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A comparative study of thermodynamic properties of binary mixtures containing alkynes

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Abstract

Literature data on molar excess enthalpies (H^E) and molar excess Gibbs energies (G^E) of linear alkynes + n-alkanes, cycloalkanes, benzene or tetrachloromethane are treated in the framework of DISQUAC, an extended quasichemical group-contribution theory. The systems are characterized by three types of contact surfaces: acetylenic (C≡C group), aliphatic (CH_3 or CH_2 groups), cycloaliphatic (c-CH_2 group), aromatic (C_6H_6 group) and chlorine (CCl_4 group). Using a limited number of adjusted contact interchange energies parameters, the model provides a fairly consistent description of the thermodynamic properties as a function of concentration. The model may serve to predict missing data.

Keywords: Excess properties; Binary mixtures; Group contributions

1. Introduction

In continuation of our previous study on mixtures of n-alkenes + n-alkane or + cyclohexane [1] or + benzene [2] we report in this paper the results of a similar investigation of the thermodynamic properties, vapour–liquid equilibrium (VLE), excess molar Gibbs energies (G^E) and excess molar enthalpies (H^E) of binary mixtures of n-alkynes + n-alkanes, + cycloalkanes, + benzene, or + tetrachloromethane. Systematic investigation on thermodynamic behaviour of binary liquid mixtures containing n-alkanes, alkenes, alicyclic and aromatic hydrocarbons has made considerable progress. This is sharply contrasted by the scarcity of reliable studies on systems containing acetylenic hydrocarbons. Aside from solubility data on several gaseous alkynes in liquids [3–6] and some solid–liquid phase diagrams for systems alkyne + HCl [7], only very few papers have dealt with thermodynamic properties of mixtures with organic solvents [8–10]. In particular the almost complete absence of excess Gibbs energies data represents a major obstacle for an improved understanding of the influence exerted by a C≡C upon the overall thermodynamics of binary alkyne systems.

The DISQUAC model, used in this work, characterizes the X–Y interactions in terms of two sets of parameters, dispersive and quasichemical [11]. The model has been successfully applied to many classes of polar + non-polar systems [12–15].

The purpose of this and following papers of this series is to investigate the ability of the first-approximation quasichemical theory [16], on which the quasichemical term in DISQUAC is reliant, to account for the possible interactions in binary mixtures of the second component with the π-electron system and/or the active hydrogen in n-alkynes.

The sources of available experimental data and some characteristic values are collected in Tables 1 and 2. The G^E data for n-alkynes + n-alkanes are scarce and limited to 1-hexyne [17–19]. 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 [20] method.

2. Theory

DISQUAC is an extended quasichemical group-contribution model based on Guggenheim's lattice theory [11,21]. In the classic model [16], molecules are assumed to possess one

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Nomenclature

C	interchange coefficient
G	molar Gibbs energy
H	molar enthalpy
q	relative molecular area
r	relative molecular volume
s, v	any contact surfaces
x	mole fraction
α	molecular surface fraction

Subscripts

a, b, c, d, t,	type of contact surface (group) a, CH_3, CH_2; b, C_6H_6; c, c-CH_2; d, CCl_4; t, C≡C
calc.	calculated quantity
exp.	experimental quantity
i	type of molecule (component)
l	order of interchange coefficient: $l = 1$, Gibbs energy; $l = 2$, enthalpy

Superscripts

dis	dispersive
E	excess property
quac.	quasichemical

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 [22]. In the classical model, the interchange energies of every (s, v) contact generate non-randomness to the extent expressed by z, which is the same for all the contacts. For non-polar 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, non-random, contribution treated quasichemically with a constant $z = 4$.

One of the advantages of DISQUAC is the use of a single coordination number z in calculating the quasichemical term. This permits the model to apply the mixtures containing groups of different polarities. The degree of no randomness is expressed by the relative amounts of quasichemical to dispersive terms. If both groups, s and v, are non-polar, then the contact (s, v) is characterized by the dispersive coefficients $C^{\rm dis}_{sv,l}$ only, all $C^{\rm quac}_{sv,l} = 0$. If one group is polar and the other non-polar, then the contact (s, v) is characterized by both sets of coefficients, $C^{\rm dis}_{sv,l}$ and $C^{\rm quac}_{sv,l}$. In a binary non-polar or polar (component 1) + non-polar (component 2) mixture, the shapes of the calculated $G^{\rm E}$ and $H^{\rm E}$ curves, adjusted to fixed equimolar values, depend on the relative amounts of quasichemical to dispersive terms. The mole fraction, $x_1^{\rm max}$, of the maxima of the dispersive curves, $G^{\rm E,dis}_{\rm int}$ and $H^{\rm E,dis}$ versus x_1, are determined by geometrica1 factors only, $x_1^{\rm max} = 1/1 + \sqrt{q1/q2}$. The quasichemical curves, $G^{\rm E,quac}_{\rm int}$ and especially $H^{\rm E,quac}$, have the maxima shifted towards smaller x_1 values, the more, the smaller z is. Adding the two terms, one calculates with DISQUAC flatter $G^{\rm E}$ and $H^{\rm E}$ versus x_1 curves, than by using the classical quasichemical model. This being supported by experiment [11] represents another advantage of DISQUAC.

The ‘reference’ value chosen for the coordination number is $z = 4$, the same as in our previous application of DISQUAC [23,24]. This choice is to some extent, but not entirely, arbitrary. The z value is low enough to treat contacts formed by a fairly strong polar, or even weakly associating, group and a non-polar group. Contacts formed by a strongly associating group and a non-polar group would

Table 1
Molar excess Gibbs energies $G^{\rm E}$ (T; $x_1 = 0.5$) of 1-hexyne (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 $C^{\rm dis}_{sv,l}$ and $C^{\rm quac}_{sv,l}$ from Table 5

Alkyne	Solvent	T (K)	$G^{\rm E}$ (T; $x_1 = 0.5$) (J mol^{-1})		Source of experimental data
			Calc.	Exp.	
1-Hexyne	C_7H_{16}	343.15	258	257	[18]
	C_8H_{18}	303.15	293	265	[17]
		313.15	285	260	[17]
		323.15	274	248	[17]
		333.15	260	240	[17]
		343.15	248	233	[17]
	$C_{10}H_{22}$	298.15	279	276	[19]
		303.15	272	270	[19]
		313.15	256	254	[19]
		323.15	241	237	[19]
		333.15	226	224	[19]
		343.15	211	220	[19]

[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 coefficients.

Table 2
Molar excess enthalpies H^{E} (T; $x_1 = 0.5$) of n-alkynes (1) + n-alkanes, cycloalkanes, benzene or tetrachloromethane (2) mixtures at various temperatures, T, and equimolar composition: comparison of direct experimental results (Exp.) with values calculated (Calc.) using the coefficients $C^{\mathrm{dis}}_{sv,l}$ and $C^{\mathrm{quac}}_{sv,l}$ from Tables 5–8

Alkyne	Solvent	T (K)	H^{E} (T; $x_1 = 0.5$) (J mol^{-1})		Source of experimental data
			Calc.	Exp.	
1-Hexyne	C_6H_{14}	298.15	600	592	[43]
	C_7H_{16}		642	645	[8]
	$C_{10}H_{22}$		740	748	[8]
	c-C_5H_{10}		521	518	[10]
	c-C_6H_{12}		722	719	[10]
			722	726	[8]
	c-C_7H_{14}		747	712	[10]
	c-C_8H_{16}		760	700	[10]
	C_6H_6		130	131	[8]
	CCl_4		14	14	[9]
				16	[42]
3-Hexyne	C_7H_{16}	298.15	458	454	[8]
	$C_{10}H_2$		525	554	[8]
	c-C_6H_{12}		615	463	[8]
	C_6H_6		−30	−31	[8]
	CCl_4		−493	−499	[9]
				−512	[43]
1-Heptyne	C_6H_{14}	298.15	516	517	[42]
	c-C_5H_{10}		417	430	[10]
	c-C_6H_{12}		644	638	[43]
	c-C_7H_{14}		668	634	[10]
	c-C_8H_{16}		680	617	[10]
	C_6H_6		141	139	[43]
	CCl_4		−15	−12	[42]
	C_8H_{18}	298.15	500	517	[44] (see also [48])
		318.15	494	478	[44]
		308.15	497	495	[44]
	c-C_5H_{10}	298.15	374	383	[10]
	c-C_6H_{12}		587	605	[10]
	c-C_7H_{14}		609	600	[10]
	c-C_8H_{16}		620	588	[10]
	CCl_4		−16	−18	[42]
2-Octyne	C_8H_{18}	298.15	369	371	[45] (see also [48])
		318.15	363	339	[45]
	CCl_4	298.15	−378	−381	[42]
3-Octyne	C_8H_{18}	298.15	369	365	[45]
		318.15	363	330	[45]
	CCl_4	298.15	−378	−371	[42]
	C_8H_{18}	298.15	369	368	[45]
		318.15	363	328	[45]
	CCl_4	298.15	−378	−373	[42]
1-Nonyne	C_9H_{20}	298.15	456	468	[46] (see also [48])
		318.15	449	444	[46]
1-Decyne	c-$C_{10}H_{22}$	298.15	510	565	[47] (see also [48])

require a smaller value of z to reproduce the pronounced experimental asymmetry of the excess functions as, e.g. in alcohol + alkane mixtures [25]. These types of mixtures may be well at, if not beyond, the limits of accurate applicability of quasichemical models, including DISQUAC, especially in the dilute solution range.

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

2.1. Assessment of geometrical parameters

Every mixtures under study, i.e. alkynes + alkane, or + cycloalkanes, or + benzene or + tetrachloromethane are regarded as possessing three types of contact surfaces: (1) type t, acetylenic (C≡C group); (2) type a, aliphatic (CH_3, CH_2 groups, which are assumed to exert the same force field); (3) type b, aromatic (C_6H_6 group); type c, cycloaliphatic (c-CH_2 groups); or type d, chlorine (CCl_4 group).

The relative geometrical parameters r_i, q_i, and α_{si} were calculated from 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 $q_G = A_G/A_{CH_4}$ [22]. In general, for linear molecules, the V_G and A_G values calculated by Bondi [26] have been adopted.

The assessment of geometrical parameters for cyclic molecules is a more difficult problem. The segmentation into groups, e.g. of cycloalkanes into c-CH_2 groups, is not strictly justified and it seems more appropriate to treat each cyclic molecule as an independent entity. This would not be really embarrassing, as long as the parameters for any given cyclic molecule can be kept constant and have a reasonable order of magnitude. Nevertheless, a certain degree of arbitrariness is unavoidable.

For the sake of comparison, we attributed the same geometrical parameters to any given functional group *X*, whether situated in a linear or in a heterocyclic molecule. Therefore, differences between the interchange coefficients of linear and heterocyclic molecules will reflect indistinguishably changes in both the effective contact surface of *X* and in its interaction force field.

The r_G values affect the G^E_{comb} term and for molecules that do not differ too much in size, slight modifications have a negligible effect on G^E. Therefore, the $r_{c\text{-}CH_2}$ parameter has been taken the same for all the cyclic molecules and is equal to one-sixth of the total relative volume of cyclohexane.

On the contrary, the q_G values affect G^E_{int} and H^E and, consequently, all the interchange coefficients. The $q_{c\text{-}CH_2}$ parameter has been fitted to reproduce accurately the H^E curves of cycloalkanes with benzene (C_6H_6) and tetrachloromethane (CCl_4). These mixtures are non-polar and can be treated in the random mixing approximation, the mole fraction at the maximum of the H^E curve depending only on the surface ratio of the components. The surfaces of C_6H_6 and CCl_4 being established at 2.0724 and 2.4966, respectively, we calculated the relative surface of the cycloalkane $(c\text{-}CH_2)_m$ and dividing by the corresponding number *m* of c-CH_2 groups, we obtained the $q_{c\text{-}CH_2}$ increments of carbocyclic molecule [27]. The total relative molecular volumes r_i, surfaces q_i, and surface fractions α_{si}, were then calculated additively from the group increments given in Table 3 and are listed in Table 4.

2.2. Estimation of interaction parameters

It is sometimes difficult to assign unambiguously interchange coefficients to individual systems. The coefficients can be varied, indeed, within certain limits, without affecting significantly the agreement with experiment. However, considering a larger number of systems, we were able to identify a number of general and physically reasonable "rules" which we applied consistently in determining the values of the interchange coefficients. 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 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. Moreover, the values listed in Tables 5–8 were calculated with zero heat capacity coefficients. This has little effect on G^E calculated but not on H^E (calculated). The temperature dependence of our calculated H^E values results therefore from the Boltzmann factor only.

Table 3
Relative group increments for molecular volumes, $r_G = V_G/V_{CH_4}$, and areas, $q_G = A_G/A_{CH_4}$, calculated by Bondi's method [26] ($V_{CH_4} = 17.12 \times 10^{-6}\ m^3\ mol^{-1}$; $A_{CH_4} = 2.90 \times 10^5\ m^2\ mol^{-1}$)

Group	r_G	q_G	
CH_3	0.79848	0.73103	
CH_2	0.59755	0.46552	
c-CH_2	0.58645	0.56000	$m = 3$
c-CH_2	0.58645	$0.66377 - 0.0385m$	$(4 < m < 8)$
HC≡	0.67465	0.60000	
–C≡	0.47021	0.33793	

Table 4
Volumes, r_i, total surfaces, q_i, and molecular surface fractions, α_{si} (s = a, b, c, d, t) of *n*-alkynes and solvents calculated from the group increments r_G and q_G given in Table 3

Compound	r_i	q_i	α_{ai}	$\alpha_{ci}/\alpha_{bi}/\alpha_{di}$	α_{ti}
1-Hexyne	3.7360	3.0655	0.6940	0.0000	0.3060
3-Hexyne	3.7325	3.0690	0.7798	0.0000	0.2202
1-Heptyne	4.3301	3.5345	0.7346	0.0000	0.2654
1-Octyne	4.9276	3.9966	0.7653	0.0000	0.2347
2-Octyne	4.9258	4.0000	0.8310	0.0000	0.1690
3-Octyne	4.9258	4.0000	0.8310	0.0000	0.1690
4-Octyne	4.9258	4.0000	0.8310	0.0000	0.1690
1-Nonyne	5.5251	4.4621	0.7898	0.0000	0.2102
1-Decyne	6.1227	4.9276	0.8097	0.0000	0.1903
1-Heptane	4.5847	3.7897	1.0000	0.0000	0.0000
1-Octane	5.1822	4.2552	1.0000	0.0000	0.0000
1-Nonane	5.7798	4.7207	1.0000	0.0000	0.0000
1-Decane	6.3773	5.1862	1.0000	0.0000	0.0000
Cyclopentane	2.9323	2.3564	0.0000	1.0000	0.0000
Cyclohexane	3.5187	2.5966	0.0000	1.0000	0.0000
Cycloheptane	4.1052	2.7599	0.0000	1.0000	0.0000
Cyclooctane	4.6916	2.8462	0.0000	1.0000	0.0000
Benzene	2.8248	2.0724	0.0000	1.0000	0.0000
Tetrachloromethane	3.0023	2.4966	0.0000	1.0000	0.0000

Table 5
Interchange energy coefficients dispersive, $C^{\mathrm{dis}}_{\mathrm{at},l}$, and quasichemical, $C^{\mathrm{quac}}_{\mathrm{at},l}$, for n-alkyne + n-alkane mixtures ($l = 1$, Gibbs energy; $l = 2$, enthalpy)

n-alkyne	$C^{\mathrm{dis}}_{\mathrm{at},1}$	$C^{\mathrm{dis}}_{\mathrm{at},2}$	$C^{\mathrm{quac}}_{\mathrm{at},1}$	$C^{\mathrm{quac}}_{\mathrm{at},2}$
1-Hexyne	0.46	0.81	1.10	2.20
1-Heptyne	0.53[a]	0.93	1.10[a]	2.20
≥1-Octyne	0.53[a]	0.93	1.10[a]	2.20
2-Hexyne	1.00[a]	1.80[a]	1.10[a]	2.20[a]
2-Heptyne	1.20[a]	2.20[a]	1.10[a]	2.20[a]
2-Octyne	1.20[a]	2.20	1.10[a]	2.20
3-Hexyne	1.20[a]	2.20	1.10[a]	2.20
3-Heptyne	1.20[a]	2.20[a]	1.10[a]	2.20[a]
3-Octyne	1.20[a]	2.20	1.10[a]	2.20
4-Octyne	1.20[a]	2.20	1.10[a]	2.20

[a] Guessed values.

Table 6
Interchange energy coefficients dispersive, $C^{\mathrm{dis}}_{\mathrm{ct},l}$, and quasichemical, $C^{\mathrm{quac}}_{\mathrm{ct},l}$, for n-alkyne+cycloalkane mixtures ($l = 1$, Gibbs energy; $l = 2$, enthalpy)

n-alkyne	$C^{\mathrm{dis}}_{\mathrm{ct},1}$ [a]	$C^{\mathrm{dis}}_{\mathrm{ct},2}$	$C^{\mathrm{quac}}_{\mathrm{ct},1}$ [a]	$C^{\mathrm{quac}}_{\mathrm{ct},2}$
1-Hexyne	0.52	0.91	1.10	2.20
1-Heptyne	0.57	1.00	1.10	2.20
≥1-Octyne	0.57	1.00	1.10	2.20
2-Hexyne	1.10	2.00[a]	1.10	2.20[a]
2-Heptyne	1.10	2.00[a]	1.10	2.20[a]
2-Octyne	1.10	2.00	1.10	2.20
3-Hexyne	1.10	2.00	1.10	2.20
3-Heptyne	1.10	2.00[a]	1.10	2.20[a]

[a] Guessed values.

Table 7
Interchange energy coefficients dispersive, $C^{\mathrm{dis}}_{\mathrm{bt},l}$, for n-alkyne + benzene mixtures ($l = 1$, Gibbs energy; $l = 2$, enthalpy)

n-alkyne	$C^{\mathrm{dis}}_{\mathrm{bt},1}$	$C^{\mathrm{dis}}_{\mathrm{bt},2}$
1-Hexyne	0.50	0.97
1-Heptyne	0.50	0.97
2-Hexyne	0.50[a]	0.97[a]
3-Hexyne	0.50	0.97

[a] Guessed values.

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 experiment.

Table 8
Interchange energy coefficients quasichemical, $C^{\mathrm{quac}}_{\mathrm{dt},l}$, for n-alkyne + tetrachloromethane mixtures ($l = 1$, Gibbs energy; $l = 2$, enthalpy)

n-alkyne	$C^{\mathrm{quac}}_{\mathrm{dt},1}$ [a]	$C^{\mathrm{quac}}_{\mathrm{dt},2}$
1-Hexyne	0.78	1.56
1-Heptyne	0.81	1.62
1-Octyne	0.86	1.72
2-Hexyne	0.50	1.00[a]
2-Octyne	0.78	1.47
3-Hexyne	0.78	1.47
3-Octyne	0.78	1.47
4-Octyne	0.78	1.47

[a] Guessed values.

2.2.1. *n-alkynes + n-alkanes*

These systems are characterized by a single contact (a, t). G^{E} and H^{E} have been described in the past using the dispersive coefficients only, random mixing approximation [8]. DISQUAC improves representation of the experimental data if the two dispersive coefficients are reduced and a significative amount of quasichemical terms added. The rules we found as follows:

(a) the quasichemical coefficients, $C^{\mathrm{quac}}_{\mathrm{at},l}$, are the same for all the n-alkynes (1.10 for $l = 1$ and 2.20 for $l = 2$) (Table 5);
(b) the dispersive coefficients, $C^{\mathrm{dis}}_{\mathrm{at},l}$, of linear 1-alkynes increases regularly with increasing the chain length of the alkyl groups adjacent to the C≡C group;
(c) The dispersive parameters of the (a, t) contacts for the alkynes (with $n > 2$) are higher than those of 1-alkynes and show the same trend (see Fig. 1 and Table 5).

2.2.2. *n-alkynes + cycloalkanes*

Three types of contacts characterize the systems: (a, c), (a, t) and (c, t). The rules we found are as follows:

(a) the non-polar aliphatic/cycloaliphatic (a, c) interactions are represented by dispersive parameters $C^{\mathrm{dis}}_{\mathrm{ac},1} = 0.03$ and $C^{\mathrm{dis}}_{\mathrm{ac},2} = 0.120$ [28] for cyclohexane, cycloheptane and cyclooctane. Cyclopentane behaves quite differently, $C^{\mathrm{dis}}_{\mathrm{ac},2} = 0.04$, when fitted to the equimolar H^{E} (70 J mol^{-1}) with heptane at 298.15 K [29] but the composition dependence of H^{E} in cyclopentane + n-alkanes is poorly represented. Clearly, cycloalkanes do not form a homologous series in terms of c-CH$_2$ group contributions;
(b) the (a, t) contact energies, $C^{\mathrm{dis}}_{\mathrm{at},l}$ and $C^{\mathrm{quac}}_{\mathrm{at},l}$ determined independently on the basis of n-alkynes + n-alkane mixtures (see above), can be used;
(c) the quasichemical coefficients of the (c, t) contact equal the quasichemical coefficients of the (a, t) contact, i.e. $C^{\mathrm{quac}}_{\mathrm{at},l} = C^{\mathrm{quac}}_{\mathrm{ct},l}$ (Table 5);
(d) the dispersive coefficients, $C^{\mathrm{dis}}_{\mathrm{ct},l}$ of linear 1-alkynes increases regularly with increasing the chain length of the alkyl groups adjacent the C≡C and are slightly larger than $C^{\mathrm{dis}}_{\mathrm{at},l}$ (Table 6);
(e) the dispersive parameters of the (c, t) contacts for the alkynes (with $n > 2$) are higher than those of 1-alkynes and show the same trend (see Fig. 1).

Unfortunately, G^{E} data are available only for 1-hexyne (Table 1). Previous investigations of many classes of systems showed that Gibbs energy coefficients change with the structure of components but slower than the enthalpic coefficients and for the approximate representation of VLE in a limited range of temperature it may be sufficient to assume $C^{\mathrm{dis}}_{\mathrm{at},l}$ and $C^{\mathrm{dis}}_{\mathrm{ct},l}$ constant regardless of the alkyne chain length.

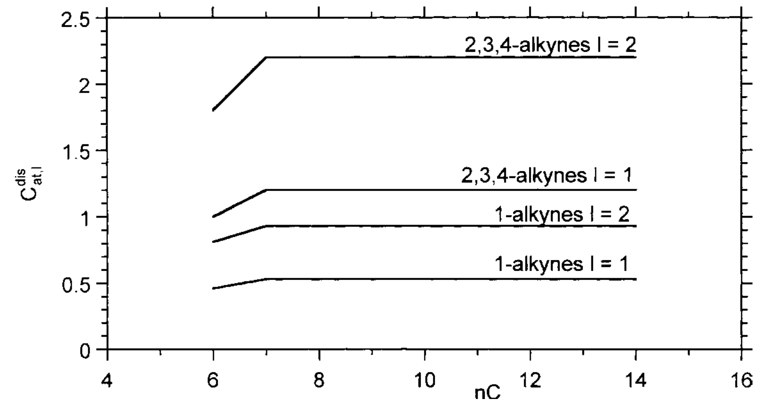

Fig. 1. Change of the dispersive interchange coefficients, $C^{\mathrm{dis}}_{\mathrm{at},l}$ for the aliphatic/acetylenic contact (a, t) in *n*-alkyne + *n*-alkane mixtures vs. *nC*, the number of carbon atoms in the *n*-alkyne.

2.2.3. *n-alkynes + benzene*

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

(a) the non-polar aliphatic/benzene (a, b) contacts are represented by dispersive parameters $C^{\mathrm{dis}}_{\mathrm{ab},1} = 0.2598$ and $C^{\mathrm{dis}}_{\mathrm{ab},2} = 0.5623$ [22]. In the case of higher alkanes (C_{14} and C_{16}) the calculated H^{E} values are smaller than the experimental data;

(b) the (a, t) contact energies, $C^{\mathrm{dis}}_{\mathrm{at},l}$ and $C^{\mathrm{quac}}_{\mathrm{at},l}$, determined independently on the basis of *n*-alkynes + *n*-alkane mixtures (see above), can be used;

(c) the quasichemical coefficients of the (b, t) contact equal zero, i.e. $C^{\mathrm{quac}}_{\mathrm{bt},l} = 0$;

(d) the dispersive coefficients, $C^{\mathrm{dis}}_{\mathrm{bt},l}$ are the same for all the *n*-alkynes (0.60 for $l = 1$ and 0.97 for $l = 2$) (Table 7).

2.2.4. *n-alkynes + tetrachloromethane*

The systems are characterized by three types of contacts: (a, d), (a, t) and (d, t). The rules we found are as follows:

(a) the non-polar aliphatic/chlorine (a, d) contacts are represented by dispersive parameters $C^{\mathrm{dis}}_{\mathrm{ad},1} = 0.093$ and $C^{\mathrm{dis}}_{\mathrm{ad},2} = 0.180$ [28]. The interchange energy parameters increase slightly with increasing the chain length of the *n*-alkane;

(b) the (a, t) contact energies, $C^{\mathrm{dis}}_{\mathrm{at},l}$ and $C^{\mathrm{quac}}_{\mathrm{at},l}$, determined independently on the basis of *n*-alkynes + *n*-alkane mixtures (see above), can be used;

(c) the dispersive coefficients of the (c, t) contact equal zero, i.e. $C^{\mathrm{dis}}_{\mathrm{ct},l} = 0$;

(d) the quasichemical coefficients, $C^{\mathrm{quac}}_{\mathrm{dt},l}$, of linear 1-alkynes increases regularly with increasing the chain length of the alkyl groups adjacent the C≡C (Table 8 and Fig. 2);

(e) the quasichemical parameters of the (c, t) contacts for the alkynes (with $n > 2$) are lower than those of 1-alkynes and shows the same trend (see Fig. 2).

3. Comparison with experiment and discussion

Using the set of dispersive and quasichemical parameters reported in Tables 5–8 a good agreement with experiment is obtained for the mixtures of *n*-alkynes + *n*-alkanes (Fig. 3),

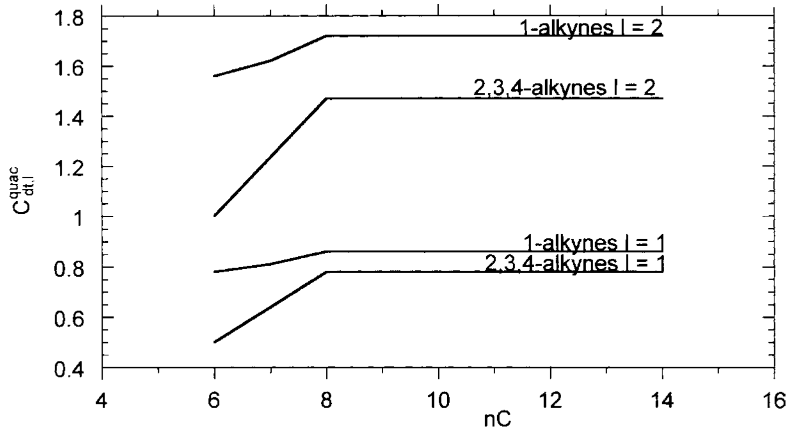

Fig. 2. Change of the quasichemical interchange coefficients, $C^{\mathrm{quac}}_{\mathrm{dt},l}$ for the chlorine/acetylenic contact (d, t) in *n*-alkyne + tetrachloromethane mixtures vs. *nC*, the number of carbon atoms in the *n*-alkyne.

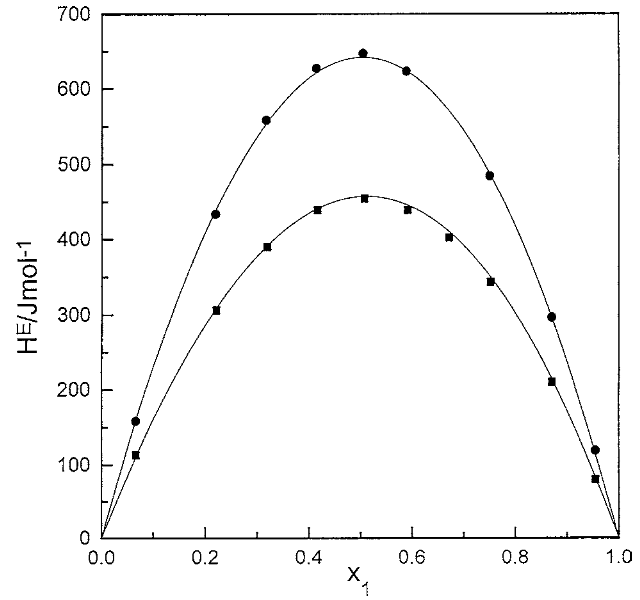

Fig. 3. Comparison of theory with experiment for the molar excess enthalpies, H^E, at 298.15 K, for n-alkyne (1) + n-heptane (2) mixtures vs. x_1, the mole fraction of alkyne: full lines: (—) predicted values; points, experimental results: (●) 1-hexyne [8]; (■) 3-hexyne [8].

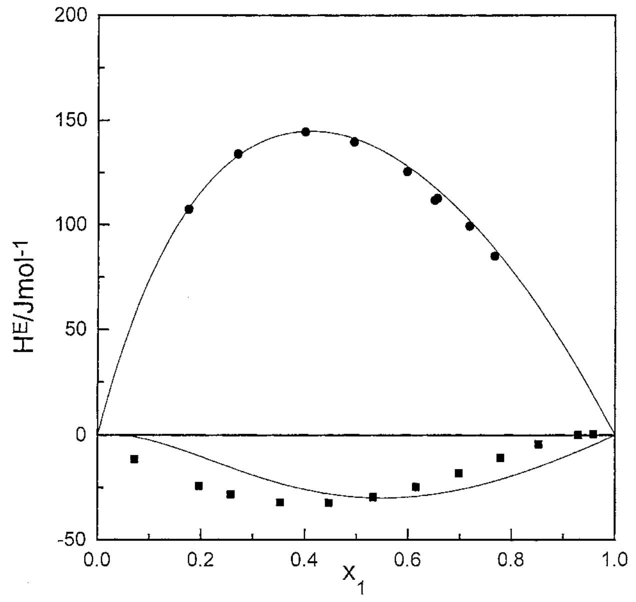

Fig. 5. Comparison of theory with experiment for the molar excess enthalpies, H^E, at 298.15 K, for n-alkyne (1) + benzene (2) mixtures vs. x_1, the mole fraction of alkyne: full lines: (—) predicted values; points, experimental results: (●) 1-heptyne [43]; (■) 3-hexyne [8].

cycloalkanes (Fig. 4), benzene (Fig. 5) or tetrachloromethane (Fig. 6) (see also Table 1).

As known, empirical group-contribution methods, such as UNIFAC [30], have a great deal of difficult with the first members of homologous series and with cyclic molecules. These difficulties arise less from the UNIFAC model itself, than from changes in the force fields of the interacting groups. The need for defining separate UNIFAC parameters for the smallest molecules, as well as for cyclic molecules, has been suggested [31], and this applies to any other group-contribution model.

In our opinion, the main advantage of using DISQUAC is, apart from the more accurate representation of all the experimentally available low-pressure phase equilibrium and

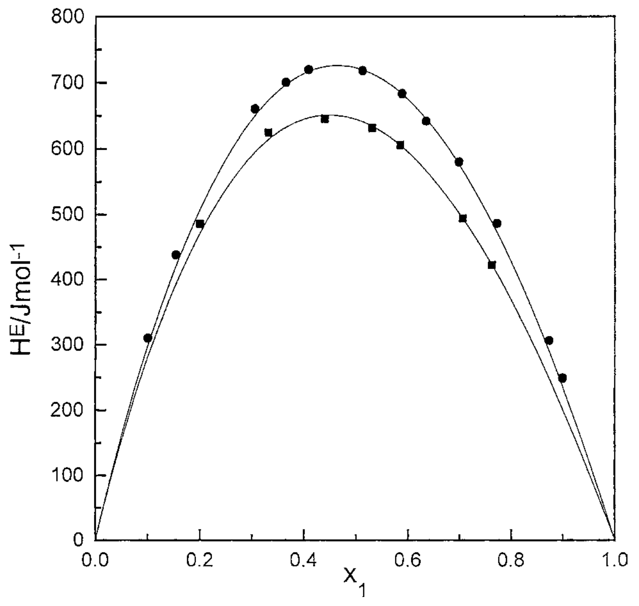

Fig. 4. Comparison of theory with experiment for the molar excess enthalpies, H^E, at 298.15 K, for n-alkyne (1) + cyclohexane (2) mixtures vs. x_1, the mole fraction of alkyne: full lines: (—), predicted values; points, experimental results: (●) 1-hexyne [10] (see also [48]); (■) 1-heptyne [43] (see also [48]).

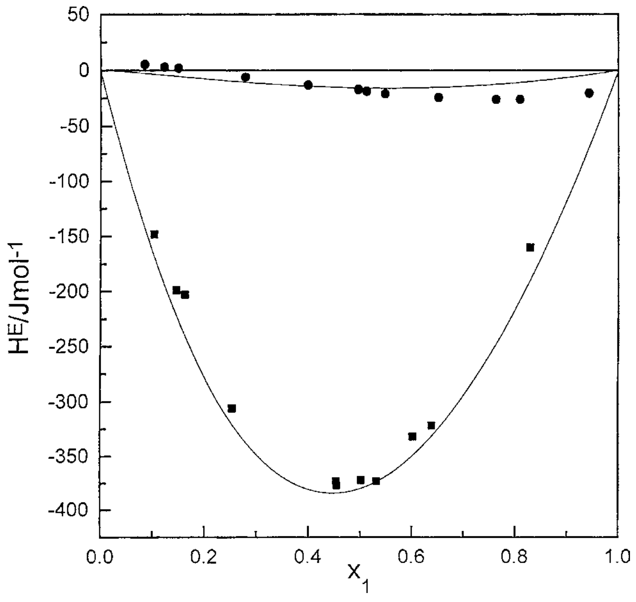

Fig. 6. Comparison of theory with experiment for the molar excess enthalpies, H^E, at 298.15 K, for n-alkyne (1) + tetrachloromethane (2) mixtures vs. x_1, the mole fraction of n-alkyne: full lines: (—) predicted values; points, experimental results: (●) 1-octyne [42] (see also [48]); (■) 4-octyne [42].

related data, the better physical significance of the parameters, than in any other group-contribution method. Despite the relatively large number of interchange coefficients (Tables 5–8), many are derived from previous adjustments on other systems and most show a regular trend conform to what one qualitatively anticipate based on molecular considerations. This confers on DISQUAC rather unique predictive capabilities, provided it is used within the limits of validity of the underlying statistical theory, the rigid quasichemical pseudo-lattice model.

Inspection of the coefficients listed in Tables 5–8 permits us to formulate several general rules. The dispersive coefficients remain almost constant or even increase for the very first members, especially when the functional group contain π-electrons, due, in our opinion, to an inductive effect. Moreover, if we compare the interchange coefficients of alkanals [32] and alkanones [33] we observe that linear alkanals have much smaller dispersive coefficients than 2-alkanones. In other words, in carbonyl compounds, replacement of hydrogen (alkanal) with methyl or higher *n*-alkyls (alkanones) increases the dispersive contribution, in terms of DISQUAC, due to enhancement of dispersive interaction between the carbonyl groups by the inductive effect of the alkyl group. The trend of the dispersive coefficients is interesting. Distinction must be made between cyclic molecules containing six or more atoms in the cycle and molecules containing less than six atoms in the cycle: the dispersive coefficients are nearly constant on mixtures of 1-alkynes with cycloalkanes containing six, seven or eight carbon atoms. On the contrary, cyclopentane has much smaller dispersive interchange coefficients (Table 6). Calculating the dispersive coefficients of benzene or tetrachloromethane with cycloalkanes it becomes clear that the behaviour of cyclopentane is peculiar. Cibulka et al. [34] arrived at the same conclusion by plotting H^{E} of tri- or tetra-chloromethane against the number of carbon atoms in the cycloalkane.

A good representation of the symmetry of the experimental H^{E} curves was obtained using a non-negligible quasichemical contribute, $C^{\mathrm{quac}}_{\mathrm{at},1} = C^{\mathrm{quac}}_{\mathrm{ct},1} = 1.10$ and $C^{\mathrm{quac}}_{\mathrm{at},2} = C^{\mathrm{quac}}_{\mathrm{ct},2} = 2.20$, constant for all the alkynes + *n*-alkanes or cycloalkanes mixtures.

It is well known that unsatured organic compounds may act as proton acceptors in hydrogen bonds [35,36]. Conversely, terminal acetylenes may act also as hydrogen bonding acids [37–39]. The fact that terminal alkynes have both proton donating and proton accepting abilities suggest that association via intermolecular hydrogen bonds might take place in the pure compounds. Contrary to expectancy, ΔH_{vap} at 25 °C is smaller for 1-hexyne ($32.1\,\mathrm{kJ\,mol^{-1}}$) than for 3-hexyne ($35.0\,\mathrm{kJ\,mol^{-1}}$). The respective normal boiling points are 71.3 °C versus 81.4 °C. The considerably smaller cohesive energy density of 1-hexyne ascertains that other factors, such as geometrical factors involved in packing, contribute significantly more to the thermodynamic behaviour of the pure 1-alkyne than intermolecular hydrogen bonding. Intuitively since 3-hexyne is a more rigid and elongated molecule as compared to 1-hexyne with its flexible “tail”.

For the mixtures of *n*-alkynes with benzene the agreement may be regarded as satisfactory using for the acetylenic–benzene (polar–polarizable contact) only dispersive interchange coefficients constant for all the *n*-alkynes investigated.

For the mixture of *n*-alkynes with tetrachloromethane, with increasing the basicity of second component, the influence of the acid hydrogen in 1-alkyne should become clearly discernible and eventually predominant. The excess enthalpy for alkynes + $\mathrm{CCl_4}$ is substantially smaller than in alkynes + *n*-alkanes systems. It is intuitively appealing to associate the exothermic contribution to H^{E} with specific interaction between $\mathrm{CCl_4}$ and the C≡C of alkyne, say of n–π type [22]. Consequently a good agreement between experimental and calculated H^{E} curves was obtained if the acetylenic/chlorine contact was considered entirely quasichemical, $C^{\mathrm{dis}}_{\mathrm{dt},l} = 0$. The $C^{\mathrm{quac}}_{\mathrm{dt},l}$ increase as the length of the alkyl chain adjacent to the polar group C≡C increases. This is attributed to the steric effect, which reduces the electrostatic 1–2 type interactions.

The influence of the inductive and steric effect of an alkyl group adjacent to a polar *X* group on the dispersive and the quasichemical interchange coefficients $C_{sx,l}$, can be more easily explained if consider that the interchange energies $\Delta\varepsilon_{sx,l}$ are related to the interaction energies ε_{sx} [22]:

$$\Delta\varepsilon_{sx,l} = \frac{|\varepsilon_{ss}| + |\varepsilon_{xx}|}{2}$$

the ε values being negative.

In polar–non-polar systems (s = a, c) where interactions are mainly of the 1-type, the inductive effect exerted by an alkyl group adjacent to the polar *X* group increases the dispersive interaction energies $|\varepsilon_{xx}|$ and consequently increases $\Delta\varepsilon_{sx,l}$ (this, in turn, causes an increase in $C^{\mathrm{dis}}_{sx,l}$).

The steric effect acts mainly on the quasichemical parameters. In polar–polar or polarizable systems decrease the electrostatic energies $|\varepsilon_{sx}|$ and consequently increases $\Delta\varepsilon_{sx,l}$ and $C^{\mathrm{quac}}_{sx,l}$.

Concerning the temperature dependence of H^{E} in all cases DISQUAC predicts the negative sign correctly, yet the absolute values are too small. As all the quantities listed in Tables 1 and 2 were calculated with zero heat capacity of interchange coefficients, $C_{\mathrm{st},3}$, dispersive and quasichemical. Accordingly, the dispersive contribution to the excess capacity (calculated) is zero and the quasichemical contribution results from the Boltzmann factor only.

It is generally admitted that the interchange “energies” in lattice-type models are temperature dependent, i.e. they must be regarded as free energies [16]. There is a priori no reason that g_{st} should be a linear function of *T*. The difficulty of using $C_{\mathrm{st},3}$ in the framework of group-contribution models results from the more complex physical significance of this parameter, and thereby its pronounced variability in a homologous series of substances. The value of $C_{\mathrm{st},3}$, adjusted for a particular system, reflects not only the true thermal coefficient of the interchange energy, but also many other inter- and intra-molecular effects that are not explicitly accounted for in the model.

4. Conclusion

This work, following the previous on chloroalkanes [28], oxaalkanes [40], alkanals [41], illustrates the advantage of applying group-contribution models in a more “flexible” manner, i.e. with structure-dependent interaction parameters. This may appear as derogation from the classical group-contribution concept. However, it reflects a physical reality, since there is no a priori reason that the force field of an atom or group of atoms should be completely independent of the intra-molecular environment. The observed regular change in the parameters with molecular structure is a decisive importance from a practical point of view, since it permits useful predictions to be made based on a relatively limited number of experimental data. The interest of the method increases with the number of classes of systems examined. One find, indeed, that the rules governing the structure dependence of the parameters are quite similar for many classes. However, in traditional group-contribution methods, the “average” interaction parameters are often only apparent constant. In reality, they depend on the number and nature of systems actually considered in the averaging. Moreover, in extreme cases, certain member of homologous series must be either ignored or treated as separate groups, with specific parameters.

It would be quite useful, and perhaps possible, to develop structure dependent parameter tables for other group-contribution models, e.g. for modified UNIFAC. It remains to investigate whether the structure/parameters relationships are comparable with those that we obtained with DISQUAC.

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References

[1] B. Marongiu, B. Pittau, S. Porcedda, M.R. Tinè, Fluid Phase Equilib. 93 (1994) 249.
[2] B. Marongiu, B. Pittau, S. Porcedda, H.V. Kehiaian, Fluid Phase Equilib. 99 (1994) 185.
[3] S.A. Miller, Acetilene, Academic Press, New York, 1965.
[4] A.C. McKinnis, Ind. Eng. Chem. 47 (1955) 850.
[5] R. Battino, H.L. Clever, Chem. Rev. 66 (1966) 395.
[6] E. Wilhelm, R. Battino, R.J. Wilcock, Chem. Rev. 77 (1977) 219.
[7] M.J. Copley, C.E. Holley, J. Am. Chem. Soc. 61 (1939) 1599.
[8] E. Wilhelm, A. Inglese, J.-P.E. Grolier, H.V. Kehiaian, Monatsh. Chem. 109 (1978) 235.
[9] E. Wilhelm, A. Inglese, J.-P.E. Grolier, H.V. Kehiaian, Monatsh. Chem. 109 (1978) 435.
[10] T.M. Letcher, S. Taylor, R.C. Baxter, J. Chem. Thermodyn. 20 (1988) 1265.
[11] H.V. Kehiaian, Pure Appl. Chem. 57 (1985) 15.
[12] B. Marongiu, S. Porcedda, H.V. Kehiaian, Fluid Phase Equilib. 87 (1993) 115.
[13] B. Marongiu, B. Pittau, S. Porcedda, Thermochim. Acta 221 (1993) 143.
[14] B. Marongiu, G. Marras, B. Pittau, S. Porcedda, Fluid Phase Equilib. 97 (1994) 127.
[15] B. Marongiu, S. Porcedda, R. Valenti, Fluid Phase Equilib. 145 (1998) 99.
[16] E.A. Guggenheim, Mixtures, Oxford University Press, London, 1952.
[17] A. Ait-Kaci, J. Jose, G. Belaribi, Int. DATA Ser., Sel. Data Mixtures 17 (1989) 105.
[18] A. Ait-Kaci, G. Belaribi, C. Michou-Saucet, J. Jose, Int. DATA Ser., Sel. Data Mixtures 20 (1992) 32.
[19] B.F. Belaribi, A. Ait-Kaci, J. Jose, Int. DATA Ser., Sel. Data Mixtures 19 (1991) 74.
[20] J.G. Hayden, J.P. O’Connell, Ind. Eng. Chem. Process Des. Dev. 14 (1975) 209.
[21] H.V. Kehiaian, Fluid Phase Equilib. 13 (1983) 243.
[22] H.V. Kehiaian, J.-P.E. Grolier, G.C. Benson, J. Chim. Phys. 75 (1978) 1031.
[23] H.V. Kehiaian, B. Marongiu, Fluid Phase Equilib. 21 (1985) 197.
[24] B. Marongiu, H.V. Kehiaian, Fluid Phase Equilib. 27 (1986) 445.
[25] M.A. Villamanan, H.C. Van Ness, Fluid Phase Equilib. 27 (1986) 181.
[26] A. Bondi, Physical Properties of Molecular Crystals, Liquids and Gases, Wiley, New York, 1968.
[27] M.R. Tinè, H.V. Kehiaian, Fluid Phase Equilib. 32 (1987) 211.
[28] H.V. Kehiaian, B. Marongiu, Fluid Phase Equilib. 40 (1988) 23.
[29] A. Inglese, J.-P.E. Grolier, Int. DATA Ser., Sel. Data Mixture 2 (1975) 98.
[30] A. Fredenslung, J. Gmehling, P. Rasmussen, Vapor–Liquid Equilibria Using UNIFAC, Elsevier, Amsterdam, 1977, p. 380.
[31] E.R. Thomas, C.A. Eckert, Ind. Eng. Chem. Process Des. Dev. 23 (1984) 194.
[32] M.R. Tinè, G. Della Gatta, H.V. Kehiaian, Fluid Phase Equilib. 54 (1990) 277.
[33] H.V. Kehiaian, S. Porcedda, B. Marongiu, L. Lepori, E. Matteoli, Fluid Phase Equilib. 63 (1991) 231.
[34] I. Cibulka, M.B. Ewung, M.L. McGlashan, J. Chem. Thermodyn. 15 (1983) 49.
[35] G.C. Pimentel, A.L. McClellan, The Hydrogen Bond, W.H. Freeman, San Francisco, 1960.
[36] Z. Yoshida, N. Ishibe, H. Ozoe, J. Am. Chem. Soc. 94 (1970) 4948.
[37] J.V. Hatton, R.E. Richards, Trans. Faraday Soc. 57 (1961) 28.
[38] J.C.D. Brand, G. Eglinton, J.F. Morman, J. Chem. Soc. 2 (1960) 2526.
[39] J.C.D. Brand, G. Eglinton, J. Tyrell, J. Chem. Soc. 5 (1965) 5914.
[40] H.V. Kehiaian, M.R. Tinè, L. Lepori, E. Matteoli, B. Marongiu, Fluid Phase Equilib. 46 (1989) 131.
[41] M.R. Tinè, B. Marongiu, Thermochim. Acta 199 (1992) 63.
[42] W. Woycicki, P. Rhensius, J. Chem. Thermodyn. 11 (1979) 153.
[43] T.M. Letcher, R.C. Baxter, J. Chem. Thermodyn. 19 (1987) 321.
[44] E.K. Otsa, L.S. Kudryavtseva, Int. DATA Ser., Sel. Data Mixtures 2 (1979) 119.
[45] E.K. Otsa, L.S. Kudryavtseva, O.G. Eisen, Monatsh. Chem. 111 (1980) 37.
[46] E.K. Otsa, V.Ya. Mikhkelson, L.S. Kudryavtseva, Zh. Fiz. Khim 35 (1979) 899.
[47] H. Wagner, R.N. Lichtenthaler, Ber. Bunsenges. Phys. Chem. 90 (1986) 8.
[48] J. Gmehling, T. Holderbaum, Heats of mixing data collection. Chemistry Data Collection, vol. III, Part 3, DECHEMA, Frankfurt, 1988.