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Thermodynamic properties of binary mixtures containing oxaalkanes

Part VI. Monoethers, acetals, diethers, cyclic mono- and di-ethers + tetrachloromethane

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Abstract The data available in the literature on thermodynamic properties concerning different oxaalkanes + tetrachloromethane mixtures are examined on the basis of the DISQUAC group contribution model. The obtained interaction parameters, dispersive and quasichemical, depend on the intramolecular environment of the O atom. The steric effect results in a regular decrease of the quasichemical interaction parameters of the oxygen/tetrachloromethane (e,d)-contact in linear ethers. The proximity effect of the O atoms generates lower coefficients in dioxaalkanes with respect to monooxaalkanes and because of the ring strain, being the quasichemical coefficients constant, the dispersive parameters in cyclic molecule are higher than in linear ethers.

Keywords DISQUAC model · Ethers · Excess properties · Tetrachloromethane

Introduction

The group contribution model DISQUAC [1, 2] is a physical model based on the rigid lattice theory developed by Guggenheim [3] for liquid mixture. DISQUAC calculates the excess thermodynamics properties as a sum of two contribution: one DIS, due to dispersive forces, always present, whatever the kind of molecule, and another QUAC, depending on specific chemical interaction. The quasichemical term is zero for mixtures of non-polar compounds, but also for mixtures containing two polar constituents. In the last case similar kind and strength of interaction exerted by the two constituents allows that a mixture maintains the same structure of the pure liquid.

This model has been successfully applied to many classes of compounds as polychloroalkanes [4], polyethers [5–7], thiaalkanes [8], dimethylsulfoxide [9] and aromatic ketones [10] with organic solvents as linear and cyclic alkanes, benzene and tetrachloromethane. Oxaalkanes represent, besides many technical important classes of substances, a particularly interesting family of molecules for the purpose of testing group-contribution models. Indeed, these molecules are formally obtained by replacing one or several CH_2 groups in an alkane by O atoms. A large variety of homomorphic molecular species are thus obtained which differ in the number and relative position of the same functional group. In parts 3–5 of this series [5–7] we have examined, in terms of DISQUAC, the thermodynamic properties and low-pressure fluid phase equilibria of mixtures containing n-alkanes or cyclohexane or benzene with linear, branched or cyclic mono- or polyoxaalkanes.

The purpose of this paper is to extend our study to binary mixtures of several families of oxaalkanes with tetrachloromethane as solvent. Based on previous experience [11, 12] we expected that DISQUAC would permit the finding of parameters of the contact tetrachloromethane\oxygen, which vary regularly with the molecular structure of compounds.

The input data are the molar excess Gibbs energies, G^E, and the molar excess enthalpies, H^E. The sources of available experimental data and some characteristic values are collected in Tables 1–2. The direct experimental isothermal P-x or P-x-y data have been reduced to obtain the molar excess Gibbs energies, G^E, using the two or three parameters Redlich–Kister equation. Vapour phase imperfection was accounted for in terms of the second virial coefficient estimated by the Hayden and O'Connell [13] method.

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In this paper we reported also the experimental H^E results of the binary mixture 2,2-diethoxypropane (1) + tetrachloromethane (2).

Experimental

Materials

2,2-diethoxypropane, declared purity 97%, was obtained from Aldrich and tetrachloromethane, 99.9%, from Riedel de Haën. Experimental densities of these chemicals were 0.82442 and 1.58424 g/cm^3, respectively.

Instrumentation

Heats of mixing were determined by means of a flow microcalorimeter (model 2277, LKB-producer AB, Bromma, Sweden). The apparatus and the experimental procedure adopted are described in detail in a previous paper [9].

Experimental results and discussion

The experimental H^E data of the binary mixture 2,2-diethoxypropane (1) + tetrachloromethane (2) are collected in Table 3. The H^E values were fitted to the smoothing Redlich–

Table 1 Molar excess Gibbs energies, G^E (T, $x_1 = 0.5$), of oxaalkane (1) + tetrachloromethane (2) mixtures at various temperatures, T, and equimolar composition: comparison of direct experimental results (exp)[a] with values calculated (calc) using the coefficients $C^{\text{dis}}_{\text{uv,l}}$ and $C^{\text{quac}}_{\text{uv,l}}$ from Tables 6, 7, 8, 9

Oxaalkane (1)	T/K	G^E (T, $x_1 = 0.5$)/J mol^{-1}		Source of experimental data
		Calc	Exp	
Linear monoethers				
Methylbutylether (1,4)	298.15	−111	−111	[15]
Diethylether (2,2)	298.15	−34	−34	[15]
Ethylbutylether (2,4)	298.15	−99	−99	[15]
Dipropylether (3,3)	298.15	−74	−74	[15]
Dibutylether (4,4)	298.15	−127	−132	[16]
			−127	[15]
	308.15	−122	−129	[17]
Linear acetals				
Dimethoxymethane	298.15	9	8	[15]
Diethoxymethane	298.15	−211	−212	[15]
Linear diethers				
1,2-Dimethoxyethane	298.15	29	29	[15]
1,2-Diethoxyethane	298.15	−186	−185	[15]
Cyclic ethers				
Tetrahydrofurane	298.15	−140	−142	[18]
			−125	[19]
	303.15	−129	−131	[18]
			−141	[20]
			−141	[21]
	308.15	−117	−120	[18]
	323.15	−82	−127	[20]
1,4-Dioxane	293.15	152	187	[22]
	298.15	159	157	[17]
			157	[18]
			171	[23]
	303.15	166	165	[18]
			187	[23]
	308.15	173	187	[18]
	313.15	180	202	[18]
			203	[23]

[a] Calculation (this work) by reduction of the original P-x or P-x-y data with the 2- or 3-parameter Redlich–Kister equation, vapour phase non-ideality corrected in terms of the second virial coefficient

Table 2 Molar excess enthalpies, H^E (T, $x_1 = 0.5$), of oxaalkane (1) + tetrachloromethane (2) mixtures at various temperatures, T, and equimolar composition: comparison of direct experimental results (exp) with values calculated (calc) using the coefficients $C_{\mathrm{uv,l}}^{\mathrm{dis}}$ and $C_{\mathrm{uv,l}}^{\mathrm{quac}}$ from Tables 6, 7, 8, 9

Oxaalkane (1)	T/K	H^E (T, $x_1 = 0.5$)/J mol^{-1}		Source of experimental data
		Calc	Exp	
Linear monoethers				
Methylbutylether (1,4)	298.15	−371	−371	[24]
Diethylether (2,2)	283.15	−445	−530	[25]
	293.15	−455	−491	[26]
	298.15	−459	−493	[27]
			−480	[25]
			−492	[24]
			−487	[28]
			−493	[29]
			−487	[30]
	303.15	−464	−463	[26]
Ethylbutylether (2,4)	298.15	−369	−354	[24]
Dipropylether (3,3)	298.15	−279	−276	[27]
			−278	[24]
			−276	[31]
Dibutylether (4,4)	298.15	−262	−262	[27]
			−262	[24]
			−217	[25]
			−261	[31]
	313.15	−263	−200	[25]
Dipentylether (5,5)	298.15	−182	−184	[27]
			−182	[24]
			−183	[31]
Dihexylether (6,6)	298.15	−131	−136	[27]
			−136	[24]
			−134	[31]
Linear acetals				
Dimethoxymethane	298.15	−364	−363	[24]
			−355	[32]
Diethoxymethane	298.15	−457	−457	[24]
			−459	[32]
Linear diethers				
1,2-Dimethoxyethane	298.15	−448	−448	[24]
1,2-Diethoxyethane	298.15	−517	−527	[32]
Branched acetals				
1,1-Dimethoxyethane	298.15	−501	−463	[32]
1,1-Diethoxyethane	298.15	−472	−508	[32]
2,2-Dimethoxypropane	298.15	−504	−541	[32]
1,1-Diethoxypropane	298.15	−440	−402	[32]
2,2-Diethoxypropane	298.15	−435	−404	This work
Cyclic ethers				
Tetrahydrofurane	283.15	−740	−874	[33]
	293.15	−774	−872	[34]
	298.15	−790	−790	[35]
	303.15	−806	−737	[21]

Table 2 continued

Oxaalkane (1)	T/K	H^E (T, $x_1 = 0.5$)/J mol^{-1}		Source of experimental data
		Calc	Exp	
			−726	[33]
			−737	[36]
Tetrahydropyrane	283.15	−694	−862	[33]
	298.15	−723	−723	[35]
	303.15	−732	−715	[33]
1,3-Dioxolane	298.15	143	164	[37]
			146	[35]
1,3-Dioxane	298.15	−119	−119	[35]
1,4-Dioxane	283.15	−190	−382	[33]
	293.15	−230	−240	[38]
	298.15	−249	−253	[39]
			−252	[40]
			−251	[41]
			−258	[42]
			−250	[43]
			−247	[44]
	303.15	−267	−236	[33]
	308.15	−286	−202	[42]
	318.15	−320	−152	[42]

Table 3 Experimental values (this work) of the molar excess enthalpies, H^E, of binary mixtures of 2,2-diethoxypropane (1) + tetrachloromethane (2), at 298.15 K

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
2,2-Diethoxypropane + Tetrachloromethane					
0.0571	−118.9	0.2876	−395.0	0.6175	−320.0
0.1315	−240.6	0.3771	−437.9	0.7078	−251.1
0.1679	−278.6	0.4759	−414.5	0.7841	−173.3
0.2324	−360.1	0.5477	−373.1		

Kister equation, with 3 parameters. We obtained $a_0 = -1616.4$, $a_1 = 889.88$, $a_2 = 318.98$. The standard deviation calculated by a least squares treatment was 6.9 J mol^{-1}.

Theory

Oxaalkane + tetrachloromethane systems are regarded as possessing a total of four types of contact surfaces: type a, aliphatic (CH_3, CH_2 and CH groups in linear or branched oxaalkanes) or type c (c-CH_2 in cyclic oxaalkanes) type d, chloro (CCl_4 in tetrachloromethane) and type e, oxygen (O group, in oxaalkane). The equations used to calculate G^E and H^E in terms of DISQUAC are the same as in other applications [1] and need not be repeated here.

The dispersive and the quasichemical interchange coefficients $C^{\text{dis}}_{\text{uv,l}}$ and $C^{\text{quac}}_{\text{uv,l}}$ where u,v = a,c,d,e, and l = 1 (Gibbs energy) or l = 2 (enthalpy) express the strength of interaction among different groups. Heat capacity coefficients, l = 3, have not been considered.

Assessment of geometrical parameters

The relative geometrical parameters as volumes, r_i, surfaces, q_i, and molecular surface fractions α_{vi}, of all the non cyclic molecular species have been calculated on the basis of the relative group parameters, the volumes, r_G, and surfaces, q_G, taking arbitrarily the volume, V_{CH_4}, and surface, A_{CH_4}, of methane as unity. Thus $r_G = V_G/V_{CH_4}$ and $q_G = A_G/A_{CH_4}$. In general, for linear molecules, the V_G and A_G values calculated by Bondi [14] have been adopted. The c-CH_2 group surface have been estimated previously. [6] The relative group parameters used in this work are reported in Table 4. Table 5 list the geometrical parameters of all the oxaalkanes referred to in this paper.

Estimation of interaction parameters

The groups investigated in the present work are non polar (contact a or c), polarizable (contact d) or weakly polar (contact e). DISQUAC should be well adapted to study mixtures formed by these groups.

In the application of the model, we make assumption that the parameters may vary with the molecular structure. This strategy improves the predictions, especially in the

Table 4 Relative group increments for molecular volumes, $r_G = V_G/V_{CH_4}$, and areas, $q_G = A_G/A_{CH_4}$, c-CH_2 is a methylene group in an *m*-atom cycle, calculated by Bondi's method [14], ($V_{CH_4} = 17.12 \times 10^{-6}\ m^3\ mol^{-1}$, $A_{CH_4} = 2.90 \times 10^5\ m^2\ mol^{-1}$)

Group	r_G	q_G
$-CH_3$	0.79848	0.73103
$-CH_2-$	0.59755	0.46552
–CH–	0.39603	0.19655
–C–	0.19451	0.00000
c-CH_2-	0.58645	0.56000 ($m = 3$)
		0.66317–0.0385m ($4 \le m \le 8$)
O	0.21612	0.20690

case of branched or cyclic molecules and for the first members of homologous series. The variation should be regular and similar classes should follow the same rules. The final selection of parameters is achieved by plotting the, usually few, adjusted values on smooth curves and estimating the other values by interpolation or extrapolation.

In this section we formulate the rules and list the selected values of the coefficients. In the following sections we discuss the physical meaning of the observed rules and compare the calculated data with experiments.

Every class of mixtures is characterized by three types of contacts; (a,d) (a,e) and (d,e) for class 1 and 2, and (c,d) (c,e) and (d,e) for class 3 and 4. In this work the interchange parameters for the contact (d,e) have been determined while the parameters for the contacts (a,d), (a,e), (c,d), and (c,e) are taken from the literature.

The rules we found as follows:

1. non cyclic mono-ethers + tetrachloromethane

(1a) (a,d)-contact. DIS. The $C^{dis}_{ad,1}$ dispersive coefficients were assumed constant for every system. The values taken from the literature [4] are: $C^{dis}_{ad,1} = 0.093$ and $C^{dis}_{ad,2} = 0.180$.

(1b) (a,e)-contact. DISQUAC. The interchange coefficients, dispersive and quasi-chemical, calculated independently from properties of aliphatic ethers + n-alkane mixtures can be used [5]. The dispersive coefficients, $C^{dis}_{ae,1}$ are constant for all linear aliphatic ethers. The quasi-chemical coefficients, $C^{quac}_{ae,1}$ decrease as the length of the molecule increases.

(1c) (d,e)-contact. DISQUAC. The dispersive coefficients, $C^{dis}_{de,1} = 9.6$ $C^{dis}_{de,2} = 11.6$, are constant and independent of the chain length, *n* and *m* ($n \le m$), of the n-alkyl groups adjacent to the oxygen atom (Table 6). The quasichemical coefficients, $C^{quac}_{de,1}$, of symmetrical ethers, *n*-O-*n*, decrease rapidly with increasing *n* and reach nearly constant values for

Table 5 Relative volumes, r_i, relative total surfaces, q_i, and molecular surface fractions, α_{vi}, (v = a, c, e) calculated from the group increments r_G and q_G given in Table 6; a (CH_3, CH_2, or CH); c (c-CH_2 or c-CH), e (O)

Compound	r_i	q_i	α_{ai}	α_{ei}	α_{ci}
CH_3–O–$(CH_2)_3CH_3$	3.6057	3.0655	0.9325	0.0675	0.0000
CH_3CH_2–O–CH_2CH_3	3.0082	2.6000	0.9204	0.0796	0.0000
CH_3CH_2–O–$(CH_2)_3CH_3$	4.2033	3.5310	0.9414	0.0586	0.0000
$CH_3(CH_2)_2$–O–$(CH_2)_2CH_3$	4.2033	3.5310	0.9414	0.0586	0.0000
$CH_3(CH_2)_3$–O–$(CH_2)_3CH_3$	5.3984	4.4621	0.9536	0.0464	0.0000
$CH_3(CH_2)_4$–O–$(CH_2)_4CH_3$	6.5935	5.3931	0.9616	0.0384	0.0000
$CH_3(CH_2)_5$–O–$(CH_2)_5CH_3$	7.7886	6.3242	0.9673	0.0327	0.0000
CH_3–O–CH_2–O–CH_3	2.6268	2.3414	0.8233	0.1767	0.0000
CH_3CH_2–O–CH_2–O–CH_2CH_3	3.8219	3.2724	0.8735	0.1265	0.0000
CH_3–O–$(CH_2)_2$–O–CH_3	3.2243	2.8069	0.8526	0.1474	0.0000
CH_3CH_2–O–$(CH_2)_2$–O–CH_2CH_3	4.4194	3.7379	0.8893	0.1107	0.0000
CH_3–O–$CH(CH_3)$–O–CH_3	3.2237	2.8034	0.8524	0.1476	0.0000
CH_3CH_2–O–$CH(CH_3)$–O–CH_2CH_3	4.4188	3.7345	0.8892	0.1108	0.0000
CH_3–O–$C(CH_3)_2$–O–CH_3	3.8207	3.3379	0.8760	0.1260	0.0000
CH_3CH_2–O–$CH(CH_2CH_3)$–O–CH_2CH_3	5.0164	4.2000	0.9015	0.0985	0.0000
CH_3CH_2–O–$C(CH_3)_2$–O–CH_2CH_3	4.9726	4.2690	0.9031	0.0969	0.0000
(c-$CH_2)_4$–O	2.5619	2.0920	0.0000	0.0989	0.9011
(c-$CH_2)_5$–O	3.1484	2.3708	0.0000	0.0873	0.9127
(c-$CH_2)_3$–O_2	2.1916	1.8276	0.0000	0.2264	0.7736
(c-$CH_2)_4$–O_2	2.7780	2.1449	0.0000	0.1929	0.8071

For tetrachloromethane, $r_2 = 3.0543$ and $q_2 = 2.5104$ ($\alpha_{d2} = 1.0000$) [4]

Table 6 Dispersive and quasichemical interchange energy coefficients for contact (d,e) in linear ethers of general formula (CH_3–$(CH_2)_{n-1}$–O–$(CH_2)_{m-1}$–CH_3) as *n*-O-*m*; *n*, *m* represents the number of C atoms of the two n-alkyl group attached to the O atom (+*n* and +*m* indicates at least *n* and *m* C atoms respectively)

Ether	$C^{dis}_{de,1}$	$C^{dis}_{de,2}$	$C^{quac}_{de,1}$	$C^{quac}_{de,2}$
1–O–1	9.60	11.60	2.60	5.00
1–O–4+	9.60	11.60	1.17	3.85
2–O–2	9.60	11.60	1.63	3.10
2–O–4+	9.60	11.60	1.04	3.10
3–O–3	9.60	11.60	1.08	2.35
4–O–4	9.60	11.60	0.83	0.63
5–O–5	9.60	11.60	0.83	0.19
+6–O–6+	9.60	11.60	0.83	0.00

$n \geq 6$. In non-symmetrical ethers, *n*-O-*m* ($n < m$), the coefficients are mainly determined by the shortest group *n*. For a given *n*, the coefficients slowly decrease with increasing *m* and for $n \geq 2$ they are almost independent of *m*.

2. non-cyclic compounds of general formula $CH_3(CH_2)_{n-1}$–O–$(CH_2)_u$–O–$(CH_2)_{m-1}CH_3$ (u = 1, acetals; u = 2, dioxaalkanes) + tetrachloromethane

    (**2a**) (a,d)-contact. See above, rule. (**1a**)

    (**2b**) (a,e)-contact. See above, rule. (**1b**).

    (**2c**) (d,e)-contact. DISQUAC. The dispersive coefficients for this class of compounds, $C^{dis}_{de,1}$, decrease with the increase in chain length, *n* and *m*, of the terminal n-alkyl groups and with the decrease of the "distance" *u* between the O atoms (Table 7). Branched acetals exhibit the same trend but the intercharge values are lower than those of the linear ones. Small values for the quasi-chemical parameters were necessary also in this case. They are constant for all the linear or branched dioxa-compounds ($C^{quac}_{de,1} = 1.5$, $C^{quac}_{de,2} = 2.5$) (Table 7) .

3. Cyclic monoethers + tetrachloromethane

Table 7 Dispersive interchange energy coefficients for contact (d,e) in compounds of general formula $CH_3(CH_2)_{n-1}$–O–$(CH_2)_u$–O–$(CH_2)_{m-1}CH_3$; *n* and *m* represent the number of C atoms of the n-alkyl groups attached to the O groups, *u* represent the number of C atom of the n-alkyl or branched alkyl group between the two O groups

n,m	*u*	Linear		Branched		$C^{quac}_{de,1}$	$C^{quac}_{de,2}$
		$C^{dis}_{de,1}$	$C^{dis}_{de,2}$	$C^{dis}_{de,1}$	$C^{dis}_{de,2}$		
1,1	1	6.70	9.21	6.20	8.85	1.5	2.5
1,1	2	6.70	9.07	–	–	1.5	2.5
2,2	1	5.35	8.46	5.80	8.29	1.5	2.5
2,2	2	5.35	8.02	–	–	1.5	2.5

Table 8 Dispersive and quasichemical interchange energy coefficients for contact (d,e) in cyclic monoether of general formula (c-$CH_2)_{p-1}$O)

p	$C^{dis}_{de,1}$	$C^{dis}_{de,2}$	$C^{quac}_{de,1}$	$C^{quac}_{de,2}$
5, tetrahydrofurane	21.00	28.57	2.0	0.2
6, tetrahydropyrane	16.34	19.95	2.0	0.2

(**3a**) (c,d)-contact. DIS. The dispersive coefficients, $C^{dis}_{cd,1}$ of the non-polar (c,d)-contact, derived from the properties of cyclohexane + tetrachloromethane mixtures [9] can be used and are constant for all the cyclic ethers (0.245 for l = 1 and 0.562 for l = 2).

(**3b**) (c,e)-contact. DISQUAC. The quasichemical coefficients of the (c,e) contact decrease with increasing ring size, *p*, and approach the values of linear ethers for $p \geq 7$ [5].

The dispersive coefficients of the (c,e) contact of cyclic ethers [(c-$CH_2)_{p-1}$ O] decrease with increasing ring size, *p*, and approach the value the values of the linear ethers for $p \geq 7$ [5].

(**3c**) (d,e)-contact. DISQUAC. The dispersive coefficients of the (d,e) contact of cyclic ethers [(c-$CH_2)_{p-1}$ O] decrease with increasing ring size, *p* (Table 8). Small values for the quasi-chemical parameters were considered to better reproduce the symmetry of the excess property curves and are constant for all the cyclic ethers ($C^{quac}_{de,1} = 2.0$, $C^{quac}_{de,2} = 0.2$) (Table 8).

4. Cyclic di-ethers + tetrachloromethane

    (**4a**) (c,d)-contact. See above, rule. (**3a**)

    (**4b**) (c,e)-contact. DISQUAC. The dispersive coefficients of the (c,e) contact of cyclic di-ethers increase with increasing ring size, *p*, from 1,3-dioxolane to 1,3-dioxane and 1,4-dioxane [6].

    The quasichemical coefficients of the (c,e) contact increase with increasing ring size, *p*, from 1,3-dioxolane to 1,3-dioxane and 1,4-dioxane [6].

    (**4c**) (d,e)-contact. DIS. The dispersive coefficients of the (d,e) contact of cyclic di-ethers increase as ring size, *p*, increases from 1,3-dioxolane to 1,3-dioxane and 1,4-dioxane (Table 9).

Table 9 Dispersive interchange energy coefficients $C^{dis}_{de,1}$, $C^{dis}_{de,2}$, for contact (d,e) in cyclic diethers (c-$CH_2)_{p-2}O_2$)

p	$C^{dis}_{de,1}$	$C^{dis}_{de,2}$
5, 1,3-dioxolane	10.14	12.90
6, 1,3-dioxane	10.45	15.95
6, 1,4-dioxane	13.26	17.10

Comparison with experiment and discussion

The systems here considered show weak deviations from ideality. Indeed, G^E at equimolar composition for the mixtures under examination are approximately in the range -200 to $+200$ J mol^{-1}.

Generally excess Gibbs energy curves of all mixtures considered in this work, as a function of the mole fraction of a component, are reproduced very well (Table 1). See for example Fig. 1 where experimental data and values calculated by using the DISQUAC model, for mixtures containing linear acetals or dioxaalkanes + tetrachloromethane are represented.

Only for the mixtures containing dioxane, a difference that reaches the maximum values of $+35$ J mol^{-1} has been obtained for $x_1 = 0.2$. Meanwhile on the right side of the curve ($x_1 > 0.5$) the agreement is very good.

H^Es are not very high and are generally negative with the exception of mixtures containing the cyclic diether, 1,3-dioxolane. Linear symmetric ethers + tetrachloromethane mixtures show, at equimolar composition and 298.15 K, exothermic effects in the range -493 J mol^{-1} for diethyl ether to -135 J mol^{-1} for dihexyl ether.

Also the differences between experimental and calculated excess enthalpies are acceptable (see Table 2 and Figs. 2–3). The temperature dependence is roughly reproduced even if the H^E are calculated with zero heat capacity of dispersive and quasi-chemical interchange coefficients, $C_{\mathrm{uv,l}}^{\mathrm{quac}}$.

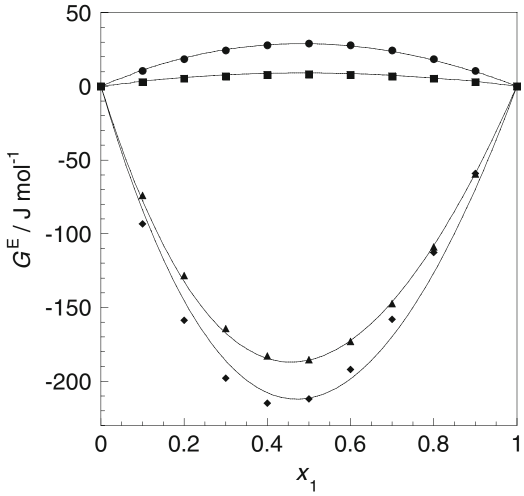

Fig. 1 Comparison of theory with experiments for the molar excess Gibbs energies, G^E, at 298.15 K, for acetal or di-oxaalkane (1) + tetrachloromethane (2) mixtures versus x_1, the mole fraction of component (1): (*full lines*) DISQUAC predictions, (*points*) experimental results from Ref. [15]: (*black circle*) 1,2-dimethoxyethane, (*black square*) dimethoxymethane, (*black up-pointing triangle*) 1,2-diethoxyethane, (*black diamond*) 1,2-diethoxymethane

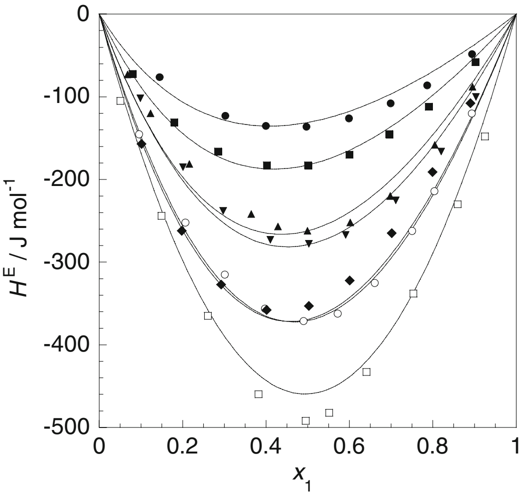

Fig. 2 Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for linear ethers (1) + tetrachloromethane (2) mixtures versus x_1, the mole fraction of component (1): (*full lines*) DISQUAC predictions, (*points*) experimental results from Ref. [24]: (*black circle*) dihexylether, (*black square*) dipentylether, (*black up-pointing triangle*) dibutylether, (*black down-pointing triangle*) dipropylether, (*black diamond*) ethylbutylether, (*white circle*) methylbuthylether, (*white square*) diethylether

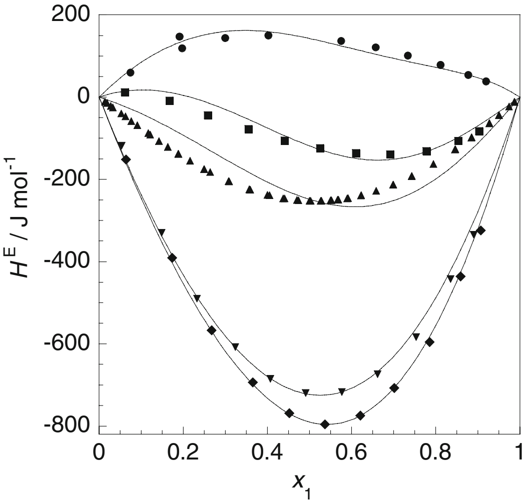

Fig. 3 Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for cyclic mono- and di- ethers (1) + tetrachloromethane (2) mixtures versus x_1, the mole fraction of component (1): (*full lines*) DISQUAC predictions, (*points*) experimental results: (*black circle*) 1,3-dioxolane [35], (*black square*) 1,3-dioxane [35], (*black up-pointing triangle*) 1,4-dioxane [40], (*black down-pointing triangle*) tetrahydropyrane [35], (*black diamond*) tetrahydrofurane [35]

As expected, the largest deviations appear in the case of branched acetals. In these system the excess function strongly depend on the contact tetrachloromethane\oxygen (d,e), and a variation of 5% in the parameters produce a difference of 100 J mol^{-1} (at $x_1 = 0.5$) on the G^E and H^E calculated values.

The substitution of a CH_2 group in an alkane by an O atom influences the intermolecular forces as a result of two opposing effects: one weakens, owing to the small dispersive forces exerted by O atoms compared with those of the CH_2 group, while the other strengthens, owing to the electrostatic interactions between the C–O dipoles.

In the case of the interactions parameters of the (d,e)-contact the steric effect of the linear alkyl groups adjacent to the O atom, affect the dispersive forces and the electrostatic forces at the same time. This may explain the constancy of the dispersive interchange coefficients in ethers.

In contrast, the quasi-chemical interactions are considerably weakened by the shorter alkyl groups attached to the O atom. The size of the other alkyl groups has less influence. Indeed the quasichemical interchange coefficients of symmetrical di-*n*-alkyl ethers (*n*-O-*n*) rapidly decrease when *n* increases. Moreover, the relative constancy of the coefficients of *n*-O-*m* type molecules can be noted when *n* is constant and *m* increases [rule (1d), Table 6].

The influence of the inductive and steric effect of an alkyl group adjacent to a polar X group (X = O) on the dispersive and quasi-chemical interchange parameters $C_{\mathrm{sx,l}}^{\mathrm{quac}}$ can be more easily explained if we consider that the interchange energies, $\Delta\varepsilon_{\mathrm{sx}}$, are related to the interaction energies, $\varepsilon_{\mathrm{sx}}$,

$$\Delta\varepsilon_{\mathrm{sx}} = (|\varepsilon_{\mathrm{ss}}| + |\varepsilon_{\mathrm{xx}}|)\backslash 2 - |\varepsilon_{\mathrm{sx}}| \qquad (1)$$

the ε values being negative.

In polar-polar/polarizable systems the inductive effect exerted by an alkyl group adjacent to the polar X group increases the dispersive interaction energies $\varepsilon_{\mathrm{sx}}$ and consequently decreases $\Delta\varepsilon_{\mathrm{sx}}$ and $C_{\mathrm{sx,l}}^{\mathrm{dis}}$.

The steric effect acts mainly on the quasi-chemical parameters. In polar-polar/polarizable systems it decreases the electrostatic energies $\varepsilon_{\mathrm{sx}}$ and consequently increases $\Delta\varepsilon_{\mathrm{sx}}$ and $C_{\mathrm{sx,l}}^{\mathrm{quac}}$.

The proximity of the two atoms in the O–$(CH_2)_u$–O group in acetals and diethers weakens the molecular interactions and the dispersive coefficients of acetals are smaller than the corresponding coefficients of ethers.

The increase of interchange coefficients of cyclic ethers (c–$CH_2)_{p-1}$–O with decreasing ring size *p* was attributed to the steric effect, the enhanced dipole moments and the increased polarizability due to electron delocalization (ring strain).

The increase of the dispersive parameters from 1,3-dioxolane to dioxane (1,3- or 1,4-isomer) can be ascribed to the ring strain effect while the decrease from 1,4-dioxane to 1,3-dioxane was attributed to the proximity effect between the two oxygen atoms.

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