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Excess Enthalpies of 1-Bromobutane + Oxaalkanes at 298.15 K. Comparison with Disquac Predictions[†]

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Excess enthalpies, H^E, at 298.15 K and atmospheric pressure are reported for binary liquid mixtures of 1-bromobutane + oxaalkane of the general formula $CH_3-(CH_2)_{s-1}-O-(CH_2)_{t-1}-CH_3$. The experimental results are interpreted in terms of the DISQUAC group contribution model. The systems are characterized by three types of contact surfaces: oxygen (O), bromo (Br), and alkane. The interchange energy parameters of the alkane/O and alkane/Br contacts were determined independently from the study of *n*-alkane + oxaalkane and *n*-alkane + bromo systems. The interaction parameters of the O/Br contacts are reported in this work. The quasichemical and the dispersive parameters depend on the environment of the O group. The model provides a fairly consistent description of the experimental data.

Introduction

One of most interesting applications of group contribution models is the prediction of thermodynamic properties of liquid polar (X) + polar (Y) mixtures. At temperatures far below the critical region (to minimize the free volume effects) and for X and Y molecules of similar size (to minimize the combinatorial effects), the mixtures show small positive deviations from ideality.

The DISQUAC model used in this work characterizes the X−Y interactions in terms of two sets of parameters, dispersive and quasi-chemical (*3*). The model has been successfully applied to many classes of polar + nonpolar systems.

The available experimental data on 1-bromobutane + oxaalkane mixtures are rather scarce; De Torre et al. (*4*) reported H^E for the 1-bromohexane + dipropyl ether at 303.5 K. No G^E (molar excess Gibbs energy) data have been reported in the literature (*5*).

In this work we have measured the H^E of 1-bromobutane + oxaalkanes with the general formula $CH_3-(CH_2)_{s-1}-O-(CH_2)_{t-1}-CH_3$. Table 1 lists the equimolar H^E values.

Table 1. Excess Molar Enthalpies, H^E ($x_1 = 0.5$), at Various Temperatures of Mixtures of 1-Bromoalkanes (1) + Oxaalkanes (2)[a]

			H^E ($x = 0.5$) J·mol^{-1}	
		T/K	exp	calc
1-bromobutane	dipropyl ether	298.15	34.3	34.3
1-bromobutane	dibutyl ether	298.15	77.5	76.9
1-bromobutane	dipentyl ether	298.15	125.2	124.6
1-bromobutane	butyl methyl ether	298.15	−52.8	−57.3
1-bromobutane	butyl ethyl ether	298.15	−6.3	−5.9
1-bromohexane	dipropyl ether[b]	303.15	7.5	5.7

[a] Comparison of direct experimental results with values calculated using the coefficients $C^{\text{dis}}_{\text{de},1}$ from Table 6 and $C^{\text{quac}}_{\text{de},1}$ from Table 7. *x* = mole fraction, exp = experimental quantity, calc = calculated quantity. [b] De Torre et al. (*4*).

Experimental Section

The molar excess enthalpies, H^E, were determined by means of a flow microcalorimeter (model 2277, LKB-producer AB, Bromma, Sweden). The apparatus and the experimental procedure are described in detail elsewhere (*6*). Fully automatic burets (ABU, from Radiometer, Copenhagen) were used to pump the liquids into the LKB unit; the volume of cylinder was 2.5 cm^3. The accuracy of the buret calibration was 0.5%. All measurements were carried out at (298.15 ± 0.10) 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 differed by <2% from literature data (*7*) over the entire composition range. The experimental uncertainties are $\sigma(x_i) = 0.0005$ and $\sigma(H^E)$/J·mol^{-1} = 0.5 + 0.02/H^E/J·mol^{-1}. All chemicals were commercial products from Fluka. They were used without further purification, and their purities, checked by gas chromatographic analysis, are reported in Table 2.

Table 2. Relative Molar Masses, M_r, Purities, and Densities, ρ, of the Pure Oxaalkanes and 1-Bromobutane at 298.15 K

compound	M_r	purity (mol %)	ρ_{exp} (g cm^{-3})	ρ_{lit} (g cm^{-3})
dipropyl ether	102.176	>99.5	0.74199	0.7419[a]
dibutyl ether	130.23	99	0.76419	0.7641[a]
dipentyl ether	158.283	99	0.78059	0.7790[a]
butyl ethyl ether	102.176	>98	0.74568	0.7448[a]
butyl methyl ether	88.1492	>99	0.73947	0.7393[b]
1-bromobutane	137.019	98	1.26643	1.2687[a]

[a] Riddick et al. (*16*). [b] TRC (*17*).

The molar excess enthalpies, H^E, have been evaluated from the formula

$$H^E = \frac{I^2 R(E/E_c)}{f} \tag{1}$$

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 *f* is the molar flow rate of the mixture.

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Table 3. Experimental Values of Molar Excess Enthalpies, H^E, for 1-Bromobutane (1) + Oxaalkanes (2) Mixtures 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}
		1-Bromobutane + Dipropyl Ether			
0.1603	18.60	0.4883	33.31	0.6562	23.46
0.2413	29.30	0.5147	37.77	0.7179	20.94
0.3889	36.34	0.5600	33.30	0.8358	19.69
0.4590	33.06	0.6292	29.58	0.8945	12.59
		1-Bromobutane + Dibutyl Ether			
0.1645	49.39	0.5415	77.48	0.8253	40.61
0.2825	65.33	0.6116	72.60	0.9043	26.27
0.3713	70.37	0.7026	67.63		
0.4405	77.04	0.7590	47.81		
		1-Bromobutane + Dipentyl Ether			
0.1898	75.11	0.4837	121.5	0.7376	103.1
0.2600	93.00	0.5554	125.2	0.7894	89.35
0.3190	98.33	0.5843	125.6	0.8332	77.87
0.4127	116.9	0.6520	120.9		
		1-Bromobutane + Butyl Methyl Ether			
0.1695	−40.98	0.4495	−57.72	0.6852	−24.86
0.2139	−47.25	0.5212	−51.16	0.7438	−23.69
0.3033	−55.04	0.5921	−38.56	0.8132	−53.34
0.3524	−57.39	0.6202	−40.97	0.8530	0.952
		1-Bromobutane + Butyl Ethyl Ether			
0.1918	−5.42	0.5032	−6.96	0.8710	0.121
0.3877	−5.88	0.5587	−6.07	0.9101	0.042
0.4577	−6.51	0.7715	0.00		
0.4871	−6.59	0.8351	0.093		

Table 4. Values of the Coefficients a_i, Eq 3, Standard Deviations $\sigma(H^E)$, Eq 4, of Experimental Excess Molar Enthalpies H^E, at 298.15 K, for 1-Bromobutane (1) + Oxaalkanes (2)

oxaalkane	a_0 (J·mol^{-1})	a_1 (J·mol^{-1})	a_2 (J·mol^{-1})	a_3 (J·mol^{-1})	$\sigma(H^E)$ (J·mol^{-1})
dipropyl ether	137.41	−35.84	3.0		
dibutyl ether	310.08	−33.70	3.6		
dipentyl ether	495.01	68.30	47.15	2.8	
butyl methyl ether	−211.38	162.04	120.29	89.35	3.0
butyl ethyl ether	−25.13	24.23	19.71	0.8	

Table 5. Relative Volumes, r_i, Total Surfaces, q_i, and Molecular Surface Fractions α_{si} (s = a, Aliphatic; e, Oxygen; d, Bromo) Calculated from the Group Increments $r_G = V_G/V_{CH4}$ and $q_G = A_G/A_{CH4}$ Estimated by Bondi's Method (Bondi, 1968) ($V_{CH4} = 17.12 \times 10^{-6}$ m^3 mol^{-1}; $A_{CH4} = 2.90 \times 10^5$ m^2 mol^{-1})

compound	r_i	q_i	α_{ai}	α_{ei}	α_{di}
1-bromobutane	3.4322	2.8448	0.7479	0.0000	0.2521
1-bromohexane	4.2249	3.2414	0.7787	0.0000	0.2213
dipropyl ether	4.2033	3.5310	0.9414	0.0586	0.0000
dibutyl ether	5.3984	4.4621	0.9536	0.0464	0.0000
dipentyl ether	6.5935	5.3931	0.9616	0.0384	0.0000
butyl methyl ether	3.6057	3.0655	0.9325	0.0675	0.0000
butyl ethyl ether	4.2033	3.5310	0.9414	0.0586	0.0000

The molar flow rate f_i of the ith component flowing into the mixing cell is given by

$$f_i = \frac{\rho_i}{M_i} F_i \tag{2}$$

where ρ_i and M_i are the density and molar mass, respectively, and F_i is the volumetric flow rate of component i.

The densities were determined with a vibrating densimeter (model DMA 58 Anton Paar) with a reproducibility of 10^{-5} g cm^{-3} at 298.15 K. The calibration of the densimeter was made with dried air ($d^\circ_{air} = 0.00118$ g/cm^3) and water ($d^\circ_w = 0.99705$ g/cm^3). Our values of density agreed within 0.2% with literature data (see Table 2).

The experimental H^E values, reported in Table 3, were fitted to the Redlich−Kister smoothing equation (where sm = smoothed quantity and x = mole fraction):

$$H^E_{sm} = x_1 x_2 \sum_{i=0}^{n-1} a_i (x_1 - x_2)^i \tag{3}$$

The values of the coefficients a_i and the standard deviations $\sigma(H^E)$ given by

$$\sigma(H^E) = \left[\frac{\sum_i (H^E_{i,sm} - H^E_{i,exp})^2}{N - n}\right]^{1/2} \tag{4}$$

were determined by least-squares analysis and are reported in Table 4. N is the number of experimental points, and n is the number of coefficients a_i.

Theory

DISQUAC is an extended quasi-chemical group-contribution model based on Guggenheim's lattice theory (*2*, *3*). In the classic model (*8*), molecules are assumed to possess one of several types of contacts s or v and occupy the sites of a lattice with coordination number z. The type of lattice and the assignment of contact points are arbitrary and irrelevant in applications to liquid mixtures and can be avoided by using the group-surface interaction version of the theory (*9*). In the classical model, the interchange energies of every (s,v) contact generate nonrandomness to the extent expressed by z, which is the same for all the contacts. For nonpolar systems, the random-mixing equations are obtained for $z = \infty$. In mixtures containing a single pair of contact, z may be treated as an adjustable parameter. DISQUAC circumvents the difficulty of treating mixtures containing pairs of groups of different polarities by taking into account a dispersive, random contribution for every contact ($z = \infty$), eventually supplemented by an electrostatic, nonrandom contribution treated quasi-chemically with a constant $z = 4$.

The equations used to calculate thermodynamic properties are the same as in other applications (*10*) and need not to be repeated here.

Assessment of Geometrical Parameters

1-Bromobutane + oxaalkanes mixtures are regarded as possessing three types of contact surfaces: type a, aliphatic (CH_3, CH_2 groups, which are assumed to exert the same force field); type e, oxygen (O); type d, bromo (Br). The three types of surface a, e, and d generate three pairs of contacts: (a,e), (a,d), and (e,d).

The adopted relative volumes, r_G, and contact surfaces, q_G, of these groups are those estimated by Bondi (*11*) and have been used to calculate additively the total volumes r_i and surfaces q_i as well as the alkane, oxygen, and bromo surface fractions α_{ai}, α_{ei}, and α_{di} (Table 5).

Estimation of Interchange Parameter

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 a 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 adjusted values, usually few, on smooth curves and estimating the other values by interpolation or extrapolation.

Table 6. Dispersive Interchange Coefficients $C^{\text{dis}}_{\text{de},1}$ and $C^{\text{dis}}_{\text{de},2}$ for Contacts (d,e) (d, Bromo; e, Oxygen) of 1-Bromobutane + Oxaalkanes Mixtures

oxaalkane	$C^{\text{dis}}_{\text{de},1}$ [a]	$C^{\text{dis}}_{\text{de},2}$
dipropyl ether	5.0	8.15
dibutyl ether	3.4	6.80
dipentyl ether	2.8	5.50
butyl methyl ether	6.0	10.5
butyl ethyl ether	5.5	9.60

[a] Guessed values.

Table 7. Quasichemical Interchange Coefficients $C^{\text{quac}}_{\text{de},1}$ and $C^{\text{quac}}_{\text{de},2}$ for Contacts (d,e) (d, Bromo; e, Oxygen) of 1-Bromobutane + Oxaalkanes Mixtures

oxaalkane	$C^{\text{quac}}_{\text{de},1}$ [a]	$C^{\text{quac}}_{\text{de},2}$
dipropyl ether	−0.4	−0.8
dibutyl ether	−0.8	−1.6
dipentyl ether	−1.0	−2.0
butyl methyl ether	−1.0	−0.2
butyl ethyl ether	−0.4	−0.8

[a] Guessed values.

Table 8. Quasichemical Interchange Coefficients, $C^{\text{quac}}_{\text{ae},1}$ and $C^{\text{quac}}_{\text{ae},2}$ for Contacts (a,e) (a, Aliphatic; e, Oxygen) of Oxaalkanes + *n*-Alkanes Mixtures (Kehiaian et al., 1989)

oxaalkane	$C^{\text{quac}}_{\text{ae},1}$	$C^{\text{quac}}_{\text{ae},2}$
dipropyl ether	2.8	2.9
dibutyl ether	2.6	1.5
dipentyl ether	2.5	1.0
butyl methyl ether	3.4	5.6
butyl ethyl ether	3.0	4.8

In other group-contribution methods, the interaction parameters, reported as constant, are in reality values that depend on the number and nature of the systems considered in the averaging.

The theoretical treatment of mixtures requires the preliminary estimation of the (a,e) and (a,d) contact parameters from thermodynamic properties of oxaalkane + *n*-alkane and 1-bromoalkane + n alkane mixtures.

Oxaalkane + *n*-Alkane Mixtures. Kehiaian et al. (*12*) have recently studied this kind of system using the DISQUAC model. The dispersive interchange parameters $C^{\text{dis}}_{\text{ae},1} = 10.6$ and $C^{\text{dis}}_{\text{ae},2} = 18.2$ are constant. However, the quasichemical parameters, $C^{\text{quac}}_{\text{ae},1}$, decrease with an increase in the number of alkyl groups adjacent to the O group (see Table 8).

1-Bromoalkane + *n*-Alkane Mixtures. The interchange parameters, $C^{\text{dis}}_{\text{ad},1}$ and $C^{\text{quac}}_{\text{ad},1}$, of the aliphatic-bromo contact have been obtained by Kehiaian and Velasco (*13*); the dispersive $C^{\text{dis}}_{\text{ad},1} = 0.200$ and $C^{\text{dis}}_{\text{ad},2} = 0.300$ and the quasi-chemical parameters $C^{\text{quac}}_{\text{ad},1} = 2.02$ and $C^{\text{quac}}_{\text{ad},2} = 3.18$ are constant.

Oxaalkane + 1-Bromoalkane Mixtures. Since the (a,e) and (a,d) contact parameters are known, it remains to determine the (d,e) contact parameters. The first point to establish was the ratio of quasi-chemical to dispersive contribution for this contact. Preliminary calculations were performed assuming that the (d,e) contact is either entirely dispersive or entirely quasi-chemical. It appeared that the shapes of the H^{E} curves are best reproduced when a nonnegligible, negative, quasi-chemical contribution, $C^{\text{quac}}_{\text{de},1}$, is considered.

The enthalpic dispersive and quasichemical coefficients (Tables 6 and 7) decrease regularly with increasing *s* and *t*, the chain length of the alkyl group adjacent to the O group.

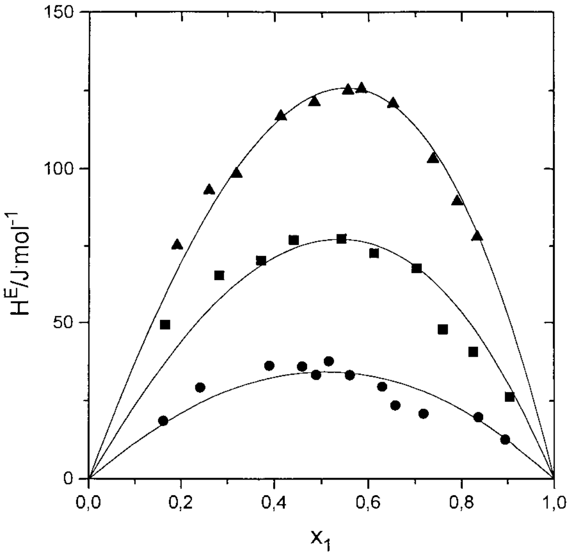

Figure 1. Comparison of theory with experiment for the molar excess enthalpies, H^{E}, at 298.15 K of bromobutane (1) + oxaalkane (2) vs x_1 , the molar fraction of bromobutane. Full lines are for predicted values, and points are for experimental H^{E} results: ●, dipropyl ether; ■, dibutyl ether; ▲, dipentyl ether.

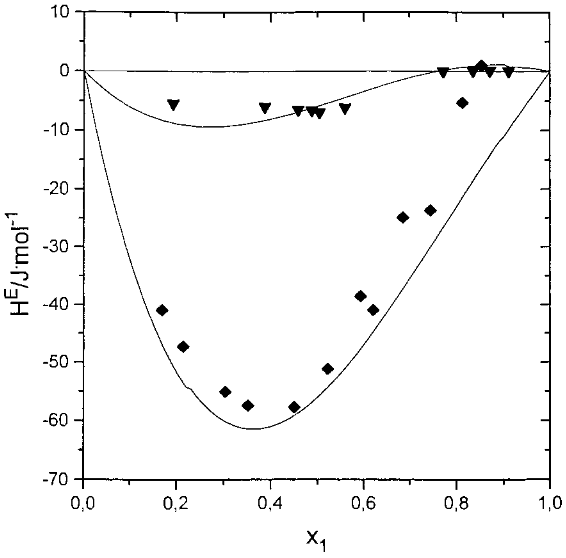

Figure 2. Comparison of theory with experiment for the molar excess enthalpies, H^{E}, at 298.15 K of bromobutane (1) + oxaalkane (2) vs x_1, the molar fraction of bromobutane. Full lines are for predicted values, and points are for experimental H^{E} results: ◆, butylmethyl ether; ▼, butylethyl ether.

Previous investigations of many classes of systems showed that the Gibbs energy coefficients change with the structure of components but more slowly than the enthalpic coefficients.

Calculated and experimental H^{E} data are compared in Table 1. Figures 1 and 2 show a comparison of the calculated and experimental molar excess enthalpies H^{E}.

Discussion and Conclusions

In previous papers (*14*, *15*) the DISQUAC model was applied to mixtures containing a polar compound + another polar or a polarizable compound; these calculations suggest that polar/polar or polar/polarizable group contacts are better described if one assumes they are entirely dipersive rather than using an entirely quasi-chemical approach.

In the present analysis it has been necessary to consider a negative quasi-chemical contribution. With respect to the model parameters representing group-pair interchange energies, the relative large dispersive term shows that the degree of orientational order changes only slightly in the process of interchanging the contacts.

In the mixing of 1-bromobutane + oxaalkane the following effects (disregarding the dispersive ones) take place: (a) disappearance of dipole−dipole interactions in the pure components (oxaalkane, bromobutane) and (b) appearance of specific Br−O interactions causing a negative contribution to the excess enthalpy. In particular the negative quasi-chemical parameters indicate that the interactions between bromobutane and an oxaalkane are very strong. In this work we have dealt with only linear monofunctional molecules, and the trend of our interchange coefficients can be interpreted in terms of steric and inductive effects only exerted by the alkyl groups adjacent to the O group of ether.

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