

THERMODYNAMIC PROPERTIES OF BINARY MIXTURES CONTAINING OXAALKANES

Part V. Monoethers, acetals, polyethers, cyclic mono- and di-ethers+benzene

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A flow microcalorimeter has been used to determine excess enthalpies, H^E , at 298.15 K of binary mixtures of dipentylether, dihexylether, 1,2-dimethoxyethane and 1,2-diethoxyethane (1)+benzene (2). These data along with the data available in the literature on H^E , molar excess Gibbs energies, G^E and liquid-vapour equilibria (LVE) of non-cyclic monoethers, acetals, polyethers and of cyclic mono- and di-ethers+benzene are examined on the basis of the DISQUAC group contribution model. Using a set of adjusted interchange energies parameters, structure dependent, the model provides a fairly consistent description of the thermodynamic properties as a function of concentration. The interaction parameters, dispersive and quasichemical, depend on the intramolecular environment of the O atom. There is clear evidence for the steric and inductive effects exerted by the alkyl groups adjacent to the O atom, for –O–C–O– proximity effect and for a ring strain effect. The steric effect results in a regular decrease of the dispersive interaction parameters of the oxygen/benzene (e,b) contact; The proximity effect of the O atoms produces a regular decrease and the ring strain a regular increase of the dispersive interaction parameters; the quasi-chemical remain constant.

Keywords: benzene, data, DISQUAC model, ethers, excess enthalpy

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 calculate the excess thermodynamics properties as a sum of two contributions: one DIS, due the dispersive forces, always present, whatever the kind of molecule and another QUAC, depending on specific chemical interaction and relate to the kind of molecule under study. The quasi-chemical term is zero for mixtures of apolar compounds.

In several papers [4–8] we have reported the results concerning the ability of this model to represent a complete set of thermodynamic properties: vapour liquid equilibria (VLE), liquid–liquid equilibria (LLE), solid–liquid equilibria (SLE), excess molar Gibbs energies (G^E), excess molar enthalpies (H^E), as well as the related partial molar excess quantities at infinite dilution. We studied systems containing: polychloroalkanes [4], polyethers [5], thioalkanes [6], dimethylsulfoxide [7] and aromatic ketones [8] with organic solvents such as alkanes, cyclohexane, benzene or CCl_4 .

Oxaalkanes represent, besides many technical important classes of substance, 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 Part 3 and 4 of this series [5, 9] we have examined, in terms of DISQUAC, the thermodynamic properties and low-pressure fluid phase equilibria of mixtures containing *n*-alkanes or cyclohexane with linear or branched mono- or poly-oxaalkanes (monoethers, acetals, polyethers), mono-xacycloalkanes and dioxacycloalkanes.

The purpose of this paper is to extend our study to binary mixtures of the same families of oxaalkanes with benzene as solvent. As expected our preliminary calculations showed that the interaction parameters of the contact benzene/oxygen in mixtures of ethers with benzene are affected by the nature and the structure of the neighbouring groups. We had the choice between estimating ‘average’ interaction parameters, with the risk of obtaining poor results in extreme cases, or studying carefully the structure dependence of the parameters. Based on previous experience [10,11] we expected that DISQUAC would permit the finding of parameters which vary regularly with the molecular structure of compounds. Thus we chose the second method.

In this paper we reported experimental H^E results of binary mixtures of dipentylether, dihexylether, 1,2-dimethoxyethane and 1,2-diethoxyethane (1)+ben-

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zene (2) and the DISQUAC analysis on mixtures of oxaalkane+benzene.

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 and 2. The direct

experimental isothermal 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 [12] method.

Table 1 Molar excess Gibbs energies G^E ($T, x_1=0.5$) of oxaalkane (1)+benzene (2) mixtures at various temperatures T and equimolar composition: comparison of direct experimental results (exp.)^a with values calculated (calc.) using the coefficients $C_{uv,1}^{\text{dis}}$ and $C_{uv,1}^{\text{quac}}$ from Tables 8–13

Oxaalkane (1)	T/K	G^E ($T, x_1=0.5$)/J mol ⁻¹		Source of experimental data
		calc.	exp.	
Linear monoethers $\text{CH}_3-(\text{CH}_2)_{s-1}-\text{O}-(\text{CH}_2)_{t-1}-\text{CH}_3$				
Methylbutylether (1,4)	343.15	42.9	41.1	[13]
Diethylether (2,2)	273.15	14.7	6.7	[14]
	293.15	15.6	20.4	[14]
		15.6	-75.8	[15]
	303.15	16.3	4.8	[15]
Dipropylether (3,3)	323.15	34.6	-5.1	[16]
	333.15	30.4	27.3	[16]
	343.15	26.2	40.1	[16]
		26.2	38.0	[17]
Dibutylether (4,4)	298.15	28.8	27.6	[18]
	308.15	19.1	18.0	[18]
Branched monoethers				
Diisopropylether	313.15	38.6	106.4	[19]
	323.15	34.4	135.8	[16]
	333.15	30.2	110.3	[16]
	343.15	26.0	111.6	[13]
		26.0	111.6	[13]
		26.0	126.0	[16]
Linear acetals				
Dimethoxymethane	308.15	-6.0	107.1	[20]
	343.15	-10.6	-10.9	[13]
1,2-Diethoxyethane	343.15	-8.8	-10.3	[13]
Cyclic mono- and di-ethers				
Tetrahydrofurane	303.15	-130.7	-131	[20]
1,4-Dioxane	293.15	46.7	64.7	[21]
	298.15	47.9	47.6	[22]
		47.9	125.6	[23]
	303.15	49.5	53.1	[22]
	313.15	53.3	65.8	[22]

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

BINARY MIXTURES CONTAINING OXAALKANES

Table 2 Molar excess enthalpies $H^E(T, x_1=0.5)$ of oxaalkane (1)+benzene (2) mixtures at various temperatures T and equimolar composition: comparison of direct experimental results (exp) with values calculated (calc) using the coefficients $C_{uv,1}^{dis}$ and $C_{uv,1}^{quac}$ from Tables 8–13

Oxaalkane (1)	T/K	$H^E(T, x_1=0.5)/J\ mol^{-1}$		Source of experimental data
		calc	exp	
Linear monoethers $CH_3-(CH_2)_{n-1}-O-(CH_2)_{m-1}-CH_3$				
Methylbutylether (1,4)	298.15	108.7	103.2	[24]
Diethylether (2,2)	298.15	-5.4	-8.7	[35]
Ethylbutylether (2,4)	298.15	154.3	200	[24]
Dipropylether (3,3)	298.15	170.5	169.5	[24]
Dibutylether (4,4)	298.15	316.6	319.6	[18]
	308.15	316.6	305.8	[18]
Dipentylether (5,5)	298.15	405.2	403.2	this work
Dihexylether (6,6)	298.15	422.0	424.7	this work
Branched monoethers				
Diisopropylether	303.15	169.5	137.3	[19]
	308.15	169.5	161.7	[26]
Linear acetals				
Dimethoxymethane	298.15	55.4	56.1	[27]
		55.4	45.0	[25]
Diethoxymethane	298.15	70.6	71.5	[27]
1,2-Dimethoxyethane	298.15	-163.6	-164.4	this work
		-163.6	-170.0	[24]
1,2-Diethoxyethane	298.15	-283.6	-282.8	this work
Branched acetals				
1,1-Dimethoxyethane	298.15	-72.5	-72.9	[27]
1,1-Diethoxyethane	298.15	-22.6	-21.9	[27]
2,2-Dimethoxypropane	298.15	93.8	93.1	[27]
1,1-Diethoxypropane	298.15	84.4	33.3	[27]
2,2-Diethoxypropane	298.15	97.6	99.6	[28]
Linear polyethers				
2,5,8-Trioxanonane	298.15	-279.8	-286.9	[24]

to be continued

Table 2 Continued

Oxaalkane (1)	<i>T</i> /K	$G^E(T, x_1=0.5)/\text{J mol}^{-1}$		Source of experimental data
		calc.	exp.	
3,6,9-Trioxaundecane	298.15	-346.1	-428.9	[24]
Cyclic ethers				
Tetrahydrofuran (c-CH ₂) ₄ -O	298.15	-365.8	-365.8	[29]
		-365.8	-395.3	[30]
	303.15	-390.3	-353.8	[31]
		-390.3	-270.0	[21]
Tetrahydropyran (c-CH ₂) ₄ -O	298.15	-255.5	-255.5	[32]
1,3-Dioxolane (c-CH ₂) ₃ -O ₂	298.15	-78.1	-78.8	[33]
1,3-Dioxane (c-CH ₂) ₄ -O ₂	298.15	-140.6	-140.3	[32]
1,4-Dioxane (c-CH ₂) ₄ -O ₂	288.15	-1.1	-34.2	[32]
	293.15	-17.7	-2.3	[34]
	298.15	-34.0	-32.2	[32]
		-34.0	-39.8	[35]
	313.15	-82.2	-29.0	[36]
	318.15	-97.9	-19.5	[34]

Table 3 Supplier, molar masses, purities and densities at 298.15 K of oxaalkanes and benzene

Compound	Supplier	$M/\text{g mol}^{-1}$	Purity/%	$\rho_{\text{exp}}/\text{g cm}^{-3}$	$\rho_{\text{lit}}/\text{g cm}^{-3}$
Dipentylether	Aldrich	158.29	97.0	0.7814	0.7790 ^b
Dihexylether	Aldrich	186.34	97.0	0.7902	0.7894 ^b
1,2-Dimethoxyethane	Aldrich	90.12	99.9	0.8612	0.8637 ^a
1,2-Diethoxyethane	Fluka	118.18	99.0	0.8375	0.8351 ^a
Benzene	Aldrich	78.113	99.9	0.8736	0.8736 ^a

^a[37], ^b[38]

Experimental

Materials

Chemicals were commercial products from Aldrich or Fluka. They were used without further purification and their purities, as checked by gas chromatographic analysis, were $\geq 99\%$.

The purities declared by the companies as well as the molar mass and the liquid densities we measured at 298.15 K along with those found in literature are collected in Table 3.

Instrumentation

Heats of mixing were determined by means of a flow micro-calorimeter (model 2277, LKB-producer AB, Bromma, Sweden). The apparatus and the experimental procedure are described in detail elsewhere [39]. Fully

automatic burettes (ABU80, Radiometer, Copenhagen, Denmark) were used to pump the liquid into the LKB unit. The molar flow rate m_i (mol s^{-1}), of component i flowing into the mixing cell is given by:

$$m_i = \Phi_i \rho_i / M_i \quad (1)$$

where Φ_i is the volumetric flow rate, ρ_i the density and M_i the molar mass. The necessary densities were determined with a vibrating tube densimeter (Anton Paar, model DMA 58, Graz, Austria) with a reproducibility of $1 \cdot 10^{-5} \text{ g cm}^{-3}$. The molar excess enthalpies have been evaluated from the formula

$$H^E = I^2 R (E/E_c) / m_i \quad (2)$$

where I and R are the electrical current and resistance in the electrical calibration experiment, E and E_c are the voltage readings for measurement and electrical calibration, respectively and m is the molar flow rate

Table 4 Experimental values of the molar excess enthalpies, H^E , of binary mixtures of mono- and di-ethers+benzene, at 298.15 K

x_1	$H^E/\text{J mol}^{-1}$	x_1	$H^E/\text{J mol}^{-1}$	x_1	$H^E/\text{J mol}^{-1}$
dipentylether+benzene					
0.0994	241.7	0.3983	428.7	0.7018	276.1
0.1808	352.5	0.4688	419.8	0.8153	182.8
0.2273	393.3	0.5406	385.3	0.8412	158.3
0.3062	422.6	0.6384	327.9		
dihexylether+benzene					
0.0866	248.6	0.4313	451.4	0.7913	215.3
0.1122	301.5	0.5028	421.0	0.8505	157.6
0.2749	460.6	0.6026	368.2		
0.3358	463.8	0.6946	303.3		
1,2-dimethoxyethane+benzene					
0.1246	-79.6	0.3629	-158.9	0.7193	-134.3
0.1760	-95.7	0.4607	-159.7	0.7736	-114.3
0.2217	-112.6	0.5617	-158.7	0.8368	-86.4
0.2993	-141.4	0.6308	-154.2	0.8952	-63.0
1,2-diethoxyethane+benzene					
0.0955	-103.9	0.3879	-277.2	0.7171	-209.6
0.1367	-141.0	0.4579	-290.0	0.7917	-167.2
0.1744	-181.2	0.4873	-284.9	0.8637	-120.6
0.2406	-216.9	0.5589	-268.3		
0.2970	-250.8	0.6553	-241.2		

Table 5 Values of the coefficients, a_i , standard deviations, $\sigma(H^E)$, of molar excess enthalpies, H^E at 298.15 K, for ethers (1)+benzene (2) mixtures

Components	a_0	a_1	a_2	a_3	$\sigma(H^E)/\text{J mol}^{-1}$
Dipentylether+benzene	1612.80	-804.08	439.00	-292.57	3.2
Dihexylether+benzene	1698.70	-921.29	685.10	-425.10	2.5
1,2-Dimethoxyethane+benzene	-657.75	14.95	-	-	3.3
1,2-Diethoxyethane+benzene	-1131.20	170.66	51.08	-	4.1

of the mixture. All enthalpy measurements were carried out at 298.15 K. The accuracy of the LKB bath temperature is 0.1 K. The reliability of the apparatus and procedure adopted were checked by performing H^E measurements on the test system benzene+cyclohexane. Our results concerning this system differed by <2% from reliable literature data [40] over the entire composition range.

Results and discussion

The experimental H^E data are collected in Table 4. The H^E values were fitted to the smoothing Redlich–Kister equation:

$$H^E = x_1 x_2 \sum_{i=0}^{p-1} a_i (x_1 - x_2)^i \quad (3)$$

where x_1 is the mole fraction of oxygenated compound (1) and p is the number of coefficients. The values of the coefficients a_i and the standard deviation of the fit, $\sigma(H^E)$, obtained by a least squares treatment, are given in Table 5.

Theory

Oxaalkane+benzene systems are regarded as possessing three 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 b, aromatic (C_6H_6 in benzene), type e, oxygen (O group, in oxaalkane). The equations used to calculate G^E and H^E are the same as in other applications [1] and need not be repeated here.

Table 6 Relative group increments for molecular volumes, $r_G=V_G/V_{CH_4}$ and areas, $q_G=A_G/A_{CH_4}$, c-CH₂ and c-CH are respectively, a methylene or a methine group in an m -atom cycle, calculated by Bondi's method [15], ($V_{CH_4}=17.12\cdot 10^{-6}$ m³ mol⁻¹, $A_{CH_4}=2.90\cdot 10^5$ m² 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	$m=3$
		0.66317-0.0385 m	$4\leq m\leq 8$
c-CH-	0.38496	0.29103	$m=3$
		0.39480-0.0385 m	$4\leq m\leq 8$
O	0.21612	0.20690	

Table 7 Relative volumes, r_i , total surfaces, q_i and molecular surface fractions, α_{vi} , ($v=a, e, c$) calculated from the group increments r_G and q_G given in Table 6: a (CH₃, CH₂, or CH); b (C₆H₆); c (c-CH₂ or c-CH), e (O)

Compound	r_i	q_i	α_{ai}	α_{ei}	α_{ci}
CH ₃ -O-(CH ₂) ₃ CH ₃	3.6057	3.0655	0.9325	0.0675	0.0000
CH ₃ CH ₂ -O-CH ₂ CH ₃	3.0082	2.6000	0.9204	0.0796	0.0000
CH ₃ CH ₂ -O-(CH ₂) ₃ CH ₃	4.2033	3.5310	0.9414	0.0586	0.0000
CH ₃ (CH ₂) ₂ -O-(CH ₂) ₂ CH ₃	4.2033	3.5310	0.9414	0.0586	0.0000
CH ₃ (CH ₂) ₃ -O-(CH ₂) ₃ CH ₃	5.3984	4.4621	0.9536	0.0464	0.0000
CH ₃ (CH ₂) ₄ -O-(CH ₂) ₄ CH ₃	6.5935	5.3931	0.9616	0.0384	0.0000
CH ₃ (CH ₂) ₅ -O-(CH ₂) ₅ CH ₃	7.7886	6.3242	0.9673	0.0327	0.0000
(CH ₃) ₂ CH-O-CH(CH ₃) ₂	4.2021	3.5241	0.9413	0.0587	0.0000
CH ₃ -O-CH ₂ -O-CH ₃	2.6268	2.3414	0.8233	0.1767	0.0000
CH ₃ CH ₂ -O-CH ₂ -O-CH ₂ CH 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 ₃ CH ₂ -O-(CH ₂) ₂ -O-CH ₂ CH 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 ₃ CH ₂ -O-CH(CH ₃)-O-CH ₂ CH 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 ₃ CH ₂ -O-CH(CH ₂ CH ₃)-O-CH ₂ CH ₃	5.0164	4.2000	0.9015	0.0985	0.0000
CH ₃ CH ₂ -O-C(CH ₃) ₂ -O-CH ₂ CH ₃	4.9726	4.2690	0.9031	0.0969	0.0000
CH ₃ -O-[(CH ₂) ₂ -O] ₂ -CH ₃	4.6355	3.9448	0.8427	0.1573	0.0000
CH ₃ CH ₂ -O-[(CH ₂) ₂ -O] ₂ -CH ₂ CH ₃	5.8306	4.8759	0.8727	0.1273	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 parameters of benzene, $r_2=2.8248$ and $q_2=2.0727$ ($\alpha_{b2}=1.0000$) [41]

The temperature dependence of the interaction parameters has been expressed in terms of the dispersive or quasi-chemical interchange coefficients $C_{uv,l}^{dis}$ and $C_{uv,l}^{quac}$ where $u, v=a, b, e$ and $l=1$ (Gibbs energy) or $l=2$ (enthalpy). 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 vol-

umes 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 [42] have been adopted. The c-CH₂ and c-CH group surfaces have been estimated previously [9] (Table 6). Table 7 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 no polar (contact a or c), polarizable (contact b) or weakly polar (contact e). DISQUAC should be well adapted to study mixtures formed by these groups.

In the application of the DISQUAC model, we make the physically reasonable assumption that the parameters may vary with the molecular structure. The assumption improves the predictions, especially in the case of branched or cyclic molecules and for the first members of homologous series. A basic requirement is that the variation is regular and that similar classes 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.

1. Non-cyclic mono-ethers or polyethers+benzene

These systems are characterized by three types of contact: (a,b), (a,e) and (b,e). The rules we found as follows:

(1a) (a,b)-contact. The $C_{ab,1}^{dis}$ dispersive coefficients were assumed constant for every system. The values taken from literature [41] are: $C_{ab,1}^{dis} = 0.26$ and $C_{ab,2}^{dis} = 0.56$.

(1b) (a,e)-contact. The interchange coefficients, dispersive and quasi-chemical, calculated independently from properties of aliphatic ethers+n-alkanes mixtures can be used [2]. The dispersive coefficients, $C_{ae,1}^{dis}$ are constant for all linear aliphatic ethers. The quasi-chemical coefficients, $C_{ae,1}^{quac}$ decrease as the length of the molecule increase.

(1c) (b,e)-contact. The quasi-chemical parameters were equal zero for all the mono-ether linear or branched here considered. The dispersive coefficients, $C_{be,1}^{dis}$ decrease with increase in chain length, n and m ($n \leq m$), of the n -alkyl groups adjacent to the n -O- m atom (Table 8). The coefficients of symmetrical groups, n -O- n decrease rapidly with increasing n and reach nearly constant values for $n \geq 6$. In non-symmetrical n -O- m groups ($n < m$) 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 .

(1d) (b,e)-contact. In the case of the polyethers small values for the quasi-chemical parameters were considered to better reproduce the symmetry of the excess properties curves and are constant for all the polyethers ($C_{be,1}^{quac} = 1.4$, $C_{be,2}^{quac} = 2.6$) (Table 9). When ascertaining the n and m values of the n -O- m groups in polyethers one should ignore the other O atoms; the dispersive coefficients used in the calculation are the same of the monoethers. For example the parameters for the polyether 2,5,8-trioxanonane are the same of the dibutylether and for the polyether 3,6,9-trioxaundecane the parameters are the same of the dipentylether (Table 10).

Table 8 Dispersive interchange energy coefficients $C_{be,1}^{dis}$ and $C_{be,2}^{dis}$ for contact (b,e), b (C₆H₆) and e (O atom in, n -O- m group); n represents the number of C atoms of the n -alkyl group attached to the O group, $+n$ indicates $\geq n$; m represents the number of C atoms of the alkyl or branched-alkyl group attached to the O group, $m+$ indicates at least m C atoms

Type of O atoms	$C_{be,1}^{dis}$	$C_{be,2}^{dis}$
1-O-1	11.00*	18.00*
1-O-4 +	10.40	16.00
2-O-2	10.10	15.00
2-O-4 +	10.10*	15.00
3-O-3	9.70	13.10
4-O-4	9.50	11.50
5-O-5	9.50*	10.40
+ 6-O-6 +	9.50*	9.00

*guessed value

Table 9 Quasi-chemical interchange energy coefficients $C_{be,1}^{quac}$ and $C_{be,2}^{quac}$ for contacts (b,e), b (C₆H₆) and e (O atom in oxaalkane)

Oxaalkane	$C_{be,1}^{quac}$	$C_{be,2}^{quac}$
Ethers	0.00	0.00
Polyethers	1.40	2.60
Acetals	1.40	2.60
Cyclic mono-ethers	1.40	2.60
Cyclic di-ethers	1.00	3.40

Table 10 Dispersive interchange energy coefficients $C_{be,1}^{dis}$ and $C_{be,2}^{dis}$ for contact (b,e), b (C₆H₆) and e (O atoms in linear polyethers)

Linear polyether	$C_{be,1}^{dis}$	$C_{be,2}^{dis}$
CH ₃ -O-[(CH ₂) ₂ -O] ₂ -CH ₃	9.50*	11.50
CH ₃ CH ₂ -O-[(CH ₂) ₂ -O] ₂ -CH ₂ CH ₃	9.50*	10.40

*guessed value

Table 11 Dispersive interchange energy coefficients $C_{be,1}^{dis}$, $C_{be,2}^{dis}$ for contact (b,e), b (C_6H_6) and e (O atom in acetals 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 group attached to the O groups, u represents the number of C atom of the n -alkyl or branched alkyl group between the two O groups

$CH_3(CH_2)_{n-1}-O-(CH_2)_u-O-(CH_2)_{m-1}CH_3$			Linear		Branched	
n, m	u	$C_{be,1}^{dis}$	$C_{be,2}^{dis}$	$C_{be,1}^{dis}$	$C_{be,2}^{dis}$	
1, 1	1	5.81	8.93	4.52*	7.00*	
2, 2	1	5.20	8.14	3.43*	6.00*	
1, 1	2	5.00*	7.86	5.34*	8.28	
2, 2	2	5.00	5.87	5.34*	7.30	
1, 1	3	5.00*	7.50*	5.34*	8.82	
2, 2	3	5.00*	5.40*	5.34*	7.50	

* guessed value

2. Non-cyclic acetals+benzene

These systems are characterized by three types of contact: (a,b), (a,e) and (b,e). The rules we found as follows:

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

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

(2c) (b,e)-contact. The dispersive coefficients, $C_{be,1}^{dis}$ decrease with increase in chain length, n and m , of the n -alkyl groups adjacent to the n -O- m atoms and decrease with increase with the 'distance' u between the O atoms (Table 11). For the branched acetals we observed an increase of the parameters with increase u .

(2d) (b,e)-contact. Small values for the quasi-chemical parameters were considered to better reproduce the symmetry of the excess properties curves. They are constant for all the linear or branched acetals ($C_{be,1}^{quac}=1.4$, $C_{be,2}^{quac}=2.6$).

3. Cyclic monoethers+benzene

(3a) (b,c)-contact the dispersive coefficients, $C_{be,1}^{dis}$ of the non-polar (b,c)-contact, derived from the properties of benzene+cyclohexane mixtures [10] 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. The quasi-chemical coefficients of the (c,e) contact decrease with increasing ring size, p and approach the values of linear ethers for $p \geq 7$ [2].

(3c) (c,e)-contact. The dispersive coefficients of the (c,e) contact of cyclic ethers $[(c-CH_2)_{p-1}O]$ decrease with increase ring size, p and approach the values of the linear ethers for $p \geq 7$ [2].

(3d) (b,e)-contact. Small values for the quasi-chemical parameters were considered to better reproduce the symmetry of the excess properties curves and are constant for all the cyclic ethers ($C_{be,1}^{quac}=1.4$, $C_{be,2}^{quac}=2.6$) (Table 9).

(3e) (b,e)-contact. The dispersive coefficients of the (b,e) contact of cyclic ethers $[(c-CH_2)_{p-1}O]$ decrease with increase ring size, p (Table 12).

Table 12 Dispersive interchange energy coefficients $C_{be,1}^{dis}$, $C_{be,2}^{dis}$ for contact (b,e), b (C_6H_6) and e [O atom in cyclic monoether $(c-CH_2)_{p-1}O$]

$(c-CH_2)_{p-1}O$	$C_{be,1}^{dis}$	$C_{be,2}^{dis}$
$p=4$, tetrahydrofuran	20.95	24.84
$p=5$, tetrahydropyran	14.27*	16.93

* guessed value

Table 13 Dispersive interchange energy coefficients $C_{be,1}^{dis}$, $C_{be,2}^{dis}$ for contact (b,e), b (C_6H_6) and e (O atom in cyclic diethers)

$(c-CH_2)_{p-1}O_2$	$C_{be,1}^{dis}$	$C_{be,2}^{dis}$
$p=3$, 1,3-dioxolane	7.00*	7.28
$p=4$, 1,3-dioxane	9.20*	9.97
$p=5$, 1,4-dioxane	11.00	12.00

* guessed value

4. Cyclic di-ethers+benzene

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

(4b) (c,e)-contact. The quasi-chemical coefficients of the (c,e) contact increase with increasing ring size, p , from 1,3-dioxolane to 1,3-dioxane and 1,4-dioxane [9].

(4c) (c,e)-contact. The dispersive coefficients of the (c,e) contact of cyclic di-ethers increase with increase ring size, p , from 1,3-dioxolane to 1,3-dioxane and 1,4-dioxane [9].

(4d) (b,e)-contact. Small values for the quasi-chemical parameters constant for all the cyclic di-ethers ($C_{be,1}^{quac}=1.0$, $C_{be,2}^{quac}=3.4$) (Table 9), were adopted.

(4e) (b,e)-contact. The dispersive coefficients of the (b,e) contact of cyclic di-ethers increase with increase ring size, p , from 1,3-dioxolane to 1,3-dioxane and 1,4-dioxane (Table 13).

Comparison with experiment and discussion

The differences between experimental and calculated excess Gibbs energies and enthalpies rarely exceed 2% and this may be well within the limit of experimental error of certain measurements (Tables 1 and 2 and Figs 1–4). The temperature dependence is roughly reproduced even if the H^E are calculated with zero heat capacity of dispersive and quasi-chemical interchange coefficients, $C_{uv,1}^{\text{quac}}$. As expected the largest deviations appear in the case of the branched ethers or acetals. The experimental H^E of the ethylbutylether seem too high and they may need confirmation.

In these system the excess function strongly depend on the contact benzene\oxygen (b,o) 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 (b,e)-contact the steric effect of the linear or branched 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 quasi-chemical interchange coefficients in each given class of oxaalkane: ethers and polyethers [rule (1c) and (1d)], acetals [rule (2d)], cyclic monoethers [rule (3d)] and cyclic di-ethers [rule (4d)].

In contrast the dispersive 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 dispersive interchange coefficients of symmetrical di- n -alkyl ethers containing n -O- n atoms rapidly decrease when n increases. Moreover can be noted the relative constancy of the coefficients of n -O- m type atoms when n is constant and m increases [rule (1c), Table 9].

The influence of the inductive and steric effect of an alkyl group adjacent to a polar X group ($X=\text{O}$) on the dispersive and quasi-chemical interchange parameters $C_{sx,1}^{\text{quac}}$ can be more easily explained if we consider that the interchange energies $\Delta\epsilon_{sx}$ are related to the interaction energies ϵ_{sx}

$$\Delta\epsilon_{sx} = (|\epsilon_{ss}| + |\epsilon_{xx}|)2 - |\epsilon_{sx}| \quad (4)$$

the ϵ values being negative.

In polar–polar or polarizable systems the inductive effect exerted by an alkyl group adjacent to the polar X group increase the dispersive interaction energies ϵ_{sx} and consequently decreases $\Delta\epsilon_{sx}$ and $C_{sx,1}^{\text{dis}}$.

The steric effect acts mainly on the quasi-chemical parameters. In polar-polar or polarizable systems

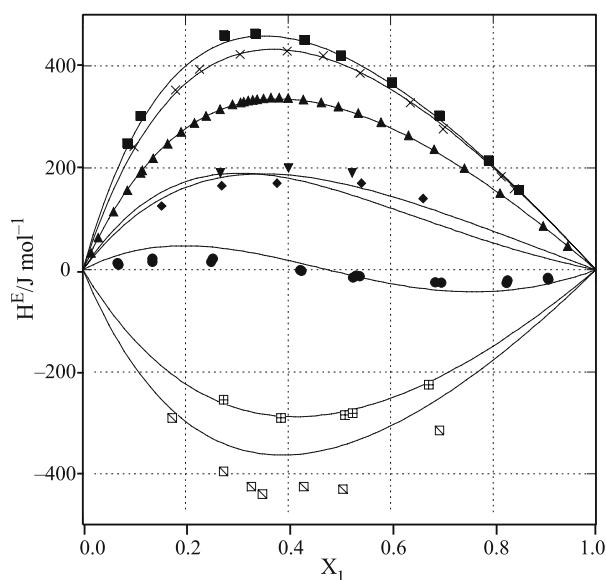


Fig. 1 Comparison of theory with experiments for the molar excess enthalpies, H^E , at 298.15 K, for linear monoethers or polyethers (1)+benzene (2) mixtures vs. x_1 , the mole fraction of component (1): full lines, DISQUAC predictions; points – experimental results: ● – diethylether, [25]; ■ – dihexylether, this work; ▼ – ethylbutylether, [24]; ▲ – dibutylether, [18]; ◆ – dipropylether, [24]; × – dipentylether, this work; + – 2,5,8-trioxanonane, [24] and \ – 3,6,9-trioxaundecane, [24]

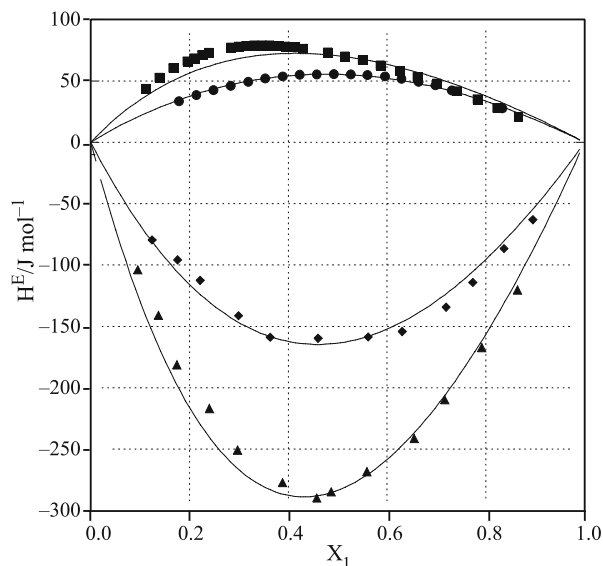


Fig. 2 Comparison of theory with experiments for the molar excess enthalpies, H^E , at 298.15 K, for linear acetals (1)+benzene (2) mixtures vs. x_1 , the mole fraction of component (1): full lines, DISQUAC predictions; points – experimental results: ● – dimethoxymethane, [27]; ■ – diethoxymethane, [27]; ▲ – 1,2-dimethoxyethane, this work; ◆ – dipropylether, [24]

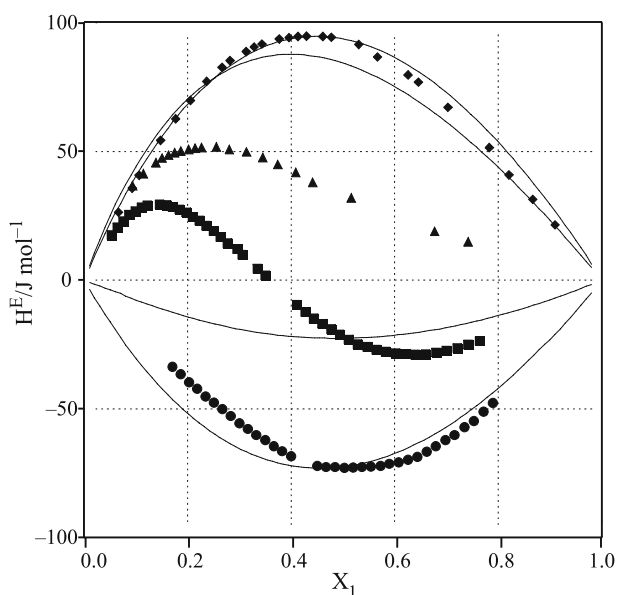


Fig. 3 Comparison of theory with experiments for the molar excess enthalpies, H^E , at 298.15 K, for branched acetals (1)+benzene (2) mixtures vs. x_1 , the mole fraction of component (1): full lines, DISQUAC predictions; points – experimental results:
 ● – 1,1-dimethoxyethane, [27];
 ■ – 1,1-diethoxyethane, [27];
 ▲ – 2,2-dimethoxypropane, [28];
 ◆ – 1,1-dimethoxypropane, [27]

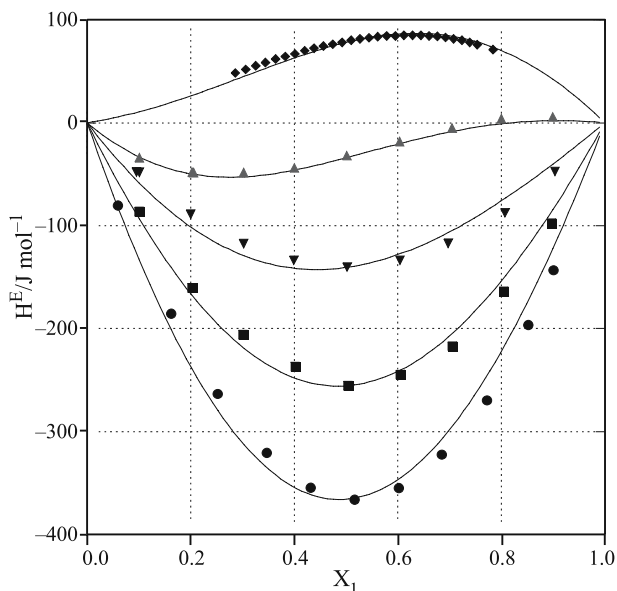


Fig. 4 Comparison of theory with experiments for the molar excess enthalpies, H^E , at 298.15 K, for cyclic ethers(1)+benzene (2) mixtures vs. x_1 , the mole fraction of component (1): full lines, DISQUAC predictions; points – experimental results: ● – tetrahydrofuran, [29]; ■ – tetrahydropyran, [32]; ▲ – 1,4-dioxane, [32]; ◆ – 1,3-dioxolane, [27]; ▼ – 1,3-dioxane, [32]

decrease the electrostatic energies ϵ_{sx} and consequently increase $\Delta\epsilon_{sx}$ and $C_{sx,1}^{quac}$.

The O atom has a relatively small volume compared with that of CH_2 (Table 6) and we can thus ignore its steric effect when calculating the interchange parameters of polyethers [rule (1d) and Table 10].

The proximity of the two atoms in the $\text{O}-(\text{CH}_2)_n-\text{O}$ group in acetals 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 $(c\text{-CH}_2)_{p-1}-\text{O}$ 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 cyclization of open chain ether (cyclic mono-ethers) and of acetals (cyclic di-ethers) results in an increase in the quasi-chemical parameters, while the increase of the dispersive parameters can be ascribed to the ring strain effect.

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