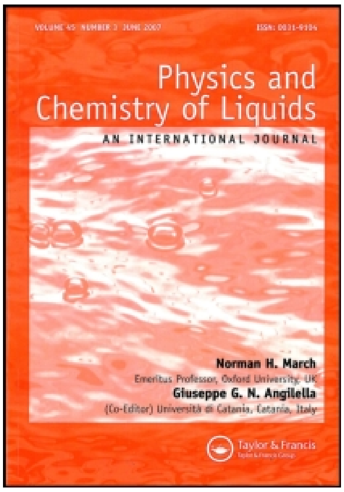

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Analysis of {α,ω-Dichloroalkane or α,ω-Dibromoalkane] Benzene and α,ω-Dichloroalkane Tetrachloromethane} Mixtures in Terms of Group Contributions

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ANALYSIS OF {[α,ω-DICHLOROALKANE OR α,ω-DIBROMOALKANE] + BENZENE AND α,ω-DICHLOROALKANE + TETRACHLOROMETHANE} MIXTURES IN TERMS OF GROUP CONTRIBUTIONS

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Molar excess enthalpies, H_m^E, at 298.15 K and atmospheric pressure have been determined for three binary liquid mixtures [x {1,3-dichloropropane or 1,4-dichlorobutane and 1,6-dichlorohexane} + $(1-x)$ tetrachloromethane]. These experimental results along with the data available in the literature on molar excess Gibbs energies, G_m^E, activity coefficients at infinite dilution, $\ln\gamma_i^\infty$, and molar excess enthalpies, H_m^E, for α,ω-dihaloalkanes + benzene or + tetrachloromethane mixtures are examined on the basis of the DISQUAC group contribution model.

Keywords: Dihaloalkanes; calorimetry; DISQUAC group contribution model; dihaloalkane-solvent interactions

INTRODUCTION

Mono- and poly-haloalkanes represent a class of technically important compounds, used in industry as intermediates or as final products. In view of the variety of possible mixtures, the applicability of predictive

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methods is of great interest. The DISQUAC group contribution method [1] pretends to improve the quality of the predictions by using structure-dependent interactions parameters. It has been applied succesfully to many classes of substances including mixtures containing fluoro-, chloro-, bromo, or iodoalkanes [2–9].

In this work, we have measured the molar excess enthalpies, H_m^E, at 298.15 K and atmospheric pressure, for three binary liquid mixtures [x {1,3-dichloropropane or 1,4-dichlorobutane and 1,6-dichlorohexane} + $(1 - x)$ tetrachloromethane]. These experimental results along with our previous one on molar excess enthalpies, H_m^E, of α,ω-dibromoalkane + benzene [10] and the data available in the literature on molar excess Gibbs energies, G_m^E, activity coefficients at infinity dilution, $\ln \gamma_i^\infty$, and molar excess enthalpies, H_m^E, for α,ω-dihaloalkanes + benzene and α,ω-dichloroalkane + tetrachloromethane mixtures are examined on the basis of the DISQUAC group contribution model.

EXPERIMENTAL

$Cl(CH_2)_3Cl$ (99 moles per cent pure) and $Cl(CH_2)_6Cl$ (98 moles per cent pure) were purchased from Aldrich; $Cl(CH_2)_4Cl$ (99 moles per cent pure) and CCl_4 (> 99.5 moles per cent) were provided by Fluka. All the products were used directly without further purification. The results from measurements of density ρ and refractive index n_D at the temperature 298.15 K agreed well with literature values and are listed in Table I. Densities have been measured with an Anton Paar Model

TABLE I Refractive index, n_D, and density, ρ, for the pure liquids

	$n_D(293.15\,K)$		$n_D(298.15\,K)$		$\rho(298.15\,K)/g\,cm^{-3}$	
Compounds	*this work*	*Ref.* [11]	*this work*	*Ref.* [11]	*this work*	*Ref.* [11]
1,3-dichloropropane	1.44762	1.4487	1.44588	1.4460	1.17866	1.1818
1,4-dichlorobutane	1.45336	1.4547	1.45190	1.4522	1.13375	1.1353
1,6-dichlorohexane	1.45648	1.4572 [b]			1.07000 [a]	1.0677 [b]
tetrachloromethane	1.45878	1.4601	1.45692	1.4570	1.58459	1.58436

[a] 293.15 K.

[b] Ref. [12].

DMA 60 densimeter equipped with a DMA 602 cell; refraction indices were determined with a Zeiss refractometer with a precision of ± 0.00002.

The excess enthalpies were determined using a calorimeter and a experimental technique described by Gutiérrez Losa and Gracia [13]. The estimated accuracy of the H_m^E measurements is 2%.

RESULTS

The experimental values of $H_{m,\mathrm{exp}}^E$, at 298.15 K, are given in Table II. They were fitted to the smoothing Redlich – Kister equation:

$$H_m^E = x(1-x)\sum_{i=1}^{n} a_i(2x-1)^{(i-1)} \qquad (1)$$

where x is the mole fraction of the compound different from the α,ω-dichloroalkane. The values for the coefficients a_i and the standard

TABLE II Experimental values of molar excess enthalpies, H_m^E, at $T = 298.15\,\mathrm{K}$ for binary mixtures studied

x_1	$H_m^E (J\,mol^{-1})$	x_1	$H_m^E (J\,mol^{-1})$	x_1	$H_m^E (J\,mol^{-1})$
1,3-dichloropropane (1) + tetrachloromethane (2)					
0.0550	95	0.4137	280	0.6811	200
0.1176	170	0.4485	281	0.7352	172
0.1846	219	0.4495	280	0.8398	104
0.2715	262	0.5280	262	0.8433	101
0.3568	279	0.5926	244	0.8831	75
1,4-dichlorobutane (1) + tetrachloromethane (2)					
0.0501	76	0.4860	219	0.7464	110
0.1550	178	0.5201	210	0.7639	101
0.2183	215	0.5532	203	0.8302	70
0.2819	235	0.6562	157	0.9099	39
0.3568	241	0.7033	136	0.9482	20
0.4219	236				
1,6-dichlorohexane (1) + tetrachloromethane (2)					
0.0892	50	0.4601	17	0.7746	− 30
0.1416	63	0.5056	8	0.7994	− 29
0.1518	62	0.5758	− 17	0.8410	− 23
0.2788	56	0.6580	− 32	0.9392	− 5
0.3871	35	0.6911	− 36		

TABLE III Values of the coefficients a_i, Eq. (1), and standard deviations $\sigma(H_m^E)$, Eq. (2), of experimental molar excess enthalpies, H_m^E, at 298.15 K, for the studied mixtures

Mixtures	a_0	a_1	a_2	a_3	a_4	$\sigma(H_m^E)$ $(J mol^{-1})$
tetrachloromethane (2) +						
1,3-dichloropropane (1)	1079.6	− 417.7	147.8	− 298.1		2
1,4-dichlorobutane (1)	868.7	− 621.6	125.8			2
1,6-dichlorohexane (1)	21.0	− 553.8	105.9	172.9	366.2	2

deviation, $\sigma(H_m^E)$, given by

$$\sigma(H_m^E) = \left[\sum \left(H_{m,\mathrm{exp.}}^E - H_{m,\mathrm{calc.}}^E\right)\Big/N\right]^{1/2} \tag{2}$$

where N is the number of experimental points, were determined by least – squares analysis and are reported in Table III.

THEORY

α,ω-dihaloalkane + tetrachloromethane or benzene systems are regarded as possessing three types of surfaces: (i) type a (CH_3 or CH_2 groups in α,ω-dihaloalkane); (ii) type h, (halogen group, h = Cl or Br in α,ω-dihaloalkane) and (iii) type d, (solvent; d = tetrachloromethane or benzene). The three types of surfaces, a, h and d, generate three pairs of contacts: (a,h), (a,d) and (h,d).

The equations used to calculate G_m^E and H_m^E are the same as in other publications [1, 14]. The interactional terms in the thermodynamic properties under consideration, G_m^E and H_m^E, are given by the DISQUAC model as the sum of a dispersive contribution, $G_{m,\mathrm{INT}}^{E,\mathrm{dis}}$ or $H_{m,\mathrm{INT}}^{E,\mathrm{dis}}$, and a quasichemical contribution, $G_{m,\mathrm{INT}}^{E,\mathrm{quac}}$ or $H_{m,\mathrm{INT}}^{E,\mathrm{quac}}$, thus:

$$G_m^E = G_{m,\mathrm{COMB}}^E + G_{m,\mathrm{INT}}^{E,\mathrm{dis}} + G_{m,\mathrm{INT}}^{E,\mathrm{quac}} \tag{3}$$

$$H_m^E = H_{m,\mathrm{INT}}^{E,\mathrm{dis}} + H_{m,\mathrm{INT}}^{E,\mathrm{quac}} \tag{4}$$

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

The temperature dependence of the dispersive or quasichemical g_{st} parameters $(s, t = a, h)$ has been expressed by a three-constant equation of the type:

$$\frac{g_{st}(T)}{RT} = C_{st.1} + C_{st.2}\left[\frac{T^0}{T} - 1\right] + C_{st.3}\left[Ln\frac{T^0}{T} - \frac{T^0}{T} + 1\right] \qquad (5)$$

where $T^0 = 298.15\,\mathrm{K}$ is the scaling temperature.

Accordingly,

$$\frac{h_{st}(T)}{RT} = C_{st.2}\frac{T^0}{T} - C_{st.3}\left[\frac{T^0}{T} - 1\right] \qquad (6)$$

$$C_{st.1} = \frac{g_{st}(T^0)}{RT^0}, \quad C_{st.2} = \frac{h_{st}(T^0)}{RT^0} \quad \text{and} \quad C_{st.3} = \frac{Cp.st(T)}{R}$$

are termed interchange energy coefficients. In our approach, we have considered zero third interchange coefficient.

The relative molecular volumes, r_i, the total relative surfaces, q_i, and the surface fractions, α_{si} $(s, t = a, h, d)$ $(i = 1, 2)$, of all molecular species have been calculated on the basis of the group volumes, V_G, and surfaces, A_G, recommended by Bondi [15], taking arbitrarily the volume and surface of methane as unity. Table IV lists the geometrical parameters of all compounds referred in this paper.

The dispersive and quasichemical interchange parameters for the contacts aliphatic-halogen (a, h), $C^{\mathrm{dis}}_{ah,l}$ and $C^{\mathrm{quac}}_{ah,l}$ $(l = 1, 2; h = \mathrm{Br\ or\ Cl})$ have been determined previously by $(a, h = \mathrm{Br})$ Artal [16] and $(a, h = \mathrm{Cl})$ Kehiaian [3]. Dispersive coefficients are constant with the chain length, except the dihalomethane, whereas quasichemical coefficients change up to the pentane derivative; the variation is a consequence of the "proximity effect" between halogen atoms sites in the same molecule.

TABLE IV Volumes, r_i, total surfaces q_i, and molecular surface fractions α_{si} ($s = a$, aliphatic; $s = t$, tetrachloromethane; $s = b$, benzene; $s = h$, bromo and $s = h'$, chloro) of studied compounds calculated from the group increments r_G and q_G of Bondi [15]

Compound	r_i	q_i	α_{ai}	α_{hi}	$\alpha_{h'i}$
$BrCH_2Br$	2.3032	2.0362	0.2921	0.7079	0.0000
$Br(CH_2)_2Br$	2.8772	2.3655	0.3936	0.6064	0.0000
$Br(CH_2)_3Br$	3.4749	2.8310	0.4933	0.5067	0.0000
$Br(CH_2)_4Br$	4.0724	3.2966	0.5649	0.4351	0.0000
$Br(CH_2)_5Br$	4.6700	3.7621	0.6187	0.3813	0.0000
$Br(CH_2)_6Br$	5.2675	4.2276	0.6607	0.3393	0.0000
$Br(CH_2)_8Br$	6.4626	5.1586	0.7219	0.2781	0.0000
$ClCH_2Cl$	2.0275	1.8500	0.3215	0.0000	0.6785
$Cl(CH_2)_2Cl$	2.5526	2.1724	0.4286	0.0000	0.5714
$Cl(CH_2)_3Cl$	3.1501	2.6379	0.5294	0.0000	0.4706
$Cl(CH_2)_4Cl$	3.7477	3.1035	0.6000	0.0000	0.4000
$Cl(CH_2)_5Cl$	4.3452	3.5690	0.6522	0.0000	0.3478
$Cl(CH_2)_6Cl$	4.9428	4.0345	0.6923	0.0000	0.3077
C_6H_6	2.8248	2.0724	0.0000	0.0000	0.0000
CCl_4	3.0543	2.5104	0.0000	0.0000	0.0000

For the CCl_4, $\alpha_{ti} = 1.0000$; for the C_6H_6 $\alpha_{bi} = 1.0000$.

The interchange parameters of the aliphatic-solvent contacts, (a, d), where solvent is tetrachloromethane or benzene, are known from Ait–Kaci works [17]. Then the representation of G_m^E and H_m^E of α,ω-dihaloalkane + solvent mixtures requires only the fitting of the (h, d) contact parameters. Based on our previous experience with other contacts in polar–polar or polar–polarizable mixtures, it was assumed the quasichemical coefficients to be equal zero, $C_{hd,l}^{\text{quac}}$ ($l = 1$, 2; h = Br or Cl and $d = CCl_4$ or C_6H_6).

The $C_{hd,1}^{\text{dis}}$ parameters were estimated on the basis of the G_m^E experimental values reported in the bibliography [18–25, 38–51]. The $C_{hd,2}^{\text{dis}}$ parameters for halogen / solvent contact were estimated on the basis of H_m^E experimental values from the literature [6, 10, 19, 20, 38–66], and from our experimental H_m^E values (Tab. II).

These parameters increase with increasing chain of the α,ω-dihaloalkane and reach the values for 1-monohaloalkane + solvent for $n \geq 5$, in which there is not "proximity effect". However, when DISQUAC was applied to bibliographic data of $C_nH_{2n+1}X + CCl_4$ or $+ C_6H_6$ mixtures [2–6] the parameters obtained changed with the chain length of the 1-monohaloalkane to reach a constant value from a certain

n different for different X. In this case, we think that there is only reason for the parameters to change (to be different) in the first compounds of the series and that from $n = 4$ the parameters should be constant.

The values of all interchange energy coefficients are listed in the Table V.

TABLE V Interchange energy coefficients $C^{\mathrm{dis}}_{st,l}$ and $C^{\mathrm{quac}}_{st,l}$ for contacts (s, t) ($s, t = a$, aliphatic; $s, t = t$, tetrachloromethane; $s, t = b$, benzene; $s, t = h$, bromo; $s, t = h'$, cloro) ($l = 1$, Gibbs energy; $l = 2$, enthalpy); n is the number of atoms of Carbon in the α,ω-dihaloalkane

Contact	n	$C^{dis}_{st,1}$	$C^{dis}_{st,2}$	$C^{quac}_{st,1}$	$C^{quac}_{st,2}$
(a, t)[a]	≥3	0.093	0.180	0.0000	0.0000
	4	0.096	0.181	0.0000	0.0000
	5	0.096	0.186	0.0000	0.0000
	6	0.097	0.190	0.0000	0.0000
(a, b)[a]	≥6	0.251	0.560	0.0000	0.0000
(a, h)[b]	1[c]	0.050	0.100	0.860	1.95
	2	0.200	0.300	1.30*	2.30
	3	0.200	0.300	1.72	2.73
	4	0.200	0.300	1.90*	3.10
	≥5	0.200	0.300	2.02*	3.18
(a, h')[d]	1	0.026	0.050	1.15	2.11
	2	0.093	0.180	1.67	3.20
	3	0.093	0.180	2.08*	3.46
	4	0.093	0.180	2.28*	3.68
	≥5	0.093	0.180	2.34	3.75
(t, h')	1	0.75	1.21	0.0000	0.0000
	2	1.13	1.85	0.0000	0.0000
	3	1.45	1.87	0.0000	0.0000
	4	1.68	1.90	0.0000	0.0000
	≥5	1.70*	1.98	0.0000	0.0000
(b, h)	1	0.053	0.479	0.0000	0.0000
	2	0.564	0.856	0.0000	0.0000
	3	0.69*	0.750	0.0000	0.0000
	4	0.79*	0.720	0.0000	0.0000
	≥5	0.815	0.703	0.0000	0.0000
(b, h')	1	0.193	0.268	0.0000	0.0000
	2	0.588	0.891	0.0000	0.0000
	3	0.769	0.840	0.0000	0.0000
	4	0.88*	0.820	0.0000	0.0000
	≥5	0.970	0.813	0.0000	0.0000

* Estimated values.

[a] Ref. [17].

[b] Ref. [16].

[c] Ref. [67].

[d] Ref. [7].

COMPARISON WITH EXPERIMENT AND DISCUSSION

Tables VI, VII and VIII and Figures 1 and 2 show a comparison of DISQUAC with experiment for the isothermal vapor–liquid equilibria and excess molar enthalpies of α,ω-dichloroalkane or α,ω-dibromoalkane + benzene. DISQUAC reproduce quite satisfactorily both the simmetry and the magnitude of the G_m^E or H_m^E-composition curves

TABLE VI Molar excess Gibbs energies, $G_m^E(x_1 = 0.5)$ of α,ω-dihaloalkane + benzene mixtures at various temperatures and equimolar composition. Comparison of direct experimental results (Exp.) with values calculated (Calc.) using the coefficients from Table V

		$G_m^E/J\,mol^{-1}$		
α,ω-dihaloalkane	*T/K*	*Calc.*	*Exp.*	*Reference*
$BrCH_2Br$	308.15	−113	−105	Ref. [18]
$Br(CH_2)_2Br$	283.15	144	180	Ref. [19]
			146	Ref. [20]
			144	Ref. [21]
	288.15	142	140	Ref. [21]
	293.15	140	159	Ref. [22]
			139	Ref. [21]
	298.15	138	250	Ref. [23]
			138	Ref. [21]
	303.15	136	172	Ref. [19]
			134	Ref. [21]
	308.15	134	279	Ref. [23]
			131	Ref. [21]
	313.15	133	128	Ref. [21]
	318.15	131	126	Ref. [21]
	323.15	129	122	Ref. [21]
$ClCH_2Cl$	293.15	−75	−76	Ref. [24]
	298.15	−75	−75	Ref. [24]
			−70	Ref. [25]
	303.15	−75	−74	Ref. [24]
	348.00	−73	−67	Ref. [25]
$Cl(CH_2)_2Cl$	293.15	56	33	Ref. [38]
	298.15	55	57	Ref. [62]
			19	Ref. [26]
			48	Ref. [27]
	303.15	55	14	Ref. [28]
	308.15	55	44	Ref. [62]
	313.15	55	5	Ref. [63]
$Cl(CH_2)_3Cl$	298.15	7	7	Ref. [29]

TABLE VII Molar excess enthalpies, $H_m^E(x_1 = 0.5)$ of α,ω-dihaloalkane + benzene mixtures at various temperatures and equimolar composition. Comparison of direct experimental results (Exp.) with values calculated (Calc.) using the coefficients from Table V

		$H_m^E/J\,mol^{-1}$		
α,ω-dihaloalkane	*T/K*	*Calc.*	*Exp.*	*Reference*
$BrCH_2Br$	298.15	130	140	Ref. [57]
			131	Ref. [10]
	303.15	129	53	Ref. [57]
$Br(CH_2)_2Br$	288.15	259	299	Ref. [58]
	293.15	256	300	Ref. [19]
			289	Ref. [20]
	298.15	253	252	Ref. [39]
			299	Ref. [58]
			246	Ref. [40]
			253	Ref. [10]
	308.15	248	298	Ref. [58]
	318.15	242	293	Ref. [58]
$Br(CH_2)_3Br$	298.15	27	14	Ref. [10]
$Br(CH_2)_4Br$	298.15	−96	−28	Ref. [10]
$Br(CH_2)_5Br$	298.15	−103	−85	Ref. [10]
$Br(CH_2)_6Br$	298.15	−78	−97	Ref. [10]
$Br(CH_2)_8Br$	298.15	−7	−93	Ref. [10]
$ClCH_2Cl$	298.15	−82	−82	Ref. [41]
			−82	Ref. [42]
			−82	Ref. [43]
			−82	Ref. [44]
			−82	Ref. [45]
			−83	Ref. [46]
			−82	Ref. [47]
			−78	Ref. [44]
$Cl(CH_2)_2Cl$	280.75	87	90	Ref. [48]
	288.15	77	67	Ref. [49]
	293.15	71	83	Ref. [38]
	297.85	66	63	Ref. [50]
			60	Ref. [51]
	298.15	65	63	Ref. [60]
$Cl(CH_2)_2Cl$	298.15	65	64	Ref. [48]
			64	Ref. [41]
			65	Ref. [61]
			65	Ref. [62]
			66	Ref. [49]
	303.15	60	46	Ref. [63]
	308.15	54	53	Ref. [64]
			54	Ref. [62]
			55	Ref. [49]
	315.00	47	44	Ref. [48]
	318.15	44	55	Ref. [49]
	343.15	21	58	Ref. [65]

TABLE VII (Continued)

α,ω-dihaloalkane	T/K	$H_m^E/J\,mol^{-1}$		Reference
		Calc.	Exp.	
$Cl(CH_2)_3Cl$	298.15	−47	−75	Ref. [66]
$Cl(CH_2)_4Cl$	298.15	−101	−131	Ref. [66]
$Cl(CH_2)_5Cl$	298.15	−102	−123	Ref. [66]
$Cl(CH_2)_6Cl$	298.15	−76	−123	Ref. [66]

TABLE VIII Logarithm of activity coefficients at infinite dilution, $\ln\gamma_2^\infty$, of α,ω-dihaloalkane + benzene mixtures at various temperatures. Comparison of direct experimental results (Exp.) with values calculated (Calc.) using the coefficients from Table V

α,ω-dihaloalkane	T/K	$\ln\gamma_2^\infty$		Reference
		Calc.	Exp.	
$ClCH_2Cl$	337.2	0.089	0.058	Ref. [30]
	355.0	0.086	0.039	Ref. [30]

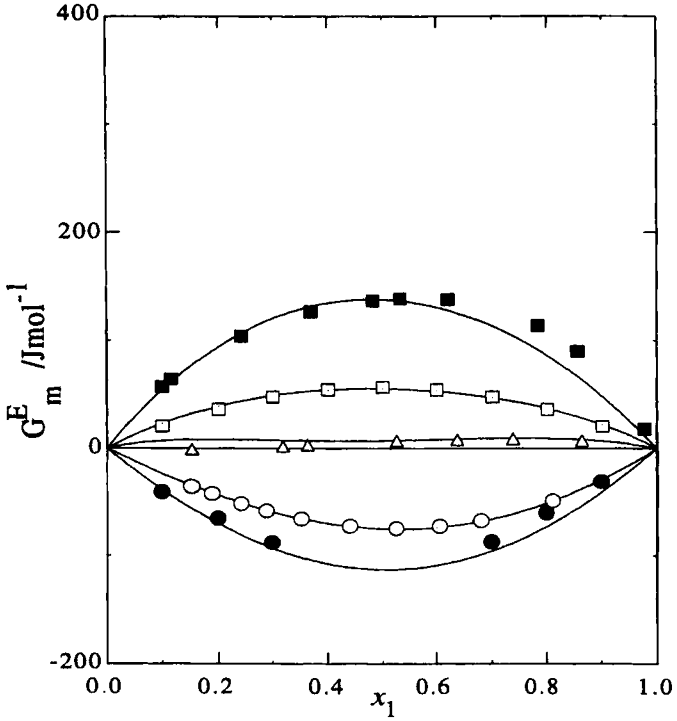

FIGURE 1 Molar excess Gibbs energies, G_m^E of α,ω-dichloroalkane, $Cl(CH_2)_nCl$ (○, $n = 1$; □, $n = 2$; △, $n = 3$) or α,ω-dibromoalkane, $Br(CH_2)_nBr$(●, $n = 1$; ■, $n = 2$) + benzene mixtures; lines, DISQUAC prediction.

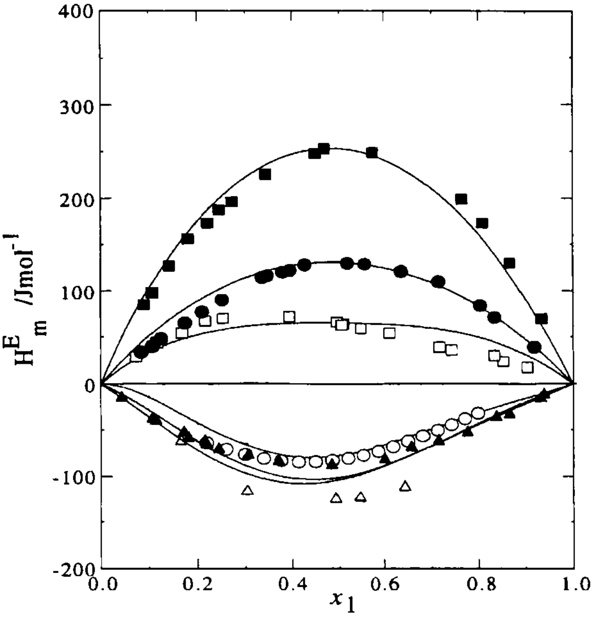

FIGURE 2 Molar excess enthalpies, H_m^E of α,ω-dichloroalkane, $Cl(CH_2)_nCl$ (○, $n = 1$; □, $n = 2$; △, $n = 5$) or α,ω-dibromoalkane, $Br(CH_2)_nBr$ (●, $n = 1$; ■, $n = 2$, ▲, $n = 5$) + benzene mixtures; lines, DISQUAC prediction.

TABLE IX Molar excess Gibbs energies, $G_m^E(x_1 = 0.5)$ of α,ω-dichloroalkane + tetrachloromethane mixtures at various temperatures and equimolar composition. Comparison of direct experimental results (Exp.) with values calculated (Calc.) using the coefficients from Table V

		$G_m^E/J\ mol^{-1}$		
α, ω-dichloroalkane	*T/K*	*Calc.*	*Exp.*	*Reference*
$ClCH_2Cl$	303.15	331	253	Ref. [31]
			330	Ref. [32]
			307	Ref. [33]
	308.15	327	242	Ref. [31]
	312.15	324	261	Ref. [31]
	318.15	318	265	Ref. [34]
$Cl(CH_2)_2Cl$	298.15	404	417	Ref. [27]
			220	Ref. [35]
	303.15	400	400	Ref. [32]
	313.15	393	371	Ref. [33]
			367	Ref. [35]
	322.00	387	507	Ref. [35]
	350.00	369	337	Ref. [36]
	353.15	368	365	Ref. [37]
$Cl(CH_2)_3Cl$	298.15	389	282	Ref. [29]
	303.15	389	390	Ref. [32]
$Cl(CH_2)_4Cl$	303.15	366	360	Ref. [32]

TABLE X Molar excess enthalpies, H_m^E ($x_1 = 0.5$) of α,ω-dichloroalkane + tetrachloromethane mixtures at various temperatures and equimolar composition. Comparison of direct experimental results (Exp.) with values calculated (Calc.) using the coefficients from Table V

		$H_m^E/J\ mol^{-1}$		
α, ω-dichloroalkane	*T/K*	*Calc.*	*Exp.*	*Reference*
$ClCH_2Cl$	297.85	594	588	Ref. [50]
	298.15	594	596	Ref. [59]
			596	Ref. [52]
			608	Ref. [6]
$Cl(CH_2)_2Cl$	288.15	641	653	Ref. [49]
	298.15	628	626	Ref. [53]
			667	Ref. [6]
			666	Ref. [49]
	303.15	622	663	Ref. [54]
	308.15	616	664	Ref. [49]
	313.15	610	654	Ref. [49]
$Cl(CH_2)_3Cl$	288.15	417	262	Ref. [56]
	298.15	399	509	Ref. [6]
			276	Ref. [56]
			270	This work
	303.15	391	265	Ref. [55]
	308.15	383	287	Ref. [56]
	318.15	368	302	Ref. [56]
$Cl(CH_2)_4Cl$	298.15	238	342	Ref. [6]
			217	This work
	303.15	228	224	Ref. [55]
$Cl(CH_2)_5Cl$	298.15	180	236	Ref. [6]
$Cl(CH_2)_6Cl$		111	156	Ref. [6]
			5	This work

for these type of mixtures, taking into account the ocurrence of intramolecular effects (especially the proximity effect) in the dihalocompounds.

In the case of the mixtures with tetrachloromethane as solvent (Tabs. IX and X), DISQUAC reproduce less satisfactorily the simmetry of the curves G_m^E-composition of α,ω-dichloroalkane $+ CCl_4$ (Fig. 3). However, H_m^E-composition curves (Fig. 4), are reasonably well represented. It should be remembered that the excess functions of polar + polar or + polarizable mixtures are given DISQUAC by the difference between two terms, dispersive and quasichemical. Hence the difficulty in representating accurately (in terms of relative errors) the experimental data in mixtures with low values of H_m^E as is the case of 1,6-dichlorohexane $+ CCl_4$.

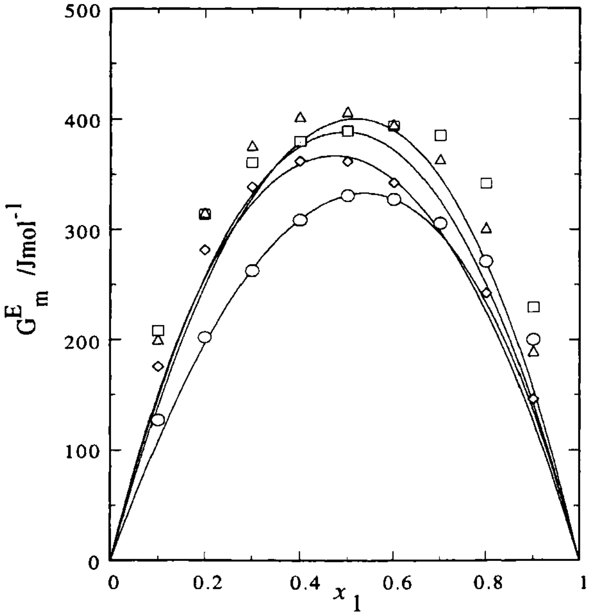

FIGURE 3 Molar excess Gibbs energies, G^E_m of α,ω-dichloroalkane, $Cl(CH_2)_nCl$ (○, n = 1; △, n = 2; □, n = 3; ◇, n = 4) + tetrachloromethane mixtures; lines, DISQUAC prediction.

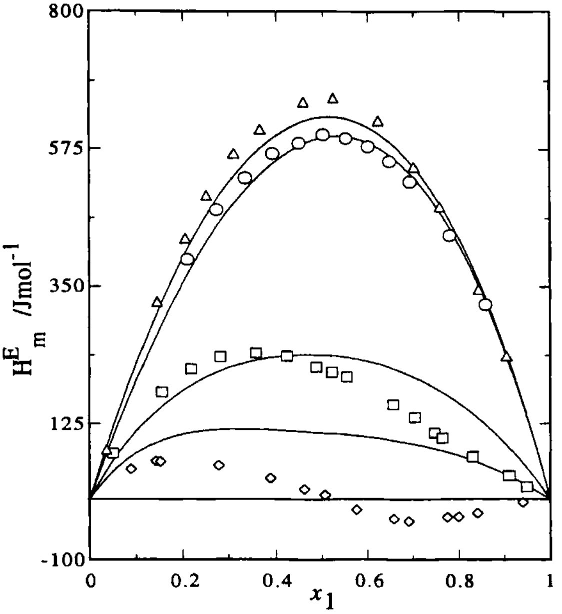

FIGURE 4 Molar excess enthalpies, H^E_m of α, ω-dichloroalkane, $Cl(CH_2)_nCl$ (○, n = 1; △, n = 2; □, n = 4; ◇, n = 6) + tetrachloromethane mixtures; lines, DISQUAC prediction.

References

[1] Kehiaian, H. V. (1985). *Pure & Appl. Chem.*, **57**, 15.
[2] Artal, M., Fernández, J., Muñoz Embid, J., Velasco, I., Otín, S. and Kehiaian, H. V. (1990). *J. Sol. Chem.*, **20**, 3.
[3] García Vicente, I., García-Lisbona, N., Velasco, I., Otín, S., Muñoz Embid, J. and Kehiaian, H. V. (1989). *Fluid Phase Equilibria*, **49**, 251.
[4] García-Lisbona, N., García Vicente, I., Muñoz Embid, J., Velasco, I., Otín, S. and Kehiaian, H. V. (1989). *Fluid Phase Equilibria*, **45**, 191.
[5] Soriano, M. J., Velasco, I., Otín, S. and Kehiaian, H. V. (1990). *Fluid Phase Equilibria*, **45**, 205.
[6] Kehiaian, H. V. and Marongiu, B. (1988). *Fluid Phase Equilibria*, **42**, 141.
[7] Kehiaian, H. V. and Marongiu, B. (1988). *Fluid Phase Equilibria*, **40**, 23.
[8] Kehiaian, H. V. and Velasco, I. (1987). *Fluid Phase Equilibria*, **38**, 227.
[9] Muñoz Embid, J., Otín, S., Velasco, I., Gutiérrez Losa, C. and Kehiaian, H. V. (1987). *Fluid Phase Equilibria*, **38**, 1.
[10] Blanco, S. T., Artal, M., Fernández, J., Muñoz Embid, J. and Otín, S. (1993). *J. Chem. Eng. Data*, **38**, 587.
[11] *TRC Thermodynamics Tables Non-Hydrocarbons*, 1994. Thermodynamics Research Center, The Texas A&M University System: College Station, TX.
[12] *Hanbook of Chemistry and Physics*, 73^{RD}, 1992. The Chemical Rubber Co: Cleveland.
[13] Gutiérrez Losa, C. and Gracia, M. (1971). *Rev. Acad. Cienc. Exactas Fis.-Quim. Nat. Zaragoza*, **26**, 101.
[14] Kehiaian, H. V., Grolier, J.-P. E. and Benson, C. G. (1978). *J. Chim. Phys.*, **75**, 1031.
[15] Bondi, A. (1968). Physical Properties of Molecular Crystals, *Liquids and Glasses*, John Wiley, New York.
[16] Artal, M., Muñoz Embid, J., Otín, S., Velasco, I. and Kehiaian, H. V. (1991). *Fluid Phase Equilibria*, **70**, 267.
[17] Ait-Kaci, A. (1982). *Ph.D. Thesis*, University of Lyon, France.
[18] Singh, P. P. and Sharma, V. K. (1989). *Fluid Phase Equilibria*, **44**, 347.
[19] Neckel, A. and Volk, H. (1958). *Monatsh. Chem.*, **89**, 755.
[20] Liebermann, E. and Fried, V. (1972). *Ind. Eng. Chem. Fundam.*, **11**, 350.
[21] Gracia, M., Pérez, P. and Valero, J. (1994). *Fluid Phase Equilibria*, **97**, 147.
[22] Birdi, G. S., Vij, J. N. and Mahl, B. S. (1974). *Thermochim. Acta*, **10**, 253.
[23] Kalra, K. C., Singh, K. C. and Spah, D. C. (1990). *J. Chem. Thermodyn.*, **22**, 771.
[24] Nigam, R. K. and Mahl, B. S. (1971). *Ind. J. Chem.*, **9**, 1250.
[25] Srivastava, R. and Smith, B. D. (1985). *J. Chem. Eng. Data*, **30**, 313.
[26] Kato, M. (1982). *Bull. Chem. Soc. Jpn.*, **55**, 23.
[27] López, J. A., Pérez, P., Gracia, M. and Gutiérrez Losa, C. (1988). *J. Chem. Thermodyn.*, p. 447.
[28] Mahl, B. S., Khurma, J. R. and Viji, J. N. (1977). *Thermochim. Acta*, **9**, 1250.
[29] Pérez, P., Valero, J., Gracia, M. and Gutiérrez Losa, C. (1989). *J. Chem. Thermodyn.*, **21**, 259.
[30] Thomas, E. R., Newman, B. A., Nicolaides, G. L. and Eckert, C. A. (1982). *J. Chem. Eng. Data*, **27**, 233.
[31] Mueller, C. R. and Ignatowski, A. J. (1960). *J. Chem. Phys.*, **32**, 1430.
[32] Azpiazu, Y., Royo, F. and Gutiérrez Losa, C. (1984). *J. Chem. Thermodyn.*, **16**, 561.
[33] Muñoz Embid, J., Roux, A. H. and Grolier, J.-P. E. (1990). *Int. Data Ser., Sel. Data Mixtures*, ser. A., p. 59.
[34] Rulewicz, G., Schuberth, H. and Leibnitz, E. (1968). *J. Prakt, Chem.*, **37**, 122.
[35] Kireev, V. A. and Skvortsova, A. A. (1936). *Zh. Fiz. Khim.*, **7**, 63.

[36] Rathbone, P. (1975). *Proc. 4th Int. IUPAC Conf. Chem. Thermodynamics*, **6**, 64.
[37] Sagnes, M. and Sanchez, V. (1971). *J. Chem. Eng. Data*, **16**, 351.
[38] Sieg, L., Crützen, J. L. and Jost, W. (1951). *Z. Phys. K. Chem.*, **198**, 263.
[39] Mahl, B. S., Kooner, Z. S. and Khurma, J. R. (1976). *Thermochim. Acta*, p. 256.
[40] Spah, D. C., Verma, P. K., Singh, K. C. and Kalra, K. C. (1989). *Thermochim. Acta*, **146**, 187.
[41] Ottersted, J.-E. A. and Missen, R. W. (1966). *J. Chem. Eng. Data*, **11**, 360.
[42] Murakami, S. and Benson, G. C. (1969). *J. Chem. Thermodyn.*, **1**, 559.
[43] Tanaka, R., Murakami, S. and Fujishiro, R. (1972). *Bull. Chem. Soc. Jpn.*, **45**, 2107.
[44] Nigam, R. K. and Mahl, B. S. (1972). *J.C.S. Faraday Trans. I*, **68**, 1508.
[45] Grolier, J.-P. E. and Inglese, A. (1976). *Can. J. Chem.*, **54**, 1952.
[46] Featherstone, J. D. B. and Dickinson, N. A. (1976). *J. Chem. Thermodyn.*, **8**, 985.
[47] Costigan, M. J., Hodges, L. J., Marsh, K. N., Stokes, R. H. and Tuxford, C. W. (1980). *Aus. J. Chem.*, **33**, 2103.
[48] Ruiter, L. H. (1955). *Rec. Trav. Chim.*, **74**, 1131.
[49] Baños, I., Valero, J., Gracia, M. and Gutiérrez Losa, C. (1983). *Ber. Bunsenges. Phys. Chem.*, **87**, 866.
[50] Cheesman, G. H. and Whitaker, A. M. B. (1952). *Proc. Roy. Soc. London*, **A212**, 406.
[51] Korvezee, A. E., Ruiter, L. H. and Stuyts, A. L. (1953). *Rec. Trav. Chim.*, **72**, 462.
[52] Siddiqi, M. A. and Lucas, K. (1983). *J. Chem. Thermodyn.*, **15**, 1181.
[53] Amaya, K. and Fujishiro, R. (1958). *Bull. Chem. Soc. Jpn.*, **31**, 90.
[54] Muñoz Embid, J., Berro, C., Otín, S. and Kehiaian, H. V. (1990). *J. Chem. Eng. Data*, **35**, 266.
[55] Royo, F., Gracia, M. and Gutiérrez Losa, C. (1980). *Rev. Acad. Cienc. Exactas Fis.-Quim. Nat. Zaragoza*, **35**, 75.
[56] Baños, I., Valero, J., Pérez, P., Gracia, M. and Gutiérrez Losa, C. (1990). *J. Chem. Thermodyn.*, **22**, 67.
[57] Singh, P. P., Nigam, R. K. and Sharma, V. K. (1984). *Fluid Phase Equilibria*, **18**, 313.
[58] Pérez, P., Florián, A., Lázaro, A., Gracia, M., Gutiérrez Losa, C. and Valero, J. (1983). *Ber. Bunsenges. Phys. Chem.*, **87**, 5.
[59] Nagata, I., Tamura, K. and Tokuriki, S. (1982). *Fluid Phase Equilibria*, **8**, 75.
[60] Brown, I. and Fock, W. (1955). *Aus. J. Chem.*, **8**, 361.
[61] Mahl, B. S. and Khurma, J. R. (1977). *J.C.S. Faraday Trans. I*, **73**, 29.
[62] Nigam, R. K., Singh, P. P., Singh, K. C., Singh, M. and Mishra, R. (1980). *Can. J. Chem.*, **58**, 1902.
[63] Kohler, F. (1969). *Monatsch. Chem.*, **100**, 1151.
[64] Patel, H. R., Sundaram, S. and Viswanath, D. S. (1979). *J. Chem. Eng. Data*, **24**, 40.
[65] Stavely, L. A. K., Tupman, W. I. and Hart, K. R. (1955). *Trans. Faraday Soc.*, **51**, 323.
[66] Grolier, J.-P. E. and Kehiaian, H. V. (1973). *J. Chim. Phys.*, **70**, 807.
[67] Blanco, S. T., Muñoz Embid, J. and Otín, S. (1993). *Fluid Phase Equilibria*, **91**, 281.