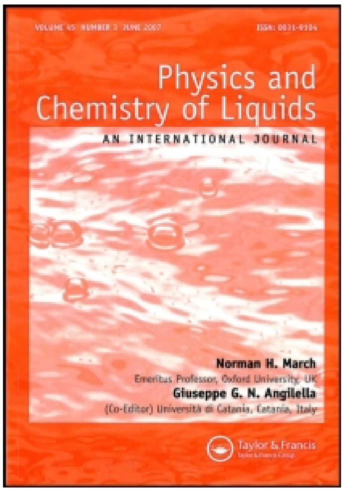

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Thermodynamics of 1-alkanol + linear alkanoate mixtures

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1-Alkanol + linear alkanoate mixtures have been investigated in the framework of the DISQUAC model. The interaction parameters for the OH/COO contacts are reported. The quasichemical parameters are independent of the mixture compounds. The dispersive parameters change with the molecular structure of the components. The same behaviour is observed for the OH/CO (carbonyl) and OH/OCOO (carbonate) contacts. DISQUAC represents well the molar excess Gibbs energies, coordinates of azeotropes and molar excess enthalpies. Using binary parameters only, DISQUAC improves meaningfully predictions on this property from the UNIFAC model for 1-alkanol + linear alkanoate + hydrocarbon systems. In contrast, the Nitta–Chao and the DISQUAC models yield similar results for the thermodynamic properties of the binary and ternary mixtures considered. 1-Alkanol + linear alkanoate mixtures are characterized by strong dipolar interactions between like molecules. In 1-alkanol + $CH_3COO(CH_2)_{u-1}CH_3$ systems, dipole–dipole interactions between ester molecules are more important for $u \leq 7$. For $u \geq 8$, the more important contribution to the excess molar enthalpy comes from the disruption of the alkanol–alkanol interactions. For systems containing a polar compound such as alkanone, alkanoate or linear organic carbonate, dipolar interactions increase in the order: alkanone < alkanoate < carbonate.

Keywords: Thermodynamics; 1-Alkanol; Linear alkanoate; Dipolar interactions

1. Introduction

In the framework of the TOM (Thermodynamics of Organic Mixtures) Project [1,2] the OCO program is developed to get a better understanding of the interactions involving one or both of the groups CO (carbonyl) and O (ether) in the same or in different molecules. So, we have investigated, experimentally and theoretically, the following classes of mixtures: linear organic carbonate (OCOO group) + alkane, + benzene or toluene, + CCl_4 [3–6] or + 1-alkanol [7,8]; organic anhydride (COOCO group) + alkane [9,10], 1-alkanol + linear alkanone (CO group) [11,12] and linear alkanone + linear ether (O group) [13].

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From the theoretical point of view, the interactions present in the mentioned mixtures are characterized in terms of the DISQUAC (*dis*persive-*quasic*hemical) [1,2] and ERAS (*e*xtended *r*eal *a*ssociated *s*olution) [14] models. This article is mainly concerned with the DISQUAC study of systems containing 1-alkanols and linear esters. DISQUAC is a purely physical model based on the rigid lattice theory developed by Guggenheim [15]. We have shown that DISQUAC is a powerful tool to study mixtures, which show strong positive deviations from the Raoul's law (1-alkanol + alkane [16], linear organic carbonate [6] or *N*,*N*-dialkylamide [17,18] + alkane), or those systems which show strong negative deviations from this law (alkanol + amine [19]). Moreover, we have shown that DISQUAC provides accurate predictions on vapor–liquid equilibria (VLE) and molar excess enthalpies (H^E) for ternary mixtures using binary parameters only, that is neglecting ternary interactions [12,20–22].

In a previous work on 1-alkanol + linear organic carbonate systems [7], it was stated that quick reference values of the DISQUAC interaction parameters for the OH/COO contacts could be obtained as mean values of those for the OH/CO and OH/OCOO contacts. Now, we provide more accurate interaction parameters for the OH/COO contacts and we test them studying the ability of DISQUAC to predict H^E of 1-alkanol + linear ester + hydrocarbon mixtures.

2. DISQUAC model

2.1. *Assessment of geometrical parameters*

When DISQUAC is applied, the total relative molecular volumes, r_i, surfaces, q_i, and the molecular surface fractions, α_{si}, of the compounds present in the mixture are usually calculated additively on the basis of the group volumes R_G and surfaces Q_G recommended by Bondi [23]. As volume and surface units, the volume R_{CH_4} and the surface Q_{CH_4} of methane are taken arbitrarily [24]. For the ester group, $r_{COO} = 0.89953$ and $q_{COO} = 0.75862$ [25]. For the hydroxyl group, $r_{OH} = 0.46963$ and $q_{OH} = 0.50345$ [16] The geometrical parameters for other groups referred to in this work are given elsewhere [24].

2.2. *Equations*

The main features of DISQUAC are: (i) the 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 dispersive forces and a quasichemical (QUAC) term which arises from the anisotropy of the field forces created by the solution molecules. Thus

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

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

where, in equation (1), G^E is the molar excess Gibbs energy and $G^{E,\mathrm{COMB}}$, the combinatorial term, represented by the Flory–Huggins equations [24,26].

(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.

The temperature dependence of the interaction parameters g_{st}, h_{st} and c_{pst} (where s, t are two groups present in the solution, $s \neq t$) has been expressed in terms of the DIS and QUAC interchange coefficients $C_{st,l}^{\mathrm{DIS}}$ and $C_{st,l}^{\mathrm{QUAC}}$ ($l = 1$, Gibbs energy, $g_{st}^{\mathrm{DIS/QUAC}}(T_{\mathrm{o}})/RT_{\mathrm{o}} = C_{st,1}^{\mathrm{DIS/QUAC}}$; $l = 2$, enthalpy $h_{st}^{\mathrm{DIS/QUAC}}(T_{\mathrm{o}})/RT_{\mathrm{o}} = C_{st,2}^{\mathrm{DIS/QUAC}}$; $l = 3$, heat capacity, $c_{pst}^{\mathrm{DIS/QUAC}}(T_{\mathrm{o}})/R = C_{st,3}^{\mathrm{DIS/QUAC}}$). The scaling temperature T_{o} is 298.15 K.

3. Estimation of DISQUAC interaction parameters

In terms of DISQUAC, 1-alkanol + linear ester mixtures are regarded as possessing three types of surfaces: (i) type a, aliphatic, CH_3 or CH_2 in 1-alkanols or esters; (ii) type d, COO in esters; and (iii) type h, OH in 1-alkanols. The three surfaces generate three types of contacts: (a,d); (a,h) and (d,h). The interchange coefficients for the (a,d) and (a,h) contacts have been previously determined on the basis of thermodynamic properties of linear ester [25] or 1-alkanol [16,27] + *n*-alkane mixtures, respectively. So, only the interaction parameters for the (d,h) contacts must be fitted. The general procedure applied in the estimation of these parameters is as follows. Firstly, the experimental database for the systems under study is carefully analyzed to select those systems which will be used in the fitting of the parameters. Secondly, the parameters are fitted to reproduce as well as possible the concentration dependence of the experimental G^{E} and H^{E} data of those systems selected for the adjustment. This is made by means of a Marquardt algorithm [28] which minimises the objective function:

$$F\left(C_{st,1}^{\mathrm{DIS/QUAC}}, C_{st,2}^{\mathrm{DIS/QUAC}}, C_{st,3}^{\mathrm{DIS/QUAC}}\right) = \sum \left(G_{\mathrm{calc}}^{\mathrm{E}} - G_{\mathrm{exp}}^{\mathrm{E}}\right)^2 / N_G + \sum \left(H_{\mathrm{calc}}^{\mathrm{E}} - H_{\mathrm{exp}}^{\mathrm{E}}\right)^2 / N_H \tag{3}$$

where the sums are taken over N_G and N_H, the number of experimental data points for G^{E} and H^{E}, respectively. Thirdly, when the required data are not available, or are considered to be unreliable, the corresponding interchange coefficients are estimated by interpolation or extrapolation of the well known parameters, taking into consideration their overall variation with the molecular structure of the mixture compounds. This procedure increases markedly the predictive ability of the model. In our previous studies on 1-alkanol + linear alkanone [11], or +linear organic carbonate [7], we showed that the QUAC parameters for the OH/CO and OH/OCOO contacts are independent of the mixture components. Here, we have kept the same restriction and calculated the $C_{dh,l}^{\mathrm{QUAC}}$(l=1, 2) coefficients (table 1) as the mean values of those for the OH/CO and OH/OCOO contacts. The remainder interaction parameters can then be determined rather directly (tables 2 and 3).

Table 1. Dispersive and quasichemical interchange coefficients, $C_{dh,l}^{\mathrm{DIS/QUAC}}$, for 1-alkanol + linear alkanoate mixtures. The coordination number for the QUAC part is $z = 4$.

$C_{dh,3}^{\mathrm{DIS}}$	$C_{dh,1}^{\mathrm{QUAC}}$	$C_{dh,2}^{\mathrm{QUAC}}$	$C_{dh,3}^{\mathrm{QUAC}}$
4.5	2.6	8.5	–2.5

Table 2. Dispersive Gibbs energy interchange coefficients, $C_{dh,1}^{\mathrm{DIS}}$, for 1-alkanol + linear alkanoate mixtures.

Alkanoate[a]	m[b]					
u-COO-v	1	2	3	4	5	≥6
1COOv	0.85	1.4	1.85	2.45	3	3.5
u-COO-v ($u \geq 2$; $v \geq 1$)	1.25	1.7	1.85	2.45	3	3.5

[a] u and v represent the number of alkyl groups attached to the COO group (e.g., for $CH_3CH_2COOCH_3$ $u = 2$ and $v = 1$).
[b] Number of C atoms in the 1-alkanol.

Table 3. Dispersive enthalpic interchange coefficients, $C_{dh,2}^{\mathrm{DIS}}$, for 1-alkanol + linear alkanoate mixtures.

	m[b]									
$u+v$[a]	1	2	3	4	5	6	7	8	9	10
2	−4.2	−3.8	−2.9	−2.15	−2[c]	−1.8	0.53	1.2	2	3
3	−4.2	−2.9	−2.05	−1.33	−1.2	−0.93	0.53	1.2	2	3
4	−4.2	−2.6	−1.75	−1.25	−0.75	0.27	0.53	1.2	2	3
5	−2.8	−2.0	−0.5	−0.33	0.1[c]	0.5	0.7	1.6	2.8[c]	4.0
6	−2.8	−1.5	−0.9[c]	−0.2	0.5[c]	1.2	1.8[c]	2.5	3.4[c]	4.0
7	−2.8	−0.1	1.5	2.35	2.5	2.75	3.5	4.0	4.0	4.0
8	−2.8	0.7	2.6	3.6	3.7	3.8	4.6	4.6	4.6	4.6
9	−2.8	1.2	3.7	5.0	5.0	5.0	5.0	5.0	5.0	5.0
10	−2.8	2.6	4.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
≥11	−2.8	4	5.8	6.4	6.4	6.4	6.4	6.4	6.4	6.4

[a] u and v represent the number of alkyl groups attached to the COO group (e.g., for $CH_3CH_2COOCH_3$ $u = 2$ and $v = 1$).
[b] Number of C atoms in the 1-alkanol.
[c] Estimated value.

4. Results

For binary mixtures, the DISQUAC results are listed in tables 4–6 for G^{E}, coordinates of azeotropes and H^{E}, respectively. Table 7 shows DISQUAC predictions on H^{E} for 1-alkanol + linear alkanoate + hydrocarbon mixtures. For the sake of clarity, table 7 includes deviations between experimental and calculated H^{E} defined as:

$$\mathrm{dev}\left(H^{\mathrm{E}}\right) = \left\{ \frac{1}{N} \sum \left(\frac{H_{\mathrm{exp}}^{\mathrm{E}} - H_{\mathrm{calc}}^{\mathrm{E}}}{H_{\mathrm{exp,\,max}}^{\mathrm{E}}} \right)^2 \right\}^{1/2} \tag{4}$$

where N is the number of experimental data of the considered system. Figures 1–6 show graphically DISQUAC calculations for some selected mixtures.

Table 4. Molar excess Gibbs energies, G^E, at equimolar composition and temperature T, for 1-alkanol + linear alkanoate mixtures. Comparison of experimental (Exp) results with DISQUAC (DQ.) values calculated using the interaction parameters from tables 1–3.

		G^E (J mol^{-1})		
1-Alkanol	T (K)	Exp.	DQ.	Ref.
1-Alkanol + methyl ethanoate				
Methanol	298.15	712	708	[61]
	318.15	708	679	[61]
Ethanol	318.15	718	680	[62]
	328.15	687	654	[62]
	333.29	635	639	[63]
1-Propanol	318.15	634	646	[64]
	339.56	523	566	[63]
1-Alkanol + ethyl ethanoate				
Methanol	298.15	702	729	[61]
	328.15	711	693	[65]
Ethanol	328.15	676	656	[65]
1-Propanol	328.15	615	608	[65]
	354.79	492	511	[63]
1-Butanol	361.31	437	438	[66]
1-Alkanol + propyl ethanoate				
Ethanol	354.29	570	603	[63]
1-Propanol	367.80	478	487	[63]
1-Butanol	378.85	382	407	[66]
1-Alkanol + butyl ethanoate				
1-Butanol	390.85	307	362	[67]
1-Alkanol + methyl propanoate				
Methanol	298.15	779	774	[68]
Ethanol	298.15	750	756	[68]
	326.3	722	696	[69]
	345.54	630	646	[63]
	346.3	671	643	[69]
1-Propanol	328.15	595	606	[70]
	348.15	527	535	[70]
	355.52	500	508	[63]
1-Butanol	348.15	488	499	[71]
	363.16	400	438	[66]
1-Alkanol + ethyl propanoate				
Ethanol	352.88	640	646	[63]
1-Butanol	376.58	382	417	[66]
1-Alkanol + propyl propanoate				
Ethanol	358.25	683	643	[63]
1-Propanol	374.84	418	465	[63]
1-Butanol	389.63	358	371	[66]
1-Alkanol + butyl propanoate				
1-Butanol	395.56	273	340	[67]
	397.02	276	334	[66]
1-Alkanol + methyl butanoate				
Ethanol	326.3	753	717	[69]
	346.3	719	665	[69]
	353.67	646	643	[63]
1-Propanol	333.15	607	617	[70]
	353.15	537	546	[70]
	366.89	496	493	[63]
1-Butanol	348.15	505	530	[71]
	368.19	438	451	[71]

(*continued*)

Table 4. Continued.

1-Alkanol	T (K)	G^E (J mol^{-1}) Exp.	DQ.	Ref.
1-Alkanol + ethyl butanoate				
Ethanol	357.42	592	646	[63]
1-Propanol	373.69	423	470	[63]
1-Butanol	388.41	372	376	[66]
1-Alkanol + propyl butanoate				
Ethanol	360.74	677	625	[63]
1-Propanol	379.04	389	451	[63]
1-Butanol	397.02	276	334	[66]
1-Alkanol + butyl butanoate				
1-Butanol	402.31	210	281	[67]

Table 5. Coordinates, temperature, T_{az}, composition, x_{1az}, and pressure, P_{az}, of azeotropes for 1-alkanol (1) + linear alkanoate (2) mixtures. Comparison of experimental (Exp.) results with DISQUAC (DQ.) calculations obtained with the interaction parameters from tables 1–3.

System[a]	T_{az} (K)	x_{1az} Exp.	x_{1az} DQ.	P_{az} (kPa) Exp.	P_{az} (kPa) DQ.	Ref.
Methanol + 1COO1	298.15	0.262	0.255	31.47	31.48	[61]
	318.15	0.313	0.301	73.27	72.63	[61]
	326.95	0.670	0.686	101.325	101.8	[72]
		0.672		101.325		[73]
Methanol + 1COO2	298.15	0.641	0.641	19.90	20.08	[61]
	328.15	0.692	0.714	76.26	76.42	[65]
	343.8	0.742	0.756	141.3	138.2	[74]
Ethanol + 1COO1	318.15	0.039	0.027	65.76	65.71	[62]
	329.8	0.042	0.055	101.325	100.8	[75]
	330.05	0.047		101.325		[76]
Ethanol+ 1COO2	328.15	0.393	0.381	53.94	53.62	[65]
Ethanol + 1COO3	351.15	0.920	0.919	101.325	101.4	[77]
Ethanol + 2COO1	326.3	0.457	0.430	47.94	48.16	[69]
	346.3	0.514	0.501	103.91	104.94	[69]
Ethanol + 3COO1	326.3	0.823	0.833	35.77	35.74	[69]
	346.3	0.880	0.884	83.88	83.91	[69]
	350.97	0.909	0.883	101.325	101.68	[78]
1-Propanol + 3COO1	366.77	0.591	0.605	101.325	100.4	[78]
1-Butanol + 2COO3	389.26	0.672	0.638	101.325	105.2	[79]

[a] For symbols, see table 2.

The model represents rather accurately the thermodynamic properties examined. So, the coordinates of azeotropes at high temperatures are well described (table 5). Similarly the temperature dependence of H^E, that is the C_p^E, is well represented (figure 6).

Predictions on H^E for ternary systems were obtained on the basis of binary interactions only. Interaction parameters for OH/benzene and for COO/benzene were taken from the literature [29,30]. The deviations are independent of the mixture compounds or of the number of contacts present. So, at 298.15 K, for 1-hexanol + propyl propanoate + n-C_6 (three contacts), dev(H^E) = 0.040 and for 1-hexanol + propyl

Table 6. Molar excess enthalpies, H^E, at equimolar composition and temperature T, for 1-alkanol + linear ester mixtures. Comparison of experimental (Exp.) results with DISQUAC (DQ.) values calculated using the interaction parameters from tables 1–3.

		H^E (J mol^{-1})		
1-Alkanol	T (K)	Exp.	DQ.	Ref.
1-Alkanol + methyl ethanoate				
Methanol	298.15	1009	1067	[56]
		973		[80]
		1135		[46]
		1019		[81]
	318.15	1105	1206	[62]
Ethanol	298.15	1313	1359	[56]
		1441		[46]
1-Propanol	308.15	1724	1739	[64]
	318.15	1835	1793	[64]
1-Butanol	298.15	1886	1893	[46]
		1846		[81]
	308.15	1876	1946	[83]
		1748		[82]
1-Hexanol	298.15	2136	2113	[46]
		2083		[81]
1-Octanol	298.15	2332	2409	[46]
1-Decanol	298.15	2538	2536	[46]
		2398		[81]
1-Alkanol + ethyl ethanoate				
Methanol	298.15	923	1005	[56]
		1056		[65]
		1063		[84]
		1091		[46]
	308.15	1030	1061	[65]
Ethanol	298.15	1280	1310	[56]
		1300		[50]
		1267		[65]
		1380		[46]
		1465		[84]
	308.15	1331	1381	[65]
1-Propanol	298.15	1510	1550	[56]
		1646		[84]
	308.15	1594	1618	[65]
	318.15	1661	1682	[65]
1-Butanol	298.15	1658	1711	[56]
		1694		[46]
	308.15	1748	1783	[82]
		1695		[47]
1-Pentanol	298.15	1755	1794	[85]
		1801		[86]
1-Hexanol	298.15	1847	1869	[85]
		1865		[46]
1-Heptanol	298.15	2004	1996	[86]
1-Octanol	298.15	2003	2055	[46]
1-Nonanol	298.15	2153	2105	[86]
1-Decanol	298.15	2156	2160	[46]
1-Alkanol + propyl ethanoate				
Methanol	298.15	959	1002	[46]
Ethanol	298.15	1332	1272	[46]
1-Propanol	298.15	1237	1469	[87]
		1470		[88]
1-Butanol	298.15	1316	1581	[87]
		1566		[46]

(*continued*)

Table 6. Continued.

		H^E (J mol^{-1})		
1-Alkanol	T (K)	Exp.	DQ.	Ref.
1-Pentanol	298.15	1413	1672	[87]
1-Hexanol	298.15	1734	1781	[46]
1-Octanol	298.15	1885	1857	[46]
1-Decanol	298.15	2030	2018	[46]
1-Alkanol + butyl ethanoate				
Methanol	293.15	1161	1112	[89]
	298.15	1186	1150	[46]
Ethanol	298.15	1350	1289	[46]
1-Propanol	298.15	1300	1505	[90]
1-Butanol	298.15	1442	1563	[90]
		1506		[46]
		1480		[91]
1-Pentanol	298.15	1500	1613	[90]
1-Hexanol	298.15	1564	1674	[90]
		1701		[46]
1-Heptanol	298.15	1596	1689	[90]
1-Octanol	298.15	1663	1741	[90]
		1802		[46]
1-Nonanol	298.15	1752	1752	[90]
1-Decanol	298.15	1842	1844	[90]
		1890		[46]
1-Alkanol + pentyl ethanoate				
Methanol	298.15	1105	1158	[46]
Ethanol	298.15	1323	1310	[46]
1-Butanol	298.15	1505	1512	[46]
1-Hexanol	298.15	1600	1632	[46]
		1546		[92]
1-Octanol	298.15	1698	1691	[46]
1-Decanol	298.15	1786	1730	[46]
1-Alkanol + methyl propanoate				
Ethanol	298.15	1246	1288	[48]
1-Propanol	298.15	1556	1533	[70]
		1534		[48]
1-Butanol	298.15	1673	1697	[93]
		1667		[48]
1-Hexanol	298.15	1857	1858	[93]
		1912		[48]
1-Octanol	298.15	2041	2047	[93]
		2089		[48]
1-Decanol	298.15	2183	2153	[93]
		2257		[48]
1-Alkanol + ethyl propanoate				
1-Propanol	298.15	1481	1448	[34]
1-Butanol	308.15	1586	1629	[82]
1-Pentanol	298.15	1632	1655	[35]
1-Hexanol	298.15	1662	1765	[86]
1-Heptanol	298.15	1729	1793	[86]
1-Octanol	298.15	1796	1843	[86]
1-Nonanol	298.15	1864	1885	[86]
1-Decanol	298.15	1936	2005	[86]
1-Alkanol + propyl propanoate				
1-Hexanol	298.15	1601	1655	[36]
	308.15	1536	1702	[94]

(*continued*)

Table 6. Continued.

		H^E (J mol^{-1})		
1-Alkanol	T (K)	Exp.	DQ.	Ref.
1-Alkanol + methyl butanoate				
Ethanol	298.15	1205	1248	[48]
1-Propanol	298.15	1479	1448	[70]
		1480		[48]
1-Butanol	298.15	1595	1562	[48]
		1567		[95]
1-Pentanol	298.15	1591	1655	[95]
1-Hexanol	298.15	1673	1765	[95]
		1745		[48]
1-Heptanol	298.15	1745	1793	[95]
1-Octanol	298.15	1806	1843	[95]
		1874		[48]
1-Nonanol	298.15	1894	1885	[95]
1-Decanol	298.15	1955	2005	[95]
		2045		[48]
1-Alkanol + ethyl butanoate				
1-Butanol	308.15	1548	1616	[82]
1-Alkanol + butyl butanoate				
1-Octanol	298.15	1565	1672	[96]
	308.15	1608	1737	[97]
1-Alkanol + methyl pentanoate				
Ethanol	298.15	1255	1263	[48]
1-Propanol	298.15	1530	1482	[48]
1-Butanol	298.15	1517	1563	[93]
		1614		[48]
1-Hexanol	298.15	1615	1655	[93]
		1711		[48]
1-Octanol	298.15	1709	1724	[93]
		1766		[48]
1-Decanol	298.15	1860	1827	[93]
		1820		[48]
1-Alkanol + methyl heptanoate				
Ethanol	298.15	1347	1378	[48]
1-Propanol	298.15	1560	1547	[48]
1-Butanol	298.15	1631	1616	[48]
1-Hexanol	298.15	1643	1637	[48]
1-Octanol	298.15	1651	1672	[48]
1-Decanol	298.15	1669	1623	[48]
1-Alkanol + methyl nonanoate				
Ethanol	298.15	1430	1453	[48]
1-Propanol	298.15	1620	1646	[48]
1-Butanol	298.15	1681	1711	[48]
1-Hexanol	298.15	1644	1668	[48]
1-Octanol	298.15	1600	1613	[48]
1-Decanol	298.15	1547	1551	[48]
1-Alkanol + methyl undecanoate				
Ethanol	298.15	1497	1615	[48]
1-Propanol	298.15	1663	1739	[48]
1-Butanol	298.15	1690	1744	[48]
1-Hexanol	298.15	1614	1677	[48]
1-Octanol	298.15	1534	1609	[48]
1-Decanol	298.15	1500	1534	[48]

(*continued*)

Table 6. Continued.

1-Alkanol	T (K)	H^E (J mol^{-1}) Exp.	H^E (J mol^{-1}) DQ.	Ref.
1-Alkanol + methyl tridecanoate				
Ethanol	298.15	1590	1610	[48]
1-Propanol	298.15	1677	1726	[48]
1-Butanol	298.15	1680	1722	[48]
1-Hexanol	298.15	1544	1644	[48]
1-Octanol	298.15	1504	1569	[48]
1-Decanol	298.15	1510	1489	[48]
1-Alkanol + methyl pentadecanoate				
Ethanol	298.15	1718	1617	[48]
1-Propanol	298.15	1820	1728	[48]
1-Butanol	298.15	1784	1718	[48]
1-Hexanol	298.15	1668	1629	[48]
1-Octanol	298.15	1580	1549	[48]
1-Decanol	298.15	1502	1464	[48]

propanoate + C_6H_6 (four contacts), dev(H^E) = 0.017. The mean deviation defined by:

$$\mathrm{Mdev}\left(H^{\mathrm{E}}\right) = \sum \frac{\mathrm{dev}\left(H^{\mathrm{E}}\right)}{N_S} \tag{5}$$

where N_S, the number of systems, is 0.038 ($N_S = 8$). For the corresponding binaries ($N_S = 21$, see table 7), this deviation is 0.049. Previously, for 35 ternary systems containing one 1-alkanol and one polar compound (linear, branched or cyclic oxaalkane, alkanoate or amine) and one hydrocarbon, we had obtained $\mathrm{Mdev}\left(H^{\mathrm{E}}\right) = 0.082$ [22].

Table 7 also compares DISQUAC results on H^E for the ternary mixtures and for the constituent binaries with those obtained using the UNIFAC model [31] with parameters taken from the literature [31]. UNIFAC yields $\mathrm{Mdev}\left(H^{\mathrm{E}}\right) = 0.076$ for the ternary mixtures and 0.147 for the related binaries. Large differences between experimental and calculated results are obtained for the propyl propanoate + benzene system (table 7), indicating that the UNIFAC parameters for the COO/aromatic contacts must be improved.

The group contribution model developed by Nitta–Chao model [32] is based on the cell theory and includes, within the interaction energies, a chemical association term. This model has been applied to 1-alkanol + linear alkanoate mixtures [33]. At equimolar composition, the mean deviations between experimental and calculated values are 9.1 and 6.1% for G^E and H^E, respectively. DISQUAC provides 6.1% and 3.5%. The Nitta–Chao model has also been applied to predict H^E of the same ternary mixtures considered in the present work. For the systems 1-propanol + ethyl propanoate + n-C_6, 1-pentanol + ethyl propanoate + n-C_6 and 1-hexanol + propyl propanaote + n-C_6, the mean deviation is 4.1%, [34–36], close to the DISQUAC value (5.5%). Both models yield similar results although the Nitta–Chao theory provides information on excess molar volumes.

In the field of correlation and prediction of multicomponent data, many semi-empirical equations (i.e., geometrical methods) have been developed to establish the contribution of each one the three binaries involved in the ternary H^E [37,38].

Table 7. H^E at temperature T for 1-alkanol + linear ester + hydrocarbon mixtures. Comparison of experimental results (Exp.) with DISQUAC (DQ.) predictions using the interaction parameters from tables 1–3, or with UNIFAC (UNIF.) calculations obtained using parameters from the literature [31].

System[a]	T (K)	N[b]	$H^{E,c}_{min}$ (J mol^{-1}) Exp.	$H^{E,c}_{min}$ (J mol^{-1}) DQ.	$H^{E,d}_{max}$ (J mol^{-1}) Exp.	$H^{E,d}_{max}$ (J mol^{-1}) DQ.	dev(H^E)[e] DQ.	dev(H^E)[e] UNIF.	Ref.
1-PrOH + 2COO2 + n-C$_6$	298.15	54	196	177	1726	1625	0.041	0.110	[34]
1-PrOH + 2COO2	298.15	17			1481	1448	0.020	0.093	[34]
1-PrOH + n-C$_6$	298.15	16			550	557	0.020	0.085	[34]
2COO2 + n-C$_6$	298.15				1032	1066	0.023	0.110	[98]
1-PeOH + 2COO2 + n-C$_6$	298.15	59	291	264	1765	1724	0.033	0.113	[35]
1-PeOH + 2COO2	298.15	21			1632	1655	0.017	0.100	[35]
1-PeOH + n-C$_6$	298.15	19			508	486	0.031	0.134	[35]
1-HxOH + 1COO5 + n-C$_9$	298.15	22	598	558	1708	1633	0.043	0.037	[92]
1-HxOH + 1COO5	298.15	11			1546	1632	0.044	0.030	[92]
1-HxOH + n-C$_9$	298.15	19			635	591	0.035	0.132	[99]
1COO5 + n-C$_9$	298.15	13			935	928	0.017	0.070	[92]
1-HxOH + 2COO3 + n-C$_6$	298.15	44	981	934	1719	1653	0.040	0.122	[36]
1-HxOH + 2COO3	298.15	13			1601	1701	0.054	0.090	[36]
1-HxOH + n-C$_6$	298.15	14			458	451	0.021	0.111	[36]
2COO3 + n-C$_6$	298.15	18			821	895	0.058	0.073	[100]
1-OcOH + 3COO4 + n-C$_8$	308.15	30	880	861	1612	1693	0.024	0.118	[101]
1-OcOH + 3COO4	308.15	17			1608	1737	0.061	0.126	[97]
1-OcOH + n-C$_8$	308.15	15			626	598	0.038	0.109	[101]
3COO4 + n-C$_8$	308.15	17			678	764	0.094	0.022	[101]
1-OcOH + 3COO4 + n-C$_{12}$	308.15	40	934	876	1757	1762	0.027	0.108	[97]
1-OcOH + n-C$_{12}$	308.15	18			797	788	0.032	0.183	[97]
3COO4 + n-C$_{12}$	308.15	18			872	924	0.039	0.065	[97]
1-HxOH + 2COO3 + C$_6$H$_6$	298.15	52	126	125	1549	1585	0.017	0.030	[94]
1-HxOH + C$_6$H$_6$	298.15	18			1109	1100	0.017	0.041	[94]
2COO3 + C$_6$H$_6$	298.15	14			–102	–128	0.167	0.490	[102]
1-HxOH + 2COO3 + C$_6$H$_6$	308.15	52	150	155	1256	1235	0.080	0.080	[94]
1-HxOH + C$_6$H$_6$	308.15	20			1271	1196	0.031	0.043	[94]
1-Hexanol + 2COO3	308.15	18			1536	1702	0.091	0.073	[94]
2COO3 + C$_6$H$_6$	308.15	19			–127	–140	0.110	0.913	[102]

[a] The symbols are: 1-PrOH, 1-Propanol; 1-PeOH, 1-Pentanol; 1-HxOH, 1-hexanol; 1-OcOH, 1-Octanol; for other symbols, see table 2.

[b] Number of experimental points.

[c] Minimum value.

[d] Maximum value.

[e] Equation (4).

In the case of asymmetric equations, numbering of components is of great importance as to which component is designated as component 1 [38]. For the three systems cited above, symmetric equations such as the Kohler or Colinet equations [37,38] give mean deviations of 14.2% and 14%, respectively [34–36]. The asymmetric Tsao–Smith equation [37,38] yields deviations of 3.5% for n-C$_6$ + ethyl propanoate + 1-propanol [34]; 3% for n-C$_6$ + 1-pentanol + ethyl propanoate [35] and 4.4% for n-C$_6$ + ethyl propanoate + 1-hexanol [36].

5. Discussion

Thermodynamic properties of mixtures can be examined taking into account differences in molecular size, shape, anisotropy, dispersion forces and so forth. To investigate the impact of polarity on bulk properties, the effective dipole moment,

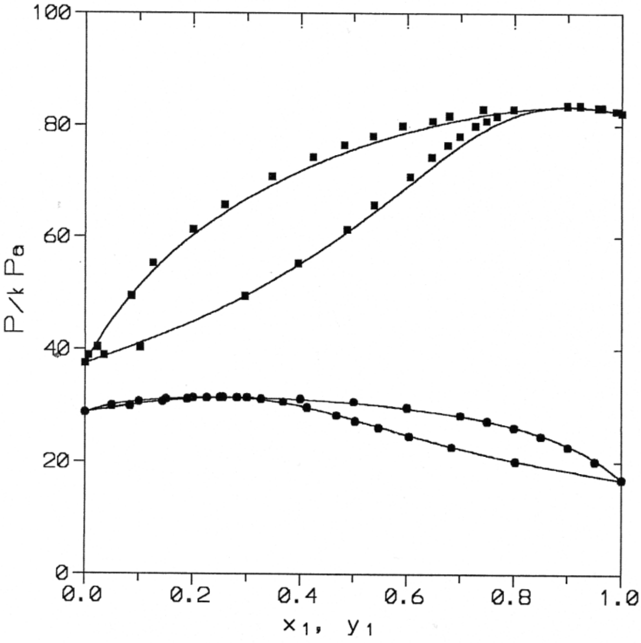

Figure 1. VLE for 1-alkanol (1) + linear alkanoate (2) mixtures. Points, experimental results: (●), methanol (1) + methyl ethanoate (2) at 298.15 K [61]; (■), ethanol (1) + methyl propanoate at 346.3 K [69]. Lines, DISQUAC calculations.

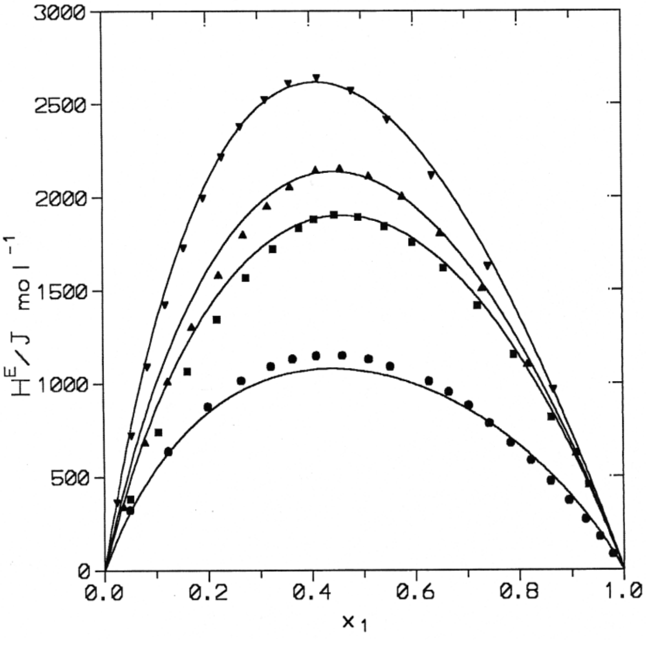

Figure 2. H^E at 298.15 K for 1-alkanol (1) + methyl ethanoate (2) mixtures. Points, experimental results [46]: (●), methanol; (■), 1-butanol; (▲), 1-hexanol; (▼), 1-decanol. Lines, DISQUAC calculations.

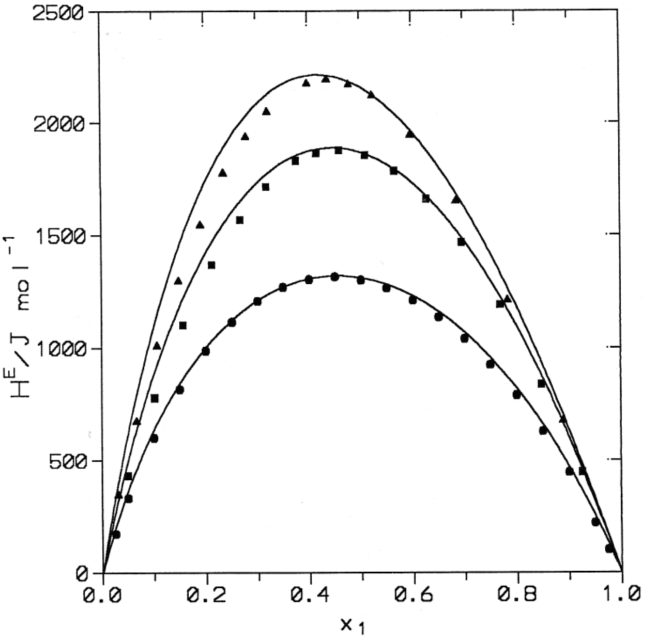

Figure 3. H^E at 298.15 K for 1-alkanol (1) + ethyl ethanoate (2) mixtures. Points, experimental results: (●), ethanol [50]; (■), 1-hexanol [46]; (▲), 1-decanol [46]. Lines, DISQUAC calculations.

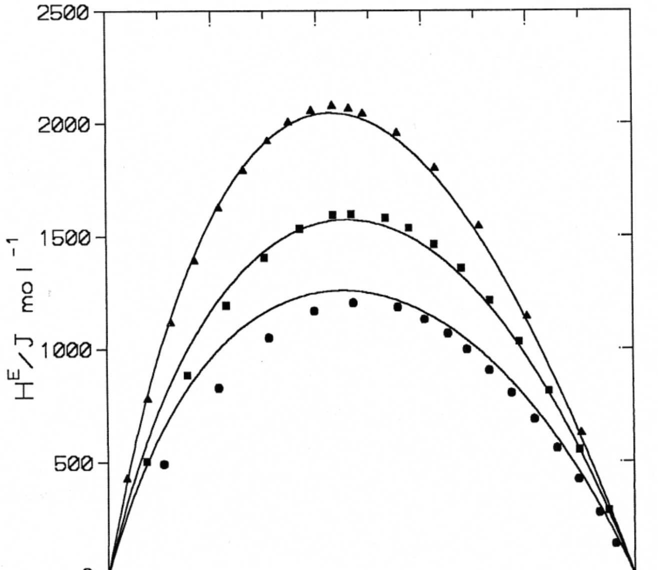

Figure 4. H^E at 298.15 K for 1-alkanol (1) + methyl butanoate (2) mixtures. Points, experimental results [48]: (●), ethanol; (■), 1-butanol; (▲), 1-decanol. Lines, DISQUAC calculations.

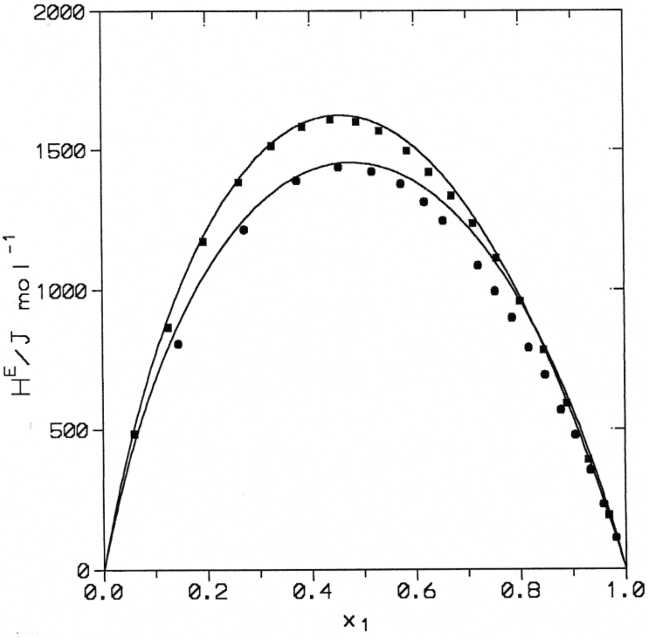

Figure 5. H^Eat 298.15 K for 1-alkanol (1) + methyl nonanoate (2) mixtures. Points, experimental results: [48] (●), ethanol; (■), 1-octanol. Lines, DISQUAC calculations.

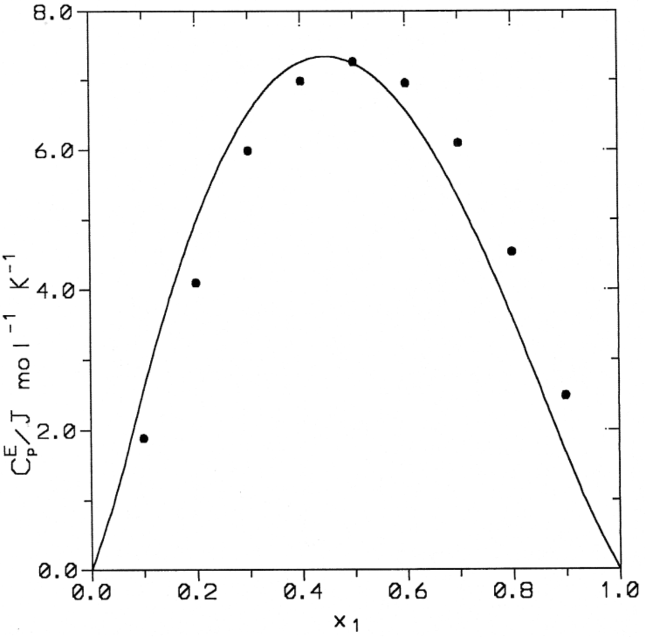

Figure 6. C_p^Eat 298.15 K for ethanol (1) + ethyl ethanoate (2) mixture. Points, experimental results [50]. Line, DISQUAC calculations.

Table 8. Physical properties of linear alkanoates: molar volume, V_m, critical temperature, T_c; critical pressure, P_c; dipole moment in gas phase, μ and effective dipole moment, $\bar{\mu}$ (equation (6)).

Alkanoate	V_m ($cm^3 mol^{-1}$)	T_c (K)	P_c (bar)	μ (D)	$\bar{\mu}$
Methyl ethanoate	$79.83^{a,b}$	506.5^{a}	47.5^{a}	1.72^{a}	0.737
Ethyl ethanoate	$98.49^{a,b}$	523.3^{a}	38.82^{a}	1.82^{a}	0.702
Propyl ethanoate	$115.66^{a,b}$	549.73^{a}	33.6^{a}	1.78^{a}	0.633
Butyl ethanoate	$132.55^{a,b}$	579^{a}	31.2^{a}	1.87^{a}	0.622
Pentyl ethanoate	$149.32^{a,b}$	605^{a}	28.1^{a}	1.87^{a}	0.586
Methyl propanoate	$95.98^{c,d}$	530.6^{c}	40.04^{c}	1.7^{e}	0.664
Ethyl propanoate	$115.54^{a,b}$	546.1^{a}	33.62^{a}	1.74^{a}	0.619
Methyl butanoate	$113.68^{c,d}$	554.4^{c}	34.7^{c}	1.7^{e}	0.610
Ethyl butanoate	$132.91^{a,b}$	566^{a}	30.64^{a}	1.74^{a}	0.577
Methyl pentanoate	$129.83^{c,d}$	567^{c}	31.9^{c}	1.76^{f}	0.591
Methyl hexanoate	$147.17^{c,d}$	597^{g}	28.1^{g}	1.75^{f}	0.552
Methyl octanoate	$180.39^{c,d}$	634^{g}	23.2^{g}	1.71^{e}	0.487
Methyl decanoate	$213.29^{c,d}$	677.5^{g}	19.4^{g}	1.71^{e}	0.448

[a][103]; [b]$T = 298.15$ K; [c][104]; [d]$T = 293.15$ K; [e][105]; [f][106]; [g]calculated using the Joback's method [105].

$\bar{\mu}$, can be used [19,39–41]. For a compound with dipole moment in gas phase, μ, $\bar{\mu}$ is defined according to [41]:

$$\bar{\mu} = \left[\frac{\mu^2 N_A}{4\pi\varepsilon_o V k_B T} \right]^{1/2} \tag{6}$$

where N_A is the Avogadro's number, ε_o, the permittivity of the vacuum, k_B, the Boltzmann's constant and V the molar volume. While for a given series, say linear alkanoates, μ varies only slightly with the chain length (table 8), by necessity $\bar{\mu}$ shows a much greater variation (table 8). For a given temperature, $\bar{\mu}$ depends on, if one discusses, e.g., a low-density gaseous system or a dense liquid phase.

5.1. *The experimental database*

Hereafter, m denotes the number of C atoms in the 1-alkanol, and we are referring to values of the molar excess properties at equimolar composition and 298.15 K.

It is well known that H^E of mixtures formed by a given n-alkane and 1-alkanols increases up to 1-propanol and then decreases, and that the H^E curves are skewed towards low mole fractions of the alcohol. C_p^E of these systems is large and positive. For example, C_p^E (ethanol + n-heptane) = 11.7 J mol^{-1} K^{-1} [42]. In addition, $G^E \approx 2H^E$ and $TS^E < 0$. Therefore, G^E(1-pentanol + n-hexane) = 1041 J mol^{-1} [43] and H^E (1-pentanol + n-hexane) = 475 J mol^{-1} [44]. All these are features of mixtures where the self-association of the alcohol plays an important role.

For systems containing a fixed n-alkane and linear alkanoates, e.g. methyl alkanoates, H^E decreases with the chain length of the ester [45]. This may be attributed to the decrease of $\bar{\mu}$ of the alkanoates (table 8). The H^E curves are nearly symmetrical and $TS^E > 0$. So, the thermodynamic properties of these systems are determined by dipole–dipole interactions between ester molecules. 1-Alkanol + linear alkanoate mixtures show similar features: (i) large positive H^E values, which are even larger than for linear alkanoate + n-alkane mixtures. So, H^E (1-hexanol + methyl ethanoate) = 2136 J mol^{-1}

[46] and H^E (methyl ethanote + n-heptane) = 1783 J mol^{-1} [47] or H^E (1-decanol + methyl pentadecanoate) = 1502 J mol^{-1} [48] and H^E (methyl pentadecanoate + n-undecane) = 453 J mol^{-1} [49] The H^E curves are rather symmetrical. (ii) positive C_p^E values as for the ethanol + ethyl ethanoate system, $C_p^E = 7.4$ J mol^{-1} K^{-1} [50], which are lower than for 1-alkanol + n-alkane mixtures. This indicates that association plays here a less important role. The expression $C_p^E > 0$ means that H^E is more positive at higher temperatures. When the temperature increases, the number of associations in the mixture decreases more than the number of self-association in the pure alkanol and this leads to a more positive contribution to H^E. In addition, the formation of cross association will on decrease increasing the temperature and this also gives a positive contribution to H^E. (iii) TS^E is large and positive. For the ethanol + methyl propanoate system $G^E = 750$ J mol^{-1} [51]; $H^E = 1246$ J mol^{-1} [48] and $TS^E = 496$ J mol^{-1}. In conclusion, mixtures involving 1-alkanols and alkanoates are mainly characterized by strong dipolar interactions between like molecules.

For 1-alkanol + $CH_3(CH_2)_{u-1}COOCH_3$ systems, H^E increases with m for a given ester ($u \leq 7$; table 6). That is, the dipolar interactions between ester molecules are more easily disrupted by alcohols with a large aliphatic surface. Note that $\bar{\mu}$ of the 1-alkanols changes in the sequence methanol = 1.024 > ethanol = 0.852 > $\cdots$ 1-hexanol = 0.547$\cdots$ >. 1-decanol = 0.443 [19]. For $m \geq 7$, H^E decreases with the increase of u (table 6) and the same behaviour is observed for shorter 1-alkanols ($2 \leq m \leq 6$). Such trends are also encountered in methyl alkanoate + n-alkane mixtures [45] and remark the importance of the dipolar interactions between alkanote molecules in the systems containing 1-alkanols, as may be ascribed to the decrease of the $\bar{\mu}$ of the alkanoates when their chain length is increased (table 8).

For $u \geq 8$, $H^E(m)$ shows a variation similar to that of 1-alkanol + a fixed n-alkane; while $H^E(u)$ increases for the shorter 1-alkanols ($2 \leq m \leq 6$). This indicates that now the more relevant contribution to H^Ecomes from the disruption of the OH–OH interactions.

For 1-alkanol + $CH_3COO(CH_2)_{u-1}CH_3$ mixtures, similar trends as those stated above are still valid. Experimental H^E results suggest that for shorter 1-alkanols, e.g., ethanol, H^E is nearly independent of u. This may be due to the fact that the decrease of COO–COO interactions are compensated by COO–OH interactions, which are also weaker due to steric effects.

It is difficult to analyze, due to discrepancies between the experimental data, the effect of different homomorphic alkanoates, $CH_3(CH_2)_{u-1}COO(CH_2)_{v-1}CH_3$, on H^E when they are mixed with a given 1-alkanol. Nevertheless, it seems that H^E increases for $u + v = 3$, 4 for mixtures including the lower alkanols, and remains practically constant from $m \geq 6$ for $u + v = 3$. So, steric effects, if they exist, only appear for the lower 1-alkanols and lead to an increase of H^E. In systems with n-alkanes, H^E is nearly independent of the u- and v-values for homomorphic alkanoates. In the case of mixtures with n-heptane: H^E (propyl ethanoate) = 1194 J mol^{-1} [52]; H^E (ethyl propanoate) = 1149 J mol^{-1} [53]; (methyl butanoate) = 1167 J mol^{-1} [54].

Finally, we note that, for a given 1-alkanol H^E increases in the sequence, linear ketone < linear alkanoate < linear organic carbonate. So, for mixtures involving methanol, H^E (2-propanone) = 694 J mol^{-1} [55] < H^E (methyl ethanoate) = 1009 J mol^{-1} [56] < H^E (dimethyl carbonate) = 1543 J mol^{-1} (value at 313.15K) [57]. The H^E variation in the mixtures with alkanes, say n-heptane, is similar: H^E (2-propanone) = 1704 J mol^{-1} [58] < H^E (methyl ethanoate) = 1783 Jmol^{-1} [47] < H^E (dimethyl carbonate) = 1988 J mol^{-1} [4]. It may be concluded that dipolar interactions in mixtures containing alkanones, alkanoates or carbonates of similar size increase as follows: alkanone < alkanoate < carbonate.

5.2. *The DISQUAC interaction parameters*

This complex behaviour is represented, in terms of the model, by means of structure-dependent interaction parameters. The interchange energy is defined by $\Delta\varepsilon_{st} = \varepsilon_{st} - (\varepsilon_{ss} + \varepsilon_{tt})/2$, where ε_{st}, ε_{ss}, ε_{tt} represent the interaction energies between the surfaces *s–t*, *s–s* and *t–t* and have negative values. In the framework of DISQUAC, $\varepsilon_{st} = g_{st}, h_{st}$. The QUAC parameters are more related to orientational effects, while the DIS parameters are related to non-specific interactions. So, the positive QUAC parameters indicate that the COO–COO and OH–OH interactions are more probable and stronger than those for COO–OH.

The QUAC interchange coefficients are independent of the mixture component and this trend is also observed, not only in systems such as 1-alkanol + *n*-alkanone [11], +linear organic carbonate [7], but also in many other alcoholic solutions: 1-alkanol + benzene, +toluene [29], +CCl_4 [59], or +propanal [60]. On the other hand, we note that $C^{\mathrm{DIS}}_{dh,2}$ coefficients show negative and positive values. The $C^{\mathrm{DIS}}_{dh,2} < 0$ may be interpreted assuming that the dipolar interactions between the COO and OH surfaces are stronger than those between like surfaces. This occurs for systems containing methanol or 1-alkanols (up to 1-hexanol) and lower or intermediate alkanoates and lead to a decrease of H^{E}.

On the other hand, the QUAC parameters for the OH/X contacts (X = CO, COO, OCOO) increase with the size of the group [7,11], in agreement with the fact that interactions between like molecules also increase with the size of the group X.

6. Conclusions

DISQUAC represents well experimental G^{E}, coordinates of azeotropes and H^{E} of the investigated systems using interaction parameters, which depend on the molecular structure. The model also provides, using only binary parameters, accurate predictions on H^{E} for 1-alkanol + linear alkanoate + hydrocarbon mixtures. DISQUAC improves results from the UNIFAC model and give similar results to those obtained from the Nitta–Chao model. 1-Alkanol + linear alkanoate mixtures are characterised by strong dipolar interactions between like molecules. In 1-alkanol + $CH_3COO(CH_2)_{u-1}CH_3$ systems, dipole–dipole interactions between ester molecules are more important for $u \leq 7$. For $u \geq 8$, the more important contribution to the excess molar enthalpy comes from the disruption of the alkanol–alkanol interactions. For systems containing a polar compound such as alkanone, alkanoate or linear organic carbonate, dipolar interactions increase in the order: alkanone < alkanoate < carbonate

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