STRUCTURAL EFFECTS AND INTERMOLECULAR INTERACTIONS IN HOMOLOGOUS SERIES OF ORGANIC SYSTEMS EVIDENCED BY THERMODYNAMIC PROPERTIES IN THE FRAME OF DISQUAC MODEL

Alexandru BÂRHALĂ,[*] Mariana TEODORESCU and Dana DRĂGOESCU

Institute of Physical Chemistry
"Ilie Murgulescu", 202 Splaiul Independenţei, 060021 Bucharest, Roumania

The data available in the literature and our recent data on vapour–liquid equilibrium (VLE), excess Gibbs energy, G^E and excess enthalpy, H^E for two homologous series of organic mixtures, namely cycloalkane + n-alkylbenzene and linear ketone + chloroalkane mixtures are examined in terms of the DISQUAC group contribution model. The sets of structure-dependent DISQUAC parameters obtained by us were used to calculate the excess thermodynamic properties (G^E, H^E) and infinite dilution functions ($\ln\gamma_i^\infty$, $H_i^{E,\infty}$), of selected mixtures from the two series. In our treatment we present also how the structural effects and different types of molecular interactions are reflected by the thermodynamic excess properties of the mentioned series mixtures.

INTRODUCTION

Both for designing separation processes of liquid mixtures and for developing new predictive methods for thermodynamic properties and testing relevant theories of liquids, the experimental data on vapour-liquid equilibria provide valuable information. For organic systems where no experimental data are available, the prediction of the thermodynamic properties is the main feature of any group contribution model.

Due to the availability of large group interaction parameter tables, UNIFAC[1] (Universal Functional Activity Coefficients) and ASOG[2] (Analytical Solution of Groups) are models which have the widest practical interest.

The review of group-contribution methods is given in general papers.[3-5] A special attention deserves DISQUAC[3] (Dispersive Quasichemical), an extended pseudo-lattice quasichemical[6] group-contribution model. The model has been successfully applied to the evaluation of thermodynamic properties from different classes of organic mixtures, in homologous series.[7-12]

In contrast to other group contribution methods where interaction parameters are average values depending on the number and nature of the systems involved in the averaging, the DISQUAC model offers a physically reasonable assumption that the parameters may also vary with the molecular structure. A basic condition requires that this variation be regular and that the similar classes of compounds follow the same rules. The final selection of DISQUAC parameters is achieved by graphical plotting of – usually a few – adjusted values so allowing estimation of other values by interpolation or extrapolation. Therefore, the proximity effects due to specific interactions are reflected in the variation of the parameters with the molecular structure.

The purpose of this paper is to test the DISQUAC model for consistent description and quality of prediction of vapour-liquid equilibria (VLE), related excess (G^E, H^E) and infinite dilution functions ($\ln\gamma_i^\infty$, $H_i^{E,\infty}$), using the sets of structure-dependent parameters obtained by us for two homologous series of organic compound mixtures, namely cycloalkane + n-alkylbenzene and linear ketone + chloroalkane mixtures. In our

---

[*] Corresponding author: abarhala@chimfiz.icf.ro

treatment we present also how the structural effects and different types of molecular interactions are reflected by the thermodynamic excess properties in the mentioned mixtures.

In order to determine the DISQUAC parameters for the first series (cycloalkyl/phenyl contact), the calculations have been performed using available literature data on VLE, equimolar G^E and/or H^E for ten mixtures[13-20] as follows: cyclohexane + benzene, + toluene, + ethylbenzene, cycloheptane + benzene, + toluene, + ethylbenzene, cyclooctane + benzene, + toluene, + ethylbenzene, + n-heptane and our data on VLE and equimolar G^E for five mixtures[21-24] namely, cyclohexane + propylbenzene, cyclooctane + ethylbenzene, + propylbenzene, + butylbenzene and + n-heptane.

For the second series (the C=O/Cl contact) the calculations were performed using selected data on VLE, G^E and H^E for ketone + chloroalkane mixtures both the literature data, and our G^E data resulting from VLE measurements of the following binary mixtures: propan-2-one + 1-chloropentane, + 1,3-dichloropropane, + 1,4-dichlorobutane, + 1,1,2,2-tetrachloroethane and + 1,1,1-trichloroethane,[25, 26] butan-2-one + 1-chloropentane, + 1,3-dichloropropane, + 1,4-dichlorobutane,[27] + 1,1,1-trichloroethane and + 1,1,2,2-tetrachloroethane,[28] pentan-3-one + 1,2-dichloroethane, + 1,3-dichloropropane,[29] + 1,4-dichlorobutane, + trichloromethane, + 1,1,1-trichloroethane and + 1,1,2,2-tetrachloroethane.[30]

The H^E data were found for the mixtures of propan-2-one + chloroalkane, [31-38] butan-2-one + chloroalkane[39–43] and pentan-3-one + chloroalkane.[35, 43, 44]

THEORETICAL ASPECTS

The DISQUAC[3] model interprets the properties of organic mixtures in terms of surface interactions using an approach which represents an extension of the quasichemical theory and where each molecule is characterised by geometrical and interaction parameters. Calculation of both the geometrical and the interaction parameters is presented in details elsewhere.[6, 8-10]

The equations used to calculate G^E and H^E are the same as described earlier; however, for the sake of clarity of presentation we remind here shortly some theoretical aspects.

The excess thermodynamic properties G^E and H^E contain a dispersive (*dis*) and a quasichemical (*quac*) term which are calculated independently by classical formulas and then simply added:

$$G^E = G^E_{comb} + G^{E,dis}_{int} + G^{E,quac}_{int} \tag{1}$$

$$H^E = H^{E,dis} + H^{E,quac} \tag{2}$$

where G^E_{comb} is the Flory-Huggins combinatorial (*comb*) term.[6] This is expressed by: $\ln \gamma^{comb}_i = \ln(\phi_i / x_i) + 1 - (\phi_i / x_i)$, where $\phi_i = r_i x_i /(r_1 x_1 + r_2 x_2)$ is the volume fraction, x_i is the mole fraction and r_i is the relative molecular volume of component i ($i = 1, 2$).
Of course, $G^E_{comb} / RT = \sum x_i \ln \gamma^{comb}_i$.

In the zeroth approximation (*quac* term zero), the natural logarithms of activity coefficients are calculated as the sum of the combinatorial ($\ln \gamma_i^{comb}$) and dispersive ($\ln \gamma_i^{dis}$) terms, where:

$$\ln \gamma^{dis}_i = q_i q_j^2 x_j^2 (g^{dis}_{12} / RT)/(q_i x_i + q_j x_j)^2 \tag{3}$$

The latter term is a partial quantity of the $G^{E,dis}_i / RT$. Similarly, the partial molar excess enthalpy is calculated as follows:

$$H^{E,dis}_i = q_i q_j^2 x_j^2 h^{dis}_{12} /(q_i x_i + q_j x_j)^2 \tag{4}$$

The temperature dependence of the interaction parameters is expressed in terms of the dispersive and quasichemical interchange coefficients $C^{dis}_{st,n}$ and $C^{quac}_{st,n}$, respectively:

$$g^{dis/quac}_{st} / RT = C^{dis/quac}_{st,1} + C^{dis/quac}_{st,2} \left[\left(298.15/T - 1 \right) \right] + C^{dis/quac}_{st,3} \left[\ln \left(298.15/T \right) - \left(298.15/T \right) + 1 \right] \tag{5}$$

$$h_{st}^{dis/quac} / RT = C_{st,2}^{dis/quac}\left(298.15/T\right) - C_{st,3}^{dis/quac}\left(298.15/T - 1\right) \tag{6}$$

where s and t denote the type of group surface (namely: a for alkyl, b for phenyl, c for cycloalkyl, d for chlorine and k for carbonyl).

The excess partial molar enthalpies, $H_i^{E,\infty}$, were derived from the Redlich-Kister equations which fit H^E calorimetric data. In particular, their infinite dilution values are given by:

$$H_1^{E,\infty} = \lim_{x_1 \to 0}(H^E / x_1 x_2) = \sum_{i=0}^{k} A_i(-1)^i \quad \text{and} \tag{7}$$

$$H_2^{E,\infty} = \lim_{x_2 \to 0}(H^E / x_1 x_2) = \sum_{i=0}^{k} A_i \tag{8}$$

A_i, being the coefficient of the fitting equation as given in the literature.

Each contact (st) is thus characterised by three dispersive interchange coefficients $C_{st,l}^{dis}$ and three quasichemical interchange coefficients $C_{st,l}^{quac}$ where $l = 1$ (Gibbs energy), 2 (enthalpy), 3 (heat capacity). For non-polar contact (st), which is the case of cycloalkyl/phenyl contact, quasichemical coefficients are zero. (Additionally to this, in our cases the heat capacity experimental data being not available, in further calculations the coefficients $C_{st,3}^{dis}$ and $C_{st,3}^{quac}$ were assumed to be zero.)

Assessment of geometrical parameters

The relative geometrical parameters, *viz.* the relative molecular volume r_i, the relative molecular surface q_i and surface fraction $\alpha_{si} = q_{si} / q_i$ of all molecular species have been calculated on the basis of the group volumes and surfaces recommended by Bondi[45] arbitrarily setting the molecular volume and surface of methane to unity.[6] The geometrical parameters of groups existing in the studied mixtures have been estimated earlier[6, 8, 46] and summarised elsewhere.[10,11,47]

Estimation of DISQUAC Interchange Parameters

A. The cycloalkane + n-alkylbenzene series

Cycloalkane + n-alkylbenzene systems are regarded as possessing three types of surface: type a, n-alkyl (CH$_3$ or CH$_2$ groups which are assumed to exert the same force field), type c, cycloalkyl (c-CH$_2$) and type b, phenyl (C$_6$H$_6$ or C$_6$H$_5$). These three types of surfaces generate three pairs of contacts, namely ab (phenyl/n-alkyl), ac (cycloalkyl/n-alkyl) and bc (cycloalkyl/phenyl).

The dispersive interchange parameters for the bc (cycloalkyl/phenyl) contact in the investigated systems have been estimated using the ac (cycloalkyl/n-alkyl) and ab (n-alkyl/phenyl) contact parameters determined independently on the basis of the two cycloalkane+ n-alkane and n-alkylbenzene + n-alkane[46] classes of non-polar mixtures. The procedure and the main steps of the estimation were presented in a previous paper.[11] The obtained bc contact parameters are presented in Table 1 for all cycloalkane + n-alkylbenzene mixtures, including the mixtures with benzene.

We note a relative constancy of $C_{bc,1}^{dis}$ values, the small differences being rather due to the inaccuracy of G^E experimental data than to the structural effects. A slight increase of $C_{bc,2}^{dis}$ values with the size of n-alkylbenzene may be attributed to the inductive effect of the n-alkyl groups, toluene being the first member of the homologous series of n-alkylbenzene.

Table 1

Dispersive interchange coefficients for the cycloalkane/phenyl contact
in cycloalkane + n-alkylbenzene mixtures

Mixture		$C_{bc,1}^{dis}$	$C_{bc,2}^{dis}$
c-C_6H_{12}	+ C_6H_6	0.25	0.54
	+ C_7H_8	0.35	0.65
	+ C_8H_{10}	0.35	0.72
	+ C_9H_{12}	0.37	0.72[a]
c-C_7H_{14}	+ C_6H_6	0.25[a]	0.56
	+ C_7H_8	0.35[a]	0.65
	+ C_8H_{10}	0.35[a]	0.71
c-C_8H_{16}	+ C_6H_6	0.24	0.55
	+ C_7H_8	0.35	0.63
	+ C_8H_{10}	0.31	0.69
	+ C_9H_{12}	0.32	0.69[a]
	+ $C_{10}H_{14}$	0.33	0.69[a]

[a] Estimated values. Note: the coefficients are average values in the temperature range under study.

If in the cycloalkane+ n-alkane mixtures the cycloalkanes do not form a homologous series, in terms of c-CH_2 group contribution, as Tine and Kehiaian[46] have evidenced, in cycloalkane + n-alkylbenzene mixtures the relatively constancy of the dispersive interchange coefficients proves that the cycloalkanes are a homologous series in the thermodynamic meaning.

B. The linear ketone + chloroalkane series

The chlorine groups of chloroakane mixtures were assigned to three types: (1) 1-chloroalkane, (2) α,ω-dichloroalkane and (3) polychloroalkane. Subsequently, the variation of the DISQUAC parameters with the chloroalkane and ketone chain length as well as with the number of chlorine atoms is taken into account.

The ketone + chloroalkane mixtures possess the three types of surface: (1) type *a*, aliphatic (CH_3, CH_2, CH, C; all these groups are assumed to exert the same force field), (2) type *d*, chlorine (Cl) and (3) type *k*, carbonyl (C=O). The three types of surface *a*, *d* and *k* form three pairs of contacts: *ad*, *ak* and *kd*. The dispersive and quasichemical interchange parameters for *ad*- and *ak*-contacts were critically evaluated from the thermodynamic properties of chloroalkane + n-alkane and ketone + n-alkane mixtures by Kehiaian *et al.*[8, 48] Since the *ad*- and *ak*-contact parameters were known, only the *kd*-contact parameters were determined by us initially, for pentane-3-one + chloroalkane[10] and propane-2-one + chloroalkane[47] and then, revised for the whole series of linear ketone + chloroalkane mixtures.[49]

We considered that the C=O/Cl contact in linear ketone + chloroalkane mixtures were of similar polarity as COO/Cl contact in n-alkyl alkanoate + chloroalkane mixtures. Therefore, taking into account the expected structural effects, the DISQUAC parameters for the *kd*-contact were determined using the same procedure as that of Avedis *et al.*[9] For this purpose, the equimolar experimental values for G^E and H^E were used, from both the literature and our recent measurements.

For the **linear ketone + 1-chloroalkane** mixtures, preliminary calculations[10] were performed under the assumption that the *kd*-contact is either entirely dispersive or entirely quasichemical. In the case of H^E data, it was shown that their dependence on composition is best modelled when the *kd*-contact is described using only the dispersive coefficients.

The obtained dispersive parameters for the *kd*-contact and their dependence on the chain length of 1-chloroalkane are given in Table 2 and shown in Fig. 1.

Table 2

Dispersive interchange coefficients for the C=O group (type *k*) in linear ketone
$CH_3(CH_2)_{u-1}CO(CH_2)_{v-1}CH_3$ with Cl atom (type *d*) in 1-chloroalkane $CH_3(CH_2)_{m-2}CH_2Cl$ *

u	*v*	*m*	$C_{kd,1}^{dis}$	$C_{kd,2}^{dis}$	*u*	*v*	*m*	$C_{kd,1}^{dis}$	$C_{kd,2}^{dis}$
1	1	4	2.55	2.97	1	3	6	2.25[a]	2.39
		5	2.74	3.16[a]			≥7	2.38[a]	2.52
		6	2.84[a]	3.26[a]	1	4	4	2.08[a]	2.22[a]

(continues)

Table 2 (continued)

u	v	col	val1	val2	u	v	col	val1	val2
		≥7	2.92[a]	3.34[a]			5	2.22[a]	2.36[a]
1	2	4	2.06	2.22			6	2.25[a]	2.51
		5	2.21[a]	2.37			≥7	2.38[a]	2.51
		6	2.27[a]	2.43	2	2	4	1.54[a]	1.68
		≥7	2.57[a]	2.73			5	1.73[a]	1.87[a]
1	3	4	2.09[a]	2.23			6	1.79[a]	1.93[a]
		5	2.22[a]	2.36			≥7	2.04[a]	2.18[a]

[*] The quasichemical interchange coefficients $C_{kd,1}^{quac} = C_{kd,2}^{quac} = 0$;   [a] Estimated value.

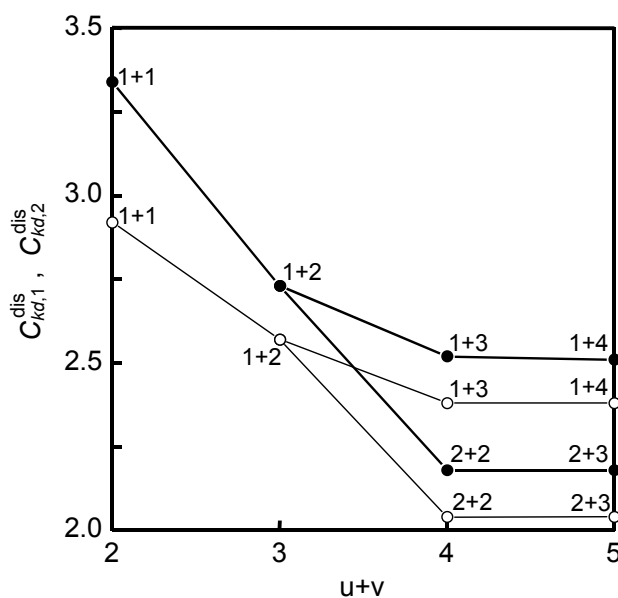
Fig. 1 – Dependence of $C_{kd,1}^{dis}$ (o) and $C_{kd,2}^{dis}$ (•) interchange coefficients on $u+v$ in the 1-chloroalkane + ketone $CH_3(CH_2)_{u-1}CO(CH_2)_{v-1}CH_3$ mixture ($u+v$ indicated in diagram).

For the **ketone + α,ω-dichloroalkane** mixtures it was found that, the *kd*-contact contributes with a non-negligible quasichemical term similarly as do the n-alkyl alkanoate + α,ω-dichloroalkane mixtures.[10] Assuming that the dispersive *kd*-contact parameters of α,ω-dichloroalkane are the same as for 1-chloroalkane ($m \geq 7$, Table 2, Fig. 1), we adjusted the quasichemical interchange parameters $C_{kd,n}^{quac}$ using the most reliable equimolar G^E and H^E data available. Table 3 summarises the obtained values and Fig. 2 illustrates the change of $C_{kd,n}^{quac}$ parameters with aliphatic chain length m between the chlorine groups in α,ω-dichloroalkanes. It was observed that $C_{kd,n}^{quac}$ coefficients are independent of the nature of ketone for $m \leq 10$.

Table 3

Quasichemical interchange coefficients for C=O group (type *k*) in linear ketone
$CH_3(CH_2)_{u-1}CO(CH_2)_{v-1}CH_3$ with Cl atom (type *d*) in α,ω-dichloroalkane $ClCH_2(CH_2)_{m-2}CH_2Cl$. Values for $m \geq 5$ are estimated

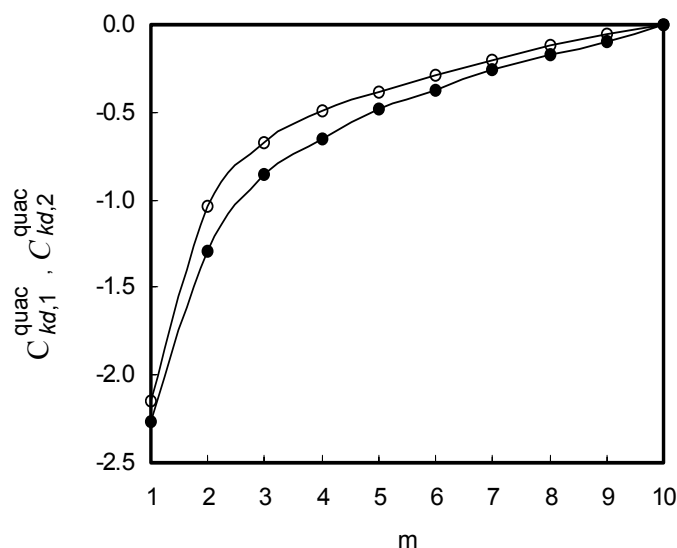| m	1	2	3	4	5	6	7	8	9	10
$C_{kd,1}^{quac}$	–2.15	–1.04	–0.67	–0.49	–0.38	–0.29	–0.20	–0.12	–0.05	0
$C_{kd,2}^{quac}$	–2.26	–1.29	–0.85	–0.65	–0.48	–0.37	–0.26	–0.17	–0.10	0

Fig. 2 – Dependence of $C_{kd,1}^{\text{quac}}$ (o) and $C_{kd,2}^{\text{quac}}$ (•) interchange coefficients on m

in the α,ω-dichloroalkane ClCH$_2$(CH$_2$)$_{m-2}$CH$_2$Cl + ketone mixtures.

For the **ketone + polychloroalkane** (trichloromethane, 1,1,1-trichloroethane, tetrachloromethane and 1,1,2,2-tetrachloroethane) mixtures, a good description of the experimental data was found using only the dispersive contribution of *kd*-contact. The parameters obtained are presented in Table 4. However, the polychloroalkanes under study are the first members of different series according to the classification by Kehiaian and Marongiu.[8] The estimation of the predictive parameters for these series of chloroalkanes would require much more additional input data. For the time being, the results are in agreement with those reported for the contact COO/Cl in mixtures of 1,1,2,2-tetrachloroethane with n-alkyl alkanoates.[50, 51]

Table 4

Dispersive interchange coefficients for C=O group (type *k*) in linear ketone
CH$_3$(CH$_2$)$_{u-1}$CO(CH$_2$)$_{v-1}$CH$_3$ with Cl atom (type *d*) in polychloroalkanes mixtures

$u+v$	CHCl$_3$		CH$_3$CCl$_3$		CCl$_4$		Cl$_2$CHCHCl$_2$	
	$C_{kd,1}^{dis}$	$C_{kd,2}^{dis}$	$C_{kd,1}^{dis}$	$C_{kd,2}^{dis}$	$C_{kd,1}^{dis}$	$C_{kd,2}^{dis}$	$C_{kd,1}^{dis}$	$C_{kd,2}^{dis}$
1+1	−1.22	−5.98	2.38	1.91	0.02	−1.00	−1.50	−6.13
1+2	−2.59	−7.86	1.10	0.77	−0.59	−2.80	−2.21	−6.84
2+2	1.07	−5.62	4.77	5.37	7.40	7.36	1.21	−1.65

COMPARISON WITH EXPERIMENT AND DISCUSSION

The comparison between the experimental data and those calculated using the DISQUAC model for the systems of the series cycloalkane + n-alkylbenzene are presented in Tables 5-7 and shown graphically, for selected mixtures in Figs. 3-5.

The model yields fairly well the dependence on concentration and temperature of VLE data (Fig. 3). The equimolar excess properties (G^{E} and H^{E}) are well described by DISQUAC (Table 5, Figs. 4, 5). The model also reproduces the change of G^{E} with temperature (G^{E} decreases with increasing temperature for the same system). The symmetry of the excess functions is also well described.

Table 5

Excess Gibbs energies, G^E, and excess enthalpies, H^E, for cycloalkane + n-alkylbenzene and n-heptane mixtures at equimolar composition and various temperatures. Comparison of experimental values with those calculated using DISQUAC coefficients given in Table 1

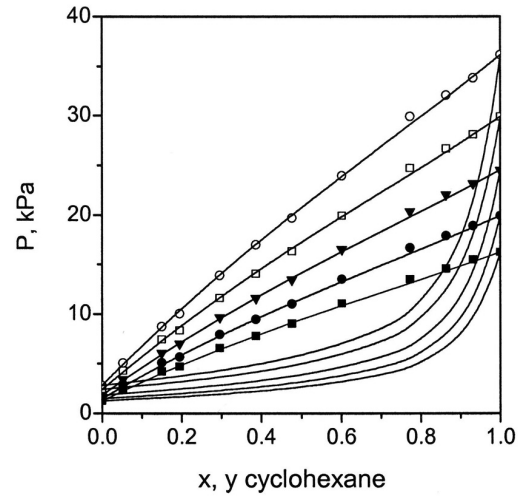| Mixture		T(K)	G^E(x = 0.5)/Jmol^{-1}		H^E(x = 0.5)/Jmol^{-1}	
			calc.	exp.[ref.]	calc.	exp.[ref.]
c-C$_6$H$_{12}$	+ C$_6$H$_6$	303.15	334	314[13]	776	776[17]
		313.15	320	296[13]		
	+ C$_7$H$_8$	303.15	283	284[14]	611	611[17]
		308.15	278	275[14]		
		313.15	272	271[14]		
	+ C$_8$H$_{10}$	298.15			550	550[18]
		303.15	219	231[15]		
		313.15	208	201[15]		
		323.15	197	191[15]		
	+ C$_9$H$_{12}$	298.15			480	
		303.15	183	196[21]		
		308.15	178	188[21]		
		313.15	173	180[21]		
		318.15	168	153[21]		
		323.15	163	148[21]		
c-C$_7$H$_{14}$	+ C$_6$H$_6$	298.15			807	821[19]
	+ C$_7$H$_8$	298.15			598	623[19]
	+ C$_8$H$_{10}$	298.15			525	548[19]
c-C$_8$H$_{16}$	+ C$_6$H$_6$	298.15	278	279[16]	817	817[19]
		313.15	250	251[16]		
		328.15	223	221[16]		
	+ C$_7$H$_8$	298.15	293	296[16]	602	602[19]
		313.15	278	278[16]		
		328.15	262	259[16]		
	+ C$_8$H$_{10}$	298.15			533	532[19]
		343.15	183	189[22]		
		353.15	173	169[22]		
		373.15	152	149[22]		
	+ C$_9$H$_{12}$	298.15			465	
		363.15	170	170[23]		
		373.15	162	152[23]		
		383.15	154	139[23]		
		393.15	146	128[23]		
	+ C$_{10}$H$_{14}$	298.15			419	
		373.15	144	164[24]		
		383.15	136	143[24]		
		393.15	129	125[24]		
c-C$_8$H$_{16}$	+ n-C$_7$H$_{16}$	298.15			228	227[20]
		343.15	144	140[24]		
		353.15	139	145[24]		

Fig. 3 – Comparison of theory with experiment for VLE of the cyclohexane + n-propylbenzene mixture at the temperatures: 303.15 (■), 308.15 (●), 313.15 (▼), 318.15 (□) and 323.15 (O) K. Lines, DISQUAC values; points, experimental results[21].
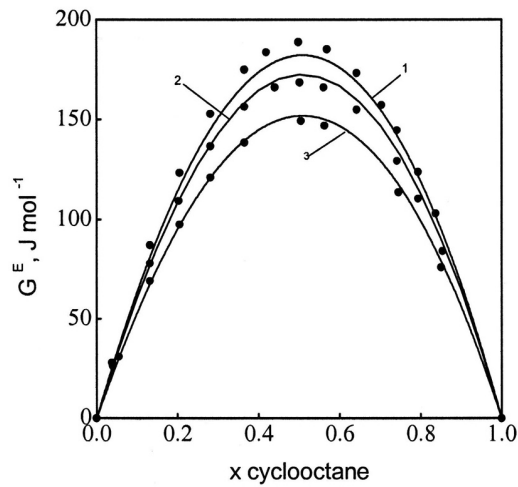

Fig. 4 – Comparison of theory with experiment for the molar excess Gibbs energy, G^E, of cyclooctane + ethylbenzene mixture at the temperatures: 343.15 (1), 353.15 (2) and 373.15 (3) K. Lines, DISQUAC values; points, experimental results[22].
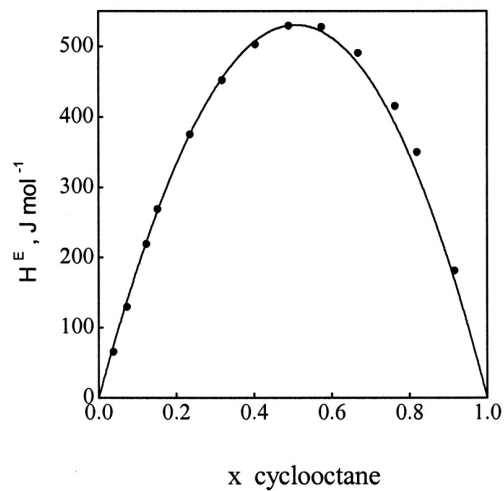

Fig. 5 – Comparison of theory with experiment for the molar excess enthalpy, H^E, of cyclooctane + ethylbenzene mixture at 298.15 K. Lines, DISQUAC values; points, experimental results[19].

The natural logarithms of activity coefficients at infinite dilution, $\ln\gamma_i^\infty$ (Table 6) are reasonably well reproduced. The existing discrepancies between the calculated and experimental values of $\ln\gamma_i^\infty$ could be due to the inaccuracy of the VLE data.

Table 6

Natural logarithms of the activity coefficients at infinite dilution, $\ln\gamma_i^\infty$, in cycloalkane + n-alkylbenzene and n-heptane mixtures at various temperatures. Comparison of experimental values[a] with those calculated using DISQUAC coefficients given in Table 1

Mixture	T(K)	$\ln\gamma_1^\infty$ exp.[ref.]	calc.	$\ln\gamma_2^\infty$ exp.[ref.]	calc.
c-C_6H_{12} + C_6H_6	303.15	0.499[13]	0.612	0.499[13]	0.384
	313.15	0.455[13]	0.592	0.455[13]	0.433
c-C_6H_{12} + C_7H_8	293.15	0.478[14]	0.477	0.497[14]	0.467
	298.15	0.466[14]	0.469	0.480[14]	0.459
	303.15	0.441[14]	0.461	0.466[14]	0.452
	308.15	0.417[14]	0.454	0.451[14]	0.444
	313.15	0.677[14]	0.447	0.519[14]	0.437
c-C_6H_{12} + C_8H_{10}	303.15	0.389[15]	0.334	0.570[15]	0.459
	313.15	0.315[15]	0.322	0.465[15]	0.443
	323.15	0.307[15]	0.312	0.446[15]	0.433
c-C_6H_{12} + C_9H_{12}	303.15	0.326[21]	0.260	0.326[21]	0.492
	308.15	0.312[21]	0.254	0.312[21]	0.484
	313.15	0.289[21]	0.250	0.289[21]	0.476
	318.15	0.242[21]	0.246	0.242[21]	0.468
	323.15	0.231[21]	0.240	0.231[21]	0.460
c-C_8H_{16} + C_6H_6	298.15	0.620[16]	0.529	0.291[16]	0.295
	313.15	0.581[16]	0.497	0.254[16]	0.235
	328.15	0.566[16]	0.467	0.211[16]	0.220
c- C_8H_{16} + C_7H_8	298.15	0.446[16]	0.498	0.514[16]	0.406
	313.15	0.401[16]	0.472	0.457[16]	0.384
	328.15	0.361[16]	0.448	0.403[16]	0.365
c- C_8H_{16} + C_8H_{10}	343.15	0.265[22]	0.304	0.265[22]	0.347
	353.15	0.230[22]	0.296	0.230[22]	0.337
	373.15	0.192[22]	0.278	0.192[22]	0.319
c- C_8H_{16} + C_9H_{12}	363.15	0.209[23]	0.256	0.209[23]	0.386
	373.15	0.195[23]	0.248	0.195[23]	0.376
	383.15	0.175[23]	0.242	0.175[23]	0.366
	393.15	0.156[23]	0.236	0.156[23]	0.356
c- C_8H_{16} + $C_{10}H_{14}$	373.15	0.234[24]	0.220	0.234[24]	0.431
	383.15	0.203[24]	0.214	0.203[24]	0.419
	393.15	0.178[24]	0.198	0.178[24]	0.409
c- C_8H_{16} + n-C_7H_{16}	343.15	0.196[24]	0.188	0.196[24]	0.334
	353.15	0.197[24]	0.182	0.197[24]	0.324

[a] From P-x or P-x-y data extrapolated at $x_i = 0$

The results for the partial molar enthalpies, $H_i^{E,\infty}$, are shown in Table 7. We note a good agreement between the calculated and experimental values of these properties. For the mixtures where experimental values of $H_i^{E,\infty}$ are missing we present the predicted values, which are in a correct sequence with the experimental ones.

Table 7

Partial molar excess enthalpies at infinite dilution, $H_i^{E,\infty}$, of cycloalkane + n-alkylbenzene and n-heptane mixtures at various temperatures. Comparison of experimental values with those calculated using DISQUAC coefficients given in Table 1

Mixture	T(K)	$H_1^{E,\infty}$ (Jmol^{-1}) exp.[ref.]	calc.	$H_2^{E,\infty}$ (Jmol^{-1}) exp.[ref.]	calc.
c-C_6H_{12} + C_6H_6	303.15	3395[17]	3499	3670[17]	2792
c-C_6H_{12} + C_7H_8	303.15	2693[17]	2459	2336[17]	2433
c-C_6H_{12} + C_8H_{10}	298.15	2600[18]	2043	—	2387
c-C_6H_{12} + C_9H_{12}	303.15	—	1673	—	2256

(continues)

c-C_7H_{14} + C_6H_6	298.15	3705[19]	3834	3530[19]	2879
c-C_7H_{14} + C_7H_8	298.15	2169[19]	2603	3232[19]	2423
c-C_7H_{14} + C_8H_{10}	298.15	1858[19]	2118	3088[19]	2329
c-C_8H_{16} + C_6H_6	298.15	3927[19]	3881	3446[19]	2826
c-C_8H_{16} + C_7H_8	298.15	2407[19]	2541	2590[19]	2293
c-C_8H_{16} + C_8H_{10}	298.15	2035[19]	2064	2491[19]	2200
c-C_8H_{16} + C_9H_{12}	298.15	—	1687	—	2074
c-C_8H_{16} + $C_{10}H_{14}$	298.15	—	1440	—	2006
c-C_8H_{16} + C_7H_{16}	298.15	651[20]	798	1557[20]	1062

The comparison of the predicted data using the estimated DISQUAC interchange parameters with the experimental data for VLE and the equimolar G^E and H^E for the chloroalkane + propan-2-one, + butan-2-one and + pentan-3-one mixtures are presented in Tables 8-10; the agreement is quite good. The VLE data are represented very well for most of ketone + chloroalkane systems with both positive and large negative deviations from ideality. As examples, the *P-x* diagram for the propan-2-one + 1,1,1-trichloroethane is shown in Fig. 6.

The temperature dependence of G^E is also well described by the DISQUAC model as can be seen from Tables 8-10. The dependence of G^E on composition is shown in Figs. 7 and 8 for butan-2-one + chloroalkane and pentan-3-one + chloroalkane, respectively mixtures.

Table 8

Excess Gibbs energy and excess enthalpy for the propan-2-one + chloroalkane mixtures at equimolar composition

Chloroalkane	*T*, K	$G^E(x = 0.5)$, J mol^{-1}		$H^E(x = 0.5)$, J mol^{-1}	
		calc.	exp.[ref]	calc.	exp.[ref]
1-Chlorobutane	298.15	333	333[31]	455	455[31]
1-Chloropentane	298.15	419	405[25]		
	303.15	417	392[25]		
	308.15	414	386[25]		
	313.15	412	376[25]		
Dichloromethane	303.15	−537	−406[32]	−873	−896[32]
1,2-Dichloroethane	273.15	−145	−226[33]		
	298.15			−321	−405[35]
1,3-Dichloropropane	298.15	−25	−9[25]	−113	−50[36]
	303.15	−24	−16[25]		
	308.15	−22	−16[25]		
	313.15	−21	−28[25]		
1,4-Dichlorobutane	298.15	25	36[26]	7	−7[36]
	303.15	25	26[26]		
	308.15	26	24[26]		
	313.15	26	25[26]		
Trichloromethane	298.15			−1921	−1925[32]
	323.15	−510	−510[32]		
1,1,1-Trichloroethane	298.15	271	265[25]		
	303.15	272	269[25]		
	308.15	272	275[25]		
	313.15	273	280[25]		
	363.15			227	228[37]
1,1,2,2-Tetrachloroethane	298.15	−792	−779[26]	−2183	−2146[39]
	303.15	−769	−798[26]		
	308.15	−746	−754[26]		
	313.15	−724	−699[26]		
Tetrachloromethane	318.15	131	131[34]	264	264[52]

Table 9

Excess Gibbs energy and excess enthalpy for the butan-2-one + chloroalkane mixtures at equimolar composition

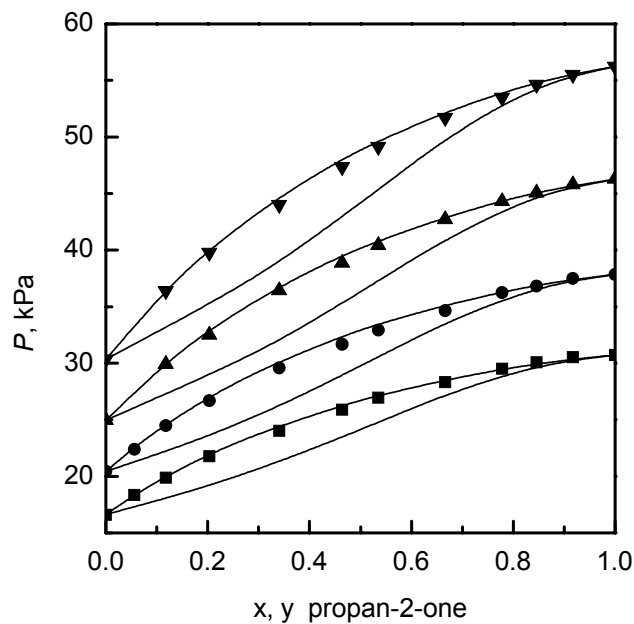| Chloroalkane	T, K	$G^E(x = 0.5)$, J mol^{-1}		$H^E(x = 0.5)$, J mol^{-1}	
		calc.	exp.[ref]	calc.	exp.[ref]
1-Chlorobutane	298.15			233	197[39]
	350.30	220	177[53]		
1-Chloropentane	298.15	267	391[54]	311	289[39]
	303.15	267	412[54]		
	308.15	266	408[54]		
	313.15	265	398[54]		
	318.15	264	396[54]		
Dichloromethane	288.15	−558	−640[40]		
1,2-Dichloroethane	333.15	−132	−208[41]		
1,3-Dichloropropane	298.15	−82	75[54]	−295	−216[42]
	303.15	−78	76[54]		
	308.15	−74	82[54]		
	313.15	−71	83[54]		
	318.15	−67	66[54]		
1,4-Dichlorobutane	298.15	−44	44[54]	−200	−181[42]
	303.15	−42	50[54]		
	308.15	−39	20[54]		
	313.15	−36	46[54]		
	318.15	−34	71[54]		
Trichloromethane	303.15	−702	−603[32]		
	318.15	−632	−735[32]		
	308.15			−2118	−2106[32]
1,1,1-Trichloroethane	298.15	84	60[54]		
	303.15	86	82[54]		
	313.15	90	101[54]		
	318.15	91	110[54]		
	363.15			−36	−27[37]
1,1,2,2–Tetrachloroethane 298.15	−632	−615[54]	−2023	−2965	
	303.15	−609	−649[54]		
	313.15	−563	−562[54]		
	318.15	−540	−456[54]		
Tetrachloromethane	298.15			−73	−80[43]

Fig. 6 – VLE diagram for the propan-2-one + 1,1,1-trichloroethane mixture at 298.15 K (■), 303.15 K (●), 308.15 K (▲), 313.15 K (▼). Lines, DISQUAC values; points, experimental results[25].

Table 10

Excess Gibbs energy and excess enthalpy for the pentan-3-one + chloroalkane mixtures at equimolar composition

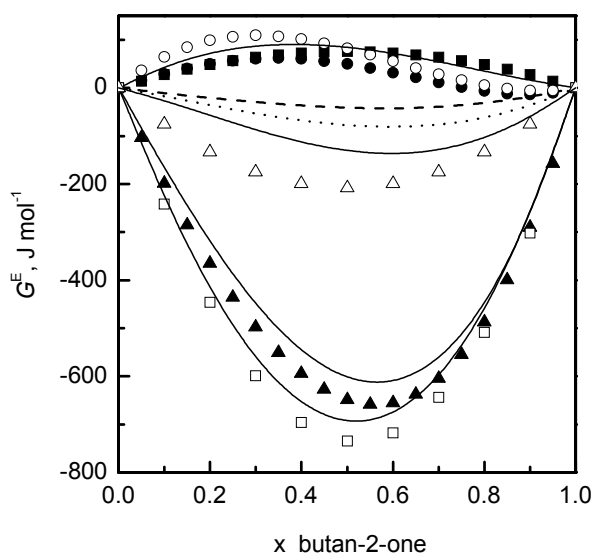| Chloroalkane	T, K	$G^E(x = 0.5)$, J mol^{-1}		$H^E(x = 0.5)$, J mol^{-1}	
		calc.	exp.[ref]	calc.	exp.[ref]
1-Chlorobutane	298.15			36	36[39]
1,2-Dichloroethane	298.15			−434	−433[43]
	323.15	−341	−213[29]		
	333.15	−339	−214[29]		
	343.15	−337	−194[29]		
	353.15	−336	−204[29]		
1,3-Dichloropropane	343.15	−144	−147[29]		
	353.15	−140	−138[29]		
	363.15	−137	−131[29]		
	373.15	−133	−133[29]		
	358			−285	−318[55]
1,4-Dichlorobutane	343.15	−83	−89[30]		
	353.15	−78	−86[30]		
	363.15	−74	−82[30]		
	373.15	−70	−78[30]		
	358			−226	−216[55]
Trichloromethane	313.15	−848	−800[30]		
	323.15	−784	−736[30]		
	333.15	−720	−698[30]		
	343.15	−656	−658[30]		
	358			−2881	−2848[55]
1,1,1-Trichloroethane	323.15	−18	−20[30]		
	333.15	−13	−11[30]		
	343.15	−7	−8[30]		
	353.15	−2	−3[30]		
	338			−200	−200[55]
Tetrachloromethane	298.15			−160	−160[55]
	353.15	604	604[35]		
1,1,2,2–Tetrachloroethane	343.15	−713	−712[30]		
	353.15	−678	−672[30]		
	363.15	−644	−644[30]		
	373.15	−610	−608[30]		
	358			−1893	−1892[55]

Fig. 7 – Molar excess Gibbs energy G^E at 303.15 K for the systems: butan-2-one + 1,3-dichloropropane[54] (■, …..), + 1,4-dichlorobutane[54] (•, – – –), + trichloromethane[32] (□, ——), + 1,1,1-trichloroethane[54] (O, ——), + 1,1,2,2-tetrachloroethane[54] (▲, ——) and + 1,2-dichloroethane[41] (at 333.15 K) (∆, ——). Lines, DISQUAC values; points, experimental results.
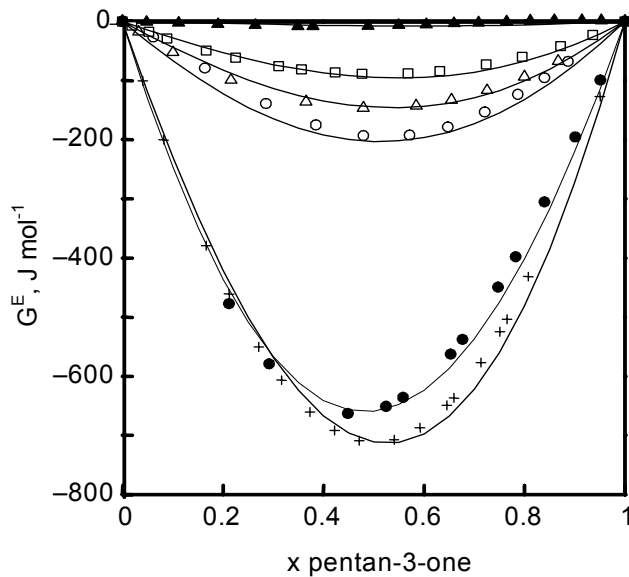
Fig. 8 – Molar excess Gibbs energy G^E at 343.15 K for the systems pentan-3-one + 1,2-dichloroethane (O), + 1,3-dichloropropane (Δ), + 1,4-dichlorobutane (□), + trichloromethane (●), + 1,1,1-trichloroethane (·), and + 1,1,2,2-tetrachloroethane (+). Lines, DISQUAC values; points, experimental results[29, 30].

The larger differences between calculated and experimental G^E values for the propan-2-one + 1,2-dichloroethane (Table 8) and butan-2-one + 1,2-dichloroethane, + 1,3-dichloropropane, + 1,4-dichlorobutane (Table 9) may be due to the inaccuracy of the experimental data and/or to the inadequacy of the Flory-Huggins equation to represent the combinatorial entropy.

The experimental H^E is in a good agreement with predicted values and the dependence of H^E on the composition is shown in Fig. 9.
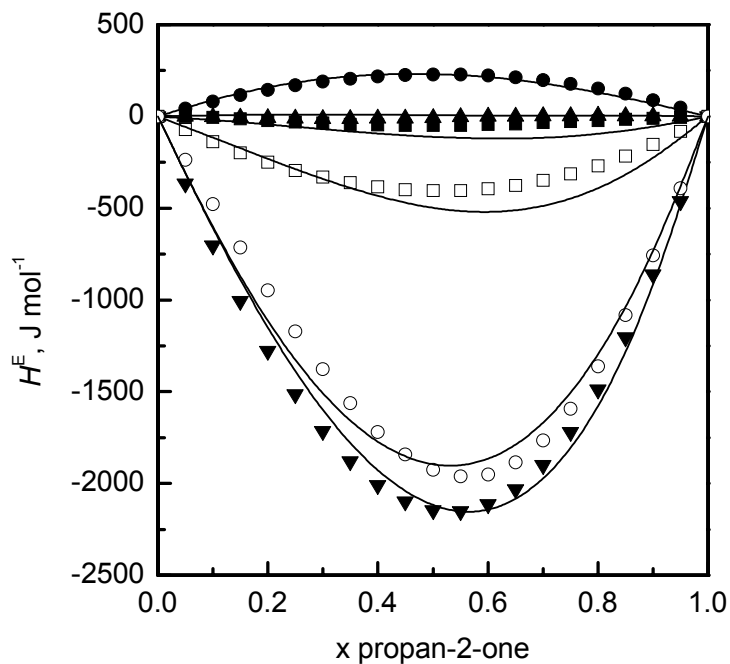

Fig. 9 – Molar excess enthalpy H^E at 298.15 K for the systems propan-2-one + 1,2-dichloroethane[35] (□), + 1,3-dichloropropane[36] (■), + 1,4-dichlorobutane[36] (▲), + trichloromethane[32] (O), + 1,1,1-trichloroethane[37] (●) (at 363.15 K), and + 1,1,2,2-tetrachloretane[39] (▼). Lines, DISQUAC values; points, experimental results.

Example of the comparison of predicted data for the natural logarithms of activity coefficients at infinite dilution, $\ln\gamma_i^\infty$ and the partial molar enthalpies, $H_i^{E,\infty}$ in the case of propane-2-one + chloroalkane mixtures are shown in Tables 11 and 12. The calculated $\ln\gamma_i^\infty$ and $H_i^{E,\infty}$ are in agreement with the experimental values.

Table 11

Natural logarithms of the activity coefficients at infinite dilution, $\ln\gamma_i^\infty$, in 2-propanone + chloroalkanes mixtures at various temperatures

Mixture	T(K)	$\ln\gamma_1^\infty$		$\ln\gamma_2^\infty$	
		exp.[ref.]	calc.	exp.[ref.]	calc.
$C_3H_6O + CH_3\text{-}(CH_2)_2\text{-}CH_2Cl$	298.15	0.518[31]	0.495	0.614[31]	0.629
$C_3H_6O + CH_3(CH_2)_3\text{-}CH_2Cl$	298.15	0.594[25]	0.548	0.792[25]	0.784
	303.15	0.612[25]	0.535	0.745[25]	0.766
	308.15	0.563[25]	0.522	0.699[25]	0.748
	313.15	0.543[25]	0.510	0.634[25]	0.731
$C_3H_6O + ClCH_2Cl$	303.15	-0.608[32]	-0.377	-0.774[32]	-0.792
$C_3H_6O + ClCH_2\text{-}CH_2Cl$	273.15	-0.717[33]	-0.242	-0.791[33]	-0.506
$C_3H_6O + ClCH_2\text{-}CH_2\text{-}CH_2Cl$	298.15	0.066[25]	-0.0097	0.025[25]	-0.0377
	303.15	0.049[25]	-0.0096	0.005[25]	-0.0355
	308.15	0.033[25]	-0.0095	0.000[25]	-0.0332
	313.15	-0.013[25]	-0.0094	0.074[25]	-0.0312
$C_3H_6O + ClCH_2\text{-}(CH_2)_2\text{-}CH_2Cl$	298.15	0.054[26]	0.0295	0.063[26]	0.0787
	303.15	0.037[26]	0.0294	0.045[26]	0.0787
	308.15	0.030[26]	0.0294	0.045[26]	0.0786
	313.15	0.026[26]	0.0293	0.050[26]	0.0783
$C_3H_6O + CHCl_3$	323.15	-0.549[32]	-0.254	-0.835[32]	-1.354
$C_3H_6O + CH_3\text{-}CCl_3$	298.15	0.410[25]	0.455	0.473[25]	0.496
	303.15	0.416[25]	0.446	0.436[25]	0.394
	308.15	0.409[25]	0.438	0.464[25]	0.392
	313.15	0.439[25]	0.430	0.429[25]	0.390
$C_3H_6O + Cl_2CH\text{-}CHCl_2$	298.15	-1.055[26]	-0.435	-1.185[26]	-2.919
	308.15	-1.011[26]	-0.401	-1.141[26]	-2.640
	313.15	-0.817[26]	-0.385	-1.048[26]	-2.511
$C_3H_6O + CCl_4$	318.15	1.054[34]	0.913	0.725[34]	-0.805

[a] From P-x or P-x-y data extrapolated at $x_i = 0$

Table 12

Partial molar excess enthalpies at infinite dilution, $H_i^{E,\infty}$, of 2-propanone (1) + chloroalkanes (2) mixtures at various temperatures

Mixture	T(K)	$H_1^{E,\infty}$ (Jmol^{-1})		$H_2^{E,\infty}$ (Jmol^{-1})	
		exp.[ref.]	calc.	exp.[ref.]	calc.
$C_3H_6O + CH_3(CH_2)_2\text{-}CH_2Cl$	298,15	1970[32]	1648	2086[32]	3320
$C_3H_6O + CH_3(CH_2)_3\text{-}CH_2Cl$	298,15		1929		2701
	303,15		1955		2727
	308,15		1980		2753
	313,15		2004		2778
$C_3H_6O + ClCH_2Cl$	303,15	-3117[32]	-1600	-3530[32]	-4717
$C_3H_6O + ClCH_2\text{-}CH_2Cl$	273,15		-684		-2299
	298,15	-1560[35]		-1507[35]	
$C_3H_6O + ClCH_2\text{-}CH_2\text{-}CH_2Cl$	298,15	19[36]	-5	-85[36]	-248
	303,15		-12		-344
	308,15		-19		-341
	313,15		-27		-338
$C_3H_6O + ClCH_2\text{-}(CH_2)_2\text{-}CH_2Cl$	298,15	11[36]	3	8[36]	6
	303,15		4		11
	308,15		5		21
	313,15		7		31
$C_3H_6O + CHCl_3$	298,15	-4280[32]		-7588[32]	
	323,15		2061		-2867
$C_3H_6O + CH_3\text{-}CCl_3$	298,15		1274		256
	303,15		1271		274
	308,15		1267		290

(continues)

Table 12 (continued)

	313,15		1263		306
	363,15	915[37]		1006[37]	
C_3H_6O + $Cl_2CH-CHCl_2$	298,15	-7780[39]	-2623	-9339[39]	-21682
	303,15		-2614		-21300
	308,15		-2606		-20921
	313,15		-2599		-20548
C_3H_6O + CCl_4	318,15	5330[52]	6513	3650[52]	-6117

Analogously to the COO/Cl contact in the 1-chloroalkane + n-alkyl alkanoate systems,[8] the C=O/Cl contact in ketone + 1-chloroalkane mixtures is best described by an entirely dispersive parameter. For the mixtures with α,ω-dichloroalkanes, the interaction energy of C=O/Cl or COO/Cl contact is much stronger than the average energies of Cl/Cl, C=O/C=O or COO/COO contacts. The H atoms in the −CH₂Cl groups interact specifically with the C=O (or COO) group (weak H-bond) due to the inductive effects of two Cl atoms. This may explain both the negative quasichemical interchange coefficients for short chain α,ω-dichloroalkanes (Table 3) and the observed proximity effect. The inductive effect of Cl atoms is more evident in ketone (or n-alkyl alkanoate[9]) + trichloromethane or + 1,1,2,2-tetrachloroethane systems where the specific interactions between unlike molecules are stronger.

The negative or largely negative values of G^E and H^E and a well-defined minimum of their dependence on composition (around equimolar) indicate that there are specific interactions in these mixtures with formation of complexes between the two components due to H-bonds.

CONCLUSIONS

The DISQUAC model applied to the selected mixtures of the cycloalkane + n-alkylbenzene evidenced the constancy of $C_{bc,1}^{dis}$ and $C_{bc,2}^{dis}$ values starting with toluene as the first member of n-alkylbenzene series. The slight increase of $C_{bc,2}^{dis}$ values with the size of n-alkylbenzene may be attributed to the inductive effect of the n-alkyl group in series of n-alkylbenzene.

The DISQUAC interchange parameters for the C=O/Cl contact extended to the whole class of linear ketones with 1-chloroalkanes, α,ω-dichloroalkanes and some polychloroalkanes binary mixtures evidenced some regularities. The $C_{kd,n}^{dis}$ and $C_{kd,n}^{quac}$ coefficients obey rather simple rules: (a) $C_{kd,1}^{dis}$ and $C_{kd,2}^{dis}$ coefficients for the 1-chloroalkane + ketone [CH₃(CH₂)$_{u-1}$CO(CH₂)$_{v-1}$CH₃] mixtures vary regularly with the $u+v$ length of hydrocarbon chain of ketone; (b) for small molecules of α,ω-dichloroalkanes, where the proximity effects are high, the $C_{kd,n}^{quac}$ coefficients vary with the aliphatic chain length m between the chlorine groups (for $m \leq 10$ the $C_{kd,n}^{quac}$ coefficients are independent of the nature of ketone, too).

Estimation of the predictive parameters for the series of polychloroalkanes would require much more experimental data; the polychloroalkanes under study being only the first members of different series. Nevertheless, the results are in agreement with those reported for the contact COO/Cl in mixtures of 1,1,2,2-tetrachloroethane with n-alkyl alkanoates.[51]

For mixtures of linear ketones with chloroalkanes possessing longer molecules where proximity effects disappear, the DISQUAC group contribution model can be successfully used for predictions of thermodynamic properties using a unique set of parameters.

Until more accurate experimental data are available in the literature, we believe the parameters collected in the present work could be with success used in the prediction of VLE, G^E, H^E, $\ln\gamma_i^\infty$ and $H_i^{E,\infty}$ for the mixture containing the same type of interactions and for which no experimental data are available.

REFERENCES

1.   Aa. Fredenslund, J. Gmehling and P. Rasmunsen, "Vapor-Liquid Equilibria Using UNIFAC", Elsevier, Amsterdam, 1977.
2.   K. Kojima and K. Tochigi, "Prediction of vapor-liquid equilibria by the ASOG method", Kodansha Ltd., Tokyo, 1979.
3.   H. V. Kehiaian, *Fluid Phase Equilib.,* **1983,** *13,* 243-252.
4.   J. Gmehling, *Fluid Phase Equilib.,* **1986,** *30,* 119 -134.
5.   Aa. Fredenslund and J.M. Sorensen, "Group-Contribution Estimation Methods". in (Sandler, S. I. Ed.) "*Models for Thermodynamic and Phase-equilibria calculations*", Ch. 4, Marcel Dekker, New York, 1994, p. 287-361.
6.   H. V. Kehiaian, J. P. E. Grolier and G. C. Benson, *J. Chim. Phys.-Chim. Biol*., **1978,** *75,* 1031-1048.
7.   H. V. Kehiaian, *Pure Appl. Chem.,* **1985,** 5*7*, 15-30.
8.   H. V. Kehiaian and B. Marongiu, *Fluid Phase Equilib.* **1988,** *40*, 23-78.
9.   G. Avedis, J. P. E. Grolier, J. Fernandez and H. V. Kehiaian, *J. Sol Chem*., **1994,** *23*, 135-152.
10. M. Teodorescu and I. Wichterle, *Collect. Czech. Chem. Commun.,* **2000,** *65*, 1559-1572.
11. M. Teodorescu, D. Drăgoescu and A. Bârhală, *Rev. Roum. Chim*., **2001,** *46*, 487-495.
12. I. Bâtiu, *Fluid Phase Equilib.*, **2005**, *227*, 113 -124.
13. J. Zielkiewicz, P. Oracz and S. Warycha, *Fluid Phase Equilib.*, **1990**, 58, 191-209.
14. E. G. Konakbaeva, E. Kh. Anisimova and M. I. Shakhparonov, *Vestn. Mosk. Univ., Ser. Khim.,* **1974***, 15*, 30-36.
15. D. V. S. Jain and O. P. Yadav, *Indian J. Chem.,* **1974***, 12*, 718-720.
16. R. C. Mitra, S. C. Guhaniyogi and S. N. Bhattacharyya, *J. Chem. Eng. Data,* **1973***, 18*, 147-151.
17. M. Karvo, *J. Chem. Thermodyn.,* **1980***, 12,* 635-639.
18. S. Murakami and R. Fujishiro, *Bull. Chem. Soc. Japan,* **1967***, 40*, 1784-1789.
19. E. Wilhelm, A. Inglese and J. P. E. Grolier, *Thermochim. Acta,* **1993***, 229*, 271-280.
20. E. Wilhelm, A. Inglese and J. P. E. Grolier, *J. Chem. Eng. Data,* **1983***, 28*, 202-204.
21. D. Drăgoescu, A. Bârhală and R. Vîlcu, *ELDATA: The Int. Electron. J. of Phys.- Chem. Data,* **1997***, 3,* 85-90.
22. M. Teodorescu, A. Bârhală, D. I. Marchidan and O. Landauer, *Fluid Phase Equilib.,* **1996***, 126,* 127-134.
23. M. Teodorescu, A. Bârhală, D. I. Marchidan and O. Landauer, *ELDATA: The Int. Electron. J. of Phys.- Chem. Data,* **1996***, 2,* 97-102.
24. M. Teodorescu, A. Bârhală and O. Landauer, *ELDATA: The Int. Electron. J. of Phys.- Chem. Data,* **1996***, 2,* 169-174.
25. D. Drăgoescu, A. Bârhală and R Vîlcu, *Fluid Phase Equilib.,* **1998,** *146*, 247-259.
26. D. Drăgoescu, A. Bârhală and R Vîlcu, *Fluid Phase Equilib.,* **1999**, *157*, 41-51.
27. A. Bârhală, D. Drăgoescu and R. Vîlcu, Proc. 11th Int. Conf. Chem. and Chem. Eng., Bucharest, Roumania, 30 September – 2 October*,* 1999, 68-73.
28. A. Bârhală, D. Drăgoescu and R. Vîlcu, Proc. 12th Roumanian Int. Conf. Chem. and Chem. Eng., RICCCE 12, Vol. Phys. Chem. Biochem. Chem. Eng., Bucharest, Roumania, 13-15 September*,* 2001*,* 7-12.
29. M. Teodorescu, A. Bârhală and O. Landauer, *ELDATA: Int. Electron. J. Phys.-Chem. Data,* **1997**, *3*, 101-108.
30. M. Teodorescu, K. Aim and I. Wichterle, *Fluid Phase Equilib.*, **1998**, *147*, 215-228.
31. J. Fernandez, J. L. Legido, J. Vijiande, J. Garcia and M. I. Paz Andrade, Proc. 6. Med. CAT. 95 Giornate Mediteranee di Calorimetria ed Analisi Termica, Cagliari, Italy, September 12-16*,* 1995**,** Ediservice STEF, Cagliari, 1995, 117-120.
32.   D. R. Lide and H. V. Kehiaian, "CRC Handbook of Thermophysical and Thermochemical Data", CRC Press, Boca Raton, FL, USA, 1994.
33. J. Nath and A. P. Dixit, *Fluid Phase Equilib.*, **1990**, *60*, 205-212.
34. I. Brown and F. Smith, *Austral. J. Chem*., **1957**, *10*, 423-428.
35. R. Kechawarz, J. Dubes and F. Tachoire, *Int. DATA Ser. Sci., Sel. Data Mixtures*, *Ser. A* **1994**, 24.
36. E. R. Lopez, J. Garcia, J. Fernandez and M. I. Paz Andrade, *J. Chem. Thermodyn.*, **1993**, *25*, 1127-1132.
37. J. Gmehling, *J. Chem. Eng. Data,* **1993**, *38*, 143-146.
38. A. D. Tripathi, *J. Chem. Eng. Data*, **1995**, *40*, 1262-1263.
39. M. J. Pico, P. C. Menaut, J. Fernandez, L. J. Legido and I. M. Paz Andrade, *J. Solution Chem.,* **1991**, *20*, 115-124.
40. J. R. Nath and R. Saini, *Fluid Phase Equilib.*, **1991**, *68*, 281-290.
41. V. Dohnal, D. Bláhová and R. Holub, *Fluid Phase Equilib.*, **1982**, *9*, 9-22.
42. C. P. Menaut, J. M. Pico, J. Fernandez, J. L. Legido and M. I. Paz Andrade, *Can. J. Chem*., **1994**, *72*, 304-307.
43. O. Kiohara, G. C. Benson and J.-P. E. Grolier, *Int. DATA Ser. Sci., Sel. Data Mixtures*, *Ser. A,* **1991**, 64.
44. R. Kechavarz, *PhD. Thesis*, University of Provence, Aix-Marsille I 1985.
45. A. Bondi, "Physical Properties of Molecular Crystals, Liquids and Glasses", Wiley-Interscience, New York, 1968.
46. M. R. Tine and H. V. Kehiaian, *Fluid Phase Equilib.,* **1987***, 32*, 211-248.
47. D. Drăgoescu and A. Bârhală, *Rev. Roum. Chim.*, **2001**, *46*, 847-855.
48. H. V. Kehiaian, S. Porcedda, B. Marongiu, L. Lepori and E. Matteoli, *Fluid Phase Equilib.,* **1991***, 63,* 231-257.
49. D. Drăgoescu, M. Teodorescu, A. Bârhală and I. Wichterle, *Collect. Czech. Chem. Commun*., **2003**, *68,* 1175–1192.
50. J. Ortega and J. Placido, *ELDATA Int. Electron. J. Phys. Chem. Data*, **1996**, *2*, 85-96.
51. J. Fárková, I. Wichterle and H. V. Kehiaian, *Fluid Phase Equilib.,* **1995**, *112*, 23-32.
52. V. Belousov and A. G. Morachevskii, Teploty smeshcheniya zhidkostei, Izd. "Khimia"*,* 1970, Leningrad.
53. J. Wisniak, *Thermochim. Acta,* **1995**, *257*, 51-58.
54. D. Drăgoescu, *PhD. Thesis*, University of Bucharest, 2003 (in Roumanian).
55. M. Teodorescu, *PhD. Thesis*, "Politehnica" University of Bucharest, 1998 (in Roumanian).