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Thermodynamic properties of *n*-alkylbenzene+*n*-alkane or cyclohexane mixtures. Comparison with disquac predictions[1]

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Abstract

The molar excess enthalpies (H^E), at 298.15 K, of some mixtures of alkylbenzenes with *n*-heptane or cyclohexane were measured using a flow calorimeter. These data, along with the literature data on molar excess enthalpies (H^E), molar excess Gibbs energies (G^E), molar excess heat capacity (C_p^E) and activity coefficients at infinite dilution (γ_i^∞) of mixtures in *n*-alkanes or cyclohexane of mono-alkylbenzenes of general formula, C_6H_5–$(CH_2)_{n-1}CH_3$, isomeric dimethylbenzenes (xylenes) and isomeric trimethylbenzenes were treated within the framework of DISQUAC, an extended group contribution model, in the simplified 'dispersive' version. The systems were characterized by three types of contact surfaces: phenyl (C_6H_5 group), alkane (CH_3 or CH_2 groups) and cyclohexane (*c*-CH_2 group). The interchange energy parameters of the alkane/cyclohexane contacts were determined previously, the interaction parameters of the alkane/phenyl and cyclohexane/phenyl contacts are reported in this study. The dispersive parameters depend on the environment of the phenyl group and the number of alkyl groups adjacent to the phenyl group. The model provides a fairly consistent description of the experimental data as a function of concentration. © 1998 Elsevier Science B.V.

Keywords: Excess enthalpies; Gibbs energies; Group contributions; Heat capacity; Microcalorimetry

1. Introduction

The thermodynamic excess functions of organic liquid mixtures depend on the chemical nature, the size and the shape of the constituent molecules. For molecules of similar chemical structure, e.g. alkanes, the size and shape factors yield the main contributions, viz. the free-volume contribution and the combinatorial entropy of mixing. Recently, it has been suggested [1] that additional contributions arise in systems containing molecules of anisotropic shape (orientational order) or of different degrees of internal motion (conformational effects) [2].

For molecules of dissimilar molecular nature but nearly the same size and shape, the differences in force fields produce the main contribution to the thermodynamic excess functions. Orientational effects, conditioned by the energy differences and molecular inhomogeneity, become rather important and also need to be taken into account.

Since it is impossible to predict quantitatively the chemical contribution, one has to adjust a few parameters for each binary system in order to describe the properties of mixtures. A significant saving of adjus-

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[1] This paper is a contribution to the TOM Project [6–8].

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Table 1
Molar excess Gibbs energies G^E (T; x_1=0.5) of *n*-alkylbenzene (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 $C_{sv,l}$ from Tables 9 and 10 (m is the number of C atoms in the alkane, *c*-6 means cyclohexane)

m	T (K)	G^E (T; x_1=0.5) (J mol^{-1})		Source of experimental data
		Calc.	Exp.	
Methylbenzene				
6	313.15	275	297	[24]
	343.15	250	181	[25]
7	298.15	287	282	[27]
			296	[28]
			161	[26]
			283	[29]
	303.15	282	268	[30]
			264	[28]
	313.15	272	272	[24]
			269	[28]
			255	[31]
	328.15	257	290	[32]
	363.15	227	171	[33]
8	313.15	259	237	[24]
	333.15	238	240	[34]
10	313.15	215	186	[24]
c-6	293.15	302	301	[35]
			301	[36]
	298.15	297	295	[35]
	303.15	291	284	[35]
			284	[36]
	308.15	286	279	[35]
	313.15	281	272	[35]
			272	[36]
	323.15	271	208	[37]
Ethylbenzene				
6	313.15	263	286	[24]
7	298.15	287	290	[38]
	313.15	275	276	[24]
			282	[38]
	327.80	264	273	[38]
	373.15	238	222	[39]
8	313.15	275	219	[24]
	373.15	236	204	[39]
10	313.15	253	214	[24]
c-6	303.15	233	224	[40]
	313.15	222	208	[40]
	323.15	212	201	[40]
1,2-Dimethylbenzene				
7	348.15	267	271	[41]
			287	[42]
	358.15	263	259	[42]
	368.30	259	267	[42]
c-6	303.15	328	331	[43]
	323.15	308	317	[43]

Table 1 (continued)

1,3-Dimethylbenzene				
7	348.15	215	217	[41]
c-6	298.15	308	297	[44]
	323.15	286	230	[43]
1,4-Dimethylbenzene				
6	313.15	211	252	[24]
7	298.15	226	220	[38]
	313.15	221	220	[38]
			220	[24]
	328.15	215	209	[38]
	348.15	209	211	[41]
	363.15	204	160	[25]
8	313.15	219	199	[24]
10	313.15	194	146	[24]
c-6	298.15	298	296	[45]
	318.15	281	246	[45]
	323.15	277	251	[43]
	328.15	273	244	[45]

Experimental data listed in this table have been obtained by reduction of the original P–x data with the 2- or 3-parameter Redlich–Kister equation, vapor phase nonideality corrected in terms of the second virial coefficients.

table parameters can be realized for classes of organic molecules which are ensembles of distinct functional groups, whereby each 'group' consists of a few atoms and is situated in a given intramolecular environment. A large number of compounds can thus be formed from a relatively small number of groups. Interaction parameters are adjusted to characterize each pair of groups and the properties of binary or multicomponent mixtures may be predicted in terms of these parameters. For this purpose, one needs either a solution model or, at least, some more or less empirical equations. The different group-contribution methods proposed so far depend on the choice of the models and equations [3]. For example, the recent UNIFAC method [4] describes excess Gibbs energies by means of two adjustable parameters per pair of groups. The combinatorial entropy is estimated by using the Flory–Huggins equation and the UNIQUAC equation [5] is used to estimate the contribution due to molecular interactions. The UNIFAC model should, therefore, be regarded as an empirical method for estimating liquid–vapor equilibria in fairly complex systems. For several years, we have interpreted [6–11] the properties of organic mixtures in terms of group surface interactions by using DISQUAC, an extended quasi-chemical pseudo-lattice group contribution model [8].

Substances that were investigated in this paper can be classified as follows:

n-alkanes, CH_3–$(CH_2)_{m-2}$–CH_3, linear molecules formed by CH_2 and CH_3 segments;
cyclohexane, a globular non-polar molecule;
benzene, a spheroidal non-polar molecule; and
alkylbenzene, weakly-polar molecules (electric dipole moment, $\mu<0.5$ Debye) of irregular shape, formed by C_6H_5, CH_2 and CH_3 segments.

Between alkane and cyclohexane and between benzene and alkylbenzene, dispersive intermolecular forces act on the molecules, these forces are stronger in the second type of mixtures than in the first type because of the presence of π electrons.

Alkylbenzenes represent, besides many technically important classes of substance, a particularly interesting family of molecules for the purpose of testing group-contribution models. As it is well known [12], mixtures of aromatic and alkane compounds have much larger values for G^E and H^E than the mixtures of alkanes. This is probably due to the relatively strong interactions between aromatic π-electrons (π–π interactions) compared with aliphatic–aliphatic and aromatic–aliphatic interactions. Alkylation of the benzene ring, reducing the aromatic fraction on the molecules, produces a decrease in H^E and the G^E.

Table 2
Molar excess enthalpies H^E (T; x_1=0.5) of *n*-alkylbenzene (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 $C_{sv,l}$ from Tables 9 and 10 (*m* is the number of *C* atoms in the alkane, *c*-6 means cyclohexane)

m	*T* (K)	H^E (T; x_1=0.5) (J mol^{-1})		Source of experimental data
		Calc.	Exp.	
Methylbenzene				
6	293.15	576	463	[46]
	298.15	570	585	[47]
	323.15	539	491	[47]
7	293.15	609	560	[46]
	298.15	602	564	[49]
			554	[48]
			521	[50]
			532	[51]
			553	[52]
	308.15	588	525	[51]
	323.15	568	524	[52]
10	298.15	676	577	[53]
12	298.15	712	605	[53]
14	298.15	740	690	[53]
			703	[51]
16	298.15	764	750	[52]
			733	[53]
	323.15	661	650	[52]
c-6	293.15	629	590	[46]
	298.15	624	629	[54]
			611	[55]
			623	[56]
			613	[57]
			347	[47]
	303.15	609	610	[58]
	316.15	570	519	[59]
				[75]
Ethylbenzene				
7	288.15	552	529	[60]
	298.15	537	540	[49]
			545	[61]
			561	[62]
	308.15	520	528	[60]
8	298.15	564	567	[63]
			699	[64]
c-6	298.15	572	573	[62]
			541	[65]
Propylbenzene				
7	298.15	435	440	[61]
8	298.15	459	429	[60]
	308.15	442	427	[60]
Butylbenzene				
7	298.15	361	375	[61]

Table 2 (continued)

1,2-Dimethylbenzene				
6	298.15	411	449	[47]
	308.15	406	422	[66]
	323.15	399	399	[47]
7	298.15	437	410	[67]
c-6	298.15	627	626	[62]
			316	[68]
1,3-Dimethylbenzene				
6	298.15	352	385	[47]
	308.15	347	373	[67]
	323.15	340	354	[47]
7	298.15	374	378	[69]
			403	[52]
	323.15	361	388	[52]
c-6	298.15	574	574	[52]
			337	[68]
	308.15	557	516	[65]
	323.15	530	530	[52]
1,4-Dimethylbenzene				
6	298.15	325	351	[47]
	323.15	313	267	[47]
7	298.15	345	345	[69]
			326	[51]
10	298.15	392	324	[51]
	303.15	386	318	[51]
	308.15	381	310	[51]
14	298.15	435	353	[51]
16	298.15	451	393	[51]
c-6	288.15	577	581	[70]
	298.15	560	563	[54]
			551	[71]
			302	[68]
			552	[70]
	300.15	556	532	[72]
	308.15	542	530	[70]
	313.15	533	533	[73]
1,2,4-Trimethylbenzene				
7	298.15	272	273	[74]
10		313	251	[74]
12		334	248	[74]
14		351	257	[74]
16		365	264	[74]
c-6	298.15	628	628	[54]
1,3,5-Trimethylbenzene				
7	298.15	306	307	[69]
16		410	350	[69]
c-6		605	608	[54]

Table 3
Logarithm of activity coefficients at infinite dilution, $\ln \gamma_i^\infty$, in *n*-alkylbenzene (1)+*n*-alkane or cyclohexane (2) mixtures at various temperatures, *T*. Comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficients $C_{\mathrm{sv},l}$ from Tables 9 and 10 (*m* is the number of *C* atoms in the alkane, *c*-6 means cyclohexane)

m	*T* (K)	$\ln \gamma_1^\infty$		$\ln \gamma_2^\infty$	
		Calc.	Exp.	Calc.	Exp.
Methylbenzene					
6	293.15			0.55	0.55 [85]
	304.75	0.39	0.46 [76]		
	322.75	0.35	0.38 [76]		
16	312.05	−0.02	0.05 [77]		
	313.15	−0.02	−0.04 [78]		
	316.95	−0.03	−0.04 [77]		
	333.15	−0.07	−0.10 [79]		
	343.15	−0.09	−0.43 [78]		
	363.15	−0.13	−0.48 [78]		
	393.15	−0.18	−0.21 [79]		
	453.15	−0.26	−0.27 [79]		
18	303.35	−0.07	0.04 [80]		
	313.45	−0.10	−0.08 [80]		
	323.35	−0.12	−0.11 [80]		
	324.55	−0.12	0.03 [77]		
	333.15	−0.14	0.04 [77]		
	333.15	−0.14	−0.12 [80]		
	341.95	−0.16	0.04 [77]		
	351.95	−0.18	0.04 [77]		
20	326.35	−0.20	−0.12 [81]		
	347.25	−0.24	−0.15 [81]		
	367.05	−0.28	−0.16 [81]		
24	324.45	−0.32	−0.27 [77]		
	333.75	−0.34	−0.21 [77]		
	343.55	−0.36	−0.26 [77]		
	349.15	−0.37	−0.27 [82]		
	353.15	−0.38	−0.27 [82]		
	355.15	−0.38	−0.31 [77]		
	357.15	−0.39	−0.27 [82]		
	361.15	−0.39	−0.29 [82]		
28	353.35	−0.50	−0.40 [83]		
	373.45	−0.54	−0.41 [83]		
	393.35	−0.57	−0.43 [83]		
Ethylbenzene					
16	313.15	0.08	−0.36 [78]		
	343.15	0.03	−0.40 [78]		
	363.15	0.01	−0.43 [78]		
	393.15	−0.02	−0.16 [79]		
	453.15	−0.03	−0.22 [79]		
18	303.15	−0.04	0.03 [80]		
	313.15	0.01	0.00 [80]		
	323.15	−0.01	−0.01 [80]		
	333.15	−0.02	0.11 [77]		
	333.15	−0.02	−0.03 [80]		
	341.95	−0.04	0.12 [77]		
	351.95	−0.05	0.12 [77]		

Table 3 (continued)

24	324.45	−0.19	−0.16 [77]		
	333.75	−0.21	−0.12 [77]		
	343.55	−0.22	−0.16 [77]		
	349.15	−0.23	−0.19 [82]		
	353.15	−0.23	−0.20 [82]		
	355.15	−0.24	−0.24 [77]		
	357.15	−0.24	−0.20 [82]		
	361.15	−0.24	−0.20 [82]		
Propylbenzene					
16	343.15	0.06	−0.36 [78]		
	363.15	0.05	−0.39 [78]		
	453.15	0.02	−0.16 [79]		
18	303.35	0.07	0.06 [80]		
	313.15	0.05	0.03 [80]		
	323.15	0.03	0.01 [80]		
	333.15	0.02	0.00 [80]		
Butylbenzene					
16	343.15	0.10	−0.33 [78]		
	363.15	0.08	−0.36 [78]		
Octylbenzene					
6	287.95			−0.03	0.40 [84]
1,2-Dimethylbenzene					
18	303.35	0.05	0.00 [80]		
	313.15	0.03	−0.03 [80]		
	323.15	0.01	−0.05 [80]		
	333.15	−0.01	−0.07 [80]		
24	349.15	−0.03	−0.22 [82]		
	353.15	−0.03	−0.24 [82]		
	357.15	−0.04	−0.24 [82]		
	361.15	−0.04	−0.24 [82]		
28	353.35	−0.33	−0.34 [83]		
	373.45	−0.36	−0.35 [83]		
	393.35	−0.38	−0.36 [83]		
1,3-Dimethylbenzene					
18	303.35	−0.02	−0.03 [80]		
	313.15	−0.04	−0.07 [80]		
	323.15	−0.05	−0.09 [80]		
	333.15	−0.07	−0.11 [80]		
24	349.15	−0.27	−0.24 [82]		
	353.15	−0.28	−0.25 [82]		
	357.15	−0.28	−0.25 [82]		
	361.15	−0.29	−0.26 [82]		
28	353.35	−0.39	−0.35 [83]		
	373.45	−0.42	−0.36 [83]		
	393.35	−0.44	−0.36 [83]		
1,4-Dimethylbenzene					
6	293.15			0.37	0.36 [85]
16	453.35	−0.08	−0.19 [79]		

(*continued overleaf*)

Table 3 (continued)

m	*T* (K)	$\ln \gamma_1^\infty$		$\ln \gamma_2^\infty$	
		Calc.	Exp.	Calc.	Exp.
18	303.35	−0.04	−0.07 [80]		
	313.15	−0.05	−0.11 [80]		
	323.15	−0.07	−0.12 [80]		
	333.15	−0.08	−0.13 [80]		
24	349.15	−0.27	−0.26 [82]		
	353.15	−0.28	−0.27 [82]		
	357.15	−0.28	−0.27 [82]		
	361.15	−0.29	−0.27 [82]		
c-6	293.15			0.46	0.30 [85]
1,3,5-Trimethylbenzene					
18	303.35	−0.03	−0.05 [80]		
	313.15	−0.05	−0.06 [80]		
	323.15	−0.06	−0.05 [80]		
	333.15	−0.07	−0.07 [80]		

The Flory's theory has been shown to predict H^E and V^E fairly well by means of a single interchange parameter [13,14].

The interactional terms in the thermodynamic properties under consideration are given by the DISQUAC model as the sum of the dispersive (DIS) and the quasi-chemical (QUAC) contributions. Owing to the non-polar nature of the molecule under examination, we used DISQUAC in the simple dispersive version, i.e. we set $C_{\mathrm{sv},1}^{\mathrm{quac}} = 0$ for all the contacts, according to preliminary calculations on the systems reported by Guieu et al. [15] and Kehiaian et al. [16].

The sources of available experimental data and some characteristic values are collected in Table 1–4. The G^E and γ_i^∞ data for alkylbenzene+*n*-alkane or cyclohexane are scarce and limited to methyl- and dimethyl-benzene.

The direct experimental isothermal *x*–*y* data (*x* and *y* are the mole fractions of the components, respectively, in the liquid and vapor phase) have been reduced to obtain the molar excess Gibbs energies, G^E, using the two- or three-parameter Redlich–Kister equation. Vapor-phase imperfection was accounted for in terms of the second virial coefficient, estimated by the Hayden and O'Connell method [17].

From the VLE (vapor–liquid equilibria) data reported by several authors [26–32] on methylbenzene and *n*-heptane mixture, G^E values have been calculated and found to be in 161–296 J mol^{-1} range. The most recent VLE data [24] indicate that the upper limit is more likely to be correct.

It should be noted that the Gibbs–Helmholtz consistency is acceptable for ethylbenzene and dimethylbenzene mixtures but fails for the toluene and *n*-heptane mixtures.

The value used for Gibbs energy interchange coefficient relative to the alkane/benzene contact, $C_{\mathrm{ab},1}$, has been obtained by adjustment to the experimental SLE curves of methylbenzene+*n*-heptane by Kehiaian et al. [15,16] and it is also close to the interchange coefficient derived from G^E by Goral [24] and Ashcroft [28].

Likewise, there is much controversy on the H^E of methylbenzene, ethylbenzene and 1,2-dimethylbenzene (Table 2), so we decided to remeasure the molar excess enthalpies of ethylbenzene and 1,2-dimethylbenzene+*n*-heptane and cyclohexane mixtures.

2. Experimental

The molar excess enthalpies, H^E, were determined by means of a flow microcalorimeter (model 2277, LKB-producer AB, Bromma, Sweden) [18]. Fully automatic burettes (ABU, from Radiometer, Copenhagen) were used to pump the liquids into the LKB unit; the volume of cylinder was 2.5 cm^3. The accu-

Table 4
Molar excess heat capacity, C_p^E (T; x_1 =0.5) of n-alkylbenzene (1)+n-alkane (2) mixtures at T=298.15 K and equimolar composition: comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficients $C_{sv,3}$ from Table 10 (m is the number of C atoms in the n-alkane)

m	C_p^E (T; x_1=0.5) (J mol^{-1} K^{-1})		Source of experimental data
	Calc.	Exp.	
Methylbenzene			
6	−1.23	−1.22	[86]
7	−1.37	−1.35	[87]
		−1.30	[88]
8	−1.70	−1.29	[86]
10	−2.10	−1.76	[86]
12	−2.39	−2.40	[86]
14	−3.72	−3.74	[88]
16	−4.14	−4.15	[86]
Ethylbenzene			
7	−1.62	−1.62	[88]
10	−2.63	−2.48	[88]
12	−3.25	−3.02	[88]
14	−4.37	−4.30	[88]
Propylbenzene			
7	−1.41	−1.42	[88]
14	−3.94	−3.95	[88]
Butylbenzene			
7	−1.38	−1.39	[88]
14	−4.42	−4.28	[88]
1,4-Dimethylbenzene			
6	−0.47	−0.48	[86]
16	−2.14	−2.14	[86]
1,2,4-Trimethylbenzene			
7	0.33	0.32	[74]
10	0.66	0.66	[74]
14	−0.09	−0.09	[74]

racy of the burette calibration was ±0.5%. All measurements were carried out at (298.15±0.10) K. The accuracy of the bath temperature was 0.1 K. The reliability of the apparatus and procedure adopted were checked by performing H^E measurements on the benzene+cyclohexane test system. Our results differed by <2% from literature data [19] over the entire composition range.

The molar excess enthalpies, H^E, were evaluated from the following formula:

$$H^E = \frac{I^2 R(E/E_c)}{f} \tag{1}$$

where I and R are the electrical current and resistance in the electrical calibration experiment, E and E_c the voltage readings for measurement and electrical calibration and f the molar flow rate of the mixture.

The molar flow rate f_i of the ith component, flowing into the mixing cell, is given by:

$$f_i = \frac{\rho_i}{M_i} F_i \tag{2}$$

where ρ_i and M_i are the density and molar mass, respectively, and F_i the volumetric flow rate of component i.

Table 5
Relative molar masses, M_r, purities and densities, ρ, (exp., experimental values; lit., literature values drawn from Ref. [89]) of the pure alkylbenzenes and solvents at 298.15 K

Compound	M_r	Purity (mol%)	ρ (g cm^{-3})	
			Exp.	Lit.
Ethylbenzene	106.167	99	0.86775	0.86253
1,2-Dimethylbenzene	106.167	99	0.87525	0.87594
n-Heptane	100.203	99	0.67945	0.67946
Cyclohexane	84.161	99.9	0.77379	0.77389

The densities were determined with a vibrating densimeter (model DMA 58 Anton Paar) with a reproducibility of 10^{-5} g cm^{-3} at 298.15 K. Our values agreed within better than 0.2% of literature data (see Table 5).

The experimental values of H^E, reported in Table 6, were fitted to the Redlich–Kister smoothing equation in order to obtain the values of a set of cofficients, a_i, for every binary mixture:

$$H^E_{sm} = x_1 x_2 \sum_{i=0}^{n-1} a_i (x_1 - x_2)^i \tag{3}$$

The values of the coefficients a_i and the standard deviations $\sigma(H^E)$ are given by:

$$\sigma(H^E) = \left[\frac{\sum_i (H^E_{i,sm} - H^E_{i,exp})^2}{N-n}\right]^{1/2} \tag{4}$$

were determined by the least-squares analysis and are reported in Table 6. Here, N is the number of experimental points and n the number of coefficients a_i.

Table 6
Experimental values of molar excess enthalpies, H^E, for alkylbenzene (1)+*n*-heptane or cyclohexane (2) mixtures at 298.15 K; coefficients a_i, from Eq. (3) and standard deviations, σ (H^E) from Eq. (4)

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
Ethylbenzene+*n*-heptane					
0.1076	211.4	0.4748	547.5	0.8282	336.1
0.1843	325.7	0.5466	568.9	0.8785	248.2
0.3113	475.7	0.6164	543.3	0.9060	195.2
0.3761	509.0	0.6439	530.3	0.9234	167.7
0.4456	545.7	0.7068	493.6		
a_0=2244.4; a_1=279.0; a_2=669.0; a_3=−333.3; σ=6.0					
Ethylbenzene+cyclohexane					
0.0816	219.3	0.3721	566.3	0.6400	504.2
0.1290	305.6	0.4000	573.0	0.7033	447.0
0.1818	367.2	0.4706	584.2	0.8421	283.8
0.2500	453.6	0.5424	563.3	0.8989	149.3
0.3077	523.4	0.5714	559.3		
a_0=2314.2; a_1=−268.3; a_2=−614.5; a_3=−444.2; σ=13.0					
1,2-Dimethylbenzene+cyclohexane					
0.1008	274.2	0.4727	631.7	0.7820	383.0
0.1439	354.4	0.5445	615.9	0.8271	314.4
0.2301	492.5	0.5736	588.1	0.8997	190.9
0.3095	571.7	0.6420	551.5		
0.4021	623.7	0.7290	455.8		
a_0=2502.9; a_1=−417.6; a_2=645.1; a_3=−202.4; σ=4.1					

3. Theory

DISQUAC is an extended quasi-chemical group-contribution model based on the Guggenheim lattice theory. In the classic model [20], molecules are assumed to possess one of the several types of contacts s 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 when applying to liquid mixtures and can be avoided by using the group–surface interaction version of the theory [21]. In the classical model, the interchange energies of every (s,v) contact generate an extent of non-randomness, 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, non-random contribution treated quasi-chemically with a constant $z=4$.

The equations used to calculate thermodynamic properties are the same as in other applications [8] and need not to be repeated here.

4. Assessment of geometrical parameters

The molecules under study, i.e. alkanes, cyclohexane and alkylbenzene are regarded as possessing three types of contact surfaces: (1), type a, aliphatic (CH_3, CH_2 groups, which are assumed to exert the same force field); (2), type b, benzene (C_6H_6) or phenyl (C_6H_5); and (3), type c, cycloaliphatic (c-CH_2).

In the theory, each type of molecule, i, is characterized by the following set of geometrical parameters: the total surface, q_i; the molecular surface fractions, α_{si}; and the volume r_i. In order to account for the constitution on organic molecules realistically, we consider them as ensembles of identifiable structural units corresponding to the main chemical groups.

We have adopted the method developed by Bondi [22]. In this elaborate method, each atom is considered to be spherical and the volume V_G and the surface A_G of a given group G, composed of various atoms, are calculated on the basis of the geometry of bonded atoms with interpenetrating surfaces. The fraction surface left for a possible contact is calculated from the covalent radii and the Van der Waals radii [21].

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 [22], ($V_{CH_4} = 17.12 \times 10^{-6}$ m^3 mol^{-1}; $A_{CH_4} = 2.90 \times 10^5$ m^2 mol^{-1})

Group	r_G	q_G
CH_3	0.79848	0.73103
CH_2	0.59755	0.46552
C_6H_{12}	3.51870	2.59660
C_6H_6	2.82480	2.07280
C_6H_5-	2.67757	1.83793

As volume and surface units, we arbitrarily decided to take the volume and surface of methane, CH_4.

The geometrical parameters, i.e. the relative group increments r_G and q_G, concerned in this study are given in Table 7, and have been used to calculate, additively, the total volumes r_i and surfaces q_i as well as the aliphatic, cyclohexane and phenyl surface fractions, α_{ai}, α_{bi} and α_{ci} (Table 8).

5. Estimation of interchange parameters

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, expecially 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, usually few, the 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. The three types of surfaces generate three pairs of contacts: (a,c), (a,b) and (c,b).

As different authors have pointed out, the value of z plays a major role in correlating different types of mixtures. For mixtures of homogeneous molecules,

Table 8
Relative molecular volumes, r_i, relative total molecular surfaces, q_i, and molecular surface fractions, α_{si}, (s=a,b,c) of alkylbenzenes and solvents calculated from the group increments r_G and q_G given in Table 7

Compound [a]	r_i	q_i	α_{ai}	α_{bi}	α_{ci}
Benzene	2.8248	2.0728	0.0000	1.0000	0.0000
Methylbenzene	3.4760	2.5690	0.2846	0.7154	0.0000
Ethylbenzene	4.0736	3.0345	0.3943	0.6057	0.0000
Propylbenzene	4.6711	3.5000	0.4749	0.5251	0.0000
Butylbenzene	5.2686	3.9655	0.5365	0.4635	0.0000
Octylbenzene	7.6589	5.8276	0.6846	0.3154	0.0000
Dimethylbenzene	4.1273	3.0655	0.4769	0.5231	0.0000
Trimethylbenzene	4.7786	3.5621	0.6157	0.3843	0.0000
Cyclohexane	3.5187	2.5966	0.0000	0.0000	1.0000

[a] For the parameters r_2 and q_2 of *n*-alkanes (α_{a2}=1.0000) see Kehiaian et al. [21].

the symmetry of the excess functions is only slightly affected by the value of z. For the sake of simplicity one may use $z=\infty$ (a random mixing).

Kehiaian et al. [21] determined the dispersive interchange parameters of the contact non-polar–non-polar alkane/cyclohexane ($C_{ac,1}$=0.05123 and $C_{ac,2}$=0.1533), of the nonpolar–polarizable contact alkane/benzene ($C_{ab,1}$=0.2598 and $C_{ab,2}$=0.5623) and of cyclohexane/benzene ($C_{cb,1}$=0.2445 and $C_{cb,2}$=0.5619). From structural considerations (intramolecular inductive effect and liquid-structure breaking effect of the alkyl substituents on the benzene ring and enthalpy–entropy compensation effect), we think that the interchange parameters for monoalkylbenzenes, dimethylbenzenes and trimethylbenzenes may be different from those of benzene and, consequently, we have determined the interchange coefficients from the available experimental data of these systems.

It is sometimes difficult to unambiguosly assign 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, a number of general and physically reasonable 'rules' were identified and these were applied consistently in determining the value of the interchange coefficients.

5.1. Monoalkylbenzenes

The rules are as follows:

(1a) The dispersive coefficients, $C_{ab,1}$, of the alkane/phenyl contact (Table 9 and Fig. 1) increase regularly with increasing n, the chain length of the alkyl group adjacent to the phenyl group of monoalkylbenzenes, from benzene to ethylbenzene and remain nearly constant for higher *n*-alkylbenzenes (increasing inductive effect).

Table 9
Interchange energy coefficients, $C_{sb,l}$, for contacts (s,b), s=a or c: a (aliphatic group in *n*-alkane or *n*-alkyl group); c (cyclohexane); b (phenyl group) of mixtures of *n*-alkylbenzene, dimethylbenzene, trimethylbenzene in *n*-alkane or cyclohexane (1=1, Gibbs energy; 1=2, enthalpy)

Alkylbenzene	$C_{ab,1}$	$C_{ab,2}$	$C_{cb,1}$	$C_{cb,2}$
Benzene	0.2598	0.5623	0.2445	0.5619
Methylbenzene	0.32	0.62	0.33	0.66
Ethylbenzene	0.38	0.70	0.35	0.72
1,2-Dimethylbenzene	0.51	0.76	0.57	0.91
1,3-Dimethylbenzene	0.42	0.65	0.50	0.80
1,4-Dimethylbenzene	0.40	0.60	0.48	0.76
1,2,4-Trimethylbenzene	0.43	0.81	0.55	1.13
1,3,5-Trimethylbenzene	0.48	0.91	0.65	1.16

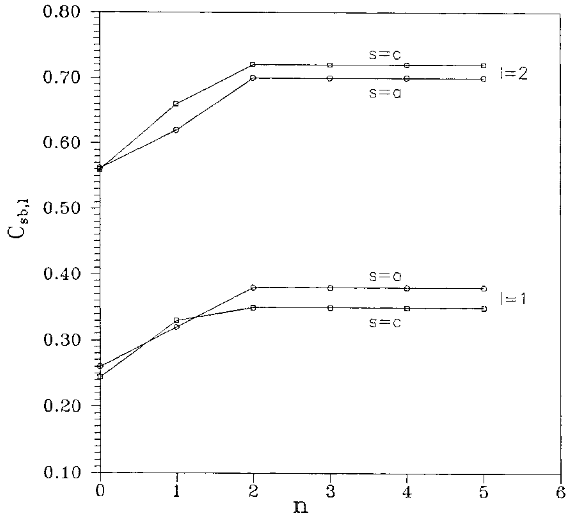

Fig. 1. Change of the dispersive interchange coefficients, $C_{sb,l}$, for the C_6H_5/aliphatic or cycloaliphatic contact (s=a or c) in *n*-alkylbenzene+*n*-alkane or cyclohexane mixtures versus *n*, the number of alkyl groups in the alkylbenzene.

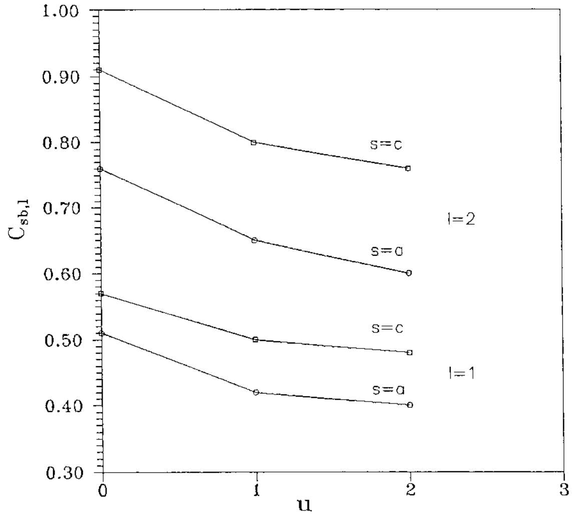

Fig. 2. Change of the dispersive interchange coefficients, $C_{sb,l}$, for the C_6H_5/aliphatic or cycloaliphatic contact (s=a or c) in dimethylbenzene+*n*-alkane or cyclohexane mixtures vs. *u*, the distance, expressed by the number of CH units in the benzene ring, between the two methyl groups in the dimethylbenzene isomers.

(2a) The dispersive coefficients, $C_{bc,1}$, of the cyclohexane/phenyl contact are slightly larger than $C_{ab,1}$ and have the same trend with *n*, the chain length of alkyl groups.

5.2. Dimethylbenzenes and trimethylbenzenes

(1b) The dispersive interchange energy coefficients $C_{ab,l}$ and $C_{bc,l}$, (Table 9) increase in the series benzene<monoalkylbenzenes<dimethylbenzenes< trimethylbenzenes and decrease regularly on increasing the distance between the two methyl groups in the isomeric dimethylbenzenes Fig. 2 or in the isomeric trimethylbenzenes.

(2b) The dispersive coefficients, $C_{bc,l}$, of the cyclohexane/phenyl contact are slightly larger than $C_{ab,l}$.

6. Comparison with experiment and discussion

First the validity of the model was tested on the main properties (G^E and H^E) related to phase equilibria. Then the derived properties, which are often more difficult to represent using a theoretical model were examined. These are partial molar quantities at infinite dilution (γ_i^∞). Finally, we extended the comparison to long-chain molecules.

6.1. Gibbs free energies

The model predicts G^E accurately. The differences between G^E (exp) and G^E (calc) rarely exceed 30 J mol^{-1} (Table 1 and Figs. 3 and 4) and this may be well within the limits of the experimental error of certain measurements. The G^E value reported by Mato [26] is considerably smaller than other experimental values.

6.2. Enthalpies

The calculated excess enthalpies H^E agree within 30 J mol^{-1} of the available measurements (Table 2 and Figs. 5–8): The H^E (exp) of some alkylbenzenes+cyclohexane, reported by Paz Andrade et al. [68], seem too small.

6.3. Activity coefficients

Activity coefficients at infinite dilution, γ_i^∞, have been determined for many compounds considered in

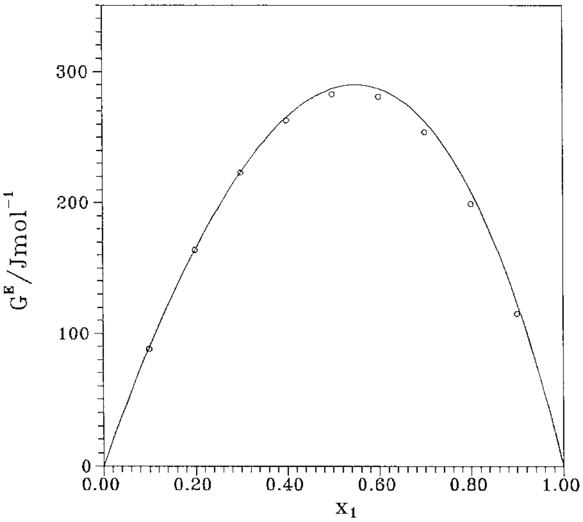

Fig. 3. Comparison of theory with experiment for the molar excess Gibbs energies, G^E, at 298.15 K, for methylbenzene (1)+n-heptane (2) mixtures versus x_1, the mol fraction of methylbenzene: full lines: ———, predicted values; points, experimental results [29].

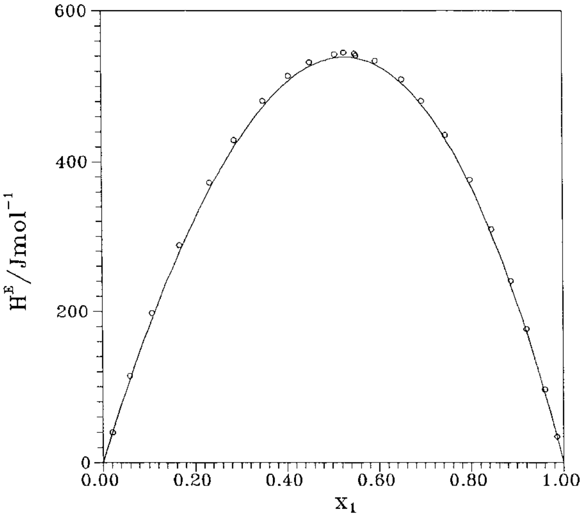

Fig. 5. Comparison of theory with experiment for the molar excess enthalpies, H^E, at 298.15 K, for ethylbenzene (1)+n-heptane (2) mixtures versus x_1, the mole fraction of ethylbenzene: full lines: ———, predicted values; points, experimental results [49].

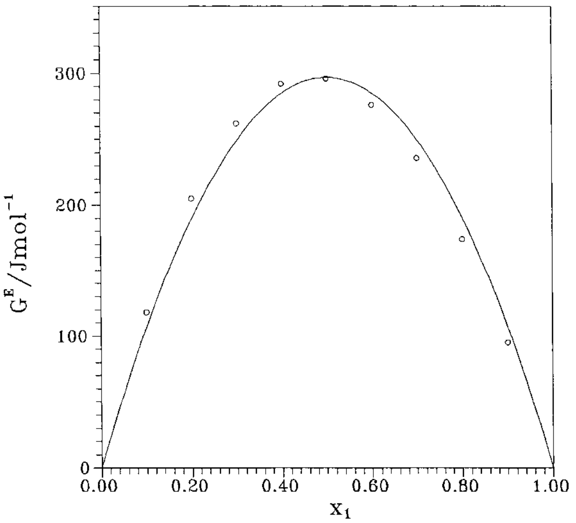

Fig. 4. Comparison of theory with experiment for the molar excess Gibbs energies, G^E, at 298.15 K, for methylbenzene (1)+cyclohexane (2) mixtures versus x_1, the mole fraction of methylbenzene: full lines: ———, predicted values; points, experimental results [45].

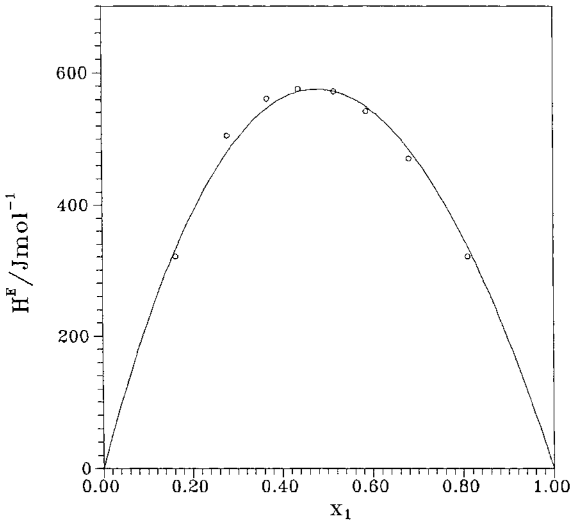

Fig. 6. Comparison of theory with experiment for the molar excess enthalpies, H^E, at 298.15 K, for 1,3-dimethylbenzene (1)+cyclohexane (2) mixtures versus x_1, the mole fraction of dimethylbenzene: full lines: ———, predicted values; points, experimental results [52].

this work (Table 3). The data have been taken from various sources, who used different techniques and temperatures. Nevertheless, the representation on the ensemble of measured values permits us to draw general conclusions similar to those of previous studies [8]. The differences between ln γ_i^∞ (exp) and ln γ_i^∞ (calc) increase rapidly with decrease in the ratio of molecular volumes of solute and solvent. As it is

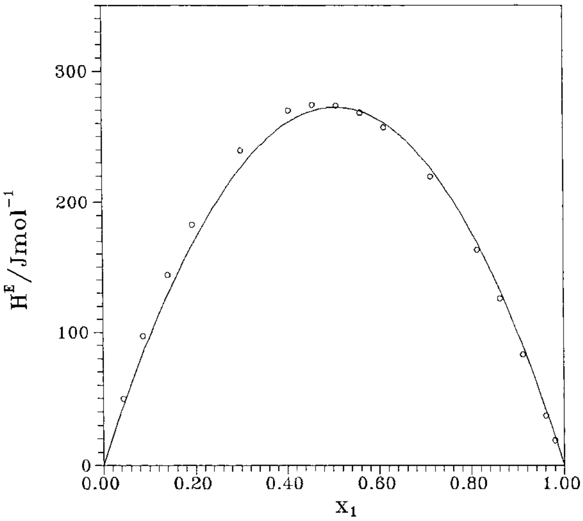

Fig. 7. Comparison of theory with experiment for the molar excess enthalpies, H^E, at 298.15 K, for 1,2,4-trimethylbenzene (1)+n-heptane (2) mixtures versus x_1, the mole fraction of trimethylbenzene: full lines: ———, predicted values; points, experimental results [74].

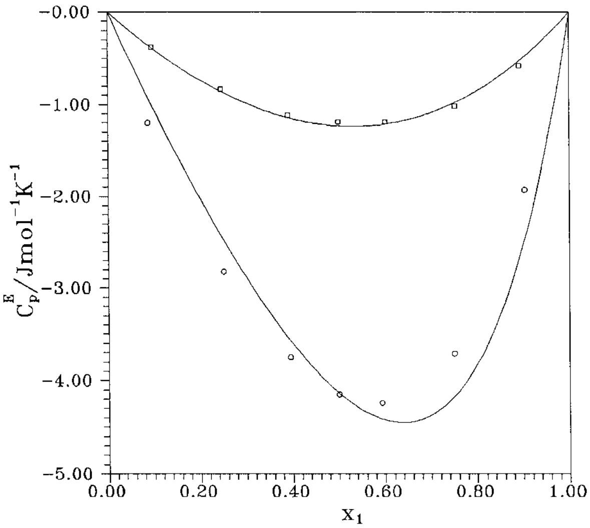

Fig. 8. Comparison of theory with experiment for the molar excess heat capacities, C_p^E, at 298.15 K, for methylbenzene (1)+n-alkane (2) mixtures versus x_1, the mole fraction of methylbenzene: full lines: ———, predicted values; points, experimental results: □, +n-hexane [86]; ○, +n-hexadecane [86].

known, the differences result, at least in part, from the Flory–Huggins equation which overestimates the combinatorial entropy.

6.4. Mixtures containing long-chain n-alkanes

In recent years, Patterson et al. [1] have presented much evidence for additional 'cooperative' effects associated with molecular size and shape. It has been shown that the orientations of long-chain n-alkane molecules in the liquid state are correlated. The mixing of the higher n-alkane (above n-octane) with more or less globular molecules acting as 'order destroyers' results in an endothermic contribution to H^E. This cooperative effect has been discussed quantitatively by Heinz and Lichtenthaler using a theoretical model [90,91]. An opposite, quite surprising, exothermic effect has been found by Wilhelm [23] for the case of mixtures of some cyclic polar compounds with n-alkanes. The first examples studied were chlorobenzenes+n-alkanes. Benzene behaves normally, the increase of H^E with the n-alkane chain length being almost accurately predicted by the random quasi-lattice group contribution formula. For chlorobenzenes, the variation of H^E decreases with increasing chain length of alkane. For the mixture of alkylbenzenes+long-chain n-alkanes, the H^E values calculated by the model are higher than experimental values. These results have been discussed in terms of creation of order of some sort in the mixtures, i.e. intramolecular and intermolecular ordering. Under isothermal conditions, the population of various conformational states of n-alkane may be altered by changes in density as well as by admixture of another substance. This 'Wilhelm' effect may be due to induced conformational changes in n-alkanes. The substituted planar aromatic ring induces an increase of 'gauche-conformation' of the alkane and it is associated with the exothermic contribution.

6.5. Excess heat capacities

As a first approximation, the interchange enthalpies, $C_{sv,2}$, are assumed to be independent of the temperature, i.e. $C_{sv,3}$=0. It is generally admitted that the interchange 'energies' in lattice-type models are temperature dependent, i.e. they must be regarded as free energies [21]. There is no a-priori reason that g_{sv} should be a linear function of T, i.e. $C_{sv,3}$=0. The difficulty in using $C_{sv,3}$ in the framework of group-contribution models results from the more complex physical significance of this parameter, and thereby its pronounced variability in a homologous series of substances. The value of $C_{st,3}$, adjusted for a particular system (Table 10), reflects not only the true thermal coefficient of interchange energy, but also, to a much larger extent than $C_{sv,1}$ and $C_{sv,2}$, many other inter- and intramolecular effects that are not explicity accounted for in the model. Preliminary calculations [15,16] showed that in alkylbenzenes from toluene to octylbenzene C_p^E changes by more than 100%. As expected, C_p^E data cannot be correlated by simple group contribution methods, the excess capacity being a property particularly sensitive to the conformational changes occurring during the mixing process. The analysis of the scarce C_p^E data available for alkylbenzene+alkane systems (Table 4 and Fig. 8) revealed that temperature coefficients of $C_{sv,2}$ depend weakly on the nature of alkylbenzene, but strongly on the size of *n*-alkane. In other words, systems which behave 'normally' with respect to H^E (and G^E) in a limited temperature range may show, at much lower temperatures, the positive enthalpic Patterson effect (stronger correlation of molecular orientations) and the negative enthalpic Wilhelm effect at much higher temperatures.

Table 10
Interchange heat-capacity coefficients, $C_{sb,3}$, for contacts (s,b), s=a or c: a (aliphatic group in *n*-alkane or *n*-alkyl group); c (cyclohexane); b (phenyl group) of mixtures of *n*-alkylbenzene, dimethylbenzene, trimethylbenzene in *n*-alkane or cyclohexane (*m* is the number of *C* atoms in the alkane; *c*-6 means cyclohexane)

Alkylbenzene	*m*	$C_{sb,3}$
Methylbenzene	6	−4.0
	7	−4.2
	8	−5.0
	10	−5.8
	12	−6.2
	14	−9.3
	16	−10.0
	c-6	−0.80
Ethylbenzene	6	−0.56
	7	−0.63
	8	−0.72
	10	−0.90
	12	−1.05
	14	−1.35
	16	−1.38
	c-6	−1.00
Propylbenzene	6	−0.58
	7	−0.68
	8	−0.80
	14	−1.47
	16	−1.50
	c-6	−1.10
Butylbenzene	6	−0.64
	7	−0.80
	8	−0.98
	14	−1.95
	16	−2.00
	c-6	−1.20
1,4-Dimethylbenzene	6	−0.26
	7	−0.32
	8	−0.40
	14	−0.78
	16	−0.85
	c-6	−0.50
1,2,4-Trimethylbenzene	7	0.29
	10	0.51
	14	−0.06
	c-6	0.45

Alkylbenzenes are treated as 'heterogeneous' molecules, in the sense of Guggenheim [20], i.e. they have several types of contact. Alkanes are regarded as 'homogeneous' molecules, i.e. they have a single type of contact. In the pure liquid, the heterogeneous molecules are oriented or 'associated'. As disorientation is an endothermic process, the degree of orientation decreases with increasing temperature. In very dilute solutions, the polar molecules dissociate completely, yielding the maximum enthalpy of solution. Accordingly, in very dilute solutions, a negative C_p^E is calculated. The sign of C_p^E (calc) in more concentrated solutions depends on the degree of orientation in the pure liquid. Weakly oriented molecules may give $C_p^E > 0$, the increase in temperature favouring disorientation in concentrated solutions. A better understanding of the order/conformational effect would clarify but only in part, the magnitude of C_p^E. The shape of C_p^E curves is considerably influenced by the non-randomness effects and that the model, at least, in its present version, fails to reproduce them satisfactorily. The study of C_p^E may appear to be of theoretical interest only, as this function has only a minor influence on phase-diagram calculations for technical applications. This is true for VLE or SLE (solid–liquid equilibrium), but not for liquid–liquid equilibrium (LLE) calculations. Very accurate and extensive C_p^E measurements will probably play an increasing role in the development of group-contribution models, provided that G^E and H^E data are also available for the same classes of systems.

Benzene has a partly ordered liquid structure that, along with the attraction force between π-electrons, contributes to its great mixing enthalpy when it is added to *n*-alkane or cyclohexane.

Methylation of benzene, because of the inductive effect, makes stronger π–π interactions and reduces the degree of order. The enthalpic interchange (dispersive) parameter increases weakly from benzene to methylbenzene (0.62>0.56). The enthalpy–entropy compensation, at least, partly diminishes the order effect, and the remaining inductive effect that is responsible for the greater Gibbs energy parameter for methylbenzene than for benzene (0.38>0.26).

In ethylbenzene, the stronger inductive effect exerted by the additional CH_2 group induces an increase of interchange energy coefficients which thereafter remain constant. As a consequence of the above-mentioned effect, intermolecular interaction rise in the order trimethylbenzene>dimethylbenzene>monoalkylbenzene for a given alkyl group.

The interchange energy coefficients trend in dimethylbenzene isomers: 1,2>1,3>1,4 and in trimethylbenzene isomers: 1,3,5>1,2,4 agree with the evolution of dipolar moments and of enthalpy of vaporisation.

The analysis of the experimental data presented in this paper demonstrated that DISQUAC, in the simplified version of the random mixing, is an accurate predictive model for systems containing alkylbenzenes+alkane or cyclohexane at low reduced temperatures. Larger discrepancies appear in the presence of molecules containing more than 10 carbon atoms, but these are regular and can be predicted a priori and, therefore, corrected.

The group-structure/interaction-parameters relationship illustrated in Figs. 1 and 2 are typical for DISQUAC and suggest that the model has a better physical basis than other models. The relationships are also of pratical importance, since they allow the evaluation of experimental data and estimation of interaction parameters.

However, we do not expect that the present version of DISQUAC will give satisfactory results in the case of strongly interacting groups (molecules with hydrogen bonds, etc.) because of the approximations involved in the quasi-chemical treatment and the assumed additivity of the dispersive and quasi-chemical contributions. Indeed, one should always bear in mind the inherent simplifications of the quasi-chemical model in which the real distance- and angle-dependent intermolecular potentials are crudely represented by a few quantities: isotropic group interchange parameters; molecular surface fractions that simulate the anisotropy of the force field; and a coordination number, which weights, via the Boltzmann factor, the contact probabilties.

7. List of symbols

A	molecular area
C	interchange coefficient
G	molar Gibbs energy
H	molar enthalpy
q	relative molecular area
r	relative molecular volume
V	molecular volume
x	mole fraction
α	molecular surface fraction
ρ	density

8. Subscripts

a,b,c	type of contact surface (group): a, CH_3, CH_2; b, C_6H_6; c, C_6H_{12}
calc	calculated quantity
exp	experimental quantity
G	type of group
i	type of molecule (component)
l	order of interchange coefficient: l=1, Gibbs energy; l=2, enthalpy l=3, heat capacity
s,v	any type of contact surface

9. Superscripts

dis	dispersive
E	excess property
quac	quasi-chemical
∞	infinite dilution property

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References

[1] D. Patterson, Pure Appl. Chem. 47 (1976) 305.
[2] P. de Saint-Romain, PhD Thesis, McGill University, Montreal, Canada, 1977.
[3] H.V. Kehiaian, Ber. Bunsenges. Physik. Chem. 81 (1977) 908.
[4] A. Fredenslung, R.L. Jones, J.M. Prausnitz, AIChe J. 21 (1975) 1086.
[5] D.S. Abrams, J.M. Prausnitz, AIChe J. 21 (1975) 116.
[6] H.V. Kehiaian, Ber. Bunsenges. Physik. Chem. 81 (1977) 908.
[7] H.V. Kehiaian, Fluid Phase Equil. 13 (1983) 243.
[8] H.V. Kehiaian, Pure Appl.Chem. 57 (1985) 15.
[9] H.V. Kehiaian, B. Marongiu, Fluid Phase Equil. 40 (1988) 23.
[10] B. Marongiu, B. Pittau, S. Porcedda, Thermochim. Acta 221 (1993) 143.
[11] B. Marongiu, B. Pittau, S. Porcedda, M.R. Tinè, Fluid Phase Equil. 93 (1994) 249.
[12] J.S. Rowlinson, Liquid and Liquid Mixtures, Butterworths, London, 1969.
[13] D.V.S. Jain, R.K. Dewan, K.K. Tewari, Indian J. Chem. 6 (1968) 511.
[14] D.V.S. Jain, B.S. Lark, S.S. Chamak, P. Chander, Indian J. Chem. 8 (1970) 66.
[15] R. Guieu, A. Faradjzadeh, L. Carbonnel, Int. DATA Ser., Sel. Data Mixt., (1980) 50.
[16] H.V. Kehiaian, R. Guieu, A. Faradjzadeh, L. Carbonnel, Ber. Bunsenges. Physik. Chem. 85 (1981) 132.
[17] J.G. Hayden, J.P. O'Connell, Ind. Eng. Chem. Process Des. Dev. 14 (1975) 209.
[18] P. Monk, I. Wadsö, Acta Chem. Scand. 22 (1968) 1842.
[19] K.N. Marsh, Int. DATA Ser., Sel. Data Mixt., Ser. A, (1973) 1.
[20] E.A. Guggenheim, Mixtures, Clarendon Press, Oxford, 1952.
[21] H.V. Kehiaian, J.P.-E. Grolier, G.C. Benson, J. Chim. Phys. 75 (1978) 1031.
[22] A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, J. Wiley, New York, 1968.
[23] E. Wilhelm, Ber. Binsenges. Physik. Chem. 81 (1977) 1150.
[24] M. Goral, Fluid Phase Equil. 102 (1994) 275.
[25] I. Wichterle, L. Boublikova, Ind. Eng. Chem. Fundam. 8 (1969) 585.
[26] F. Mato, F. Fernandez-Polanco, M. Uruena, An. Quim. 76 (1980) 114.
[27] T. Katayama, E.K. Sung, E.N. Lightfoot, Lightfoot. AIChe J. 11 (1965) 924.
[28] ST. Ashcroft, A.D. Clayton, R.B. Shearn, J. Chem. Eng. Data 24 (1979) 195.
[29] J. Surovy, J. Heinrich, Sb. Pr. Chem. Fak. Svst., 201 (1966).
[30] N.P. Markuzin, L.M. Pavlova, Zh. Prikl. Khim. (Leningrad) 44 (1971) 311.
[31] J. Dojcansky, L. Sakalosova, J. Survoy, Chem. Zvesti 28 (1974) 161.
[32] H. Kirss, L.S. Kudryavtseva, O. Eisen, Eesti NSV Tead. Kad. Toim., Keem. Geol. 24 (1975) 15.
[33] I. Wichterle, Coll. Czech. Chem. Commun. 30 (1965) 3388.
[34] C. Berro, F. Laichoubi, E. Rauzy, J. Chem. Thermodyn. 26 (1994) 863.
[35] Z.Kh. Anisimova, E.G. Konakbaeva, Teplofiz. Svojstva Vescesty i Materialov 7 (1973) 167.
[36] E.G. Konakbaeva, Z.Kh. Anisimova, M.I. Shakhparonov, Vestn. Mosk. Univ. Khim. 15 (1974) 30.
[37] V.T. Zharov, A.G. Morachevsky, L.G. Shapil, T.A. Buevich, Zh. Prikl. Khim. 41 (1968) 2443.
[38] R.A. Mentzer, R.A. Greenkorn, K.C. Chao, J. Chem. Thermodyn. 14 (1982) 817.
[39] B. Wisniewska, J. Chem. Thermodyn. 19 (1987) 897.
[40] D.V.S. Jain, O.P. Yadav, Indian J. Chem. 12 (1974) 718.
[41] M. Diaz Pena, A. Compostizo, A. Crespo Colin, J. Chem. Thermodyn. 12 (1980) 259.
[42] P.C. Proust, A.L. Ramirez, J. Yianatos, J. Chem. Eng. Data 25 (1980) 329.
[43] D.V.S. Jain, O.P. Yadav, J. Chem. Thermodyn. 5 (1973) 541.
[44] K.L. Young, R.A. Mentzer, R.A. Greenkorn, K.C. Chao, J. Chem. Thermodyn. 9 (1977) 979.
[45] D.V.S. Jain, O.P. Yadav, K.M. Kamra, Indian J. Chem. 9 (1971) 1262.
[46] A.R. Mathieson, J.C.J. Thynne, J. Chem. Soc., London, (1956) 3708.
[47] M.D.C. Baluja Santos, Acta Cient. Compostelana 7 (1970) 3.
[48] E.K. Otsa, V. Ya Mikhkelson, L.S. Kudryavtseva, Zh. Piz. Khim. 55 (1979) 899.
[49] K. Tamura, S. Murakami, R. Fujishiro, J. Chem. Thermodyn. 7 (1975) 1089.
[50] C.C. Tsao, J.M. Smith, Chem. Eng. Prog. Symp. Ser. 49 (1953) 107.
[51] D. Kuchenbecker, Thesis (Leipzig), 1980.
[52] G.W. Lundberg, J. Chem. Eng. Data 9 (1964) 193.
[53] R.L. Arenosa, C. Menduina, G. Tardajos, M. Diaz Pena, J. Chem. Thermodyn. 11 (1979) 825.
[54] K. Hsu, H.L. Clever, J. Chem. Thermodyn. 7 (1975) 434.
[55] K. Amaya, Bull. Chem. Soc. Jpn. 34 (1961) 1271.
[56] A.E.P. Watson, I.A. McLure, J.E. Bennett, G.C. Benson, J. Phys. Chem. 69 (1965) 2753.
[57] D. Diez, B. Ruiz, F.M. Royo, C. Gutierrez Losa, J. Chem. Thermodyn. 18 (1985) 803.
[58] M. Karvo, J. Chem. Thermodyn. 12 (1980) 635.
[59] M.I. Paz Andrade, Acta Cient. Compostelana 1 (1964) 117.
[60] J. Krug, Thesis (Berlin), 1985.
[61] H.V. Kehiaian, K. Sosnkowska-Kehiaian, R. Hryniewicz, J. Chim. Phys.-Chim. Biol. 68 (1971) 922.
[62] A. Cannas, B. Marongiu, S. Porcedda, this work.
[63] R.L. Arenosa, R.G. Rubio, C. Menduina, M. Diaz Pena, J. Chem. Eng. Data 30 (1985) 24.
[64] P.S. Murti, M. Van Winkle, AIChe J. 3 (1957) 517.

[65] S. Murakami, R. Fujishiro, Bull. Chem. Soc. Jpn. 40 (1967) 1784.
[66] M.I. Paz Andrade, S. Castromil, M.C. Baluja, J. Chem. Thermodyn. 2 (1970) 775.
[67] M.I. Paz Andrade, E. Jimenez, M.C. Baluja, An. Quim. 66 (1970) 955.
[68] M.I. Paz Andrade, M.P. Amor, An. Quim. 66 (1970) 717.
[69] E. Picquenard, H.V. Kehiaian, L. Abello, Bull. Soc. Chim. Fr. 1 (1972) 120.
[70] H.T. French, R.H. Stokes, J. Chem. Soc. Faraday Trans. 81 (1985) 1459.
[71] I. Nagata, Y. Ogasawara, Thermochim. Acta 52 (1982) 155.
[72] S.C. Sharma, M.L. Lakhanpal, M.L. Rumpaul, Indian J. Chim. a20 (1981) 225.
[73] A. Nissema, T. Kaivamo, M. Karvo, J. Chem. Thermodyn. 15 (1983) 1083.
[74] E. Wilhelm, A. Inglese, A.H. Roux, J.P.-E. Grolier, Fluid Phase Equil. 34 (1987) 49.
[75] J. Guedeling, T. Holderbaum, Heats of mixing data collection, Dechema Data Series, vol 111, Part 4, Frankfurt/Maine 1991.
[76] E.R. Thomas, B.A. Newman, G.L. Nicolaides, C.A. Eckert, J. Chem. Eng. Data 27 (1982) 233.
[77] P. Alessi, I. Kikic, A. Alessandrini, M. Fermeglia, J. Chem. Eng. Data 27 (1982) 445.
[78] P.S. Snyder, J.F. Thomas, J. Chem. Eng. Data 13 (1968) 527.
[79] E.A. Turek, D.W. Arnold, R.A. Greenkorn, K.C. Chao, Ind. Eng. Chem. Fundam. 18 (1979) 426.
[80] G.M. Janini, D.E. Martire, J. Phys. Chem. 78 (1974) 1644.
[81] D.E. Martire, L.Z. Pollara, J. Chem. Eng. Data 10 (1965) 40.
[82] Y.B. Tewari, D.E. Martire, J.P. Sheridan, J. Phys. Chem. 74 (1970) 2345.
[83] U. Weidlich, Thesis, Dortmund, 1985.
[84] P. Alessi, I. Kikic, private communication, 1986.
[85] E.R. Thomas, B.A. Newman, T.C. Long, D.A. Wood, C.A. Eckert, J. Chem. Eng. Data 27 (1982) 399.
[86] M. Costas, D. Patterson, Int. DATA Ser., Sel. Data Mixtures, Ser. A 3 (1985) 217.
[87] J.K. Holzhauer, W.T. Ziegler, J. Phys. Chem. 79 (1975) 590.
[88] J.-P.E. Grolier, Int. DATA Ser., Sel. Data Mixt. Ser. A 2 (1979) 132.
[89] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic solvents, Physical Properties and Methods of Purification, J. Wiley and Sons, New York, 1986.
[90] A. Heintz, R.N. Lichtenthaler, Ber. Bunsenges. Phys. Chem. 81 (1977) 921.
[91] A. Heintz, R.N. Lichtenthaler, Ber. Bunsenges. Phys. Chem. 84 (1980) 890.