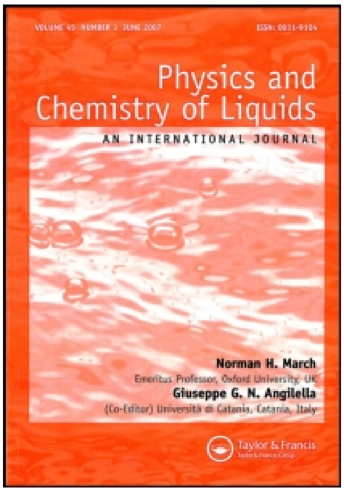

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Thermodynamics of binary mixtures with strongly negative deviations from Raoult's Law. X. linear alkanoate + $CHCl_3$ or + 1,1,2,2-tetrachloroethane

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Thermodynamics of binary mixtures with strongly negative deviations from Raoult's Law. X. linear alkanoate + $CHCl_3$ or + 1,1,2,2-tetrachloroethane

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Mixtures formed by linear alkanoates and $CHCl_3$ or 1,1,2,2-tetrachloroethane, which show strongly negative deviations from the Raoult's law, have been studied in the framework of the *dis*persive–*qua*si*c*hemical (DISQUAC) model. Systems involving CH_2Cl_2; CCl_4, Cl_3C–CH_3 or $ClCH_2$–CH_2Cl have also been briefly considered in order to carry out a more complete study. The corresponding interaction parameters are reported. As in other previous applications, the first (Gibbs energy) and third (heat capacity) quasichemical interaction parameters do not depend on the mixture components. DISQUAC represents fairly well vapor–liquid equilibria, VLE, and molar excess enthalpies, H^E, of the systems considered. VLE of the methyl ethanoate + $CHCl_3$ + benzene mixture is also well described by the model neglecting ternary interactions. UNIFAC (*uni*versal *f*unctional *a*ctivity *c*oefficient) fails when representing H^E of systems containing very long alkanoates. The mixture structure is investigated using the concentration–concentration structure factor, $S_{CC}(0)$. Heterocoordination is prevalent even at very high temperatures.

Keywords: Mixtures; Alkanoates; Chloroalkanes; Molecular interactions

1. Introduction

In this series of articles [1–9], our general aim is the characterization, using different models, of interactions between unlike molecules in systems which exhibit very strong negative deviations from the Raoult's law. We have shown that DISQUAC (*dis*persive–*qua*si*c*hemical) [10,11], a purely physical model based on the rigid lattice theory developed by Guggenheim [12], is a powerful tool to describe thermodynamic properties of the mentioned solutions assuming structure-dependent interaction parameters. It is remarkable that DISQUAC provides similar results as when association models are used. This is shown when DISQUAC results are compared with those

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obtained from the UNIQUAC (*uni*versal *qua*sichemical) association solution model for 1-alkanol + propanal systems [1], from the ideal association solution theory for linear ketone [1], or oxaalkane [2] + $CHCl_3$ mixtures, or from the ERAS (*e*xtended *r*eal *a*ssociated *s*olutions) model [13] for 1-alkanol + propanal [1], or + primary, secondary or tertiary amines [3,4].

Chloroalkane + alkane mixtures are very interesting from a theoretical point of view as they allow us to study many different effects. So, it is possible to investigate the change of the thermodynamic properties of such systems when, in a given chloroalkane, H atoms are replaced by Cl atoms (e.g, in the series CH_2Cl_2; $CHCl_3$; CCl_4). Proximity effects can also be analysed from the properties of α, ϖ-dichloroalkane + alkane mixtures. Similar effects are also present in linear alkanoate + chloroalkane systems, which exhibit an even more complex behavior. For example, the methyl ethanoate + 1-chlorobutane mixture shows positive deviation from the Raoult's law with, $H^E(x_1 = 0.5;\ T = 298.15\,K) = 527\,J\,mol^{-1}$ [14]. In contrast, linear alkanoate + $CHCl_3$ or + 1,1,2,2-tetrachloroethane mixtures present strong negative deviations from the Raoult's law, as their large and negative H^E values reveal [15–19]. So, at 298.15 K and equimolar composition, H^E (methyl ethanoate + chloroform) = $-1854\,J\,mol^{-1}$ [18]. Solid–liquid equilibria measurements show the existence of solid-compound formation in the 4-butyrolactone + $CHCl_3$ system [20]. In the framework of the UNIFAC model (Dortmund version), interaction parameters for the carboxylate (COO)/chlorine (Cl) contacts are available [21]. Linear ethyl ester (from formate to butanoate) + 1-chloroalkane systems have been treated [22] using the Nitta–Chao model [23]. The purpose of this work is to study linear alkanoate + $CHCl_3$ or 1,1,2,2-tetrachloroethane mixtures in terms of DISQUAC. At this end, the needed interaction parameters are reported. For a more complete study, systems containing CH_2Cl_2; CCl_4; $Cl_3C–CH_3$ and $ClH_2C–CH_2Cl$ are also briefly considered. In addition, we analyse the mixture structure in terms of the so-called concentration–concentration structure factor [24]. Previously, some systems including linear alkanoate and 1,1,2,2-tetrachloroethane have been investigated using DISQUAC under the assumption that the COO/Cl contacts are represented by dispersive interaction parameters only [25].

2. Models

2.1. *DISQUAC*

In the framework of DISQUAC, linear alkanoate + chloroalkane mixtures are regarded as possessing three types of surfaces: (i) type a, aliphatic, CH_3, CH_2, CH or C in alkanoates or chloroalkanes; (ii) type d, Cl in chloroalkanes; (iii) type k, COO in alkanoates.

When DISQUAC is applied, the total molecular volumes, r_i, surfaces, q_i, and the molecular surface fractions, α_i, of the mixture components are calculated additively on the basis of the group volumes R_G and surfaces Q_G recommended by Bondi [26], taking arbitrarily, as volume and surface units, the volume R_{CH_4} and surface Q_{CH_4} of methane [27]. The geometrical parameters for the groups referred to in this work are given elsewhere [28,29].

The main features of DISQUAC are: (i) The interactional partition function is factorized into two terms, in such a way that the excess functions are calculated as the sum of two contributions: A dispersive (DIS) term which represents the contribution from the intermolecular dispersive forces and a quasichemical (QUAC) term which arises from the anisotropy of the field forces created by the solution molecules. Thus:

$$G^{\mathrm{E}} = G^{\mathrm{E,\,COMB}} + G^{\mathrm{E,\,DIS}} + G^{\mathrm{E,\,QUAC}} \tag{1}$$

$$H^{\mathrm{E}} = H^{\mathrm{E,\,DIS}} + H^{\mathrm{E,\,QUAC}} \tag{2}$$

where in equation (1), G^{E} is the molar excess Gibbs energy and $G^{\mathrm{E,COMB}}$, the combinatorial term, represented by the Flory–Huggins equation [27,30]; (ii) The interaction parameters are assumed to be dependent on the molecular structure; (iii) The value $z = 4$ for the coordination number is used for all the polar contacts. This represents one of the most important shortcomings of the model, and is partially removed via the hypothesis of considering structure-dependent interaction parameters; (iv) The temperature dependence of the interaction parameters is expressed in terms of the DIS and QUAC interchange coefficients [29], $C_{st,l}^{\mathrm{DIS}}$; $C_{st,l}^{\mathrm{QUAC}}$ where $\mathrm{s} \neq \mathrm{t} = \mathrm{a, d, k}$, and $l = 1$ (Gibbs energy); $l = 2$ (enthalpy); $l = 3$ (heat capacity).

2.2. *UNIFAC*

Modified UNIFAC [21] differs from the original UNIFAC [31] by the combinatorial term and the temperature dependence of the group interaction parameters. The equations used to calculate G^{E} and H^{E} are obtained from the fundamental equation for the activity coefficient γ_i of component i:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{COMB}} + \ln \gamma_i^{\mathrm{RES}} \tag{3}$$

where $\ln \gamma_i^{\mathrm{COMB}}$ is the combinatorial term and $\ln \gamma_i^{\mathrm{RES}}$ is the residual term. Equations are given elsewhere [4].

2.2.1. Assessment of geometrical and interaction parameters. In modified UNIFAC, linear alkanoates are characterized by two main groups CCOO and HCOO. The former is subdivided into two subgroups: CH_3COO and CH_2COO. The latter is introduced to represent alkyl formates. Chloroalkanes are characterized by several main groups: CCl; CCl_2; CCl_3; CCl_4 and $CHCl_3$. The groups CCl_4 and $CHCl_3$ are main groups by themselves. The other two groups are subdivided into different groups: CCl contains the subgroups CH_2Cl; CHCl; CCl and CCl_2 is divided into CH_2Cl_2; $CHCl_2$ and CCl_2.

The subgroups have different geometrical parameters, but the subgroups within the main group are assumed to have identical group energy-interaction parameters.

The geometrical parameters, the relative van der Waals volumes and the relative van der Waals surfaces of the different subgroups are not calculated from molecular parameters like in the original UNIFAC, but fit together with the interaction parameters to the experimental values of the thermodynamic properties considered. The geometrical and interaction parameters were taken from the literature and used without modification [21].

3. Estimation of the DISQUAC interaction parameters

The three surfaces, a, d, k, generate three types of contacts: (a, d); (a, k) and (d, k). The DIS and QUAC interchange coefficients for the (a, d) and (a, k) contacts have been previously determined on the basis of thermodynamic properties of linear ester [28] or chloroalkane [29] + *n*-alkane mixtures, respectively. So, only the interaction parameters for the (d, k) contacts must be fitted. The general procedure for estimating the model parameters has been explained in detail elsewhere [32] and will not be repeated. Final parameters are given in tables 1–3.

Table 1. Dispersive and quasichemical interchange coefficients, $C^{\mathrm{DIS}}_{dk,l}$ and $C^{\mathrm{QUAC}}_{dk,l}$ ($l=1$, Gibbs energy; $l=2$, enthalpy; $l=3$, heat capacity) for (d,k) contacts[a] in linear alkanoate + trichloromethane mixtures.

Alkanoate *u*COO*v*[b]	$C^{\mathrm{DIS}}_{dk,1}$	$C^{\mathrm{DIS}}_{dk,2}$	$C^{\mathrm{DIS}}_{dk,3}$	$C^{\mathrm{QUAC}}_{dk,1}$	$C^{\mathrm{QUAC}}_{dk,2}$	$C^{\mathrm{QUAC}}_{dk,3}$
1COO1	1.25	−11	−7	−0.4	7.85	4
1COO2	0.64	−11	−7	−0.4	6.9	4
2COO1	0.4[c]	−11	−7	−0.4	7.05	4
1COO3	0.2[c]	−11	−7	−0.4	6	4
$u+v=4$	0.2[c]	−11	−7	−0.4	6.2	4
1COO4	0.2[c]	−6.35	−7	−0.4	1.6	4
2COO3	−0.1[c]	−6.35	−7	−0.4	1.85	4
$u+v=5$	−0.1[c]	−6.35	−7	−0.4	2	4
1COO5	−0.1[c]	−3	−7	−0.4	−0.75	4
$u+v=6$	−0.1[c]	−3	−7	−0.4	−0.95	4
$u+v=7$	−0.1[c]	−1	−7	−0.4	−2.5	4
$u+v=8$	−0.1[c]	2.05	−7	−0.4	−4.95	4
$u+v=9,10$	−0.1[c]	2.05	−7	−0.4	−5.15	4
$u+v\geq 11$	−0.1[c]	2.05	−7	−0.4	−5.5	4

[a] Type d, Cl in trichloromethane; type k, COO in linear alkanoates.
[b] *u* and *v* are the number of alkyl groups attached to the COO group (e.g., 1COO1 is methyl ethanoate).
[c] Estimated value.

Table 2. Dispersive and quasichemical interchange coefficients, $C^{\mathrm{DIS}}_{dk,l}$ and $C^{\mathrm{QUAC}}_{dk,l}$ ($l=1$, Gibbs energy; $l=2$, enthalpy; $l=3$, heat capacity) for (d,k) contacts[a] in linear alkanoate + 1,1,2,2-tetrachlorethane mixtures.

Alkanoate *u*COO*v*[b]	$C^{\mathrm{DIS}}_{dk,1}$	$C^{\mathrm{DIS}}_{dk,2}$	$C^{\mathrm{DIS}}_{dk,3}$	$C^{\mathrm{QUAC}}_{dk,1}$	$C^{\mathrm{QUAC}}_{dk,2}$	$C^{\mathrm{QUAC}}_{dk,3}$
1COO1	1[c]	−9	−2	−0.4	5.85	4
1COO2	0.4	−9	−2	−0.4	4.75	4
2COO1	0.2[c]	−9	−2	−0.4	5	4
1COO3	−0.1	−3	−2	−0.4	−0.9	4
$u+v=4$	−0.1	−3	−2	−0.4	−0.25	4
1COO4	−0.1	−0.8	−2	−0.4	−3	4
2COO3	−0.3	−0.8	−2	−0.4	−2.75	4
$u+v=5$	−0.3	−0.8	−2	−0.4	−2.5	4
1COO5	−0.3	0.75	−2	−0.4	−4.5	4
$u+v=6$	−0.3	0.75	−2	−0.4	−4.25	4
$u+v=7,8$	−0.3	4	−2	−0.4	−6.85	4
$u+v=9,10$	−0.3	6.25	−2	−0.4	−9.05	4
$u+v=11,12$	−0.3	6.25	−2	−0.4	−9.35	4
$u+v\geq 13$	−0.3	6.25	−2	−0.4	−9.5	4

[a] Type d, Cl in 1,1,2,2-tetrachloroethane; type k, COO in linear alkanoates.
[b] *u* and *v* are the number of alkyl groups attached to the COO group (see table 1).
[c] Estimated value.

Table 3. Dispersive and quasichemical interchange coefficients, $C_{dk,l}^{\mathrm{DIS}}$ and $C_{dk,l}^{\mathrm{QUAC}}$($l = 1$, Gibbs energy; $l = 2$, enthalpy; $l = 3$, heat capacity) for (d,k) contacts[a] in linear alkanoate + chloroalkane mixtures.

Alkanoate uCOOv[b]	$C_{dk,1}^{\mathrm{DIS}}$	$C_{dk,2}^{\mathrm{DIS}}$	$C_{dk,3}^{\mathrm{DIS}}$	$C_{dk,1}^{\mathrm{QUAC}}$	$C_{dk,2}^{\mathrm{QUAC}}$	$C_{dk,3}^{\mathrm{QUAC}}$
linear alkanoate + dichloromethane						
1COO1	0.4[c]	3.6	−7	−0.4	−3.25	4
$u + v = 3$	0.02	2.8	−7	−0.4	−3.25	4
linear alkanoate + 1,2-dichloroethane						
1COO1	0.8[c]	4.75	−7	−0.4	−3.25	4
1COO2	0.8[c]	4.05	−7	−0.4	−3.25	4
2COO1	0.8[c]	4.3	−7	−0.4	−3.25	4
linear alkanoate + 1,1,1-trichloroethane						
1COO1	2.5[c]	2.52	−3.75	−0.4	0.82	4
1COO2	2.5[c]	2.1	−3.75	−0.4	0.82	4
2COO1	2.5[c]	2.1	−3.75	−0.4	0.9	4
linear alkanoate + CCl_4						
1COO1	3.2[c]	4.9		0	0	0
1COO2	3.2[c]	4.6		0	0	0
2COO1	3.2[c]	4.73		0	0	0

[a] Type d, Cl in CH_2Cl_2; $ClCH_2$-CH_2Cl, Cl_3C-CH, CCl_4; type k, COO in linear alkanoates.
[b] u and v are the number of alkyl groups attached to the COO group (see table 1).
[c] Estimated value.

4. Results

Results from the DISQUAC model compared with experimental data for G^{E}, VLE and H^{E} are presented in tables 4–5. For the sake of clarity, these tables list deviations for the pressure, P, and for the H^{E} defined, respectively, as:

$$\sigma_r(P) = \left\{ 1/N \sum \left[(P_{\mathrm{exp}} - P_{\mathrm{calc}})/P_{\mathrm{exp}} \right]^2 \right\}^{1/2} \tag{4}$$

$$\mathrm{dev}(H^{\mathrm{E}}) = \left\{ 1/N \sum \left[(H^{\mathrm{E}}_{\mathrm{exp}} - H^{\mathrm{E}}_{\mathrm{calc}})/H^{\mathrm{E}}_{\mathrm{exp}}(x_1 = 0.5) \right]^2 \right\}^{1/2} \tag{5}$$

where N is the number of experimental measurements for each system. Figures 1–7 show graphically DISQUAC calculations for some selected mixtures. DISQUAC describes fairly well the thermodynamic properties examined. Table 6 lists DISQUAC results on VLE for the methyl ethanoate + $CHCl_3$ + C_6H_6 mixture and for the constituent binaries. This system is characterized by the contacts: (a,b), (a,d), (a,k), (b,d), (b,k) and (d,k), where the surface type b = C_6H_6. Except for the (b,d) contacts, the interaction parameters for the remainder contacts are known (see above and [33,34]). The $C_{bd,l}^{\mathrm{DIS}}$ and $C_{bd,l}^{\mathrm{QUAC}}$coefficients were determined in this work. The values obtained using experimental data from [35,36] are: $C_{bd,1}^{\mathrm{DIS}} = -0.82$; $C_{bd,2}^{\mathrm{DIS}} = -0.92$; $C_{bd,1}^{\mathrm{QUAC}} = 0.7$ and $C_{bd,2}^{\mathrm{QUAC}} = 0.6$. As usual [37–40], calculations for the ternary system were carried out neglecting ternary interactions, i.e., using binary parameters only. The deviation for the pressure is similar to the mean deviation obtained for the set of 39 mixtures previously studied (≈2.2%) [37].

UNIFAC provides worse results for VLE than DISQUAC (tables 4 and 6). Deviations between experimental and calculated values are very large for H^{E} of

Table 4. Molar excess Gibbs energies, G^E, at equimolar composition and temperature T, for linear alkanoate + chloroalkane mixtures. Comparison of experimental results (exp.) with DISQUAC (DQ.) calculations obtained using the interchange coefficients from tables 1–3 and with UNIFAC (UNIF.) results with parameters taken from the literature [21].

Alkanoate			G^E/J mol^{-1}			σ_r (P)[c]			
uCOOv[a]	T/K	N[b]	Exp.	DQ.	UNIF.	Exp.	DQ.	UNIF.	Ref.
linear alkanoate + dichloromethane									
1COO2	298.21	15	−495	−495	−442	0.0001	0.007	0.017	[60]
	398.17	15	−367	−376	−447	0.001	0.009	0.010	[60]
linear alkanoate + $CHCl_3$									
1COO1	313.15	16	−526	−523	−571	0.002	0.021	0.014	[15]
	323.15	16	−516	−485	−544	0.002	0.024	0.026	[35]
1COO2	313.15	12	−738	−733	−626	0.004	0.030	0.039	[15]
	323.15	9	−680	−692	−601	0.003	0.025	0.026	[15]
linear alkanoate + 1,1,2,2-tetrachloroethane									
1COO2	330	15	−735	−728	−459	0.008	0.022	0.097	[61]
	350	21	−677	−631	−449	0.010	0.033	0.089	[61]
1COO3	340	10	−690	−731	−445	0.006	0.014	0.066	[61]
	370	14	−621	−629	−457	0.003	0.007	0.046	[61]
2COO2	340	13	−819	−810	−314	0.002	0.007	0.130	[61]
	370	18	−668	−680	−329	0.006	0.008	0.110	[61]
2COO3	360	14	−686	−690	−312	0.002	0.005	0.100	[61]
	380	13	−613	−604	−341	0.003	0.005	0.066	[61]
3COO2	360	16	−581	−713	−312	0.003	0.031	0.076	[61]
	380	14	−521	−633	−341	0.004	0.026	0.046	[61]
3COO3	380	12	−596	−546	−331	0.001	0.011	0.059	[61]
	400	12	−528	−474	−385	0.001	0.011	0.030	[61]

[a] For symbols, see table 1.
[b] Number of experimental data.
[c] Equation (4).

Table 5. Molar excess enthalpies, H^E, at equimolar composition and temperature T, for linear alkanoate + chloroalkane mixtures. Comparison of experimental results (exp.) with DISQUAC (DQ.) calculations obtained using the interchange coefficients from tables 1–3 and with UNIFAC (UNIF.) results with parameters taken from the literature [21].

Alkanoate			H^E/J mol^{-1}			dev(H^E)[c]			
uCOOv[a]	T/K	N[b]	Exp.	DQ.	UNIF.	Exp.	DQ.	UNIF.	Ref.
linear alkanoate + CH_2Cl_2									
1COO1	298.15	15	−793	−776	−897	0.002	0.019	0.102	[14]
	298.15		−798						[62]
	318.15		−777	−731					[62]
1COO2	298.15	18	−955	−931	−855	0.004	0.015	0.054	[14]
2COO1	298.15	18	−945	−951	−727	0.001	0.022	0.126	[14]
linear alkanoate + $CHCl_3$									
1COO1	298.15	19	−1829	−1814	−1989	0.007	0.071	0.100	[18]
			−1548						[63]
	308.15	17	−1574	−1770		0.001	0.121	0.077	[15]
1COO2	276.15[d]		−2277	−2121					[64]
	298.15	22	−2088	−2074	−1971	0.003	0.062	0.092	[19]
			−2025						[65]
			−1937						[63]
	308.15	16	−1914	−2053		0.003	0.078	0.073	[15]
1COO3	298.15	21	−2265	−2244	−1898	0.003	0.037	0.107	[19]
	308.15		−1671		−1619				[66]

(*continued*)

Table 5. Continued.

Alkanoate			H^E/J mol^{-1}			dev(H^E)[c]			
*u*COO*v*[a]	*T*/*K*	*N*[b]	Exp.	DQ.	UNIF.	Exp.	DQ.	UNIF.	Ref.
2COO1	298.15	20	−2086 −1820	−2078	−1807	0.004	0.047	0.100	[18] [63]
2COO2	298.15	20	−2289	−2228	−1709	0.003	0.034	0.170	[19]
2COO3	298.15	21	−2420	−2291	−1600	0.003	0.031	0.228	[19]
3COO1	298.15	18	−2169	−2295	−1709	0.005	0.040	0.157	[18]
3COO2	298.15	20	−2373	−2291	−1600	0.003	0.029	0.226	[19]
3COO3	298.15	20	−2439	−2295	−1488	0.002	0.039	0.265	[19]
4COO1	298.15	18	−2207	−2291	−1600	0.005	0.059	0.197	[18]
5COO1	298.15	18	−2199	−2295	−1488	0.006	0.055	0.228	[18]
6COO1	298.15	18	−2170	−2177	−1378	0.006	0.036	0.256	[18]
7COO1	298.15	19	−2123	−2140	−1273	0.004	0.035	0.282	[18]
8COO1	298.15	17	−2034	−2083	−1174	0.005	0.038	0.285	[18]
9COO1	298.15	17	−1984	−1966	−1080	0.003	0.027	0.333	[18]
10COO1	298.15	19	−1922	−1962	−991	0.005	0.033	0.334	[18]
11COO1	298.15	17	−1834	−1854	−908	0.007	0.032	0.357	[18]
12COO1	298.15	17	−1767	−1753	−829	0.005	0.022	0.372	[18]
13COO1	298.15	18	−1705	−1659	−756	0.005	0.026	0.386	[18]
14COO1	298.15	18	−1630	−1569	−686	0.007	0.028	0.412	[18]
Linear alkanoate + CCl_4									
1COO1	298.15	15	258	260		0.004	0.038		[67]
1COO2	298.15	21	−52	−52		0.008	0.096	0.250	[67]
2COO1	298.15	19	−53	−60		0.004	0.157	0.577	[67]
Linear alkanoate + 1,2-dichloroethane									
1COO1	298.15	18	−307	−308		0.001	0.030		[14]
1COO2	298.15	12	−455	−452		0.004	0.021		[14]
2COO1	298.15	14	−407	−404		0.005	0.012		[14]
Linear alkanoate + 1,1,1-trichloroethane									
1COO1	298.15	17	123	122		0.003	0.041	0.360	[67]
1COO2	298.15	16	−146	−147		0.002	0.011	0.406	[67]
	363.15	17	−101	−106		0.003	0.044	0.454	[68]
2COO1	298.15	16	−161	−158		0.001	0.013	0.460	[67]
Linear alkanoate + 1,1,2,2-tetrachloroethane									
1COO1	298.15	21	−2286	−2202	−1120	0.007	0.035	0.360	[16]
1COO2	298.15	19	−2593	−2539	−1079	0.003	0.062	0.406	[17]
1COO3	298.15	17	−2801	−2739	−993	0.002	0.036	0.454	[17]
2COO1	298.15	17	−2467	−2485	−914	0.007	0.045	0.460	[16]
2COO2	298.15	15	−2513	−2470	−807	0.006	0.064	0.493	[17]
2COO3	298.15	17	−2740	−2632	−696	0.006	0.034	0.525	[17]
3COO1	298.15	17	−2485	−2470	−808	0.008	0.040	0.498	[16]
3COO2	298.15	16	−2347	−2514	−696	0.004	0.098	0.529	[17]
3COO3	298.15	16	−2701	−2574	−587	0.002	0.034	0.573	[17]
4COO1	298.15	16	−2531	−2514	−696	0.006	0.047	0.542	[16]
5COO1	298.15	18	−2515	−2574	−587	0.007	0.052	0.581	[16]
6COO1	298.15	17	−2469	−2470	−483	0.009	0.032	0.603	[16]
7COO1	298.15	20	−2387	−2302	−384	0.007	0.026	0.624	[16]
8COO1	298.15	16	−2346	−2382	−292	0.010	0.043	0.703	[16]
9COO1	298.15	19	−2249	−2232	−206	0.011	0.028	0.689	[16]
10COO1	298.15	18	−2179	−2199	−126	0.009	0.035	0.722	[16]
11COO1	298.15	19	−2072	−2060	−51	0.009	0.028	0.739	[16]
12COO1	298.15	17	−1952	−1930	20	0.013	0.036	0.804	[16]
13COO1	298.15	19	−1884	−1853	86	0.011	0.034	0.796	[16]
14COO1	298.15	17	−1822	−1731	148	0.017	0.032	0.828	[16]

[a] For symbols, see table 1.
[b] Number of experimental data.
[c] Equation (5).
[d] $x_1 = 0.487$.

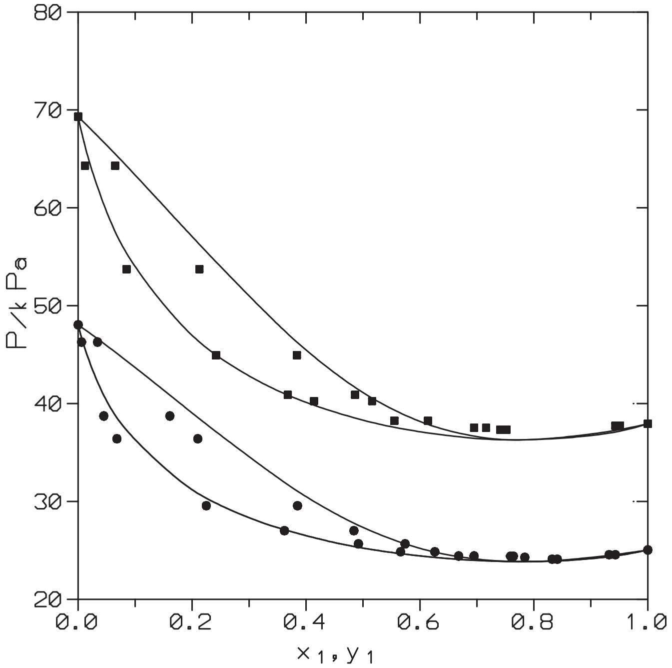

Figure 1. VLE for the ethyl ethanoate(1) + $CHCl_3$(2) system. Points, experimental results [15]: (●), $T = 313.15$ K; (■), $T = 323.15$ K. Solid lines, DISQUAC calculations.

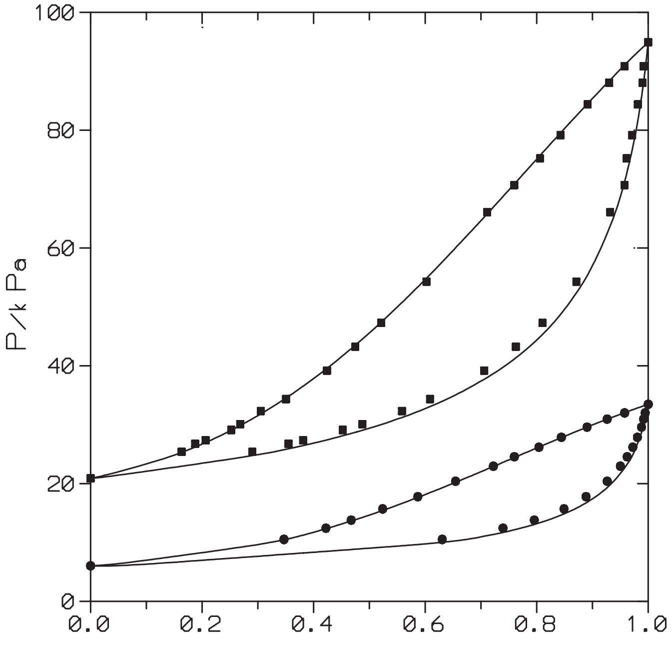

Figure 2. VLE for the ethyl propanoate(1) + $Cl_2CH–CHCl_2$(2) system. Points, experimental results [61]: (●), $T = 340$ K; (■), $T = 370$ K. Solid lines, DISQUAC calculations.

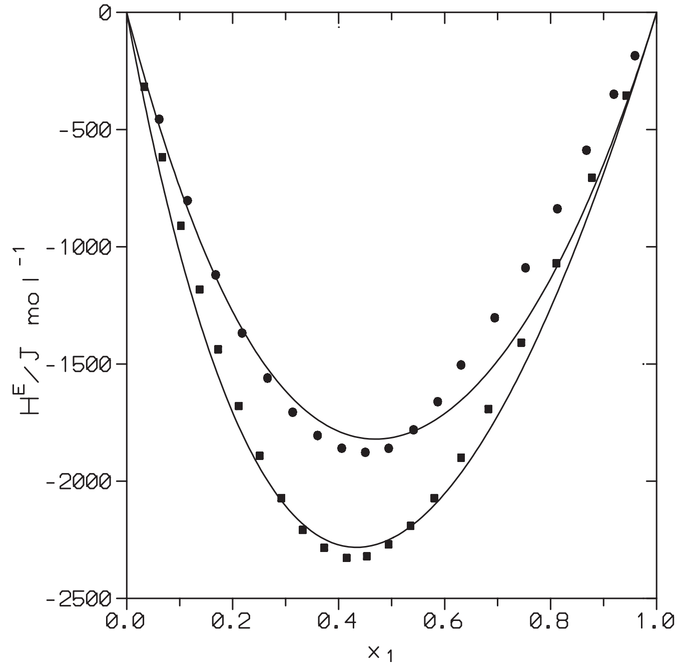

Figure 3. H^E at 298.15 K for alkyl ethanoate(1) + $CHCl_3$(2) systems. Points, experimental results: (●), methyl ethanoate [18]; (■), propyl ethanoate [19]. Solid lines, DISQUAC calculations.

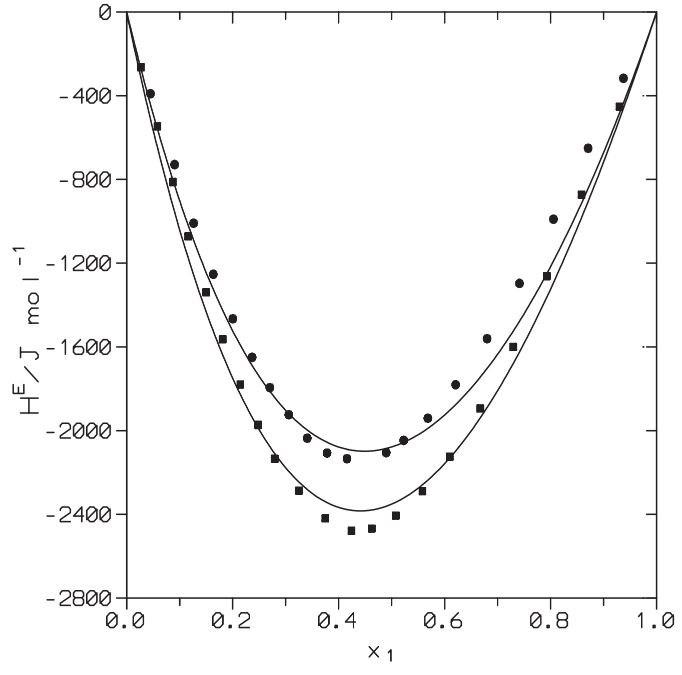

Figure 4. H^E at 298.15 K for alkyl propanoate(1) + $CHCl_3$(2) systems. Points, experimental results: (●), methyl propanoate [18]; (■), propyl propanoate [19]. Solid lines, DISQUAC calculations.

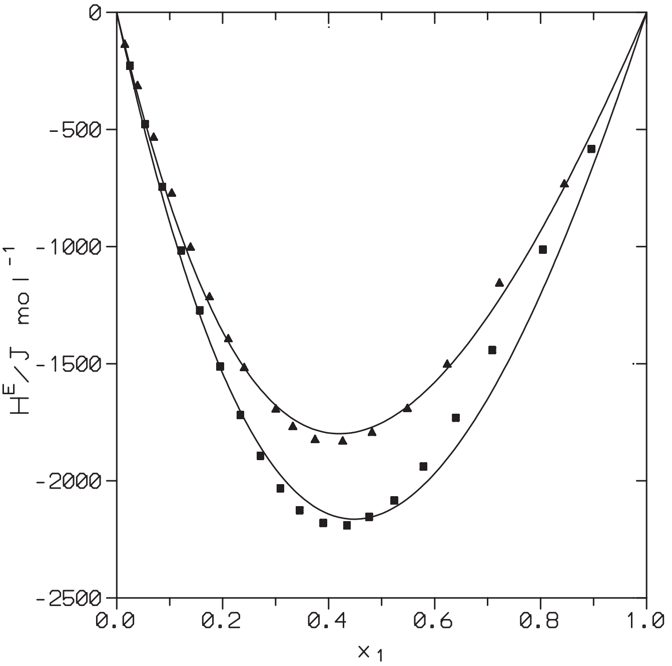

Figure 5. H^E at 298.15 K for methyl alkanoate(1) + $CHCl_3$(2) systems. Points, experimental results [18]: (■), methyl octanoate; (▲), methyl tridecanoate. Solid lines, DISQUAC calculations.

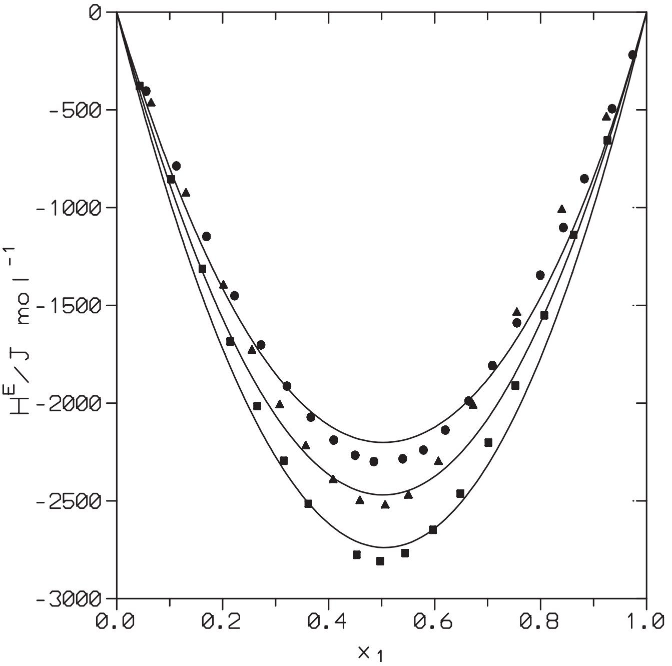

Figure 6. H^E at 298.15 K for linear alkanoate (1) + $Cl_2CH–CHCl_2$(2) systems. Points, experimental results: (●), methyl ethanoate [16]; (■), propyl ethanoate [17]; (▲), ethyl propanoate [17]. Solid lines, DISQUAC calculations.

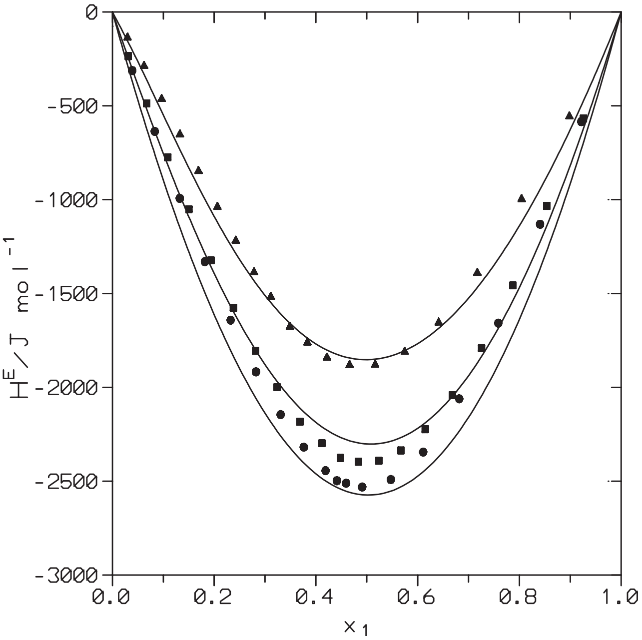

Figure 7. H^E at 298.15 K for methyl alkanoate (1) + $Cl_2CH–CHCl_2$(2) systems. Points, experimental results [16]: (●), methyl hexanoate; (■), methyl octanoate; (▲), methyl tetradecanoate. Solid lines, DISQUAC calculations.

Table 6. Predictions from the DISQUAC and UNIFAC models for VLE of the methyl ethanoate + $CHCl_3$ + C_6H_6 system at 323.15 K and for its constituent binaries.

System	N[a]	σ_r(P)[b] DQ.[c]	σ_r(P)[b] UNIF.[d]	Ref.
Methyl ethanoate + $CHCl_3$ + C_6H_6	64	0.033	0.083	[35]
Methyl ethanoate + $CHCl_3$	16	0.024	0.026	[35]
Methyl ethanoate + C_6H_6	12	0.009	0.010	[69]
$CHCl_3$ + C_6H_6	19	0.003	0.004	[35]

[a] Number of experimental data.
[b] Equation (4).
[c] DISQUAC results using the interaction parameters from tables 1–3.
[d] UNIFAC results using the interaction parameters from the literature [21].

mixtures involving long alkanoates and $CHCl_3$, probably because such systems were not considered when fitting the UNIFAC interaction parameters. On the other hand, systems with CH_2Cl_2 and $Cl_2CH–CHCl_2$ are represented in the framework of UNIFAC by the same interaction parameters. The large deviations obtained for H^E of mixtures with $Cl_2CH–CHCl_2$ (table 5) merely underline that it is very difficult to describe proximity effects in terms of the classical group contribution methods [29].

Finally, it should be mentioned that UNIFAC yields a very high value for the molar excess heat capacity at constant pressure (C_p^E) for the methyl ethanoate + $CHCl_3$ system (29.7 J mol^{-1} K^{-1}, at equimolar composition and 298.15 K). The DISQUAC value is

$4.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$, closer to the experimental result ($3.9\,\mathrm{J\,mol^{-1}\,K^{-1}}$ [41]). However, DISQUAC does not represent the very unsymmetrical C_p^{E} curve.

Mixture structure can be studied using the so-called concentration–concentration structure factor, $S_{CC}(0)$ [24], defined as [24,42,43]:

$$S_{CC}(0) = \frac{RT}{(\partial^2 G^M/\partial x_1^2)_{P,T}} = \frac{x_1 x_2}{D} \tag{6}$$

with

$$D = \frac{x_1 x_2}{RT}(\partial^2 G^M/\partial x_1^2)_{P,T} = 1 + \frac{x_1 x_2}{RT}\left(\frac{\partial^2 G^{\mathrm{E}}}{\partial x_1^2}\right)_{P,T} \tag{7}$$

D is a function closely related to thermodynamic stability [43,44]. For ideal mixtures, $G^{\mathrm{E,id}} = 0$; $D^{\mathrm{id}} = 1$ and $S_{CC}(0) = x_1x_2$. As stability conditions require, $S_{CC}(0) > 0$, and if the system is close to phase separation, $S_{CC}(0)$ must be large and positive (∞, when the mixture presents a miscibility gap). In contrast, if compound formation between components appears, $S_{CC}(0)$ must be very low (0, in the limit). So, if $S_{CC}(0) > x_1x_2$, i.e., $D < 1$, the dominant trend in the system is the separation of the components (homocoordination), and the mixture is less stable than the ideal. If $0 < S_{CC}(0) < x_1x_2 = S_{CC}(0)^{\mathrm{id}}$, i.e., $D > 1$, the fluctuations in the system have been removed, and the dominant trend in the solution is compound formation (heterocoordination). In this case, the system is more stable than ideal.

DISQUAC results for $S_{CC}(0)$ at equimolar composition are in good agreement with the experimental data (table 7). For methyl or ethyl ethanoate + $CHCl_3$ mixtures, DISQUAC predicts rather symmetrical curves, while the experimental curves are

Table 7. Concentration–concentration structure factor, $S_{CC}(0)$, at temperature T and equimolar composition for linear alkanoate + chloroalkane mixtures. Comparison of experimental (exp.) results with DISQUAC (DQ) calculations using the interchange coefficients from tables 1–3.

		$S_{CC}(0)$		
System	T/K	Exp.	DQ.	Ref.
Ethyl ethanoate + dichloromethane	298.21	0.175	0.179	[60]
	398.17	0.205	0.205	[60]
Methyl ethanoate + chloroform	313.15	0.183	0.175	[15]
	323.15	0.180	0.180	[35]
Ethyl ethanoate + chloroform	313.15	0.173	0.158	[15]
	323.15	0.176	0.162	[15]
Ethyl ethanoate + 1,1,2,2-tetrachloroethane	330	0.154	0.162	[61]
	350	0.161	0.173	[61]
Propyl ethanoate + 1,1,2,2-tetrachloroethane	350	0.171	0.166	[61]
	370	0.177	0.177	[61]
Ethyl propanoate + 1,1,2,2-tetrachloroethane	330	0.160	0.153	[61]
	370	0.174	0.173	[61]
Propyl propanoate + 1,1,2,2-tetrachloroethane	340	0.171	0.171	[61]
	370	0.180	0.181	[61]
Ethyl butanoate + 1,1,2,2-tetrachloroethane	360	0.179	0.169	[61]
	380	0.188	0.179	[61]
Propyl butanoate + 1,1,2,2-tetrachloroethane	380	0.182	0.187	[61]
	400	0.190	0.196	[61]

skewed to low mole fractions of the chloroalkane. This may be interpreted assuming that several alkanoate molecules are associated to one molecule of chloroalkane. The thermodynamic properties of these solutions have been successfully described in terms of the ideal associated solution theory assuming interactions of the 1 : 2 type [15,45]. Similar interactions are also encountered for ethyl ethanoate + Cl_2CH–$CHCl_2$ system. It is interesting to note that $S_{CC}(0) < 0.25$ at very high temperatures. That is, heterocoordination is present even at those conditions. This contrasts with the behavior observed for other mixtures which also present strong negative deviation from the Raoult's law. For example, for 1-propanol + di-*n*-propylamine, at equimolar composition, $S_{CC}(0) = 0.198$ ($T = 298.15$ K) and $S_{CC}(0) = 0.254$ ($T = 373.15$ K) [9].

5. Discussion

5.1. *Excess enthalpies*

H^E of mixtures formed by $CH_3(CH_2)_{u\text{-}1}COOCH_3 + CHCl_3$, Cl_2HC–$CHCl_2$ or + a short chain 1-alkanol [46] varies similarly with u. So, H^E decreases for $1 \le u < 5$, and then increases (table 4; [16,18]). This may be attributed to: (i) interactions between unlike molecules are weakened, as the COO group is more sterically hindered for the longer alkanoates; (ii) Esters with a larger aliphatic surface break more easily interactions between chloroalkanes. Note that H^E of $CHCl_3$ or Cl_2HC–$CHCl_2$ + *n*-alkane mixtures increases with the size of the alkane [47,48]. In contrast, H^E decreases with the chain length of the methyl alkanoate for mixtures with a given alkane [49], as a consequence of the weakening of the dipole–dipole interactions between ester molecules. Similarly, H^E also decreases for systems involving $CH_3(CH_2)_{u-1}COO(CH_2)_{v-1}CH_3$ when v increases for a given u.

The variation of H^E with the chloroalkane, for a given alkanoate, is similar to that encountered in chloroalkane + fixed alkane mixtures. So, in systems with *n*-C_6, at equimolar composition and 298.15 K, H^E (ClH_2C–CH_2Cl) = 1618 J mol^{-1} [50] > H^E (Cl_2HC–$CHCl_2$) = 1200 J mol^{-1} [48] and H^E (Cl_2CH_2) = 1319 J mol^{-1} [51] > H^E ($CHCl_3$) = 756 J mol^{-1} [51]. For mixtures including methyl ethanoate, and the same chloroalkanes, a similar trend is observed (table 5). This behavior may be ascribed to: (i) interactions between chlorinated molecules are more easily broken for those chloroalkanes where there are no acidic H atoms; (ii) a higher ability of certain chloroalkanes to interact with alkanoates via H-bonding. So, the H^E values of CCl_4 + linear alkanoate systems (table 5) indicate that the globular molecule of CCl_4 interacts weakly with alkanoates. These interactions are probably of the dipole-induced dipole type. The large and negative H^E for solutions with $CHCl_3$ or Cl_2HC–$CHCl_2$ reveals that H-bonds between unlike molecules are formed, which may be due to the presence of acidic H atoms in the mentioned chloroalkanes.

5.2. *The interaction parameters*

We note that the $C^{\mathrm{QUAC}}_{dk,l}$ ($l = 1, 3$) coefficients are independent on the mixture components (tables 1–3), except for those systems with CCl_4. This behavior has been found for other mixtures previously investigated in terms of DISQUAC:

1-Alkanol + alkane [52,53], + tertiary alkyl ethers [54], 2-alkoxyethanol + alkane [55] or 1-alkanol + di-*n*-alkylamide [56].

It is remarkable that the COO/CCl_4 contacts are represented by DIS parameters only. The same occurs for contacts such as: Aliphatic/CCl_4 [29]; CCl_4/C_6H_6 [27]; CCl_4/Cl [57], CCl_4/F [58]; CCl_4/OCOO (organic carbonate) [59]. This is a typical behavior for many polar-polarizable group contacts.

On the other hand, the $C_{dk,2}^{\mathrm{DIS/QUAC}}$ coefficients strongly depend on the molecular structure of the mixture components. The variation of the $C_{dk,2}^{\mathrm{DIS}}$ coefficients with the alkanoate for systems including $CHCl_3$ or $Cl_2HC–CHCl_2$ is similar to that encountered for 1-alkanol + linear alkanoate mixtures, which are also characterized by constant QUAC enthalpic parameters [46]. As usual, the $C_{dk,2}^{\mathrm{DIS/QUAC}}$ coefficients are constant for the longer alkanoates.

In chloroalkane + *n*-alkane systems, the increase of Cl atoms in the chloroalkane (e.g., $CH_2Cl–CH_2Cl$; $Cl_2CH–CHCl_2$) leads to a decrease of the QUAC parameters, while the DIS parameters are constant or increase [29]. Proximity effects cause an increase of both DIS and QUAC interaction parameters [29]. In linear alkanoate + chloroalkane mixtures, proximity effects seem to increase the DIS parameters (table 3). The increase of the Cl atoms in the chloroalkane increases the QUAC parameters and decreases the DIS ones (tables 1–3).

6. Conclusions

Linear alkanoate + $CHCl_3$ or + $Cl_2HC–CHCl_2$ mixtures have been studied in the framework of DISQUAC. The interaction parameters are reported. DISQUAC represents the experimental data better than UNIFAC. Heterocoordination is present even at very high temperatures.

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