Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 1, 145–154

A COMPARATIVE STUDY OF THERMODYNAMIC PROPERTIES OF BINARY MIXTURES CONTAINING PERFLUOROALKANES

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Literature data on molar excess enthalpies and molar excess Gibbs energies, liquid–liquid equilibria, activity coefficients at infinite dilution and partial molar enthalpies at infinite dilution of binary mixtures of *n*-perfluoroalkanes (C_5–C_8)+*n*-alkanes (C_5–C_8) and of *n*-perfluorohexane+linear monoethers of general formula, $CH_3(CH_2)_m$–O–$(CH_2)_n$–CH_3 (m,n=1–4), are treated in the framework of DISQUAC, an extended quasichemical group contribution theory. The systems are characterized by two or three types of contact surfaces: aliphatic (CH_3, CH_2, CH and C groups), fluorine (F group) and oxygen (O group). Using a limited number of adjusted contact interchange energies parameters, structure dependent, 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: *alkane, binary mixtures, DISQUAC contributions, ethers, excess properties, perfluoroalkane*

Introduction

In the course of our investigation on the capability 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 have studied systems of polychloroalkanes [1], oxaalkanes [2], alkanones [3], alkanals [4], thioalkanes [5], nitroalkanes [6], alkanenitriles [7], alkenes [8], alkanoates [9], alkynes [10] and tetrachloroethylene [11] with organic solvents such as alkanes, cyclohexane, benzene or CCl_4: i.e. with inert or unassociated but active components (particularly, non-polar but polarizable molecules).

However, until now, systems containing fluorocompounds have not been considered in the framework of DISQUAC, except for linear monofluoroalkanes+alkane [12]. So the aim of the present paper is to study the mixtures of perfluoroalkanes with different organic solvent (alkanes and monoethers).

The anomalous behaviour of fluorocarbon (FC) solution has been extensively investigated during the fifties. The existing data at the time on vapour pressures, solubilities, heats of mixing and volume changes were the subject of a review article by Scott [13]. Fluorocompounds have been further investigated in recent years due the great importance they have either in biomedical and in industrial applications. After the Montreal Protocol and its successive amendments stating to phase out the ozone depleting chlorinated and fluorochlorinated compounds, FC's and their mixtures were proposed as alternative environmentally friendly refrigerants, fire-extinguishers, foam blowing agents and solvents. More recently the interest of refrigerant industry shifted towards FC mixtures with alkanes or fluorinated ethers in order to ensure high performance refrigerants. As a consequence, the thermophysical properties of fluoro- and halofluoro-compound containing mixtures have attracted the focus of much interest [14–16].

In order that the great number of potential mixtures may be used, the availability of thermodynamic data of mixing and predictive models is of the utmost importance.

The purpose of this and following papers of this series is to investigate the ability of the first-approximation quasi-chemical theory [1], on which the quasi-chemical term in DISQUAC is reliant, to account for the possible interactions in binary mixtures of the polar group F.

The sources of available experimental data and some characteristic values are collected in Tables 1–3.

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1388–6150/$20.00

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Table 1 Molar excess Gibbs energies G^E (T; x_1=0.5) of perfluoroalkane (1)+n-alkane or ether (2) mixtures at various temperatures, T, and equimolar composition: comparison of direct experimental results (exp.)[a] with values calculated (calc.) using the coefficients $C^{\text{dis}}_{\text{sv},1}$ and $C^{\text{quac}}_{\text{sv},1}$ from Tables 8–9; m and n represent the number of C atoms of the alkyl groups attached to the O group in the monoethers

Perfluoroalkane (1)	Solvent (m–O–n) (2)	T/K	G^E (T; x_1=0.5)/J mol^{-1} calc.	G^E (T; x_1=0.5)/J mol^{-1} exp.	Source of experimental data
C_5F_{12}	C_5H_{12}	278.15	1172	1234	[13]
	C_6H_{14}	293.15	1286	1287	[28]
C_6F_{14}	C_6H_{12}	293.15	1156	1140	[28]
	C_6H_{14}	298.15	1322	1304	[28]
			1322	1348	[29]
	C_7H_{16}	298.15	1466	1450[a]	[28]
	C_8H_{18}	298.15	1544	1493[a]	[30]
	iso-C_8H_{18}	323.15	1516	1376	[13]
	2–O–2	293.15	1233	1231	[30]
	3–O–3	323.15	1520	1472	[30]
	4–O–4	313.15	1658	1746	[30]
	1–O–4	298.15	1362	1364	[30]
		317.65	1289	1262	[30]
	2–O–4	323.15	1414	1429	[30]
C_7F_{16}	C_6H_{14}	303.15	1334	1271	[28]
	C_7H_{16}	328.15	1428	1310	[13]
	3–CH_3–C_7H_{15}	343.15	1521	1510	[13]
C_8F_{18}	C_6H_{14}	313.15	1314	1294	[28]

[a] Extrapolated value

Theory

DISQUAC model [17, 18] is a physical model based on the rigid lattice theory developed by Guggenheim [19] for liquid mixtures. The main features of the DISQUAC are: (a) the partition function is factorized in two terms, in such a way that the excess function are calculated as the sum of two contributions: a dispersive term which represent the contribution from dispersive forces, and a quasi-chemical term which arises from the anisotropy of the field forces created by the solution molecules; in the case of G^E, the combinatorial entropy is represented by the Flory–Huggins equation [20]; (b) the interaction parameters are assumed to be structure dependent; (c) mixtures are studied systematically in order of increasing complexity of molecular structure and intermolecular interactions.

In the classic quasichemical model [20], 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 [20]. In the classical model, the interchange energies of every (s, v) contact generate no 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=∞. 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=∞), eventually supplemented by an electrostatic, non-random, contribution treated quasi-chemically with a constant coordination number z.

The use of a single coordination number z in calculating the quasichemical term is one of the advantages of DISQUAC. This permits the model to apply to mixtures containing groups of different polarities. The degree of non randomness is expressed by the relative amounts of quasi-chemical to dispersive terms. If both groups, s and v, are non polar, then the contact (s, v) is characterized by the dispersive coefficients $C^{\text{dis}}_{\text{sv},1}$ only, all $C^{\text{quac}}_{\text{sv},1}$=0. If one group is polar and the other non-polar, then the contact (s, v) is characterized by both sets of coefficients, $C^{\text{dis}}_{\text{sv},1}$ and $C^{\text{quac}}_{\text{sv},1}$. In a binary non-polar or polar (component 1)+non-polar

Table 2 Molar excess enthalpies H^E (T; x_1=0.5) of n-perfluoroalkanes (1)+n-alkanes or ether (2) mixtures at various temperatures, T, and equimolar composition: comparison of direct experimental results (exp.)[a] with values calculated (calc.) using the coefficients $C^{\text{dis}}_{\text{sv},1}$ and $C^{\text{quac}}_{\text{sv},1}$ from Tables 8–9; m and n represent the number of C atoms of the alkyl groups attached to the O group in the monoethers

Perfluoroalkane (1)	Solvent (m–O–n) (2)	T/K	H^E (T; x_1=0.5)/J mol^{-1} calc.	exp.	Source of experimental data
C_5F_{12}	C_5H_{12}	277.15	1804	1549	[13]
	C_6H_{14}	293.15	1977	1937	[31]
C_6F_{14}	C_5H_{12}	293.15	1906	1986	[31]
	C_6H_{14}	298.15	2100	2093	[31]
			2100	2173	[29]
		313.15	2100	2373	[13]
		308.15	2100	2135	[29]
	C_7H_{16}	298.15	2274	2291[a]	[31]
	2-$CH_3C_7H_{15}$	288.05	2433	2050[a]	[31]
		298.15	2433	2170[a]	[31]
	C_8H_{18}	298.15	2433	2162[a]	[31]
	2–O–2	293.15	2249	2247	[31]
	3–O–3	298.15	2636	2520[a]	[31]
	4–O–4	298.15	2914	2447[a]	[31]
	1–O–4	298.15	2388	2347[a]	[31]
C_7F_{16}	2–O–4	298.15	2547	2429[a]	[31]
	C_6H_{14}	298.15	2203	2389[a]	[31]
	iso-C_8H_{18}	303.15	2572	2110	[29]
C_8F_{18}	C_6H_{14}	298.15	2291	2367[a]	[31]

[a] Extrapolated value

(component 2) mixture, the shapes of the calculated G^E and H^E curves, adjusted to fixed equimolar values, depend on the relative amounts of quasi-chemical to dispersive terms. The mole fraction, x_1^{max}, of the maxima of the dispersive curves, $G^{\text{E,dis}}_{\text{int}}$ and $H^{\text{E,dis}}$ $vs.$ x_1, are determined by geometrical factors only, $x_1^{\text{max}} = 1/(1+\sqrt{q1/q2})$. The quasi-chemical curves, $G^{\text{E,quac}}_{\text{int}}$ and especially $H^{\text{E,quac}}$, 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^E and H^E $vs.$ x_1 curves, than by using the classical quasi-chemical model. This being supported by experiment [18] represents another advantage of DISQUAC.

In this work the ‘reference’ value chosen for the coordination number is z=4, the same as in our previous application of DISQUAC [17, 21]. 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 require a smaller value of z to reproduce the pronounced experimental asymmetry of the excess functions as, e.g., in alcohol+alkane mixtures [22]. 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 (aliphatic), weakly polar (ether) and polar (fluorine). DISQUAC should be well suitable to study mixtures formed by these groups. The relevant thermodynamic properties are listed in Tables 1–5.

Assessment of geometrical parameters

Every mixtures under study, i.e. perfluoroalkane+alkane, or +ethers are regarded as possessing three types of contact surfaces: (1), type f, fluorine (F group); (2), type a, aliphatic (CH_3, CH_2 and C groups, which are assumed to exert the same force field); (3), type e, (O group in ethers).

The total relative molecular volumes r_i, surfaces q_i, and surface fractions α_{si}, were calculated on the basis of the relative group parameters, the volumes r_G and surfaces q_G, recommended by Bondi [23], taking arbitrarily the volume V_{CH_4} and

Table 3 Upper critical solution temperature, UCST, of *n*-perfluoroalkanes (1)+*n*-alkanes or ether (2) mixtures: comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficients $C^{\mathrm{dis}}_{\mathrm{sv},1}$ and $C^{\mathrm{quac}}_{\mathrm{sv},1}$ from Tables 8–9; *m* and *n* represent the number of C atoms of the alkyl groups attached to the O group in the monoethers

Perfluoroalkane (1)	Solvent (*m*–O-*n*) (2)	$\mathrm{UCST_{calc}}$	$\mathrm{UCST_{exp}}$	Source of experimental data
C_5F_{12}	C_5H_{12}	296	266	[32]
	C_6H_{14}	311	288	[32]
C_6F_{14}	C_5H_{12}	307	273	[32]
	C_6H_{14}	326	294	[29]
		326	296	[32]
	C_7H_{16}	340	315	[29]
		340	316	[32]
	C_8H_{18}	350	324	[29]
		350	335	[32]
	C_9H_{20}	356	354	[32]
	1–O–4	301	313	[30]
	2–O–4	315	322	[30]
	3–O–3	316	322	[30]
	4–O–4	339	–	Fig. 11
C_7F_{16}	C_5H_{12}	315	282	[32]
	C_6H_{14}	337	302	[33]
		337	303	[32]
	C_7H_{16}	353	323	[34]
	C_8H_{18}	366	341	[35]
	C_9H_{20}	376	360	[32]
C_8F_{18}	C_6H_{14}	344	311	[36]
	C_7H_{16}	364	331	[36]
	C_8H_{18}	379	350	[36]
		379	348	[32]
		379	349	[39]
	C_9H_{20}	391	369	[36]

surface $A_{\mathrm{CH_4}}$ of methane as unity [20], and are listed in Tables 6 and 7.

Estimation of interaction parameters

It is sometimes difficult to assign unambiguously interchange dispersive and quasi-chemical 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 [24, 25]. 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.

In Tables 8 and 9 are reported respectively the dispersive and quasi-chemical interchange coefficients for contacts (a, e) and (f, e). The values listed in Tables 8, 9 were calculated with zero heat capacity dispersive coefficients.

Table 4 Activity coefficients at infinite dilution, $\ln\gamma_1^\infty$, of *n*-perfluoroalkanes (1)+*n*-alkanes or ether (2) mixtures: comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficients $C_{\mathrm{sv},1}^{\mathrm{dis}}$ and $C_{\mathrm{sv},1}^{\mathrm{quac}}$ from Tables 8–9

Component 1	Component 2	T/K	$\ln\gamma_1^\infty$		$\ln\gamma_2^\infty$		Source of exp. data
			calc.	exp.	calc.	exp.	
C_5F_{12}	C_6H_{14}	293.05	2.57	2.46	1.79	2.19	[28]
C_6F_{14}	C_5H_{12}	293.65	2.83	2.55	1.42	1.64	[28]
	C_6H_{14}	298.15	2.86	2.72	1.70	2.02	[28]
				2.89		1.72	[37]
				2.81		2.14	[40]
	C_7H_{16}	298.15	2.92	3.05	1.99	2.40	[28]
		317.65	2.64	2.55	1.80	2.18	[28]
	C_8H_{18}	313.15	2.73	2.91	2.09	2.36	[28]
C_7F_{16}	C_6H_{14}	303.15	3.11	2.78	1.60	1.82	[28]
	C_7H_{16}	298.15	3.29	3.43	1.95	2.10	[37]
C_8F_{18}	C_6H_{14}	313.15	3.24	2.83	1.46	1.75	[28]
C_6F_{14}	2–O–2	293.15	2.54	2.93	2.41	1.91	[30]
	3–O–3	298.15	2.72	3.14	2.96	2.55	[30]
		323.15	2.32	2.19	2.45	1.72	[30]
	4–O–4	313.15	2.56	3.22	3.14	2.38	[30]
	1–O–4	298.15	2.59	3.03	2.59	1.27	[30]
		317.65	2.28	2.45	2.22	1.62	[30]
	2–O–4	323.15	2.31	2.43	2.44	2.14	[30]

Table 5 Excess partial molar enthalpies at infinite dilution[a] $\overline{H}_j^\infty$ (*j*=1, 2) of *n*-perfluoroalkanes (1)+*n*-alkanes or ether (2) mixtures: comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficients $C_{\mathrm{sv},1}^{\mathrm{dis}}$ and $C_{\mathrm{sv},1}^{\mathrm{quac}}$ from Tables 8–9

Component 1	Component 2	T	$\overline{H}_1^\infty$		$\overline{H}_2^\infty$		Source of exp. data
			calc.	exp.	calc.	exp.	
C_5F_{12}	C_6H_{14}	293.15	9.6	10.9	6.7	9.8	[28]
		298.15	9.6	11.1	6.7	10.0	[28]
C_6F_{12}	C_5H_{12}	293.15	11.2	12.0	6.8	8.4	[28]
		298.15	11.2	12.2	6.8	8.6	[28]
	C_6H_{14}	298.15	11.2	12.6	6.7	9.9	[28]
	C_7H_{16}	298.15	11.2	12.7	7.7	11.3	[28]
	C_8H_{18}	298.15	11.2	13.2	8.6	12.7	[28]
	$2\text{–}CH_3C_7H_{15}$	288.05	11.2	11.6	8.6	11.0	[28]
		298.15	11.2	12.0	8.6	11.4	[28]
C_7F_{16}	C_6H_{14}	298.15	12.8	14.6	6.7	9.4	[28]
	C_7H_{16}	298.15	12.8	15.5			[38]
C_8F_{18}	C_6H_{14}	298.15	14.4	15.4	6.7	9.3	[28]
C_6F_{12}	2–O–2	293.15	11.9	14.2	5.6	9.9	[30]
	3–O–3	298.15	11.4	13.5	7.3	11.7	[30]
	4–O–4	298.15	11.2	13.6	9.0	13.8	[30]
	1–O–4	298.15	11.6	14.1	6.4	11.2	[30]
	2–O–4	298.15	11.4	13.8	7.3	12.2	[30]

[a] units: kJ mol^{-1}

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.

Perfluoroalkanes+n-alkanes

These systems are characterized by a single contact (a, f). The dispersive coefficients have been determined, in the random mixing approximation, from G^E and H^E of mixtures, totally miscibles, of perfluoropentane and perfluorohexane+*n*-pentane or +*n*-hexane. The rules we found as follows: (1a) the dispersive coefficients, $C^{\mathrm{dis}}_{\mathrm{af},1}$, are the same for all the perfluoroalkanes (0.534 for l=1 and 0.815 for l=2) (Table 8).

The values of the dispersive parameters are practically the same found by Artal *et al.* [12] for the same contact in 1-monofluoroalkanes+*n*-alkane mixtures (0.544 for l=1 and 0.838 for l=2). Being monofluoroalkanes polar compounds their mixtures with alkanes were treated using also a non negligible quasi-chemical contribution (4.266 for l=1 and 6.578 for l=2). One should expect that as increase the number of F atoms in the same molecule decrease the quasi-chemical contribution until to reach zero for perfluoroalkanes as found in previous studies on mixtures of alkanes with polychloroalkanes [1] or oxaalkanes [2] or thioalkanes [5].

Table 6 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 [27], ($V_{CH_4}=17.12\cdot10^{-6}$ m^3 mol^{-1}; $A_{CH_4}=2.90\cdot10^5$ m^2 mol^{-1})

Group	r_G	q_G
$-CH_3$	0.79848	0.73103
$>CH_2$	0.59755	0.46552
$>CH$	0.39601	0.19660
$>C<$	0.19451	0.00000
F^{-}	0.35047	0.39655
–O–	0.21612	0.20690

Table 8 Interchange energy coefficients dispersive, $C^{\mathrm{dis}}_{\mathrm{sv},1}$, for contact (a, f), (a, e) and (e, f) in the perfluoroalkane+*n*-alkane or ether mixtures (l=1, Gibbs energy; l=2, enthalpy)

$C^{\mathrm{dis}}_{\mathrm{af},1}$	$C^{\mathrm{dis}}_{\mathrm{af},2}$	$C^{\mathrm{dis}}_{\mathrm{ae},1}$	$C^{\mathrm{dis}}_{\mathrm{ae},2}$	$C^{\mathrm{dis}}_{\mathrm{ef},1}$	$C^{\mathrm{dis}}_{\mathrm{ef},2}$
0.534	0.815	10.60	18.20	6.50	18.20

Table 9 Interchange energy coefficients quasi-chemical, $C^{\mathrm{quac}}_{\mathrm{sv},1}$, for contacts (a, e) and (e, f) in the perfluoroalkane+alkane or monoether mixtures (l=1, Gibbs energy; l=2, enthalpy); *m* and *n* represent the number of C atoms of the alkyl groups attached to the O group in the monoethers

Monoether *m*–O–*n*	$C^{\mathrm{quac}}_{\mathrm{ae},1}$	$C^{\mathrm{quac}}_{\mathrm{ae},2}$	$C^{\mathrm{quac}}_{\mathrm{ef},1}$	$C^{\mathrm{quac}}_{\mathrm{ef},2}$
1–O–4	3.40	5.60	12.00	21.00
2–O–2	3.30	5.00	12.00	21.00
2–O–4	3.00	4.80	12.00	21.00
3–O–3	2.80	2.90	12.00	21.00
4–O–4	2.60	1.50	12.00	21.00

Table 7 Volumes, r_i, total surfaces, q_i, and molecular surface fractions, α_{si}, (s=a, e, f) of perfluoroalkane, alkane and ethers calculated from the group increments r_G and q_G given in Table 3

Compound	r_i	q_i	α_{ai}	α_{ei}	α_{fi}
C_5F_{12}	5.1779	4.7586	0.0000	0.0000	1.0000
C_6F_{14}	6.0736	5.5517	0.0000	0.0000	1.0000
C_7F_{16}	6.9691	6.3448	0.0000	0.0000	1.0000
C_8F_{18}	7.8645	7.1379	0.0000	0.0000	1.0000
C_5H_{12}	3.3896	2.8586	1.0000	0.0000	0.0000
C_6H_{14}	3.9871	3.3241	1.0000	0.0000	0.0000
C_7H_{16}	4.5847	3.7891	1.0000	0.0000	0.0000
C_8H_{18}	5.1823	4.2552	1.0000	0.0000	0.0000
C_9H_{20}	5.7798	4.7207	1.0000	0.0000	0.0000
$CH_3–O–(CH_2)_3CH_3$	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

Perfluoroalkanes+ethers

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

(2a) The (a, f) contact energies, $C^{\mathrm{dis}}_{\mathrm{af},1}$, determined independently on the basis of perfluoroalkane+*n*-alkane mixtures (see rule (1a)), can be used.

(2b) The aliphatic/oxygen (a, e), determined independently on the basis of monoethers+alkane mixtures [6], are represented by dispersive parameters $C^{\mathrm{dis}}_{\mathrm{ae},1}$=10.60 and $C^{\mathrm{dis}}_{\mathrm{ae},2}$=18.20 and are the same for all the monoethers.

(2c) The quasi-chemical coefficients of the (a, e)-contact, $C^{\mathrm{quac}}_{\mathrm{ae},1}$, determined independently on the basis of ethers+*n*-alkane mixture [6], decreases regularly with increasing *m* and *n*, the chain length of the alkyl groups adjacent the –O– group (Table 9).

(2d) The dispersive coefficients of the (e, f)-contact, $C^{\mathrm{dis}}_{\mathrm{ef},1}$, determined from the mixtures of perfluoroalkane+ethers, are the same for all the perfluoroalkanes (6.5 for *l*=1 and 18.2 for *l*=2) (Table 6) and remain constant with increasing *m* and *n*, the chain length of the alkyl groups adjacent the –O– group (Table 8).

(2e) The quasi-chemical coefficients of the (e, f) contact, $C^{\mathrm{quac}}_{\mathrm{ef},1}$, determined from the mixtures of perfluoroalkane+ethers, are the same for all the perfluoroalkanes (12.0 for *l*=1 and 21.0 for *l*=2) and remain constant with increasing *m* and *n*, the chain length of the alkyl groups adjacent the –O– group (Table 9).

Comparison with experiment

Using the set of parameters dispersive and quasi-chemical reported in Tables 8–9 a good agreement with experiment is obtained for the excess Gibbs energies and excess enthalpies of perfluoroalkane+*n*-alkane and +ethers (Tables 1, 2 and Figs 1–4). Activity coefficients (γ_1^∞) and excess partial molar enthalpies ($\overline{H}_j^\infty$) at infinite dilution are collected in Tables 4 and 5, respectively. Calculated γ_1^∞ of PFA are overestimated while γ_2^∞ of alkanes are underestimated. The opposite happens for activity coefficients on mixtures containing ethers. Both $\overline{H}_1^\infty$ and $\overline{H}_2^\infty$ are underestimated for PFA+alkanes and PFA+ethers mixtures.

Partially miscibility has been reported for several mixtures of a perfluoroalkane with an alkane or monoether (Table 3). Using the same parameters of Tables 8–9 we have calculated the liquid–liquid equilibrium (LLE) curves of the perfluoroalkane+*n*-alkane and +monoether mixtures (Figs 5–11). The calculated upper critical solution temperature

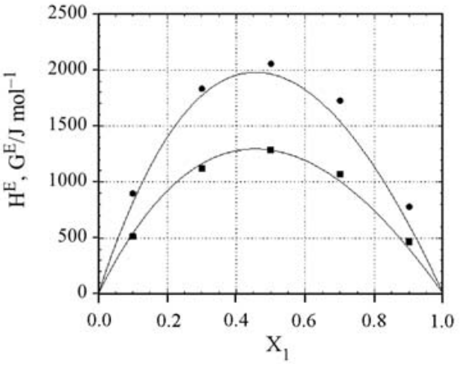

Fig. 1 Comparison of theory with experiments for the molar excess Gibbs energies, G^E, and molar excess enthalpies, H^E, at 298.15 K, for perfluoropentane (1)+*n*-hexane (2) mixtures *vs.* x_1, the mole fraction of perfluoropentane: — – predicted values; experimental results: ● – enthalpy; ■ – Gibbs energy

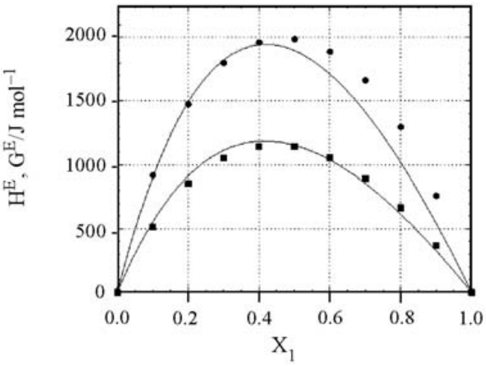

Fig. 2 Comparison of theory with experiments for the molar excess Gibbs energies, G^E, and molar excess enthalpies, H^E, at 298.15 K, for perfluorohexane (1)+*n*-pentane (2) mixtures *vs.* x_1, the mole fraction of perfluorohexane: — – predicted values; experimental results: ● – enthalpy; ■ – Gibbs energy

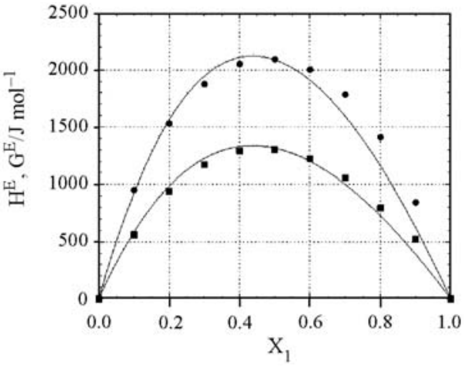

Fig. 3 Comparison of theory with experiments for the molar excess Gibbs energies, G^E, and molar excess enthalpies, H^E, at 298.15 K, for perfluorohexane (1)+*n*-hexane (2) mixtures *vs.* x_1, the mole fraction of perfluorohexane: — – predicted values; experimental results: ● – enthalpy; ■ – Gibbs energy

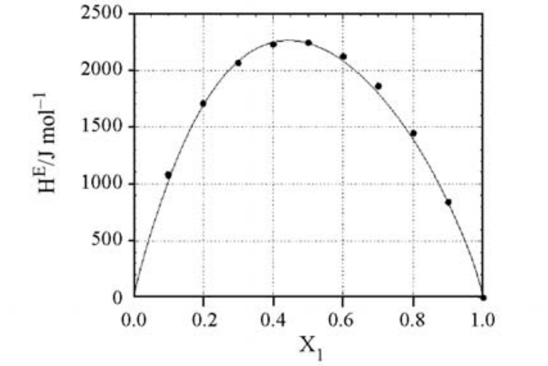

Fig. 4 Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for perfluorohexane (1)+diethylether (2) mixtures *vs.* x_1, the mole fraction of perfluorohexane: — – predicted values; ● – experimental results

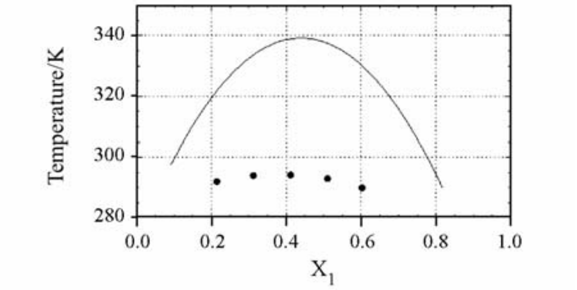

Fig. 5 Comparison of theory with experiments for the liquid–liquid equilibrium, LLE, for perfluorohexane (1)+*n*-hexane (2) mixtures *vs.* x_1, the mole fraction of perfluorohexane: — – predicted values; ● – experimental results

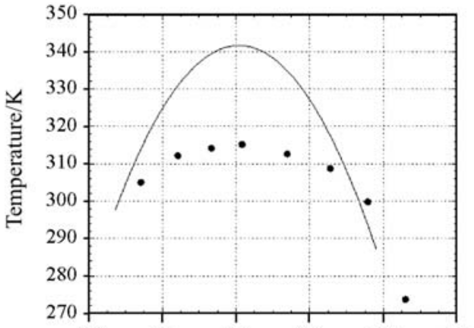

Fig. 6 Comparison of theory with experiments for the liquid–liquid equilibrium, LLE, for perfluorohexane (1)+*n*-heptane (2) mixtures *vs.* x_1, the mole fraction of perfluorohexane: — – predicted values; ● – experimental results

(UCST) are compared in Table 3 with experimental ones. In most cases experimental T^C are lower and the LLE curves flatter, than calculated values. This may well be due to the proximity of the critical solution

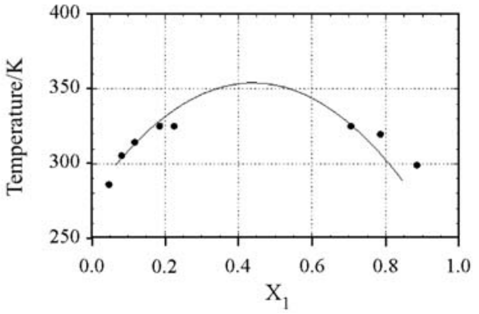

Fig. 7 Comparison of theory with experiments for the liquid–liquid equilibrium, LLE, for perfluorohexane (1)+*n*-octane (2) mixtures *vs.* x_1, the mole fraction of perfluorohexane: — – predicted values; ● – experimental results

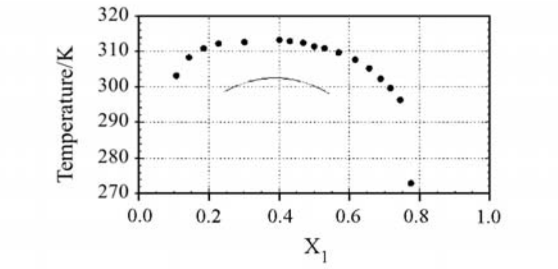

Fig. 8 Comparison of theory with experiments for the liquid–liquid equilibrium, LLE, for perfluorohexane (1)+methylbutylether (2) mixtures *vs.* x_1, the mole fraction of perfluorohexane: — – predicted values; ● – experimental results

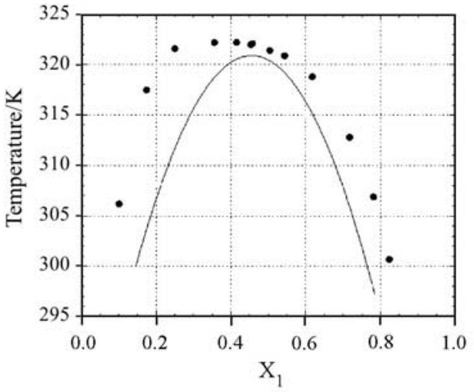

Fig. 9 Comparison of theory with experiments for the liquid–liquid equilibrium, LLE, for perfluorohexane (1)+ethylbutylether (2) mixtures *vs.* x_1, the mole fraction of perfluorohexane: — – predicted values; ● – experimental results

point. The flattening is physically understandable as a consequence of increasing non randomness at lower temperature. Although the agreement between experimental and calculated data is poor, we consider the ability to predict LLE curves by using the parameters already determined for VLE a success of DISQUAC model. As known infact, empirical group

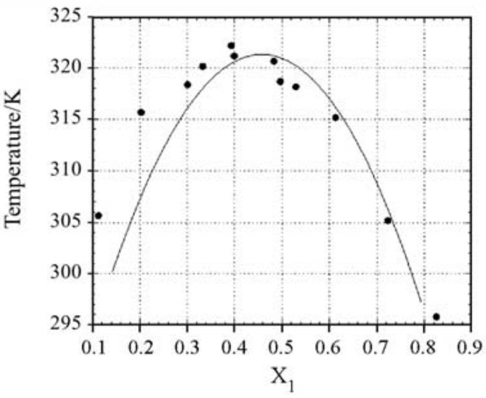

Fig. 10 Comparison of theory with experiments for the liquid–liquid equilibrium, LLE, for perfluorohexane (1)+dipropylether (2) mixtures *vs.* x_1, the mole fraction of perfluorohexane: — – predicted values; ● – experimental results

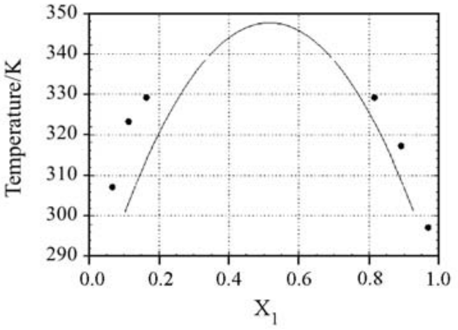

Fig. 11 Comparison of theory with experiments for the liquid–liquid equilibrium, LLE, for perfluorohexane (1)+dibutylether (2) mixtures *vs.* x_1, the mole fraction of perfluorohexane: — – predicted values; ● – experimental results

contribution methods, such as UNIFAC [26], have a great deal of difficulty in dealing the prediction of the LLE using the same parameters determined from the LVE. 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 parameters for the LLE applies to UNIFAC as well as to any other group contribution model [27].

Discussion

The main advantage of using DISQUAC, apart from the more accurate representation of all the experimentally available low-pressure phase equilibrium and related data, is the better physical significance of the parameters, than in any other group contribution method. To this purpose, the interchange enthalpy of the contact alkane-perfluoroalkane (PFA) ($C_{af,2}$=0.815) can be compared with the values for alkane-cyclohexane ($C_{ac,2}$=0.1533), alkane-benzene ($C_{ab,2}$=0.5623), alkane-CCl_4 ($C_{ad,2}$=0.1896) [20]. The positive sign of all C_{ak} indicates that the surface contacts a–k (k=b, c, d, f) between alkane and hydrocarbon (alicyclic, aromatic) or halogen atoms (Cl, F) produces a lower interaction enthalpy than the average of a–a and k–k interaction enthalpies in pure liquids. The highest value of C_{af} for alkane-PFA suggests that the attractive force between aliphatic groups and F atoms of PFA is weaker than that between alkane and any of cyclohexane, benzene and CCl_4. This is confirmed by a study on the enthalpies of solvation of PFA's, alkanes, and cyclohexane in hexane and perfluorohexane [31]. Perfluoroalkanes proved to be inert molecules that interact weakly with themselves as well as with alkanes.

The choice of adopting structure dependent parameters leads to define a relatively large number of interchange coefficients. This can be justified by the regular trends exhibited by these parameters, conform to what one qualitatively should anticipate based on molecular considerations. This confers to DISQUAC rather unique predictive capabilities, provided it is used within the limits of validity of the underlying statistical theory, the rigid quasi-chemical pseudo-lattice model. The decreasing trend of C_{ae} (Table 9) can be tentatively attributed to the decreasing O–O interaction force in pure liquid ethers with increasing steric hindrance of the aliphatic chains.

In this application, DISQUAC proved itself able to predict G^E, H^E and LLE curves of perfluoroalkane+alkane mixtures by introducing only two new dispersive coefficients characterizing the (a, f) contact. Two dispersive and two quasi-chemical coefficients for (e, f) contact were found necessary in order to predict the thermodynamic behaviour of perfluoroalkane+ether mixtures. In this case we did not need to introduce structure dependent parameters, the dependence on the structure being sufficiently accounted by the parameters previously obtained for (a, e) contact from adjustment on alkane+ether systems [2].

Concerning the temperature dependence of H^E in all cases DISQUAC predicts values too small as all the quantities listed in Tables 1–2 were calculated with zero heat capacity of interchange coefficients, $C_{sv,3}$, dispersive and quasi-chemical. Accordingly the temperature dependence of calculated H^E and G^E results from the Boltzmann factor only.

Conclusions

This work, following the previous on chloroalkanes, oxaalkanes, alkanones, 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 intramolecular 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.

Acknowledgements

We are grateful to Dr. H. V. Kehiaian for helpful suggestions and comments.

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DOI: 10.1007/s10973-007-8753-9