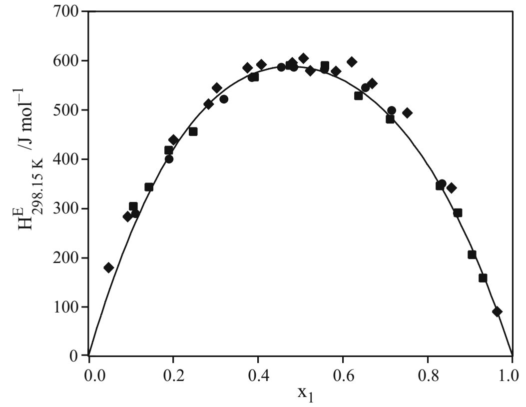

Fig. 5 Comparison of theory with experiments for the molar excess enthalpies, H^E , at 298.15 K, for DMSO (1)+C_6H_6 (2) mixtures *vs.* x_1, the mole fraction of DMSO; —– predicted values, experimental results: ● – this work, ■ – [28], ◆ – [30]

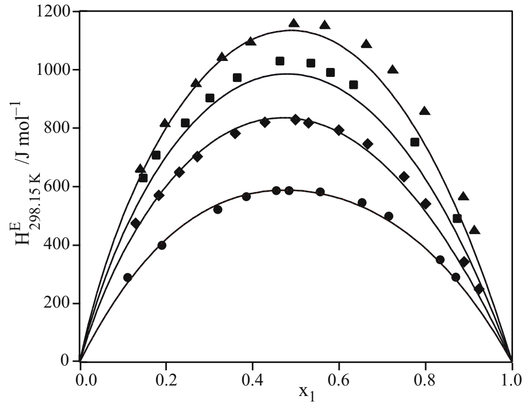

Fig. 6 Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for DMSO (1)+alkylbenzene (2) mixtures *vs.* x_1, the mole fraction of DMSO: —– predicted values, experimental results: this work: ● – benzene, ◆ – methylbenzene, ■ – ethyl benzene, ▲ – *n*-propylbenzene

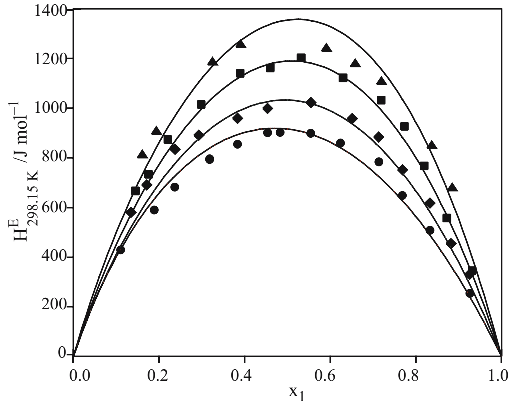

Fig. 7 Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for DMSO (1)+chloroalkane (2) mixtures *vs.* x_1, the mole fraction of DMSO: —– predicted values, experimental results: this work: ● – chloropropane, ◆ – 1-chlorobutane, ■ – chloropentane, ▲ – chlorohexane

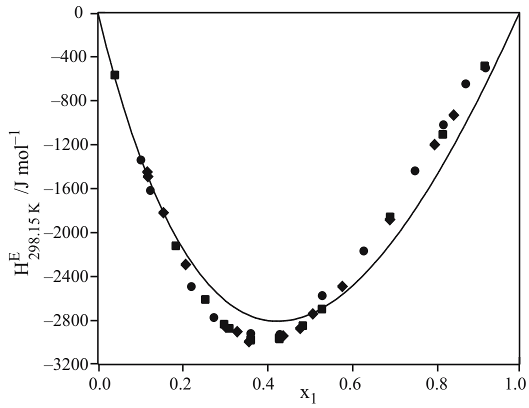

Fig. 8 Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for DMSO (1) +$CHCl_3$ (2) mixtures *vs.* x_1, the mole fraction of DMSO: –– – predicted values, experimental results: ● – this work, ■ – [27], ◆ – [26]

with alkylbenzenes). A good representation of the symmetry of the experimental H^E curves was obtained using a non-negligible quasi-chemical contribute, $C^{quac}_{bs,1}$=4.9 and $C^{quac}_{bs,2}$=1.80, constant for all the DMSO+alkylbenzene mixtures (only for mixtures with benzene are $C^{quac}_{bs,1}$=$C^{quac}_{bs,2}$=0) (Table 12).

For the mixture of DMSO with tetrachloromethane, 1,1,1-trichloroethane and monochloroalkane a good agreement between experimental and calculated H^E curves was obtained if for the sulfoxide/chlorine contact was considered both the dispersive parameters ($C^{quac}_{bs,1}$ decreasing from the tetrachloroethane to chloropropane and constant with increasing the chain length of the alkyl group of the chloroalkane) and the quasi-chemical parameters (decreasing from tetrachloro to chloropropane and decreasing as the length of the alkyl chain adjacent to the polar group Cl increases). This is attributed to the steric effect, which reduces the electrostatic 2–2 type interactions.

The influence of the inductive of an alkyl group adjacent to a polar or polarizable Y group on the dispersive interchange coefficients $C_{uv,l}$, can be more easily explained if consider that the interchange energies $\Delta\varepsilon_{uv,l}$ are related to the interaction energies ε_{uv}:

$$\Delta\varepsilon_{uv,l}=(|\varepsilon_{uu}|+|\varepsilon_{vv}|)/2-|\varepsilon_{uv}|$$

where ε values being negative.

In polar–polar or polar–polarizable systems (*u*=s, *v*=b,d) where interactions are mainly of the 1–2 type, the inductive effect exerted by an alkyl group adjacent to the polar or polarizable Y group increases the dispersive interaction energies $|\varepsilon_{uv}|$ and consequently decrease $\Delta\varepsilon_{uv,l}$ (this, in turn, causes an decrease in $C^{dis}_{uv,l}$).

The excess enthalpies of DMSO+$CHCl_3$, $CHCl_2$–$CHCl_2$ and +CH_2Cl_2 are large and negative again indicating the existence of specific interaction between the DMSO and $CHCl_3$ or $CHCl_2$–$CHCl_2$ or CH_2Cl_2. The symmetry of the H^E for dimethylsulfoxide+trichloromethane, +1,1,2,2-tetrachloroethane and +dichloromethane is shifted to the region rich in DMSO. The asymmetry of the excess function was interpreted as a result of formation of AB complexes. However, a pure physical model such as DISQUAC theory is able to represent this asymmetry using quasi-chemical enthalpy coefficient of the (d,s) contact strongly negative (Table 13). Also the quasi-chemical enthalpy coefficient for the mixtures with dichloromethane is negative.

Table 11 Dispersive and quasi-chemical interchange coefficients for the contacts (a,s) and (c,s), determined from mixtures of dimethylsulfoxide+*n*-alkane, and +cyclohexane mixtures respectively (this work)

u,v	$C^{dis}_{uv,1}$	$C^{dis}_{uv,2}$	$C^{quac}_{uv,1}$	$C^{quac}_{uv,2}$
a,s	6.8	8.0	9.0	12.0
c,s	6.8	8.0	8.8	6.0

Table 12 Dispersive and quasi-chemical interchange coefficients for the contacts (b, s) determined from mixtures of dimethylsulfoxide+alkylbenzene mixtures (this work)

Alkylbenzene	$C^{dis}_{uv,1}$	$C^{dis}_{uv,2}$	$C^{quac}_{uv,1}$	$C^{quac}_{uv,2}$
Benzene	9.76	7.69	0.00	0.00
Methylbenzene	8.69	6.05	4.90	1.80
Ethylbenzene	8.59	5.87	4.90	1.80
n-Propylbenzene	8.49	5.68	4.90	1.80
iso-Propylbenzene	8.49	5.68	4.90	1.80
n-Butylbenzene	8.39	5.50	4.90	1.80
sec-Butylbenzene	8.39	5.50	4.90	1.80
tert-Butylbenzene	8.39	5.50	4.90	1.80
Dimethylbenzene	8.34	5.60	4.90	1.80
Trimethylbenzene	8.00	5.14	4.90	1.80

Table 13 Dispersive and quasi-chemical interchange coefficients for the contacts (d,s) in different types of Cl atoms in chloroalkane+dimethylsulfoxide mixtures (this work)

Chloroalkane	$C^{dis}_{uv,1}$	$C^{dis}_{uv,2}$	$C^{quac}_{uv,1}$	$C^{quac}_{uv,2}$
CCl_4	4.03	5.25	9.57	6.66
CH_3CCl_3	4.03	5.25	5.38	1.91
$CH_3(CH_2)_2Cl$	2.00	3.00	1.93	1.02
$CH_3(CH_2)_3Cl$	2.00	3.00	1.23	0.90
$CH_3(CH_2)_4Cl$	2.00	3.00	1.00	0.90
$CH_3(CH_2)_5Cl$	2.00	3.00	1.00	0.90
CH_2Cl_2	1.20	2.30	2.20	–4.00
$CHCl_2CHCl_2$	1.40	16.30	2.40	–21.00
$CHCl_3$	1.50	18.00	2.40	–21.00

Concerning the temperature dependence of H^E in all cases DISQUAC predicts the negative sign correctly, yet the absolute values are too small. As all the quantities listed in Tables 4–6 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.

It is generally admitted that the interchange ‘energies’ in lattice-type models are temperature dependent, i.e. they must be regarded as free energies. There is a priori no reason that q_{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.

Conclusions

This work, following the previous on chloroalkanes [5], on polyethers [6], alkanones [7], alkanals [8], 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 apparent 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 remains 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
H	molar enthalpy
q	relative molecular area
r	relative molecular volume
u, v	any contact surfaces
x	mole fraction
α	molecular surface fraction

Subscripts

a,b, c, d, s	type of contact surface (group) a, CH_3, CH_2; b, C_6H_6; c, c-CH_2; d, Cl; s, SO
calc	calculated quantity
exp	experimental quantity
i	type of molecule (component)
l	order of interchange coefficient: l=1, Gibbs energy; l=2, enthalpy

Superscripts

dis	dispersive
E	excess property
quac	quasi-chemical

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