EXCESS ENTHALPIES OF AROMATIC ETHER OR AROMATIC KETONE(1)+*n*-HEPTANE(2) MIXTURES
DISQUAC analysis

Bruno Marongiu, Alessandra Piras, Silvia Porcedda and *Enrica Tuveri*

Dipartimento di Scienze Chimiche, Università di Cagliari, Cittadella Universitaria di Monserrato, 09042 Cagliari, Italy

A flow microcalorimeter has been used to determine excess enthalpies, H^E, at 298.15 K, of binary mixtures of aromatic ether or aromatic ketone(1)+*n*-heptane(2). All systems investigated are characterized by positive values of H^Es. These data along with the data available in the literature on H^E, molar excess Gibbs energies, G^E, and liquid-vapour equilibria (LVE) are treated in the framework of DISQUAC. 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 occurrence of the 'hetero-proximity effect' between C_6H_5– and –CO– or –O– groups is suggested by the variation of the interchange parameters.

Keywords: data, DISQUAC model, ethers, excess enthalpy, ketones, n-heptane

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 to dispersive forces, always present, whatever to kind of molecule, and another QUAC, depending on specific chemical interaction, and relate to the kind of molecule under study. The quasichemical term is zero for mixtures of apolar compounds.

In several papers [4–7] we have reported the results concerning the ability of DISQUAC 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], thiaalkanes [6] and alkynes [7] with organic solvents such as alkanes, cyclohexane, benzene or CCl$_4$.

One of the basic assumption in group contribution theories, independently of the particular method used, is that each group is situated in a well-defined intramolecular environment. But to better reproduce the interaction energies the model we adopted permit to found interaction parameters, between different kinds of group, $C_{st,l}$ that vary regularly with the molecular structure of compounds involved. For example the steric effect exerted by the chain length of the adjacent alkyl group (R–) in aliphatic aldehydes [8], (–CHO group), ketones [9], (CO group) or tertiary amines [10], (–N< group), is one among the many intramolecular factors which alter the values of the interchange energy parameters.

In polyfunctional molecules also the proximity of two identical or different groups in a given molecule usually has a quite strong influence on the interchange coefficients. This 'proximity effect' has previously been demonstrated for molecules containing the following pairs of identical group ('homoproximity'): –O–·····–O– [5], –S–·····–S– [6] and >N–·····–N< [11]. These examples have been confined to symmetrical molecules containing two identical groups X, X(CH$_2$)$_n$X. The variable *n* affects only the (X, CH$_2$)-contact energies. The study of asymmetrical molecules containing two different groups X and Y, X(CH$_2$)$_n$Y, is much more difficult, the variable *n* affecting the energies of three contact simultaneously: (X,CH$_2$), (Y,CH$_2$) and (X,Y).

As expected our preliminary calculations showed that the interaction parameters of mixtures of aromatic ether or aromatic ketone with alkane 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 [4, 12] 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 the DISQUAC treatment and experimental results concerning two kinds of mixtures: aromatic ether of general formula $(C_6H_5–(CH_2)_n–O–CH_3)+n$-heptane and aromatic ketone of general formula $(C_6H_5–(CH_2)_n–CO–CH_3)+n$-heptane.

The input data are the molar excess Gibbs energies, G^E, and the molar excess enthalpies, H^E, obtained from liquid-vapor equilibrium and calorimetric measurements, respectively.

Thermodynamic data are rather scarce for the mixtures under study. For several systems, in particular those containing long chain ketones and ethers, no data are available, for other only a single source of data exists. The sources of available experimental data and some characteristic values are collected in Tables 1–3. The G^E data concerning the mixtures under investigation are limited to methoxybenzene [13]. 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

Table 1 Molar excess Gibbs energies G^E (T; $x_1=0.5$) of aromatic ether or aromatic ketone(1)+n-alkane(2) mixtures at various temperatures T and equimolar composition: comparison of direct experimental results (exp.)[a] with values calculated (calc.) using the coefficients $C_{uv,l}^{dis}$ and $C_{uv,l}^{quac}$ from Tables 8–9

| Component 2 | T/K | G^E (T;$x_1=0.5$)/J mol^{-1} | | Source of exp. data |
		calc.	exp.	
		methoxybenzene(1)		
n-hexane	333.15	701	699	[13]
	343.15	686	675	[13]
n-heptane	359.15	687	644	[13]
	368.15	673	631	[13]

[a]Calculation (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

Table 2 Molar excess enthalpies H^E ($x_1=0.5$) of aromatic ether or aromatic ketone(1)+n-alkane mixtures at 298.15 K and equimolar composition: comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficients $C_{uv,l}^{dis}$ and $C_{uv,l}^{quac}$ from Tables 8–9

| Component 2 | H^E (T;$x_1=0.5$)/J mol^{-1} | | Source of exp. data |
	calc.	exp.	
	methoxybenzene(1)		
n-heptane	1277	1378	[15]
		1278	this work
	benzylmethylether(1)		
n-heptane	1213	1244	[15]
		1213	this work
	1-phenyl-2-methoxyethane(1)		
n-heptane	1149	1148	[15]
	acetophenone(1)		
n-pentane	1249	1339	[16]
n-hexane	1382	1438	[16]
n-heptane	1504	1502	this work
		1498	[17]
	phenyl-2-propanone(1)		
n-hexane	1539	1662	[16]
n-heptane	1667	1675	[17]
	4-phenyl-2-butanone(1)		
n-hexane	1479	1146	[16]
n-heptane	1605	1604	this work

Table 3 Logarithm of activity coefficients at infinite dilution, $\ln\gamma_2^\infty$ of aromatic component relative to the mixtures aromatic ether or aromatic ketone(1)+n-alkane(2) at various temperatures T: comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficients $C_{uv,l}^{dis}$ and $C_{uv,l}^{quac}$ from Tables 8–9

Component 2	T/K	$\ln\gamma_2^\infty$		Source of exp. data
		calc.	exp.	
methoxybenzene(1)				
n-pentane	293.15	3.1	3.6	[18]
n-hexane	293.15	3.7	3.9	[18]
n-heptane	293.15	4.3	4.2	[18]
acetophenone(1)				
n-pentane	293.15	5.5	6.0	[18]
	298.15	5.4	5.4	[19]
n-hexane	293.15	7.4	6.8	[18]
	298.15	7.2	6.1	[19]
			6.7	[20]
	303.15	7.0	6.0	[21]
	337.15	5.8	6.4	[22]
	352.15	5.3	5.4	[22]
n-heptane	293.15	9.8	7.6	[18]
	298.15	9.4	6.8	[19]
	337.15	7.3	7.0	[22]
	352.15	6.7	6.0	[22]
n-octane	337.15	9.2	7.7	[22]
	352.15	8.3	6.6	[22]
n-nonane	337.15	11.3	8.4	[22]
	352.15	10.1	7.3	[22]
phenyl-2-propanone(1)				
n-pentane	298.15	6.2	7.7	[23]
n-hexane	298.15	8.7	8.6	[23]

was accounted for in terms of the second virial coefficient estimated by the Hayden and O'Connell [14] method. H^Es data exist only for the mixtures in alkanes of the first three terms of both classes [15–17]. Also activity coefficient are scarce, several source report the values relative to the hydrocarbon of mixtures containing an aromatic ketone and an n-alkane [18–23].

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 ≥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 4.

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 [25]. Fully automatic burettes (ABU80, Radiometer, Copenhagen) 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:

$$m_i = \varphi_i\rho_i/M_i \qquad (1)$$

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

Table 4 Supplier, molar masses, purities and densities at 298.15 K of aromatic ethers, aromatic ketones and *n*-heptane

Compound	Supplier	M/g mol^{-1}	Purity/%	ρ_{exp}/g cm^{-3}	ρ_{lit}/g cm^{-3}
methoxybenzene	Aldrich	108.14	99.0	0.98917	0.98932[a]
benzylmethylether	Aldrich	122.17	98.0	0.95870	–
acetophenone	Aldrich	120.15	99.9	1.02382	1.02382[a]
4-phenyl-2-butanone	Aldrich	148.21	98.0	0.98434	–
n-heptane	Fluka	84.16	99.5	0.77386	0.77389[a]

[a][24]

Table 5 Experimental values of the molar excess enthalpies, H^E, of binary mixtures of aromatic ether or aromatic ketone(1)+*n*-heptane, 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}
		methoxybenzene+*n*-heptane			
0.1189	595.5	0.4028	1228.4	0.7296	1025.3
0.1443	694.9	0.4735	1269.0	0.7825	860.7
0.1836	838.8	0.5029	1275.1	0.8780	542.6
0.2522	1027.6	0.5743	1252.9	0.9310	312.9
0.3360	1159.9	0.6693	1141.9		
		benzylmethyl ether+*n*-heptane			
0.1037	506.5	0.4355	1206.5	0.7552	930.0
0.1617	714.9	0.4646	1217.0	0.8223	738.7
0.2244	908.7	0.5364	1211.1	0.9025	454.8
0.3026	1030.2	0.6067	1155.1		
		acetophenone+*n*-heptane			
0.1116	837.6	0.3858	1485.1	0.7153	1186.9
0.1732	1053.5	0.4558	1512.8	0.7903	936.5
0.2390	1309.5	0.4852	1507.7	0.8341	779.7
0.2952	1410.5	0.5568	1466.6	0.8829	579.3
0.3203	1431.3	0.6262	1364.7		
0.3665	1135.5	0.6983	1040.8		
		4-phenyl-2-butanone+*n*-heptane			
0.0892	784.5	0.4235	1601.5	0.7231	1270.8
0.1403	1048.9	0.4948	1612.9	0.7966	1026.1
0.1967	1246.2	0.5663	1561.0	0.8393	860.8
0.2686	1429.7	0.5950	1549.6	0.9073	517.2
0.3287	1530.1	0.6620	1419.6		

(Anton Paar, model DMA 58) with a reproducibility of $1 \cdot 10^{-5}$ g cm^{-3}.

The molar excess enthalpies have been evaluated from the formula

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

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 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 [26] over the entire composition range.

Results and discussion

The experimental H^E data are collected in Table 5. The H^E values were fitted to the smoothing Redlich–Kister equation:

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

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 6.

All mixtures investigated containing ether and ketone+*n*-heptane exhibit positive values of H^{E}s. At equimolar composition, values are in the range of +1213÷+1605 J mol^{-1}.

Our experimental results generally agree with data from other authors (Table 2) with the exception of the values relative to the methoxybenzene+*n*-heptane system. Our value at equimolar composition (1278 J mol^{-1}) is significantly lower than the corresponding values found by Kehiaian [15] +1348 J mol^{-1}. Moreover even if no measures were performed on 4-phenyl-2-butanone+*n*-heptane mixtures, the values of H^{E} reported in literature [16] are not congruent with our H^{E} experimental determination on the same ketone plus *n*-heptane at the same temperature.

Theory

Each class under examination: aromatic ether+alkane and aromatic ketone+alkane is regarded as possessing three types of contact surfaces: type a, aliphatic (CH$_3$, CH$_2$ groups); type b, aromatic (C$_6$H$_5$ group); type e, ether (–O– group), type k, ketone (–CO– group). The equations used to calculate G^{E} and H^{E} are the

same as in other applications [4] and need not be repeated here.

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,k 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 r_i, volume of the ith molecule, q_i, surface of the ith molecule and α_{vi}, surface fraction of the surface of type v in the ith molecule, were calculated from the relative group parameters, the volumes of each group r_G and surfaces of each group 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 [27] have been adopted. The values of r_G and q_G used to calculate the geometrical parameters of the molecule under study (reported in Table 7) are the same reported in previous papers [5, 28].

Estimation of interaction parameters

The groups investigated in the present work are no polar (contact a), polarizable (contact b) or weakly polar (contacts e and k). 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.

Table 6 Values of the coefficients, a_i, standard deviations, $\sigma(H^{E})$, of molar excess enthalpies, H^{E} at 298.15 K, for aromatic ether or aromatic ketone(1)+*n*-heptane(2) mixtures

Component (1)	$a_0/$	$a_1/$	$a_2/$	$a_3/$	$\sigma(H^{E})/$
	J mol^{-1}				
methoxybenzene	5111.4	–301.16	538.7	–	16
benzylmethyl ether	4852.4	–100.57	731.53	–	12
acetophenone	6008.9	–907.67	1477.8	–1392.9	17
4-phenyl-2-butanone	6415.1	–506.11	2038	–2270	10

Table 7 Relative volumes, r_i, relative total surfaces, q_i, and molecular surface fractions, α_{vi}, (v=a, b, e, k) of ethers, ketones and *n*-heptane. Relative quantities are calculated with respect to the values of the corresponding quantity of methane

Compound	r_i	q_i	α_{ai}	α_{bi}	α_{ki}	α_{ei}
methoxybenzene	3.6922	2.7759	0.2634	0.6621	0.0000	0.0745
benzylmethyl ether	4.2897	3.2414	0.3692	0.5670	0.0000	0.0638
acetophenone	4.1595	3.1207	0.2343	0.5889	0.1768	0.0000
4-phenyl-2-butanone	5.3546	4.0517	0.4102	0.4536	0.1362	0.0000
n-heptane	4.5847	3.7891	1.0000	0.0000	0.0000	0.0000

Table 8 Dispersive and quasichemical interchange coefficients for the contacts (a,e) and (b,e). The (a,e) contact were determined from mixtures of aliphatic ether of general formula $CH_3–(CH_2)_n–O–CH_3$+n-alkane [5]. The (b,e) contact were determined from mixtures of aromatic ether of general formula $C_6H_5–(CH_2)_n–O–CH_3$+n-alkane

n	$C_{ae,1}^{dis}$	$C_{ae,2}^{dis}$	$C_{ae,1}^{quac}$	$C_{ae,2}^{quac}$	$C_{be,1}^{dis}$	$C_{be,2}^{dis}$	$C_{be,1}^{quac}$	$C_{be,2}^{quac}$
0	10.6	18.2	4.2	7.0	19.33	27.32	6.0	12.0
1	10.6	18.2	3.8	6.4	16.14	24.41	6.0	12.0
2	10.6	18.2	3.5	5.9	14.67	22.19	6.0	12.0
≥3	10.6	18.2	3.4	5.6	14.67*	22.19*	6.0*	12.0*

*guessed values

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

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.

Aromatic ethers+n-alkanes

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. DIS. The $C_{ab,1}^{dis}$ dispersive coefficients were assumed constant for every system. The values taken from literature [29] are: $C_{ab,1}^{dis}$=0.26 and $C_{ab,2}^{dis}$=0.56.

(1b) (a,e)-contact. DISQUAC. The interchange coefficients, (collected in Table 8) were calculated from properties of aliphatic ethers+n-alkanes mixtures [5]. 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. To choose the correct (a,e) parameter we assumed that the phenyl group contained in an aromatic ether play the same role of a methyl group in an aliphatic ether.

(1c) (b,e)-contact. DISQUAC. The quasi-chemical parameters were constant for all the aromatic ethers here considered. The dispersive coefficients, $C_{be,1}^{dis}$ decrease as n (number of methylene groups interposed between the polar group and the benzene-derived group) increase. These results are reported in Table 8.

Aromatic ketones+n-alkanes

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

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

(2b) (a,k)-contact. DISQUAC. The interchange coefficients, (collected in Table 9) derived from properties of aliphatic ketones+n-alkanes mixtures [9] increase with n. The quasi-chemical coefficients, $C_{ak,1}^{quac}$ decrease as the length of the molecule increase. To choose the correct (a,k) parameter we assumed that the phenyl group contained in the aromatic ketone play the same role of a methyl group.

(2c) (b,k)-contact. DIS. Also the (b,k) parameters are reported in Table 9. The quasichemical parameters were set equal to zero to better reproduce the symmetry of the excess properties curves. The dispersive coefficients, $C_{bk,1}^{dis}$ decrease as n increase.

Table 9 Dispersive and quasi-chemical interchange coefficients for the contacts (a,k) and (b,k). The (a,k) contact were determined from mixtures of aliphatic ketone of general formula $CH_3–(CH_2)_n–CO–CH_3$+n-alkane [9]. The (b,k) contact were determined from mixtures of aromatic ketone of general formula $C_6H_5–(CH_2)_n–CO–CH_3$+n-alkane

| n	$C_{ak,1}^{dis}$	$C_{ak,2}^{dis}$	$C_{ak,1}^{quac}$	$C_{ak,2}^{quac}$	$C_{bk,1}^{dis}$	$C_{bk,2}^{dis}$	$C_{bk,1}^{quac}$	$C_{bk,2}^{quac}$
0	2.90	5.05	6.08	8.25	4.2	7.4	0.0	0.0
1	3.25	6.16	5.35	6.35	1.0	6.2	0.0	0.0
2	3.31	6.92	5.29	5.94	1.8	5.9	0.0	0.0
≥3	3.31	6.92	5.29	5.94	1.8*	5.9*	0.0*	0.0*

*guessed values

Discussion on theoretic results

Concerning the final results, since the first inter-change parameters, reported in Tables 8–9, were derived from the experimental values of methoxy-benzene+n-hexane at 333.15 K, the agreement between experimental and calculated excess Gibbs energies (Table 1) is good. Moreover, the temperature dependence is roughly reproduced.

It is satisfactory also the result of the comparison between DISQUAC predictions and experimental data for the excess enthalpies, at 298.15 K, of aromatic ethers or aromatic ketones+n-heptane (Table 2 and Figs 1 and 2). The lack of data at temperature different from 298.15 K do not permit to compare the temperature dependence, that usually is not well reproduced when, as in this case, the H^Es are calculated with zero heat capacity of dispersive and quasi-chemical interchange coefficients, $C_{uv,3}$.

In Table 3 are collected the experimental logarithm of activity coefficients at infinite dilution of the n-alkane, in γ_2^∞, and the calculated ones that often results overestimated, especially when the size of the second component increases.

The trend of the coefficients listed in Tables 8–9 may be explained by general rules. The dispersive coefficients for the (a,Y) contact are constant (Y=O) or slightly increase (Y=CO) as n increase because of inductive effect. The quasichemical coefficients for the (a,Y) contact (Y=O or CO) increase as n increase because of steric effect. The dispersive coefficients of
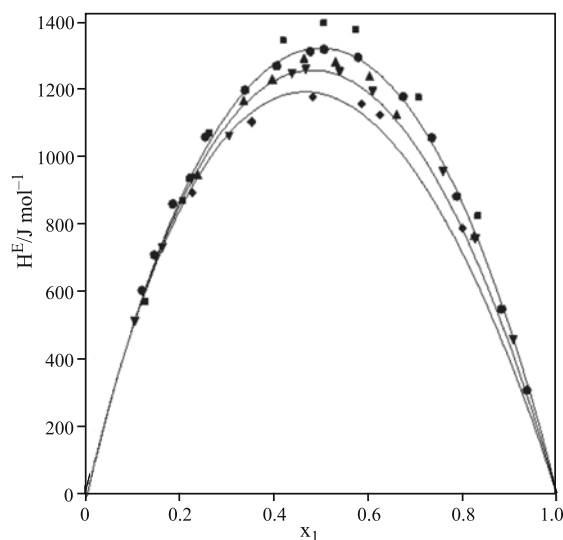
Fig. 1 Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for aromatic ether of general formula C_6H_5–O–$(CH_2)_n$ (n=0,1,2) (1)+n-heptane (2) mixtures vs. x_1, the mole fraction of component (1): full lines, DISQUAC predictions; points, experimental results: ● – n=0, this work; ■ – n=0 [14]; ▼– n=1, this work; ▲ – n=1, [14]; ◆ – n=2, [14]
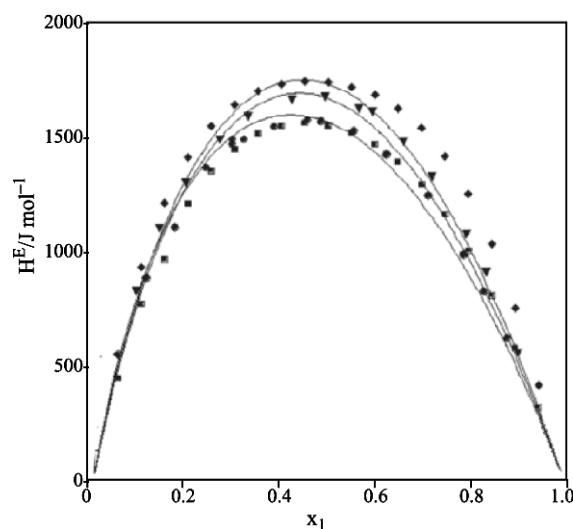
Fig. 2 Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for aromatic ketones of general formula C_6H_5–$(CH_2)_n$–CO–CH_3 (n=0,1,2) (1)+n-heptane (2) mixtures vs. x_1, the mole fraction of component (1): full lines, DISQUAC predictions; points, experimental results: ● – n=0, this work; ■ – n=0, [16]; ◆– n=1, [16]; ▼– n=2, this work

the X/Y contact (X=C_6H_5–; Y=O or CO) decrease as n increase. The X/Y quasichemical parameters are constant for both classes, i.e. they are not influenced by the reciprocal distance also when short molecules are involved. This behaviour is called proximity effect. Generally, the values of interchange coefficients, when not constant, vary only for the first three or four terms of the series so we expect that will be possible to predict the values of excess properties for mixtures containing a n-alkane and an aromatic ether or ketone with three or more CH_2– groups. The guessed values are reported in Tables 8–9 together with the other estimated coefficients.

Moreover, the value of the $C_{be,1}^{dis}$ and $C_{bk,1}^{dis}$ parameters for n≥3, should attempt the values determined from mixtures of aliphatic ether+benzene and aliphatic ketone+benzene, respectively. No papers reporting a DISQUAC treatment on ethers+ benzene are available in literature. Yahiaoui et al. [30] reported the $C_{bk,1}^{dis}$ and $C_{bk,1}^{quac}$ values obtained for an only ternary mixture containing a ketone and benzene: 2-butanone+benzene+n-octane. The authors found values that partially agree with our deductions: $C_{bk,1}^{dis}$=5.40, $C_{bk,2}^{dis}$= 5.50, $C_{bk,1}^{quac}$=0 and $C_{bk,2}^{quac}$=0.

Acknowledgements

References

1 H. V. Kehiaian, Fluid Phase Equilib., 13 (1983) 243.

2 H. V. Kehiaian, Pure Appl. Chem., 57 (1985) 15.

3 E. A. Guggenheim, Mixtures. Oxford University Press, London 1952.

4 H. V. Kehiaian and B. Marongiu, Fluid Phase Equilib., 40 (1988) 23.

5 H. V. Kehiaian, M. R. Tinè, L. Lepori, E. Matteoli and B. Marongiu, Fluid Phase Equilib., 46 (1989) 131.

6 B. Marongiu, G. Marras, B. Pittau and S. Porcedda, Fluid Phase Equilib., 97 (1994) 127.

7 D. Falconieri, B. Marongiu, A. Piras and S. Porcedda, Thermochim. Acta, 418 (2004) 85.

8 I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H. V. Kehiaian, Fluid Phase Equilib., 12 (1983) 125.

9 H. V. Kehiaian, S. Porcedda, B. Marongiu, L. Lepori and E. Matteoli, Fluid Phase Equilib., 63 (1991) 23.

10 I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H. V. Kehiaian, Fluid Phase Equilib., 9 (1982) 49.

11 I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H. V. Kehiaian, Fluid Phase Equilib., 11 (1983) 1.

12 B. Marongiu, A. Piras, S. Porcedda and E. Tuveri, J. Therm. Anal. Cal., 91 (2008) 37.

13 M. A. Yanez Torres, S, B. Bottini, E. A. Brignole, V. Sanhueza and R. Reich, Fluid Phase Equilib., 71 (1992) 85.

14 G. Hayden and J. P. O'Connell, Ind. Eng. Chem. Process Des. Dev., 14 (1975) 209.

15 H. V. Kehiaian, K. Sosnkowoska-Kehiaian and R. Hryniewicz, J. Chim. Phys.-Chim. Biol., 68 (1971) 922.

16 J.-P. E. Grolier, O. Kiyhoara and G. C. Benson, J. Chem. Thermodyn., 9 (1977) 697.

17 O. Urdaneta, S. Hamam, Y. P. Handa and G. C. Benson, J. Chem. Thermodyn., 11 (1979) 851.

18 E. R. Thomas, B. A. Newman, T. C. Long, D. A. Wood and C. A. Eckert, J. Chem. Eng. Data, 27 (1982) 399.

19 P. Vernier, C. Rainbault and H. Renon, J. Chim. Phys., 66 (1969) 429.

20 J. C. Leroi, J. C. Masson, H. Renon, J. F. Fabriees and H. Sannier, Ind. Eng. Chem., 16 (1977) 139.

21 M. N. Pul'tsin, A. A. Gaile and V. A. Proskuryakov, Zh. Fiz. Khim., 47 (1973) 751.

22 Y. I. Leitman and A. A. Gaile, Zh. Fiz. Khim., 45 (1971) 2113.

23 J.- P. Monfort, J. Vidal and H. Renon, J. Chim. Phys., 67 (1970) 748.

24 J. A. Riddick, W. B. Bunger and T. K. Sakano, Organic Solvents – Physical Properties and Methods of Purification. Wiley, New York 1968.

25 P. Monk and I. Wadsö, Acta Chem. Scand., 22 (1968) 1842.

26 K. N. Marsh, Int. DATA Ser., Sel. Data Mixtures, Ser. A (1973) 75.

27 A. Bondi, Physical Properties of Molecular Crystals, Liquids and Gases. Wiley, New York 1968.

28 H. V. Kehiaian, J.-P. E. Grolier, M. R. Kechavarz, G. C. Benson, O. Kiyhoara and Y. P. Handa, Fluid Phase Equilib., 7 (1981) 95.

29 H. V. Kehiaian, J.-P. E. Grolier and G. C. Benson, J. Chim. Phys., 75 (1978) 1031.

30 A. Yahiaoui, J. A. Gonzalez, A. Ait-Kaci, J. Jose and H. V. Kehiaian, Fluid Phase Equilib., 98 (1994) 179.