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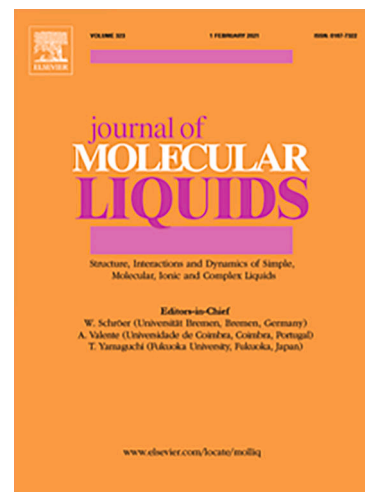
THERMODYNAMICS OF MIXTURES CONTAINING A FLUORINATED BENZENE AND A HYDROCARBON

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Abstract

Fluorobenzene, or 1,4-difluorobenzene or hexafluorobenzene + alkane mixtures and hexafluorobenzene + benzene, or + toluene, or + 1,4-dimethylbenzene systems have been investigated using thermodynamic properties from the literature and through the application of the DISQUAC and UNIFAC (Dortmund) models and the concentration-concentration structure factor (

$S_{CC}(0)$) formalism. DISQUAC interaction parameters for the contacts F/alkane and F/aromatic have been determined. UNIFAC interaction parameters available in the literature for these contacts have been used along calculations. Both models predict double azeotropy for the $C_6F_6 + C_6H_6$ system, although in different temperature ranges. The H_m^E values of the fluorobenzene, or 1,4-difluorobenzene $+$ *n*-alkane systems are positive and are accurately described by the models using interaction parameters independent of the *n*-alkane. This means that no Patterson's effect exists in such mixtures. DISQUAC calculations allow state that such conclusion is still valid for $C_6F_6 + n$-alkane mixtures. DISQUAC provides better results than UNIFAC on C_{pm}^E of solutions involving *n*-alkanes, or on H_m^E of $C_6F_6 +$ aromatic hydrocarbon systems. Mixtures with alkanes are characterized by interactions between like molecules, which are mainly of dispersive type, which is supported, e.g., by the negative C_{pm}^E values of these systems. It is shown that structural effects can contribute largely to H_m^E. This is investigated in terms of the excess molar internal energy at constant volume, U_{Vm}^E, whose values are determined for the investigated solutions. For mixtures with a given *n*-alkane, the relative variation of H_m^E and U_{Vm}^E with the fluorohydrocarbons is different. H_m^E values change in the sequence $C_6F_6 > 1,4\text{-}C_6H_4F_2 > C_6H_6 > C_6H_5F$, while U_{Vm}^E changes in the order: 1,4-$C_6H_4F_2 > C_6H_6 \approx C_6H_5F > C_6F_6$. $C_6F_6 +$ aromatic hydrocarbon mixtures are characterized by interactions between unlike molecules as it is demonstrated by their negative H_m^E values. The application of the $S_{CC}(0)$ formalism reveals that homocoordination is more important in $C_6F_6 + n$-alkane mixtures than in the corresponding systems with C_6H_5F, and that heterocoordination is dominant in the solutions of C_6F_6 with an aromatic hydrocarbon.

Keywords: Fluorinated benzenes/hydrocarbons/ dispersive interactions; structural effects

1. Introduction

There are two important effects which can be present in liquid mixtures formed by *n*-alkane and a molecule A of plate-like or of more or less globular shape [1-4]. They are the so-called Wilhelm's and Patterson's effects. The former is encountered in systems where A is a flat molecule of the type 1,2,4-trimethylbenzene, or 1-methylnaphthalene, or 1,2,4-trichlorobenzene [4,5]. These solutions

show decreasing values of molar excess enthalpies, H_m^E, when n, the number of C atoms in the n-alkane, is increased. Tentatively, such variation has been ascribed to the creation of a certain intramolecular order due to the flat component A hinders the rotational motion of the segments of the flexible molecules of longer n-alkanes. The Patterson's effect is encountered, e.g, in benzene, or toluene or cyclohexane, or CCl_4 + n-alkanes systems. Here, H_m^E values increase in line with n more sharply than expected for mixtures including longer n-alkanes. This has been explained in terms of an extra endothermic contribution to H_m^E which arises from the disruption of the local order existing in the longer n-alkanes. Issues related to order creation or order destruction have been extensively investigated by means of the Flory's theory [3,6]. Application of group contribution models is also very useful at this regards [7,8]. In fact, group contribution methods, which consider n-alkanes as homogeneous molecules, predict a more or less regular increment of H_m^E for A + n-alkane systems. Thus, if H_m^E(experimental) > H_m^E(calculated) for mixtures including longer n-alkanes, then the Patterson's effect is present in such solutions. As an example, we provide a comparison between experimental H_m^E values with the corresponding results obtained from the application of the UNIFAC (Dortmund) model [9] for benzene mixtures. At equimolar composition and 298.15 K, the experimental results are: H_m^E/J mol^{-1} = 931 (n = 7) [10]; 1101 (n = 12) [11]; 1289 (n =16) [11], while the calculated values, in the same units, are: 848 (n = 7); 1009 (n = 12); 1087 (n =16). Therefore, if one is interested in an accurate representation of H_m^E for this class of systems, interaction parameters depending on n must be considered (Figure S1, supplementary material). The zeroth approximation of DISQUAC [12,13] has been applied in this framework to the study of C_6H_6, or C_7H_8, or C_6H_{12} or CCl_4 + n-alkanes systems [7,8,14], and it has been shown that the dispersive enthalpic parameter increases for larger n values. Similarly, the systems 1,2,4-trimethylbenzene, or chlorobenzene, or 1-chloronaphthalene, or bromobenzene + n-alkane have also been investigated using the same approach [5,15,16], although no numerical values for the interaction parameters have been provided. The graphical representation of the dispersive enthalpic parameter vs. n shows that the former decreases when the latter increases, which has been considered as a main feature of systems where the Wilhelm's effect exists.

H_m^E values of binary mixtures formed by one aromatic fluorinated compound (AFC) such as fluorobenzene, or 1,4-difluorobenzene, or hexafluorobenzene and one n-alkane increase in line with n [15,17]. For C_6F_6 solutions, H_m^E (x_1 = 0.5; T = 298.15 K)/J mol^{-1} = 1119 (n =7) and 1324 (n = 14) [15]. Thus, one of the aims of this work is to investigate if Patterson's effect is present in the mentioned systems, by comparing experimental results with those provided by DISQUAC. Along the work, DISQUAC calculations are compared with results obtained from the application of the

UNIFAC (Dortmund) model using interaction parameters from the literature [9,18]. Fluorobenzene is a polar molecule (dipole moment, μ = 1.7 D [19], while both 1,4-difluorobenzene and C_6F_6 have μ = 0 D. However, the latter compound has a rather large quadrupolar moment (31.7 10^{-40} C m^2 [20]), while this magnitude is -21.0 10^{-40} C m^2 for C_6H_5F [20] and -7.7 10^{-40}C m^2 for 1,4-$C_6H_4F_2$ [21]. The study of systems with such characteristics is important for a better understanding of weak no covalent interactions, which are decisive for the prediction and control of organic solid-state structures [22]. With this purpose in mind, our study is extended to hexafluorobenzene + benzene, or + toluene, or + 1,4-dimethylbenzene (14DMBZ) mixtures. The C_6F_6 + C_6H_6 system deserves particular attention by its outstanding properties. It shows double azeotropy [23-25], negative H_m^E values [26,27] (-496 J mol^{-1} at 298.15 K and equimolar composition [27]) and, although both compounds are liquids at room temperature, form a complex of the 1:1 type in solid state [28-30], which is a typical organic crystal. Initially, the existence of this adduct was ascribed to the formation of a bond of the π–π* type between C_6H_6 and C_6F_6 [31,32]. However, spectroscopic studies do not support that the C_6F_6–benzene interactions are due to a charge transfer [33]. Investigations on the charge distributions in these complexes show that their cohesion arises from to interactions between their quadrupolar moments [20,34,35]. On the other hand, the mentioned thermodynamic data suggest that the complex still exists in liquid state, which is supported by detailed studies using neutron or x-diffraction techniques [36]. The selected systems for this study are also investigated in the framework of the concentration-concentration structure factor ($S_{CC}(0)$) formalism [37,38], whose purpose is to try to link the thermodynamic properties of a given liquid mixture with local deviations from the bulk composition. Particularly, the method, based on the Bhatia-Thorton partial structure factors [39], is concerned with the study of fluctuations in the number of molecules in a binary mixture regardless of the components, the fluctuations in the mole fraction and the cross fluctuations.

Aromatic fluorinated compounds have many applications. For example, fluorobenzene is used in the manufacturing of Li batteries [40]. On the other hand, aromatic compounds are commonly encountered in urban air arising from the fossil fuel combustion emissions [41] and the understanding of the atmospheric chemistry of these compounds is required to assess their environmental impact [42]. In this context, fluorobenzene is used in the development of new lower boiling fuels which protect the environment by reducing emissions. The design of new organic co-crystals is relevant in the pharmaceutical industry since can replace salts. In addition, complex aromatic fluorinated molecules are used as antidepressants, or as drugs to reduce cholesterol [43]. The study of aromatic-aromatic interactions involving fluorine substituted benzenes is also interesting in order to investigate the binding of drugs at their sites of action [19,44].

2. THEORIES

2.1 DISQUAC

DISQUAC is based on the rigid lattice theory developed by Guggenheim [45]. Some relevant features of the model are now described. (i) The total molecular volumes, r_i, surfaces, q_i, and the molecular surface fractions, α_i, of the compounds present in the mixture are calculated additively on the basis of the group volumes R_G and surfaces Q_G recommended by Bondi [46]. As volume and surface units, the volume R_{CH4} and surface Q_{CH4} of methane are taken arbitrarily [13]. The geometrical parameters for the groups referred to in this work are given elsewhere [13,47,48]. (ii) The partition function is factorized into two terms, and the excess functions are calculated as the sum of two contributions: a dispersive (DIS) term which represents the contribution from the dispersive forces; and a quasichemical (QUAC) term which arises from the anisotropy of the field forces created by the solution molecules. For the molar excess Gibbs energy, G_m^E, a combinatorial term, $G_m^{E,COMB}$, described by the Flory-Huggins equation [13] must be included. Thus,

$$G_m^E = G_m^{E,COMB} + G_m^{E,DIS} + G_m^{E,QUAC} \tag{1}$$

$$H_m^E = H_m^{E,DIS} + H_m^{E,QUAC} \tag{2}$$

(iii) The interaction parameters are assumed to be dependent on the molecular structure. (iv) The coordination number $z = 4$ is used for all the polar contacts. This is an important shortcoming of the model, and is partially removed via the hypothesis of considering structure dependent interaction parameters. (v) It is also assumed that there is no volume change upon mixing, that is, V_m^E, the excess molar volume, is 0.

The equations used to calculate the DIS and QUAC contributions to G_m^E and H_m^E in the framework of DISQUAC are given elsewhere [12,49]. The temperature dependence of the interaction parameters is expressed in terms of the DIS and QUAC interchange coefficients [12, 49], $C_{st,l}^{DIS}; C_{st,l}^{QUAC}$ where s ≠ t are two contact surfaces present in the mixture and $l = 1$ (Gibbs energy; $C_{st,1}^{DIS/QUAC} = g_{st}^{DIS/QUAC}(T_o) / RT_o$); $l = 2$ (enthalpy, $C_{st,2}^{DIS/QUAC} = h_{st}^{DIS/QUAC}(T_o) / RT_o$)); $l = 3$ (heat capacity, $C_{st,3}^{DIS/QUAC} = c_{pst}^{DIS/QUAC}(T_o) / R$)). $T_o = 298.15$ K is the scaling temperature and R, the gas constant.

2.2 UNIFAC (Dortmund)

Modified UNIFAC (Dortmund version) differs from original UNIFAC [50] by the combinatorial term and the temperature dependence of the interaction parameters. The equations

needed to calculate G_m^E and H_m^E are obtained from the fundamental equation for the activity coefficient γ_i of component i:

$$\ln \gamma_i = \ln \gamma_i^{COMB} + \ln \gamma_i^{RES} \tag{3}$$

where $\ln \gamma_i^{COMB}$ and $\ln \gamma_i^{RES}$ are, respectively, the combinatorial and residual terms. Equations can be found elsewhere [49]. On the other hand, in this UNIFAC version, the geometrical parameters, the relative van der Waals volumes, and the relative van der Waals surfaces of the different groups/subgroups are not calculated from molecular parameters like in the original UNIFAC, but fit together with the interaction parameters to the experimental values of the thermodynamic properties considered. In the framework of UNIFAC (Dortmund), AFCs are represented by the main group ACF (Nº 38). No subgroups are defined within this main group in such way that, e.g., hexafluorobenzene is considered as an homogeneous molecule. The geometrical and interaction parameters were taken from the literature and used without modification [9,18].

2.3 The concentration-concentration structure factor formalism

For a binary system, the $S_{CC}(0)$ function can be determined from the equation [37,38]:

$$S_{CC}(0) = \frac{x_1 x_2}{1 + \dfrac{x_1 x_2}{RT}\left(\dfrac{\partial^2 G_m^E}{\partial x_1^2}\right)_{P,T}} \tag{4}$$

In the case of ideal mixtures, $G_m^{E,id} = 0$; and $S_{CC}^{id}(0) = x_1 x_2$. Stability conditions require that $S_{CC}(0) > 0$. Thus, if a system is close to phase separation, $S_{CC}(0)$ must be large and positive and the dominant trend is the separation between components (homocoordination), and $S_{CC}(0) > x_1 x_2$. If compound formation between components exists (heterocoordination), $S_{CC}(0)$ must be very low and $0 < S_{CC}(0) < x_1 x_2$. More details can be encountered in reference [37].

3. Estimation of DISQUAC interaction parameters

In the framework of DISQUAC, C_6H_5F, or $1,4\text{-}C_6H_4F_2$, or C_6F_6 + n-alkane, or + cyclohexane, or + methylcyclohexane, or + benzene, or + toluene, or + 14DMBZ mixtures are regarded as possessing the following four types of surfaces: (i) type a, aliphatic (CH_3, CH_2, in n-alkanes, methylcyclohexane, toluene or 14DMBZ); (ii) type b, aromatic (C_6H_6 in benzene, C_6H_5- in toluene or fluorobenzene, C_6H_4- in 14DMBZ or 1,4-difluorobenzene, or aromatic ring in C_6F_6); (iii) type c, c-CH_2 or c-CH in cyclohexane or methylcyclohexane; (iv) type f, F in C_6H_5F, $1,4\text{-}C_6H_4F_2$ or C_6F_6. Detailed

explanations on the general procedure applied in the estimation of the DISQUAC interaction parameters have been given elsewhere [12,49]. Some important remarks are provided below.

3.1 The C_6H_5F, or $1,4$-$C_6H_4F_2$, or C_6F_6 + C_6H_6 systems

These mixtures are characterized only by the (b,f) contact. In view of the thermodynamic properties of the solution containing C_6F_6, described in Introduction, we have assumed that the mentioned contact in this solution is represented by DIS and QUAC interaction parameters (Table 1). The C_6H_5F, or $1,4$-$C_6H_4F_2$ + C_6H_6 systems show low H_m^E and G_m^E values. For example, at equimolar composition and 303.15 K, H_m^E/J mol^{-1} = 1 (C_6H_5F) and 65 ($1,4$-$C_6H_4F_2$) [51]. In addition, for the C_6H_5F + C_6H_6 system at x_1 = 0.5 and 348.15 K, G_m^E = 27 J mol^{-1} [52]. These experimental results suggest that the corresponding (b,f) contacts can be represented by DIS parameters only. Calculations showed that the $C_{bf,l}^{DIS}$ (l =1,2,3) coefficients are negligible. Thus, for the sake of simplicity, we have assumed that $C_{bf,l}^{DIS}$ = 0 (l =1,2,3) for the mixtures with C_6H_5F, or $1,4$-$C_6H_4F_2$.

3.2 The C_6H_5F, or $1,4$-$C_6H_4F_2$, or C_6F_6 + alkane systems

Three types of contacts exist in these mixtures: (s,b), (s,f) and (b,f), where s = a, aliphatic in *n*-alkanes or methylcyclohexane; or s = c, c-CH$_2$ or c-CH in cyclohexane or methylcyclohexane. The (s,b) contacts are described by dispersive interaction parameters only and are known from the study of alkylbenzene + alkane mixtures for systems with toluene, or 14DMBZ [47]. However, interaction parameters are not available for solutions including hexamethylbenzene and a survey of literature data using the ThermoLit application showed that there is a lack of the required experimental data to conduct a fitting of the interaction parameters for $C_6(CH_3)_6$ + alkane mixtures. As a consequence, we have considered that $C_{sb,l}^{DIS}$ = 0 (s = a,c; l =1,2,3) for systems with C_6F_6. Regarding the (b,f) contacts, the interaction parameters are already known (see above). The parameters for the (a,f) contacts (Table 1) were then determined under the following conditions: (i) the contacts are represented by DIS and QUAC interaction parameters. (ii) The QUAC parameters are considered to be the same for mixtures with C_6H_5F or $1,4$-$C_6H_4F_2$. The adjustment of the (c,f) parameters was conducted assuming that that $C_{af,l}^{QUAC} = C_{cf,l}^{QUAC}$ (l =1,2,3). In the framework of DISQUAC, this is a typical procedure applied when investigating, e.g., mixtures formed by ether [53] or chloroalkane [54], or *n*-alkanone [55], or linear organic carbonate [56] or tertiary amide [57], or 1-alkanol [58] and *n*-alkane or cyclohexane.

3.3 The C_6F_6 + toluene, or +$1,4$-dimethylbenzene systems

These mixtures are also built by three contacts: (a,b); (a,f) and (b,f). The interaction parameters for (a,b) and (a,f) contacts are already known. The determination of the parameters for the (b,f) contacts was performed under the basic assumption that the systems with benzene or toluene or 1,4-dimethylbenzene are characterized by the same QUAC coefficients but different DIS parameters (see

Table 1). A similar procedure we applied in previous studies concerned with mixtures formed by tertiary amide [57], or 1-alkanol [59], or 2-alkanol [60], or sulfolane [61] and an aromatic hydrocarbon.

4. Theoretical results

Results from DISQUAC on phase equilibria, H_m^E and C_{pm}^E are shown in Tables 2-5 and in Figures 1-6. Tables 2 and 4 contain relative deviations for pressure and for H_m^E, respectively, defined as

$$\sigma_r(P) = \{\frac{1}{N}\sum \left[\frac{P_{exp} - P_{calc}}{P_{exp}}\right]^2\}^{1/2} \tag{5}$$

$$dev(H_m^E) = \{\frac{1}{N}\sum \left[\frac{H_{m,exp}^E - H_{m,calc}^E}{H_{m,exp}^E(x_1 = 0.5)}\right]^2\}^{1/2} \tag{6}$$

where N stands for the number of data points. Similarly, results from the application of the UNIFAC model are listed in Tables 2,4 and 5.

Table 6 contains DISQUAC calculations on $S_{CC}(0)$ (see Figure 7), and a comparison between theoretical results with experimental values determined in this work using VLE data from the literature (see also Figure S2 of supplementary material). We note that DISQUAC is a reliable tool to evaluate the $S_{CC}(0)$ magnitude.

Results on the double azeotropy of the $C_6F_6 + C_6H_6$ system deserve some comments. Experimental data show that two azeotropes are encountered in the temperature range (303.15-453.15) K [23-25]. UNIFAC describes correctly this behaviour between (303.15-363.15) K. At 373.15, the model predicts only a positive azeotrope at $x_{1az} = 0.25$ and $P_{az} = 188.2$ kPa. DISQUAC only predicts the existence of positive azeotropes at the lower temperatures, i.e. in the range (303.15-350.15) K. From 353.45 K to 413.15 K, DISQUAC correctly predicts the existence of two azeotropes. In fact, at 413.15 K, we obtain $x_{1az} = 0.25$, $P_{az} = 505.1$ kPa and $x_{1az} = 0.60$, $P_{az} = 501$ kPa. The $C_6F_6 + C_6H_{12}$ system has a eutectic point at $x_{1eu} = 0.185$ and $T_{eu} = 251.6$ K [28]. The DISQUAC results, $x_{1eu} = 0.162$ and $T_{eu} = 252.3$ K, show the model can be applied in a wide range of temperature. On the other hand, neglecting ternary interactions, i.e., using binary parameters only, DISQUAC provides the following $\sigma_r(P)$ values for the VLE at 298.15 K of the ternary systems $C_6F_6 + C_6H_6$ + tetradecane ($N = 27$) [62] or + hexadecane ($N = 29$) [63]: 0.040 and 0.045, respectively, which are very close to UNIFAC results (0.049 and 0.041).

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5. Discussion

Below, we are referring to values of the thermodynamic properties at equimolar composition and 298.15 K.

5.1 Alkane mixtures

These systems show positive H_m^E values (Table 4, see below), and therefore are characterized by interactions between like molecules. As already mentioned, μ, of C_6H_5F is 1.7 D [19], while C_6F_6 and 1.4-$C_6H_4F_2$ have $\mu = 0$ D [19]. However, (C_{pm}^E / J mol^{-1} K^{-1}) values of C_6H_5F or C_6F_6 + alkane mixtures are negative (-1.12 [17] and -1.18 [15], respectively, for the corresponding heptane systems, see Table 5), which indicates that dispersive interactions are dominant. Negative C_{pm}^E values are typically ascribed to order destruction [1-3]. This is also the case of C_6H_6, or C_6H_{12} + n-alkane systems. For example, C_{pm}^E /J mol^{-1} K^{-1} = -3.34 for the benzene + heptane mixture [64]. The importance of dispersive interactions in the investigated solutions is supported by their situation in the G_m^E vs. H_m^E diagram [65-67]. In fact, they are placed between the lines $G_m^E = 1/3\ H_m^E$ and $G_m^E = 1/2\ H_m^E$, or very close to this region, which is where mixtures characterized by dispersive interactions are encountered. We give some G_m^E and H_m^E values for reference. Thus, for heptane systems: G_m^E /J mol^{-1} = 430 (C_6H_6) [68]; 435 (C_6H_5F); 488 (1,4-$C_6H_4F_2$), 644 (C_6F_6) (DISQUAC values) and H_m^E/J mol^{-1} = 931 (C_6H_6) [10]; 888 (C_6H_5F) [17]; 1050 (1,4-$C_6H_4F_2$) [15] and 1119 (C_6F_6) [15]. Obviously, all the systems show positive $TS_m^E (= H_m^E - G_m^E)$ values, which is also a main feature of systems where dispersive interactions are dominant. In addition, it should be mentioned that a number of H_m^E curves are skewed towards high concentration of the AFC (see Figures 2 and 3 and S1 of supplementary material). This is important since it seems to be a manifestation of the existence of a quadrupolar order [2,69]. In the case of polar + non-polar systems, H_m^E curves are predicted to be shifted to lower concentrations of the polar compound [2,69]. Finally, preliminary calculations on the basis of the Flory model reveal that orientational effects in these solutions are weak. In fact, we have obtained: $dev(H_m^E)$ (heptane) = 0.021 (C_6H_5F); 0.082 (1,4-$C_6H_4F_2$) and 0.074 (C_6F_6) and $dev(H_m^E)$ (hexadecane) = 0.016 (C_6H_5F); 0.020 (1,4-$C_6H_4F_2$) and $dev(H_m^E) = 0.017$ for the C_6F_6 + tetradecane mixture.

5.2 Mixtures with a given fluorobenzene

In this case, H_m^E increases with n (Table 4, Figures 2-4). The comparison between DISQUAC values for mixtures including C_6H_5F or 1,4-$C_6H_4F_2$ with experimental data show an excellent

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agreement between them (Table 4, Figures 2-3). Therefore, one can conclude that there is no Patterson's effect, since calculations were performed using enthalpic parameters independent of the *n*-alkane. This is confirmed by the results obtained from UNIFAC (Dortmund) calculations (Table 4). A similar conclusion can be stated for C_6F_6 mixtures on the basis of the results provided by DISQUAC (Table 4, Figure 4).

For the present solutions, C_{pm}^E becomes progressively more negative when *n* is increased (Table 5, Figures 5 and 6). DISQUAC describes accurately such behaviour by means of $C_{af,3}^{DIS}$ coefficients which depend on *n* (Table 1). This merely expresses that C_{pm}^E is a property closely related to the mixture structure. Nevertheless, we remark that the model still predicts the C_{pm}^E variation with *n* using a unique $C_{af,3}^{DIS}$ value. In the case of C_6H_5F systems, if $C_{af,3}^{DIS} = -0.5$, then DISQUAC yields: C_{pm}^E/J mol^{-1} K^{-1} = -0.9 ($n = 7$); -1.4 ($n = 8$); -2.0 ($n = 10$); -3.1 ($n = 12$); -4.4 ($n = 14$), in fair agreement with experimental results (Table 5).

V_m^E data also increase with *n* [15,17] (Table 7). For example, V_m^E (C_6H_5F)/cm^3 mol^{-1} = 0.246 ($n = 6$); 0.833 ($n = 16$) [17]. That is, both H_m^E and V_m^E functions have the same sign and increase in line (Table 7). This underlines the importance of the interactional contribution to V_m^E, which is supported by the fact that the H_m^E and V_m^E curves show a similar symmetry. From the few data available on V_m^E (*T*), we obtain $\dfrac{\Delta V_m^E}{\Delta T}$ / cm^3 mol^{-1} K^{-1} = 0.0016 (C_6H_5F + methylcyclohexane) [70,71]; 0.0017 (C_6H_5F + C_6H_{12}) [71,72] and 0.008 (C_6F_6 + C_6H_{12}) [73,74]. For the C_6H_6 + C_6H_{12} system, this value is 0.00064 cm^{3}mol^{-1} K^{-1}[71,75]. The mixtures with C_6H_5F or C_6F_6 are more sensitive to temperature changes probably because these liquids are more ordered.

It is to be noted that the C_6H_5F + hexane, or + C_6H_{12} systems show the same H_m^E results (869 [17] and 864 [71] J mol^{-1}, respectively) but very different (V_m^E /cm^3 mol^{-1}) values (0.246 [17] and 0.686 [70], in the same order as above), which underlines the importance of shape effects on V_m^E. We remark that some mixtures involving 1,4-$C_6H_4F_2$ or C_6F_6 show very large and positive V_m^E values (Table 7). For example, V_m^E (C_6F_6)/cm^3 mol^{-1}= 1.882 ($n = 7$); 2.093 ($n = 14$) [15]; 2.454 (cyclohexane [73]). In such cases, one can expect that the equation of state contribution (eos) to H_m^E is also large (see below). In the following, we'll see that it is crucial to take into account this fact in order to conduct a consistent discussion.

5.3 Systems with a given alkane

At this condition, H_m^E/J mol^{-1} of mixtures with heptane changes in the sequence: 888 (C$_6$H$_5$F) [17] < 1050 (1,4-C$_6$H$_4$F$_2$) [15] < 1119 (C$_6$F$_6$) [15]. The partial excess molar enthalpies at infinite dilution of the first compound (fluorinated benzene), $H_{m,1}^{E,\infty}$/kJ mol^{-1} determined from H_m^E measurements for the same systems over the entire composition range are: 3.48 [17]; 3.47 and 4.31 [15], respectively. However, these results do not provide a reliable information about interactions between AFC molecules due to the mentioned large eos contribution to H_m^E. For this reason, we conduct now a discussion in terms on the excess molar internal energies at constant volume, U_{Vm}^E. This magnitude can be determined from [76]:

$$U_{Vm}^E = H_m^E - T\frac{\alpha_p}{\kappa_T}V_m^E \qquad (7)$$

where α_p and κ_T are, respectively, the isobaric thermal expansion coefficient and the coefficient of isothermal compressibility of the system under consideration. The $T\frac{\alpha_p}{\kappa_T}V_m^E$ term is defined as the contribution from the eos term to H_m^E. The α_p and κ_T values have been calculated here assuming ideal behavior for the mixtures ($M^{id} = \phi_1 M_1 + \phi_2 M_2$; with $M_i = \alpha_{pi}$, or κ_{T_i} and $\phi_i = x_i V_{m,i}/(x_1 V_{m,1} + x_2 V_{m,2})$). For alkanes, their α_{pi}, and κ_{T_i} values were taken from the literature [77]. For aromatic compounds, these values are listed in Table S1 (supplementary material). Table 7 contains our results on U_{Vm}^E. We note that the eos contribution to H_m^E represents ca. 50% in the case of systems with C$_6$F$_6$. For heptane mixtures, U_{Vm}^E changes as follows: 557 (C$_6$F$_6$) < 765 (C$_6$H$_5$F) < 854 (1,4-C$_6$H$_4$F$_2$) (all values in J mol^{-1}). In addition, $U_{Vm,1}^{E,\infty}$ / kJ mol^{-1} = 2.94 (C$_6$H$_5$F); 2.65 (1,4-C$_6$H$_4$F$_2$) and 2.42 (C$_6$F$_6$). The corresponding value for the C$_6$H$_6$ + heptane mixture is 2.7 kJ mol^{-1} (value obtained using H_m^E and V_m^E data from references [10] and [78], respectively). From these results, some conclusions can be stated. (i) Although interactions between fluorohydrocarbon molecules are quite similar, they are stronger between C$_6$H$_5$F molecules. (ii) The fact that U_{Vm}^E (1,4-C$_6$H$_4$F$_2$) > U_{Vm}^E (C$_6$H$_5$F) should be interpreted as a consequence of that more dispersive interactions are broken upon mixing in 1,4-C$_6$H$_4$F$_2$ systems. (iii) Although $U_{Vm,1}^{E,\infty}$ is lower for C$_6$F$_6$ solutions, the lowest U_{Vm}^E values obtained for these mixtures suggest that *n*-alkanes are not good breakers of the C$_6$F$_6$ network. At this regards, the C$_6$F$_6$ + 2,2,4-trimethylpentane (TMP) mixture is very interesting. This solution shows a large and positive H_m^E value (1740 J mol^{-1}) although it is affected by rather

large error (ca. 20%) since is determined from G_m^E data at different temperatures [79]. The mentioned result is higher than that for the C_6F_6 + heptane mixture (see above). The U_{Vm}^E value of the C_6F_6 + TMP is also higher (1355 J mol^{-1}, value determined using V_m^E = 1.375 cm^3 mol^{-1} [79]). One can conclude that TMP is a good breaker of the existing order in C_6F_6. It may be pertinent to compare these results with those for C_6H_6 mixtures. For such systems, the eos contribution to H_m^E is also large, particularly for solutions including longer n-alkanes (Table 7). The H_m^E variation follows the order: C_6F_6 > 1,4-$C_6H_4F_2$> C_6H_6 > C_6H_5F, while U_{Vm}^E changes in the order: 1,4-$C_6H_4F_2$> $C_6H_6 \approx$ C_6H_5F > C_6F_6. It is to be noted, that C_6H_6 and C_6H_5F systems behave quite similarly. On the other hand, it is remarkable that U_{Vm}^E varies with n more smoothly for systems including C_6F_6 than for mixtures with, e.g. C_6H_5F. The linear regressions of U_{Vm}^E data vs. n give slopes, which are (in J mol^{-1}) 11.9 and 19.2, respectively. This seems to indicate that n-alkanes are not good breakers of the C_6F_6 network.

Mixtures with C_6H_{12} behave differently and both H_m^E and U_{Vm}^E values of C_6H_5F systems are lower than for systems containing C_6F_6. We have already mentioned that H_m^E values of C_6H_5F + hexane, or + C_6H_{12} mixtures are very similar. However, H_m^E is much higher for the C_6F_6 + C_6H_{12} mixture (1576 J mol^{-1} [26]) than for the solution with heptane, and $U_{V,m}^E$ is also higher for the former solution (Table 7). This result contrasts with that provided above for the TMP mixture. Both cyclohexane and TMP are globular molecules and one could expect similar results for the systems with C_6F_6. It seems clear that the ability of TMP for destructing the C_6F_6 network is much higher

5.4 C_6F_6 + aromatic hydrocarbon systems

At 313.2 K, the H_m^E/J mol^{-1} values of these mixtures are negative (-433 (C_6H_6); -1140 (C_7H_8); -1660 (1,4-$C_6H_4(CH_3)_2$ [27], Figure 4). This means that interactions between unlike molecules are dominant. The following features support this statement. (i) The solutions are placed in the third quarter of the the G_m^E vs. H_m^E diagram, since both magnitudes are negative (Tables 2 and 4). The 1-alkanol + linear primary amine systems, characterized by strong interactions between unlike molecules [49], are situated in the same region. (ii) From H_m^E measurements at different temperatures, it is obtained that C_{pm}^E is positive, which is indicative of order creation [1-3]. This is particularly relevant for the systems with C_7H_8 or 14DMBZ, whose values are 16.7 and 12.3 J mol^{-1} K^{-1}, respectively [27]. (iii) Accordingly, TS_m^E values are negative.

At 313.15 K, we note that V_m^E /cm^3 mol^{-1} decreases when the number of the CH$_3$ groups attached to the aromatic ring increases: 0.801 (C$_6$H$_6$), 0.416 (C$_7$H$_8$), 0.0855 (14DMBZ) [74]. That is, H_m^E and V_m^E change in line, which underlines the relevance of the interactional contribution to V_m^E. Since structural effects contribute negatively to V_m^E, the positive values of this magnitude may indicate that the positive contribution to V_m^E from the disruption of interactions between like molecules largely exceeds to those emerging from both structural effects and from the creation of interactions between unlike molecules.

It is noteworthy that the H_m^E curve of the C$_6$F$_6$ + C$_6$H$_6$ mixture shows a small region at low mole fractions of C$_6$F$_6$, with positive H_m^E values (Figure 4). Such region vanishes when U_{Vm}^E data are considered. Therefore, it may be ascribed to dominant structural effects in such region. The U_{Vm}^E value of the benzene mixture is -719 J mol^{-1}, a very different result to the theoretical one obtained from molecular simulations (-2700 J mol^{-1}) [80].

On the other hand, our calculations show that U_{Vm}^E and H_m^E change in the same sequence: C$_6$H$_6$ > C$_7$H$_8$ > 14DMBZ (Table 7). Thus, interactions between unlike molecules are expected to be stronger in the 14DMBZ solution. In addition, the melting points of the 1:1 complexes formed in solid phase changes in the order: 300.6 K (14DMBZ) > 297.2 K (C$_6$H$_6$) > 283.15 K (C$_7$H$_8$) [28] and this also supports that interactions between unlike molecules are stronger in the mixture containing 14DMBZ. The lower melting point for the toluene system may be related, in some extent, to the much lower melting point of this hydrocarbon.

5.5 The concentration-concentration structure factor formalism

$S_{CC}(0)$ of C$_6$H$_6$ + n-alkane mixtures decreases when n increases (Table 6, Figure S2, supplementary material). That is, interactions between like molecules are more easily disrupted when the system contains long chain n-alkanes. It is remarkable that $S_{CC}(0)$ values of mixtures formed by C$_6$F$_6$ and tetradecane or hexadecane are very similar and the corresponding curves are skewed towards higher C$_6$F$_6$ concentrations. These features suggest that longer n-alkanes are not good breakers of the C$_6$F$_6$-C$_6$F$_6$ interactions. The lower $S_{CC}(0)$ value of the C$_6$F$_6$ + TMP mixture reveals that the globular TMP molecule can disrupt more easily the C$_6$F$_6$ network. On the other hand, homocoordination is more important in mixtures with C$_6$F$_6$ than in systems with benzene. Since C$_6$F$_6$-C$_6$F$_6$ and C$_6$H$_6$-C$_6$H$_6$ interactions are characterized by similar $U_{Vm,1}^{E,\infty}$ values, the observed behaviour might be ascribed to C$_6$F$_6$ is more ordered liquid. Next, we discuss some results on $S_{CC}(0)$ from DISQUAC calculations. Firstly, the model correctly predicts the symmetry of the $S_{CC}(0)$ curves of the C$_6$F$_6$ + tetradecane, or + hexadecane mixtures (Figure 7). DISQUAC provides rather

similar maxima values for these systems and for the heptane solution (Table 6). It is to be noted that the curve of this mixture is more symmetrical (Figure 7). This supports our previous conclusion about longer alkanes are poorer breakers of the C_6F_6 order. DISQUAC provides $S_{CC}(0)$ values for the C_6H_5F mixtures that slightly differ from those of the C_6H_6 systems, which suggests that dipolar interactions are not relevant in solutions with fluorobenzene. In addition, DISQUAC predicts a higher homocoordination in C_6F_6 solutions, indicating that this is a more structured liquid. In the case of systems with cyclohexane, homocoordination is also higher in mixtures with C_6F_6, and is more relevant in mixtures with cyclohexane than in solutions containing an *n*-alkane of similar size. Finally, the C_6F_6 + aromatic hydrocarbon systems are characterized by heterocoordination (Table 6), which is stronger in the solution with 1,4-dimethylbenzene. Calculations in terms of the Kirkwood-Buff integrals formalism [81] show the existence of unlike aggregates at higher mole factions of C_6F_6 in the solution with benzene [82].

5.6 Mixtures with other fluorinated benzenes

Firstly, we consider mixtures of the type $C_6H_{6-u}F_u$ ($u < 6$) + C_6H_6 . Their H_m^E values strongly depend on the number and position of the F atoms attached to the aromatic ring and not on the dipole moment of the AFC involved [26]. In spite of this, some general features can be stated. (i) The H_m^E values are positive and not large [26]. The largest value is attained for the system with 1,3,5-$C_6H_3F_3$ (496 J mol^{-1} [26]). (ii) The C_{pm}^E values are negative (-1.1 J mol^{-1} K^{-1} for the mentioned solution [26]). That is, dispersive interactions are dominant. The C_6F_6 mixture behaves in different way and shows $H_m^E < 0$ and $C_{pm}^E > 0$ (see Tables 4 and 5). The H_m^E curve of the system with C_6HF_5 is S-shaped with positive H_m^E values at lower concentrations of the AFC and $C_{pm}^E = 0.16$ J mol^{-1} K^{-1} [26]. Regarding the C_6HF_5 + C_6H_{12} mixture, its H_m^E value (1527 J mol^{-1} [83] is very close to that of the mixture with C_6F_6 (1576 J mol^{-1}[27]); $C_{pm}^E = -1.1$ J mol^{-1} K^{-1} [83] and the application of the Flory model gives $dev(H_m^E) = 0.028$. It is clear that, although C_6HF_5 is a polar compound ($\mu = 1.6$ D [19]), the system under consideration is mainly characterized by dispersive interactions. On the other hand, V_m^E /cm^3 mol^{-1} values of the solutions with benzene (0.860) or with cyclohexane (2.082) are large and positive [84], which suggests that the contribution to H_m^E from the eos term will be here also very important. Using α_{pi}, and κ_{T_i} values reported in reference [85] for C_6HF_5, we have determined U_{Vm}^E /J mol^{-1} for the such solutions and the results are: -253 (benzene) and 827 (cyclohexane). We remark the negative value for the system with C_6H_6 that reveals that interactions between unlike molecules are dominant in that mixture. The S-shaped concentration dependence of H_m^E has been explained assuming that the physical interactions are described by a term which is skewed to the

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region rich in the component of lower molar volume as it occurs within the regular solution theory [83]. However, U_{Vm}^{E} values are negative over the entire concentration range and the S-shaped H_m^E curve can be related to large eos contribution to this excess function. In addition, V_m^E /cm³ mol⁻¹ values of the mixtures $C_6HF_5 + C_6H_6$ (0.860), or + C_7H_8 (0.505), or + 1,4-DMBZ (0.287) decrease when the number of the CH_3 groups attached to the aromatic ring increases [84]. The same trend is encountered for the corresponding systems with C_6F_6 (see above). This set of features reveals that a certain similarity exists between the systems with C_6F_6 or with C_6HF_5.

The DISQUAC application to this type of systems shows that the 1,3,5-$C_6H_3F_3$ + C_6H_6 mixture, characterized by one contact, can be described in terms of the DIS approximation. This is not the case for the systems C_6HF_5+ C_6H_6 or + C_6H_{12} characterized by one and three contacts respectively (see above). Nevertheless, our calculations reveal that the coefficients $C_{bf,1}^{QUAC}$ and $C_{sf,1}^{QUAC}$ (s = b,c; l =1,3) of the mixtures with C_6F_6 can be used for the systems with C_6HF_5, while the $C_{sf,2}^{DIS/QUAC}$ (s = b,c) coefficients must be modified (see Table S2 of supplementary material). A similar trend has been encountered when treating in terms of DISQUAC mixtures such as, e.g., 1-alkanol + n-alkane [86], or + benzene, or + toluene [59], or + *N,N*-dialkylamide [57], or + pyridine or + alkyl-pyridine [87], or + DMSO [88]. It must be underlined that the $C_{cf,1}^{QUAC}$ (l =1,2,3) coefficients for solutions with C_6H_5F or 1,4-$C_6H_4F_2$ are the same and that differ from those of mixtures with C_6F_6 or C_6HF_5, which suggests that the former type of systems behave differently.

5.7 The aromacity effect

H_m^E values of $CH_3(CH_2)_uF$ + n-alkane mixtures decrease when u is increased. Thus, H_m^E (hexane)/J mol⁻¹ = 481(u = 4); 416 (u =5); 294 (u = 7) [48]. This variation can be explained in terms of the effective dipole moments, $\overline{\mu}$, of 1-fluoroalkanes, an useful magnitude to examine the impact of polarity of bulk properties. It is defined by [49,76,89]:

$$\overline{\mu} = \left[\frac{\mu^2 N_A}{4\pi\varepsilon_0 V_m k_B T} \right]^{1/2} \tag{8}$$

where the symbols have the usual meaning. The dipole moments of 1-fluoroalkanes with u = 4, or 5 are, respectively, (1.85 and 1.82) D, [90] and the corresponding molar volumes (cm³ mol⁻¹) are, in the same order, 114.90 [91] and 130.03 (at 293.15 K) [92]. The $\overline{\mu}$ values are: 0.660 (u = 4) and 0.611 (u = 5). The observed decrease of H_m^E can be then ascribed to a slight weakening of the dipolar interactions between fluoroalkane molecules when u is increased. The H_m^E value for the 1-fluorohexane system is much lower than the corresponding result for the solution with fluorobenzene

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(869 J mol^{-1} [17]) and $H_{m,1}^{E,\infty}$ (hexane)/kJ mol^{-1} = 2.1 (u = 5 [48]) < 3.4 (C$_6$H$_5$F) [17]. Since $\bar{\mu}$ (fluorobenzene) = 0.664 is quite similar to the values reported above for 1-fluoroalkanes, and taking into account the lack of volumetric data for these solutions needed to U_{Vm}^E determinations, the large difference between these enthalpic data can be explained assuming that more dispersive interactions between fluorobenzene molecules are broken upon mixing (aromacity effect).

On the other hand, for benzene systems, H_m^E/J mol^{-1} = 98 (u = 4); 133 (u =5); 219 (u = 7) [48]. Therefore, H_m^E increases in line with u, which can be ascribed to the longer 1-fluoroalkanes can break more easily benzene-benzene interactions due to their larger aliphatic surface. These values are lower than the corresponding results for hexane mixtures, and reveal the existence of interactions between unlike molecules. In the case of the C$_6$H$_5$F + C$_6$H$_6$ mixture, both components have rather similar aromatic surfaces and H_m^E is 1 J mol^{-1} (at 303.15 K) [51].

6. Conclusions

Mixtures containing fluorobenzene, or 1,4-difluorobenzene or hexafluorobenzene and alkane or an aromatic hydrocarbon have been investigated on the basis of thermodynamic properties from the literature, and using the DISQUAC and UNIFAC (Dortmund) models and the $S_{CC}(0)$ formalism. It has been shown that mixtures with alkanes: (i) are characterized by interactions between like molecules; (ii) that these interactions are essentially dispersive; (iii) that the Patterson's effect does not exist in mixtures with n-alkanes; (iv) structural effects can be very important. In fact, for mixtures with a given n-alkane, H_m^E values change in the sequence C$_6$F$_6$ > 1,4-C$_6$H$_4$F$_2$ > C$_6$H$_6$ > C$_6$H$_5$F, while U_{Vm}^E changes in the order: 1,4-C$_6$H$_4$F$_2$ > C$_6$H$_6$ $\approx$ C$_6$H$_5$F > C$_6$F$_6$. On the other hand, C$_6$F$_6$ + aromatic hydrocarbon mixtures are characterized by interactions between unlike molecules. The application of $S_{CC}(0)$ formalism reveals that homocoordination is more important in C$_6$F$_6$ + n-alkane mixtures than in the corresponding systems with C$_6$H$_5$F, and that heterocoordination is dominant in the solutions of C$_6$F$_6$ with an aromatic hydrocarbon. In systems with n-alkanes, the aromacity effect leads to increased H_m^E values for mixtures with C$_6$H$_5$F in comparison to those of systems with 1-fluoroalkanes.

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7. References

[1]   D. Patterson. Structure and the thermodynamics of non-electrolyte mixtures. J. Solution Chem. 23 (1994) 105-120.

[2]   D. Patterson. Structure and the thermodynamics of non-electrolyte mixtures. Thermochim. Acta 267 (1995) 15-27.

[3]   S.-N. Bhattacharyya, M. Costas, D. Patterson, H.-V. Tra. Thermodynamics of mixtures containing alkanes. Fluid Phase Equilib. 20 (1985) 27-45.

[4]   E. Wilhelm. Thermodynamics of 1,2,4-trichlorobenzene with *n*-alkanes: a novel effect. Ber. Bunsenges. Phys. Chem. 81 (1977) 1150-1154.

[5]   E. Wilhelm, A. Inglese, A.H. Roux, J.-P.E. Grolier. Excess enthalpy, excess heat capacity and excess volume of 1,2,4-trimethylbenzene or 1-methylnaphthalene + an *n*-alkane. Fluid Phase Equilib. 34 (1987) 49-67.

[6]   A. Domínguez, G. Tardajos, E. Aicart, S. Pérez-Casas, L.M. Trejo, M. Costas, D. Patterson, H. van Tra. Van der Waals liquids, Flory theory and mixing functions for chlorobenzene with linear and branched alkanes. J. Chem. Soc. Faraday Trans. 89 (1993) 89-93.

[7]   J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova, A. Ait-Kaci. Application of the zeroth approximation of the DISQUAC model to cyclohexane + *n*-alkane mixtures using different combinatorial entropy terms. Fluid Phase Equilib. 112 (1995) 63-87.

[8]   H.V. Kehiaian. Thermodynamics of binary liquid organic mixtures. Pure Appl. Chem. 57 (1985) 15-30.

[9]   J. Gmehling, J. Li, M. Schiller. A modified UNIFAC model.2. Present parameter matrix and results for different thermodynamic properties. Ind. Eng. Chem. Res. 32 (1993) 178-193.

[10]   G.W. Lundberg. Thermodynamics of solutions XI. Heat of mixing of hydrocarbons. J. Chem. Eng. Data 9 (1964) 193-198.

[11]   M. Díaz Peña, C. Menduiña. Excess enthalpies at 298.15 K of binary mixtures of benzene with *n*-alkanes. J. Chem. Thermodyn. 6 (1974) 387-393.

[12]   J.A. González, I. García de la Fuente, J.C. Cobos. Correlation and prediction of excess molar enthalpies using DISQUAC in: E. Wilhelm, T.M. Letcher (Eds.), Enthalpy and Internal Energy: Liquids, Solutions and Vapours, Royal Society of Chemistry, Croydon 2017.

[13]   H.V. Kehiaian, J.-P.E. Grolier, G.C. Benson. Thermodynamics of organic mixtures. A generalized quasichemical model theory in terms of group surface interactions. J. Chim. Phys. 75 (1978) 1031-1048.

[14]   A. Ait-Kaci, Ph. D. Thesis, Lyon, France, 1982.

[15]   E. Wilhelm, A. Inglese, A. Laínez, A.H. Roux, J.-P.E. Grolier. Thermodynamics of (1,4-difluorobenzene + an *n*-alkane) and of (hexafluorobenzene + an *n*-alkane). Fluid Phase Equilib. 110 (1995) 299-313.

[16]   E. Wilhelm, A. Inglese, J.-P.E. Grolier, H.V. Kehiaian. Enthalpy of mixing of bromobenzene with *n*-alkanes, with cyclohexane, and with benzene. Thermochim. Acta 31 (1979) 85-92.

[17]   A.H. Roux, J.-P.E. Grolier, A. Inglese, E. Wilhelm. Excess molar enthalpies, excess molar heat capacities and excess molar volumes of (fluorobenzene + an *n*-alkane). Ber. Bunsenges. Phys. Chem. 88 (1984) 986-992.

[18]   J. Gmehling, J. Lohman, A. Jakob, J. Li, R. Joh. A modified UNIFAC (Dortmund) model. 3. Revision and extension. Ind. Eng. Chem. Res. 37 (1998) 4876-4882.

[19]   J.R. Trudell. Contributions of dipole moments, quadrupole moments, and molecular polarizabilities to the anesthetic potency of fluorobenzenes. Biophys. Chem. 73 (1998) 7-11.

[20]   J.K. Cockcroft, R.E. Ghosh, J.J. Shephard, A. Singh, J.H. Williams. Investigation of the phase behaviour of the 1:1 adduct of mesitylene and hexafluorobenzene. CrystChemCom 19 (2017) 1019-1023.

[21]   J. Hernández-Trujillo, A. Vela. Molecular quadupole moments for the series of fluoro- and chlorobenzenes. J. Phys. Chem. 100 (1996) 6524-6530.

[22]   G. R. Desiraju. Crystal engineering: from molecule to crystal. J. Am. Chem. Soc. 135 (2013) 9952–9967.

[23]   A. Aucejo, J.B. Montón, R. Muñoz, J. Wisniak. Double azeotropy in the benzene + hexafluorobenzene system. J. Chem. Eng. Data 41 (1996) 21-24.

[24]   W.J. Gaw, F.L. Swinton. Thermodynamic properties of binary systems containing hexafluorobenzene. Part 4. Excess Gibbs free energies of the three systems hexafluorobenzene + benzene, toluene and *p*-xylene. Trans. Faraday. Soc. 64 (1968) 2023-2034.

[25]   H. Quinteros-Lamas, F. Llovell, J. Wisniak. The polyazeotropic behaviour of the benzene + hexafluorobenzene system revisited. J. Chem. Thermodyn. 113 (2017) 340-349.

[26]   D.V. Fenby, R.L. Scott. Heats of mixing of non-electrolytes. IV. Mixtures of fluorinated benzenes. J. Phys. Chem. 71 (1967) 4103-4110.

[27]   A. Andrews, K.W. Morcom, W.A. Duncan, F.L. Swinton, J.M. Pollock. The thermodynamic properties of fluorocarbon + hydrocarbon mixtures. 2. Excess enthalpies of mixing. J. Chem. Thermodyn. 2 (1970) 95-103.

[28]   W.A. Duncan, F.L. Swinton. Thermodynamic properties of binary systems containing hexafluorobenzene. Part 1. Phase diagrams. Trans. Faraday Soc. 62 (1966) 1082-1089.

[29]   J.R. Goates, J.B. Ott, J. Reeder. Solid + liquid equilibria and solid compound formation in hexafluorobenzene + benzene, + pyridine, + furan, and + thiophene. J. Chem. Thermodyn. 5 (1973) 135-141.

[30]   D. Mikailitchenko, A. Marbeuf, Y. Haget, H.A.J. Oonk. Influence of the methyl-group on the complexation in the benzenic family: the toluene-hexafluorobenzene system and the *p*-xylene-hexafluorobenzene system. Mol. Liq. Crist. 319 (1998) 291-305.

[31]   D. F. R. Gilson, C. A. McDowell. Molecular motion in weak charge transfer complexes. Can. J. Chem. 44 (1966) 945-952.

[32]   J. H. Williams. The molecular electric quadrupole moment and solid-state architecture. Acc. Chem. Res. 26 (1993) 593-598.

[33]   J.H. Williams. Modeling the vibrational dynamics of solid benzene: hexafluorobenzene. The anatomy of a phase transition. Chem. Phys. 172 (1993) 171–186.

[34]   J. Hernández-Trujillo, F. Colmenares, G. Cuevas, M. Costas. MP2 ab initio calculations of the hexafluorobenzene-benzene and –monofluorobenzene complexes. Chem. Phys. Lett. 265 (1997) 503-507.

[35]   N.M.D. Brown, F. L. Swinton. The importance of quadrupolar interactions in determining the structure of solid hydrocarbon-fluorocarbon compounds. J. Chem. Soc., Chem. Commun. (1974) 770-771.

[36]   E. Bartsch, H. Bertagnolli, P. Chieux. A neutron and X-ray diffraction study of the binary liquid aromatic system benzene-hexafluorobenzene. II. The mixtures. Ber. Bunsenges Phys. Chem. 90 (1986) 34-46.

[37]   J.C. Cobos. An exact quasi-chemical equation for excess heat capacity with W-shaped concentration dependence. Fluid Phase Equilib. 133 (1997) 105-127.

[38]   L.M. Trejo, M. Costas and D. Patterson. Effect of molecular size on the W-shaped excess heat capacities: oxaalkane-alkane systems. J. Chem. Soc., Faraday Trans. 87 (1991) 3001-3008.

[39]   A.B. Bhatia, D.E. Thornton. Structural aspects of the electrical resistivity of binary alloys. Phys. Rev. B2 (1970) 3004-3012.

[40]   Z. Jiang, Z. Zeng, X. Liang, L. Yang, W. Hu, C. Zhang, Z. Han, J. Feng, J. Xie. Fluorobenzene, a low-density, economical, and bifunctional hydrocarbon cosolvent for practical lithium metal batteries. Adv. Functional Materials 31 (2021) 2005991.

[41]   J.G. Calvert, R. Atkinson, K.H. Becker, R.M. Kamens, J.H. Seinfeld, T.J. Wallington, G. Yarwood. Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons, Oxford University Press, 2002.

[42]   M.P. Sulbaek Andersen, J.W. Lengkong, J. Wallberg, F. Hasager, K. Vo, S. Thirstrup Andersen, H. G. Kjaergaard, T.J. Wallington, O. J. Nielsen. Atmospheric chemistry of hexa- and penta-fluorobenzene: UV photolysis and kinetics and mechanisms of the reactions of Cl atoms and OH radicals. Phys. Chem. Chem. Phys. 20 (2018) 28796-28809.

[43]   K. Müller, C. Faeh, F. Diederich. Fluorine in pharmaceuticals: looking beyond intuition. Science 317 (2007) 1881–1886.

[44]   J.C. Ma, D.A. Dougherty. The cation-π interaction. Chem. Rev. 97 (1997) 1303-1324.

[45]   E.A. Guggenheim, Mixtures, Oxford University Press, Oxford, 1952.

[46]   A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968.

[47]   A. Cannas, B. Marongiu, S. Porcedda. Thermodynamic properties of *n*-alkylbenzene + *n*-alkane or cyclohexane mixtures. Comparison with DISQUAC predictions. Thermochim. Acta 311 (1998) 1-19.

[48]   M. Artal, J. Fernández, J. Muñoz Embid, I. Velasco, S. Otín, H.V. Kehiaian. Excess enthalpies and molecular interactions in solutions of 1-fluoroalkanes in alkanes, benzene or tetrachloromethane. J. Solution Chem. 20 (1991) 3-16.

[49]   J.A. González, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. Part 4. Application of the DISQUAC model to mixtures of 1-alkanols with primary or secondary linear amines. Comparison with Dortmund UNIFAC and ERAS results. Fluid Phase Equilib. 168 (2000) 31-58.

[50]   A. Fredenslund, R.L. Jones, J.M. Prausnitz. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. AIChE J. 21 (1975) 1086-1099.

[51]   S. Otín, M.J. Toledo, J. Muñoz, I. Velasco, C. Gutiérrez Losa. Excess molar enthalpies of (a halogenobenzene + benzene, or + toluene) and of some (a dihalogenobenzene + benzene). J. Chem. Thermodyn. 17 (1985) 935-940.

[52]   M. Díaz Peña, A. Compostizo, A. Crespo Colín, I. Escudero. Isothermal (*p,x,y*) relations and activity coefficients for benzene + chlorobenzene, + fluorobenzene, and + thiophene at 348.15 K. J. Chem. Thermodyn. 13 (1981) 869-873.

[53]   H.V. Kehiaian, M.R. Tiné, L. Lepori, E. Matteoli, B. Marongiu. Thermodynamics of binary mixtures containing oxaalkanes. Part 3. Monoethers, polyethers, orthoesters and cyclic monoethers + *n*-alkanes or cyclohexane. Fluid Phase Equilib. 46 (1989) 131-177.

[54]   H.V. Kehiaian, B. Marongiu. A comparative study of thermodynamic properties and molecular interactions in mono- and polychloroalkane + *n*-alkane or + cyclohexane mixtures. Fluid Phase Equilib. 40 (1988) 23-78.

[55]   H.V. Kehiaian, S. Porcedda, B. Marongiu, L. Lepori, E. Matteoli. Thermodynamics of binary mixtures containing linear or cyclic alkanones + *n*-alkanes or + cycloalkanes. Fluid Phase Equilib. 63 (1991) 231-257.

[56]   J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova, H.V. Kehiaian. Calorimetric and phase equilibrium data for linear carbonates + hydrocarbons or + CCl_4 mixtures. Comparison with DISQUAC predictions. Thermochim. Acta 217 (1993) 57-69.

[57]   J.A. González, J.C. Cobos, I. García de la Fuente. Thermodynamics of liquid mixtures containing a very strongly polar compound. Part 6. DISQUAC characterization of *N,N*-dialkylamides. Fluid Phase Equilib. 224 (2004) 169-183.

[58] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova. DISQUAC predictions of phase equilibria, molar and standard partial molar excess quantities for 1-alkanol + cyclohexane mixtures J. Solution Chem. 23 (1994) 399-420

[59] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova. Estimation of DISQUAC interchange energy parameters for 1-alkanols + benzene, or + toluene mixtures Fluid Phase Equilib. 93 (1994) 1-22.

[60] J.A. González, I. García de la Fuente, J.C. Cobos. DISQUAC structure-dependent interaction parameters for mixtures containing sec-alkanols and benzene, toluene, or n-alkanones. Can. J. Chem. 76 (1998) 1418-1428.

[61] J.A. González, U. Domanska. Thermodynamics of mixtures containing a very strongly polar compound. Part I. Experimental phase equilibria (solid-liquid and liquid-liquid) for sulfolane + alkan-1-ols systems. Analysis of some mixtures including sulfolane in terms of DISQUAC. Phys. Chem. Chem. Phys. 3 (2001) 1034-1042.

[62] J. Aracil, R.G. Rubio, J. Núñez, M. Díaz Peña, J.A.R. Renuncio. Thermodynamic properties of $\{x\ C_6F_6 + (1\text{-}x)\ C_{14}H_{30}\}$ and $\{x_1C_6F_6 + x_2C_6H_6 + (1\text{-}x_1\text{-}x_2)C_{14}H_{30}\}$ at 298.15 K. J. Chem. Thermodyn. 19 (1987) 605-611.

[63] J. Aracil, R.G. Rubio, M. Cáceres, M. Díaz Peña, J.A.R. Renuncio. Excess properties of the hexafluorobenzene-n-hexadecane and hexafluorobenzene-benzene-n-hexadecane systems at 298.15 K. Fluid Phase Equilib. 31 (1986) 71-87.

[64] J.-P.E. Grolier, A. Faradjzadeh, H.V. Kehiaian. Calorimetric effects of short-range orientational order in solutions of benzene or n-alkylbenzenes in n-alkanes. Thermochim. Acta 53 (1982) 157-162.

[65] F. Kohler, J. Gaube. Temperature-dependence of excess thermodynamics properties of mixtures and intermolecular interaction. Pol. J. Chem. 54 (1980) 1987-1993.

[66] R. Fuchs, L. Krenzer, J. Gaube. Excess properties of binary mixtures composed of a polar component and an alkane. Ber. Bunsenges. Phys. Chem. 88 (1984) 642-649.

[67] K. P. Shukla, A.A. Chialvo, J.M. Haile. Thermodynamic excess properties in binary fluid mixtures. Ind. Eng. Chem. Res. 27 (1988) 664-671.

[68] D.V.S. Jain, V.K. Gupta, B.S. Lark. Thermodynamics of n-alkane mixtures. V. Vapour pressures and excess Gibbs energies of n-heptane + benzene and n-octane + benzene. J. Chem. Thermodyn. 3 (1973) 451-454.

[69] C.H. Twu, K.E. Gubbins, C.G. Gray. Excess thermodynamic properties for liquid mixtures of non-spherical molecules. Mol. Phys. 29 (1975) 713-729.

[70] S.N. Battacharyya, A. Mukherjee. Excess thermodynamic functions of some binary non-electrolyte mixtures. I. Measurements of excess Gibbs free energy, enthalpies, and volumes of mixing. J. Phys. Chem. 72 (1968) 56-63.

[71] F. Kimura, S. Murakami. Molar excess enthalpies and volumes of binary fluorobenzene systems at 298.15 K. Fluid Phase Equilib. 3 (1979) 93-112.

[72] A.V. Anantaraman, S.N. Battacharyya, S.R. Palit. Excess thermodynamic functions of binary mixtures. System: cyclohexane + fluorobenzene. Trans. Faraday. Soc. 59 (1963) 1101-1109.

[73] S. Ruenkrairergsa, D.V. Fenby, D.E. Jones. Aromatic fluorocarbon mixtures. 3. Excess volumes of $C_6H_6 + C_6F_5X$ and c-$C_6H_{12} + C_6F_5X$ (X = H,F,Cl,Br,I). J. Chem. Thermodyn. 5 (1973) 347-351.

[74] W.A. Duncan, J.P. Sheridan, F.L. Swinton. Thermodynamic properties of binary systems containing hexaflurorobenzene. Part 2. Excess volume of mixing and dipole moments. Trans. Faraday Soc. 62 (1966) 1090-1096.

[75] Z. Kolska, D. Dvorakova, J. Mika, T. Boublik. Volumetric behaviour of the binary systems benzene-cyclohexane and benzene-2-2-4-trimethylpentane at temperatures 293.15-323.15 K. Fluid Phase Equilib. 303 (2011) 157-161.

[76] J.S. Rowlinson, F.L. Swinton, Liquids and Liquid Mixtures, 3rd Edition, Butterworths, G. B., 1982

[77] F. Hevia, J.A. González, C. Alonso-Tristán, I. García de la Fuente, L.F. Sanz. Orientational effects in alkanone, alkanal or dialkyl carbonate + alkane mixtures, or in alkanone + alkanone, or + dialkyl carbonate systems. J. Mol. Liq. 233 (2017) 517-527.

[78] B. González, E.J. González, I. Domínguez, A. Domínguez. Excess properties of binary mixtures hexane, heptane, octane and nonane with benzene, toluene and ethylbenzene at T = 283.15 and 298.15 K. Phys. Chem. Liq. 48 (2010) 514-533.

[79] J. Aracil, R.G. Rubio, M. Cáceres, M. Día Peña, J.A.R. Renuncio. Thermodynamics of fluorocarbon-hydrocarbon mixtures formed by 2,2,4-trimethylpentane with hexafluorobenzene and with hexafluorobenzene-benzene J. Chem. Soc., Faraday Trans. I 84 (1988) 539-550.

[80] M.I. Cabaço, Y. Danten, M. Bernard, Y. Guissani, B. Guillot. Structural investigations of liquid binary mixtures: neutron diffraction and molecular dynamics studies of benzene, hexafluorobenzene and 1,3,5-triflurobenzene. J. Phys. Chem. B. 102 (1998) 10712-10723.

[81] J.G. Kirkwood, F.P. Buff. The statistical mechanical theory of solutions. I. J. Chem. Phys. 19 (1951) 774-777.

[82] E. Ruckenstein, I. Shulgin. Aggregation in binary solutions containing hexafluorobenzene, J. Phys. Chem. B. 103 (1999) 10266-10271.

[83] P.J. Howell, B.J. Skillerne de Bristowe, D. Stubley. Enthalpies of mixing of pentafluorobenzene with some hydrocarbons. J. Chem. Thermodyn. 4 (1972) 225-231.

[84] B.J. Skillerne de Bristowe, D. Stubley. Excess volumes of mixtures of pentafluorobenzene with some hydrocarbons. J. Chem. Thermodyn. 5 (1973) 865-871.

[85] B.J. Skillerne de Bristowe, D. Stubley. Excess enthalpies of liquid mixtures of an aromatic fluorocarbon + a hydrocarbon. Analysis in terms of lattice theory. J. Chem. Thermodyn. 6 (1974) 581-585.

[86] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova**. A characterization of the aliphatic/hydroxyl interactions using a group contribution model (DISQUAC). Ber. Bunsenges. Phys. Chem. 95 (1991) 1658-1668.

[87] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos**. Thermodynamics of binary mixtures containing amines. V. Systems with pyridines. Thermochim. Acta, 441 (2006) 53-68.

[88] J.A. González, S. Villa, N. Riesco, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing a very strongly polar compound. IV. Application of the DISQUAC, UNIFAC and ERAS models to DMSO + organic solvent systems. Phys. Chem. Liq. 41 (2003) 583-597

[89] E. Wilhelm, A. Laínez, J.-P.E. Grolier. Thermodynamics of (a halogenated ethane or ethane + an *n*-alkane). V^{E} and $C_{\mathrm{p}}^{\mathrm{E}}$ of mixtures containing either 1,1,2,2-tetrachloroethane, or tetrachlorethene). Fluid Phase Equilib. 49 (1989) 233-250.

[90] A.L. McClellan, Tables of experimental dipole moments, Vols. 1,2,3, Rahara Enterprises, El Cerrito, US, 1974.

[91] M. Artal, J. Muñoz Embid, I. Velasco. Excess enthalpies and excess volumes of (iodomethane + 1-fluoropentane or 1-chloropropane or 1-chloropentane or bromoethane or iodoethane or 1-iodobutane) at the temperature 298.15 K. J. Chem. Thermodyn. 26 (1994) 703-708.

[92] W.A.T. Macey. The physical properties of certain organic fluorides. J. Phys. Chem. 64 (1960) 254-257.

[93] Z. Atik. Measurements and calculation of vapour-liquid equilibria for the binary mixtures of fluorobenzene and alkanes at a pressure of 101.4 kPa. J. Chem. Eng. Data 52 (2007) 1503-1505.

[94] M. Díaz Peña, A. Crespo-Colín, A. Compostizo, I. Escudero. Liquid-vapor equilibriums in binary systems formed by methylcyclohexane with chlorobenzene, fluorobenzene, and thiophene J. Chem. Eng. Data, 25 (1980) 17-21.

[95] M. Díaz Peña, A. Compostizo, A. Crespo, Colín, I. Escudero. Activity coefficients and excess Gibbs free energies at 348.15 K in cyclohexane + chlorobenzene, + fluorobenzene, and + thiophene. J. Chem. Thermodyn. 12 (1980) 1051-1055.

[96] W.J. Gaw, F.L. Swinton. Thermodynamic properties of binary systems containing hexafluorobenzene. Part 3. Excess Gibbs free energy of the system hexafluorobenzene + cyclohexane. Trans. Faraday. Soc. 64 (1968) 637-647.

[97]   A. Chinikamala, G.N. Houlth, Z. Lowell Taylor. Vapor-liquid equilibria of binary systems containing selected hydrocarbons with perfluorobenzene. J. Chem. Eng. Data 18 (1973) 322-325.

[98]   R.G. Rubio, J.A.R. Renuncio, M. Díaz Peña. Vapor-liquid equilibria for *n*-tetradecane-benzene mixtures at 25 and 50 ºC. J. Solution Chem. 11 (1982) 823-830.

[99]   M. Díaz Peña, J.A.R. Renuncio, R.G. Rubio. Excess Gibbs energies for the benzene + *n*-hexadecane system at 298.15 and 323.15 K. Thermochim. Acta 56 (1982) 199-208.

[100]   S. Weissman, S.E. Wood. Vapor-liquid equilibrium of benzene-2,2,4-trimethylpentane mixtures. J. Chem. Phys. 32 (1960) 1153-1160.

[101]   H. Casas, L. Segade, C. Franjo, E. Jiménez, M.I. Paz-Andrade, Excess molar enthalpies of propyl propanoate + hexane + benzene at 298.15 K and 308.15 K.J. Chem. Eng. Data, 45 (2000) 445-449.

[102]   S. Murakami, G. C. Benson. An isothermal dilution calorimeter for measuring enthalpies of mixing. J. Chem. Thermodyn. 1 (1969) 559-572.

[103]   T.M. Letcher, D.M. Perkins. Application of the Flory theory of liquid mixtures to excess volumes and enthalpies of benzene + cycloalkane and + *n*-alkane mixtures. Thermochim. Acta 77 (1984) 267-274.

[104]   A.M. Awwad, S.F. Al-Azzawi, M.A. Salman. Volumes and viscosities of benzene + n-alkane mixtures. Fluid Phase Equilib. 31 (1986) 171-182

TABLE 1

Dispersive (DIS) and quasichemical (QUAC) interchange coefficients, $C_{sf,l}^{DIS}$ and $C_{sf,l}^{QUAC}$, for (s,f,) contacts[a] in fluorobenzene, or 1,4-difluorobenzene, or hexafluorobenzene + hydrocarbon mixtures (l = 1, Gibbs energy; l = 2, enthalpy; l = 3, heat capacity).

System	(s,f)	$C_{sf,1}^{DIS}$	$C_{sf,2}^{DIS}$	$C_{sf,3}^{DIS}$	$C_{sf,1}^{QUAC}$	$C_{sf,2}^{QUAC}$	$C_{sf,3}^{QUAC}$
C_6H_5F + *n*-alkane[b]	(a,f)	-1.7	-3	-0.82[c]	2	3.8	0.2
1,4-$C_6H_4F_2$ + *n*-alkane[b]	(a,f)	-1.7	-2.3	-0.82	2	3.8	0.2

C_6F_6 + n-alkane	(a,f)	1.035	0.32	2.9^d	-0.57	0.35	-3.06
C_6H_5F + $C_6H_{12}^e$	(c,f)	-1.55	-2.65	-0.1	2	3.8	0.2
1,4-$C_6H_4F_2$ + $C_6H_{12}^e$	(c,f)	-1.55	-2.65	-0.1	2	3.8	0.2
C_6F_6 + C_6H_{12}	(c,f)	1.25	0.83	2.7	-0.57	0.35	-3.06
C_6F_6 + C_6H_6	(b,f)	2.02	2.25	-4.4	-1.8	-2.2	4
C_6F_6 + C_7H_8	(b,f)	1.46	0.4	1	-1.8	-2.2	4
C_6F_6 + 1,4-$C_6H_4(CH_3)_2$	(b,f)	0.3	-2.32	1	-1.8	-2.2	4

^{a}type s = a, aliphatic, s = b, aromatic, s = c, cyclic; type f, fluorine; ^{b} $C_{af,1}^{DIS/QUAC}$ coefficients determined assuming that $C_{bf,1}^{DIS/QUAC} = 0$ (l = 1,2,3); ^{c} $C_{af,3}^{DIS} = -1.0$ (n-C_6); -0.82 (n-C_7); -0.58 (n-C_8); -0.5 (n-C_{10}); -0.2 (n-C_{12}); $0.1(\geq n$-C_{14}); ^{d}value for heptane; for (n-C_{14}), $C_{af,3}^{DIS} = 2.78$; ^{e} $C_{cf,1}^{DIS/QUAC}$ coefficients determined assuming that $C_{bf,1}^{DIS/QUAC} = 0$ (l = 1,2,3) (see text)

TABLE 2

Molar excess Gibbs energy, G_m^E, at equimolar composition and temperature T, for fluorobenzene(1) or hexafluorobenzene(1) + hydrocarbon(2) mixtures. Comparison of experimental results (Exp.) with DISQUAC (DQ) calculations using the interaction parameters from Table 1, or with UNIFAC (Dortmund) (UNIF) predictions obtained using interaction parameters from the literature [9,18].

Hydrocarbon	T/K	N^a	G_m^E /J mol^{-1}	$\sigma_r(P)$ ^{b}	Ref

			Exp[c]	DQ.	Exp[c]	DQ[d]	UNIF[e]	
C_6H_5F + alkane								
n-C$_6$ ($x_1 = 0.537$)	344.9		393	380				93
				377[f]				
n-C$_7$ ($x_1 = 0.491$)	359.9		330	346				93
				290[f]				
CH_3-C_6H_{12}	348.15	25	357	353	0.0005	0.001	0.015	94
C_6H_{12}	323.15	10	341	419	0.011	0.028	0.014	72
	343.15	10	357	395	0.016	0.025	0.026	72
	348.15	28	387	389	0.0005	0.004	0.025	95
C_6F_6 + hydrocarbon								
n-C$_{14}$	298.15	20	641	646	0.005	0.018	0.022	62
n-C$_{16}$	298.15	18	604	615	0.003	0.023	0.031	63
C_6H_{12}	303.15	10	797	800	0.0035	0.004	0.067	96
	333.15	10	720	707	0.0007	0.003	0.059	96
	343.15	10	698	703	0.0013	0.003	0.057	96
C_6H_6	303.15	10	− 59	− 53	0.0003	0.009	0.005	24
	313.15	10	− 44	− 39	0.0002	0.008	0.002	24
	333.15	10	− 18	− 16	0.0014	0.007	0.004	24
	343.15	10	− 4.5	− 5.3	0.002	0.006	0.004	24
Toluene	303.15	10	− 213	− 212	0.0005	0.005	0.005	24
	343.15	10	− 106	− 110	0.0006	0.003	0.016	24
14DMBZ[g]	303.15	9	− 430	− 445	0.0006	0.009	0.021	24
	323.15	9	− 353	− 365	0.0021	0.005	0.046	24
	343.15	9	− 305	− 296	0.0065	0.005	0.008	24

[a]number of data points; [b]equation (5); [c]values of the fittings of experimental data using Redlich-Kister expansions to represent G_m^E; [d]results from equation (5) obtained using DISQUAC values for P_{calc}; [e]results from equation (5) obtained using UNIFAC values for P_{calc}; [f]UNIFAC result; [g]1,4-dimethylbenzene

TABLE 3

Azeotropic data ($x_{1az}, T_{az}; P_{az}$) for fluorobenzene(1) or hexafluorobenzene(1) + hydrocarbon(2) mixtures. Comparison of experimental results (Exp.) with DISQUAC (DQ) calculations using the interaction parameters from Table 1

System	T_{az} /K	x_{1az}		P_{az} /kPa		Ref
		Exp	DQ.	Exp.	DQ.	
$C_6H_5F + n\text{-}C_6$	342	0.046[a]	0.002	101.4	101.1	93
$C_6H_5F + n\text{-}C_7$	357.6	0.896[a]	0.898	101.4	101.2	93
$C_6F_6 + n\text{-}C_6$	341.09	0.245[a]	0.261	101.3	105.0	97
$C_6F_6 + CH_3\text{-}C_6H_{11}$	353.02	0.949[a]	0.976	101.3	100.8	97
	343.15	0.468[a]	0.463	93.21	93.43	96
$C_6F_6 + C_6H_6$	302.6	0.047[a]		16.00		23
	303.15	0.048[a]	0.088	15.93	16.1	24
	305.05	0.8115[b]	n.a.[c]	16.00		23
	333.15	0.126[a]	0.143	52.64	53.2	24
	343.15	0.157[a]	0.155	74.40	75.1	24
	352.45	0.208[a]		101.3		97
	353.45		0.182[a]		104.7	
	353.45	0.813[b]	0.700	101.3	101.7	97
	357.8	0.193[a]		120.		23
	358.85		0.188[a]		120.6	
	358.85	0.774[b]	0.619	120	118.4	23

[a]positive azeotrope; [b]negative azeotrope; [c]not available: DISQUAC does not predict the existence of negative azeotropes for this system at low temperatures (see Text)

TABLE 4

Molar excess enthalpies, H_m^E, at equimolar composition and temperature T, for fluorobenzene(1), or 1,4-difluorobenzene(1) or hexafluorobenzene(1) + hydrocarbon(2) mixtures. Comparison of experimental results (Exp.) with DISQUAC (DQ) calculations using the interaction parameters from Table 1.

hydrocarbon	T/K	N^a	H_m^E/J mol^{-1}	$dev(H_m^E)$ [b]	Ref

			Exp[c]	DQ.	Exp[c]	DQ[d]	UNIF[e]	
			C_6H_5F + alkane					
n-C_6	298.15	15	869	845	0.003	0.020	0.028	17
n-C_7	298.15	15	888	901	0.001	0.012	0.005	17
n-C_8	298.15	17	941	950	0.003	0.010	0.005	17
n-C_{10}	298.15	18	1024	1034	0.0008	0.011	0.006	17
n-C_{12}	298.15	18	1092	1102	0.001	0.010	0.006	17
n-C_{14}	298.15	18	1156	1159	0.003	0.005	0.008	17
n-C_{16}	298.15	18	1201	1208	0.005	0.006	0.006	17
C_6H_{12}	298.15	21	864	878	0.001	0.016	0.059	71
	303.15	8	906	867	0.007	0.041	0.031	72
	313.15	9	885	849	0.024	0.037	0.064	72
CH_3-C_6H_{11}	283.15		790	823				70
	298.15		738	809				70
		21	823		0.001	0.018	0.063	71
	313.15		692	793				70
			1,4-difluorobenzene + n-alkane					
n-C_7	298.15	12	1050	1019	0.007	0.020	0.025	15
n-C_8	298.15	13	1083	1071	0.009	0.025	0.025	15
n-C_{10}	298.15	11	1185	1158	0.005	0.025	0.015	15
n-C_{12}	298.15	14	1290	1228	0.010	0.034	0.021	15
n-C_{16}	298.15	13	1359	1334	0.017	0.025	0.015	15
			C_6F_6 + hydrocarbon					
n-C_7	298.15	28	1119	1098	0.003	0.020	0.253	15
n-C_{14}	298.15	24	1324	1400	0.003	0.049	0.361	15
C_6H_{12}	298.15	9	1576	1577	0.006	0.016	0.167	27
	313.2	9	1517	1549	0.015	0.014	0.111	27
	333.2	5	1483	1509	0.004	0.011	0.094	27
C_6H_{11}-CH_3	298.15		1315	1275				27
Table 4 (continued)								
	333.2		1239	1235				27
C_6H_6	283.2		−447	−581				26
	298.2	12	−456	−507	0.007	0.081	0.621	27
			−496					26
	308.15		−464	−465				26
	313.2	13	−433	−446	0.009			27

	318.15		−439	−429				26
	328.2	10	−402	−396	0.005			27
	343.9	9	−351	−352	0.006	0.117	0.641	27
Toluene	313.2		−1140	−1118				27
	328.2		−908	−906				27
	343.2		−651	−702				27
14DMBZ[f]	313.2	10	−1660	−1660	0.006	0.037	0.270	27
	328.2	7	−1504	−1516	0.009	0.040	0.176	27
	343.2	8	−1430	−1379	0.021	0.041	0.087	27

[a]number of data points; [b]equation (6); [c]results from equation (6) obtained using $H_{m,calc}^{E}$ values from the fitting of experimental data to Redlich-Kister expansions; [d]results from equation (6) obtained using $H_{m,calc}^{E}$ values from the DISQUAC application; [e]results from equation (6) obtained using $H_{m,calc}^{E}$ values from the UNIFAC application using interaction parameters from the literature [9,18]. [f]1,4-dimethylbenzene

TABLE 5

Isobaric molar excess heat capacities, C_{pm}^{E}, of fluorobenzene(1), or hexafluorobenzene(1) + hydrocarbon(2) mixtures at 298.15 K and equimolar composition. Comparison of experimental results (Exp.) with DISQUAC (DQ) calculations using the interaction parameters from Table 1, or with UNIFAC (Dortmund) predictions obtained using interaction parameters from the literature [9,18].

System	$C_{p\mathrm{m}}^{\mathrm{E}}$ /J mol⁻¹ K⁻¹			Ref.
	Exp	DQ	UNIF	
$C_6H_5F + n\text{-}C_7$	-1.18	-1.20	0.16	17
$C_6H_5F + n\text{-}C_8$	-1.42	-1.45	0.19	17
$C_6H_5F + n\text{-}C_{10}$	-2.00	-2.00	0.26	17
$C_6H_5F + n\text{-}C_{12}$	-2.78	-2.74	0.33	17
$C_6H_5F + n\text{-}C_{14}$	-3.75	-3.66	0.39	17
$C_6F_6 + n\text{-}C_7$	-1.18	-1.03	12.6	15
$C_6F_6 + n\text{-}C_{14}$	-2.25	-2.13	13.9	15
$C_6F_6 + C_6H_{12}$	-2.7	-1.75	0.77	27
$C_6F_6 + C_6H_6$	1.8	4.4	-1.6	27
$C_6F_6 + C_7H_8$	16.7	15.1	0.56	27
$C_6F_6 +$ 14DMBZ[a]	12.3	10.5	1.8	27

[a] 14DMBZ, 1,4-dimethylbenzene

TABLE 6

$S_{\mathrm{cc}}(0)$ of fluorobenzene(1), or hexafluorobenzene(1), or benzene(1) + hydrocarbon(2) mixtures at temperature T and at composition x_1, where $S_{\mathrm{cc}}(0)$ shows the maximum value. Comparison of experimental results (Exp.) with DISQUAC values obtained using interaction parameters from Table 1.

System	T/K	Exp.		DQ		Ref.
		x_1	$S_{cc}(0)$	x_1	$S_{cc}(0)$	
$C_6H_5F + n\text{-}C_7$	298.15			0.54	0.378	
$C_6H_5F + n\text{-}C_{14}$	298.15			0.58	0.305	
$C_6H_5F + n\text{-}C_{16}$	298.15			0.57	0.284	
$C_6H_5F + C_6H_{12}$	298.15			0.50	0.389	
$C_6F_6 + n\text{-}C_7$	298.15			0.51	0.528	
$C_6F_6 + n\text{-}C_{14}$	298.15	0.61	0.458	0.66	0.559	62
$C_6F_6 + n\text{-}C_{16}$	298.15	0.63	0.458	0.69	0.542	63
$C_6F_6 + TMP$	298.15	0.50	0.374			79
$C_6F_6 + C_6H_{12}$	303.15	0.44	0.704	0.44	0.711	96
$C_6F_6 + C_6H_6$	303.15	0.50	0.231	0.50	0.219	24
$C_6F_6 + C_7H_8$	303.15	0.50	0.206	0.50	0.200	24
$C_6F_6 + 14DMBZ$[a]	303.15	0.50	0.177	0.50	0.177	24
$C_6H_6 + n\text{-}C_7$	298.15	0.50	0.354			68
$C_6H_6 + n\text{-}C_{14}$	298.15	0.65	0.291			98
$C_6H_6 + n\text{-}C_{16}$	298.15	0.57	0.256			99
$C_6H_6 + TMP$[b]	308.15	0.65	0.308			100

[a] 14DMBZ, 1,4-dimethylbenzene; [b] TMP, 2,24-trimethylpentane

TTABLE 7

Excess molar functions: enthalpy, H_m^E, volume, V_m^E, and internal energy at constant volume U_{Vm}^E, at equimolar composition and 298.15 K for C_6H_5F, or $1,4\text{-}C_6H_4F_2$, or C_6F_6, or benzene + organic solvent (Solv) mixtures at 298.15 K

Solv	C_6H_5F	$1,4\text{-}C_6H_4F_2$	C_6F_6	C_6H_6

	$H_m^{E\,a}$	$V_m^{E\,b}$	$U_{Vm}^{E\,a}$	$H_m^{E\,a}$	$V_m^{E\,b}$	$U_{Vm}^{E\,a}$	$H_m^{E\,a}$	$V_m^{E\,b}$	$U_{Vm}^{E\,a}$	$H_m^{E\,a}$	$V_m^{E\,b}$	$U_{Vm}^{E\,a}$
n-C_6	869[c]	0.246[c]	803							924[i]	0.403[m]	816
n-C_7	888[c]	0.431[c]	765	1050[e]	0.650[e]	854	1119[e]	1.882[e]	557	931[j]	0.562[m]	768
n-C_8	941[c]	0.532[c]	785	1083[e]	0.779[e]	842				969[k]	0.700[m]	761
n-C_{10}	1024[c]	0.664[c]	822	1185[e]	0.935[e]	886						
n-C_{12}	1092[c]	0.740[c]	863	1290[e]	0.985[e]	957				1101[k]	0.919[n]	814
n-C_{14}	1156[c]	0.789[c]	905				1330[e]	2.093[e]	640	1183[k]	1.015[o]	856
n-C_{16}	1201[c]	0.832[c]	935	1359[e]	1.080[e]	999				1256[k]	1.023[n]	926
C_6H_{12}	864[d]	0.686[d]	632				1576[f]	2.454[g]	729	800[l]	0.654[p]	576
C_6H_6							− 433[f,*]	0.801[h,*]	− 719*			
C_7H_8							− 1140[f,*]	0.416[h,*]	− 1298*			
14DM BZ[q]							− 1660[f,*]	0.0855[h,*]	− 1690*			

[a]units: J mol^{-1}; [b]units: cm^3 mol^{-1}; [c][17]; [d][71]; [e][15]; [f][26]; [g][73], [h][75]; [i][101]; [j][10]; [k][11]; [l][102]; [m][78];

[n][103]; [o][104]; [p][71]; [q]1,4-dimethylbenzene; *, values at 313.15 K.
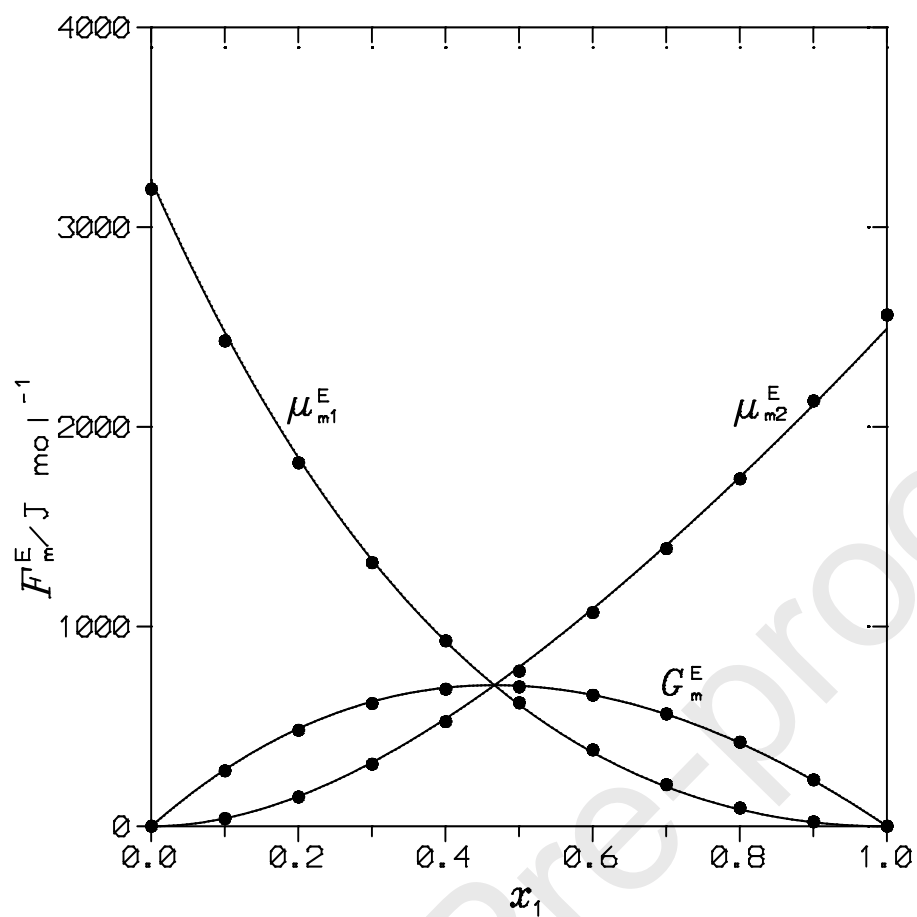
Figure 1 Excess molar Gibbs energy, $F_m^E = G_m^E$, and excess molar chemical potentials, $F_m^E = \mu_{mi}^E$ of hexafluorobenzene(1) + cyclohexane(2) mixture at 343.15 K. Points, experimental results [96]. Solid lines, DISQUAC calculations.
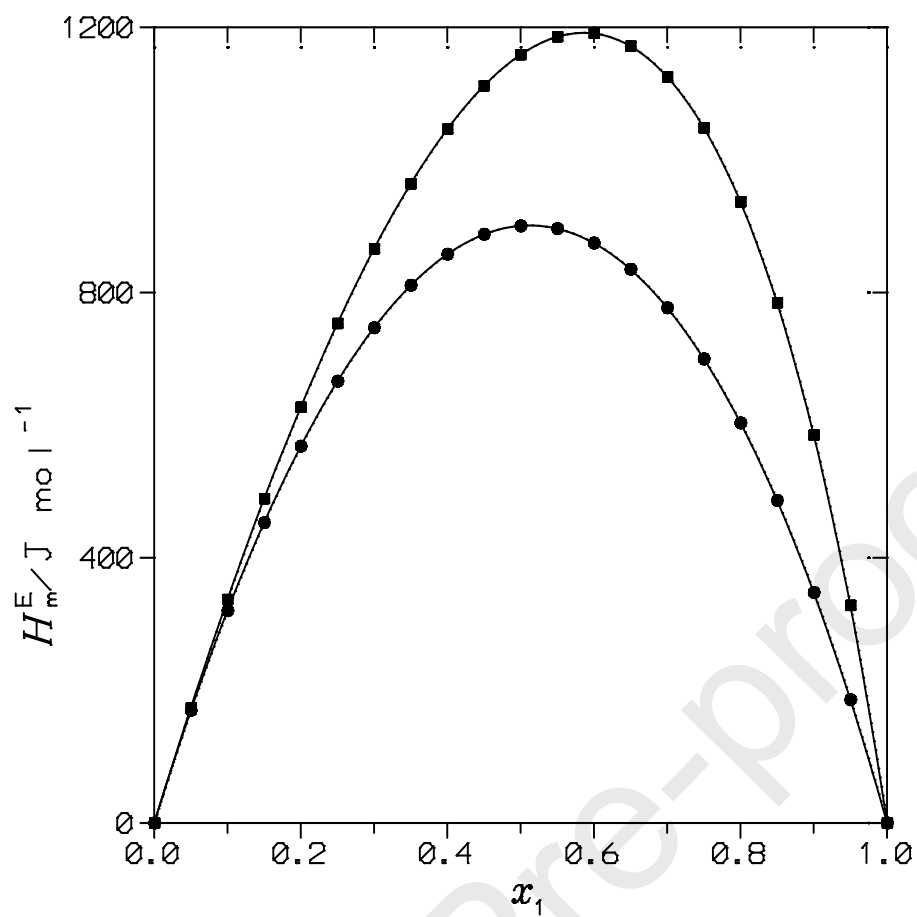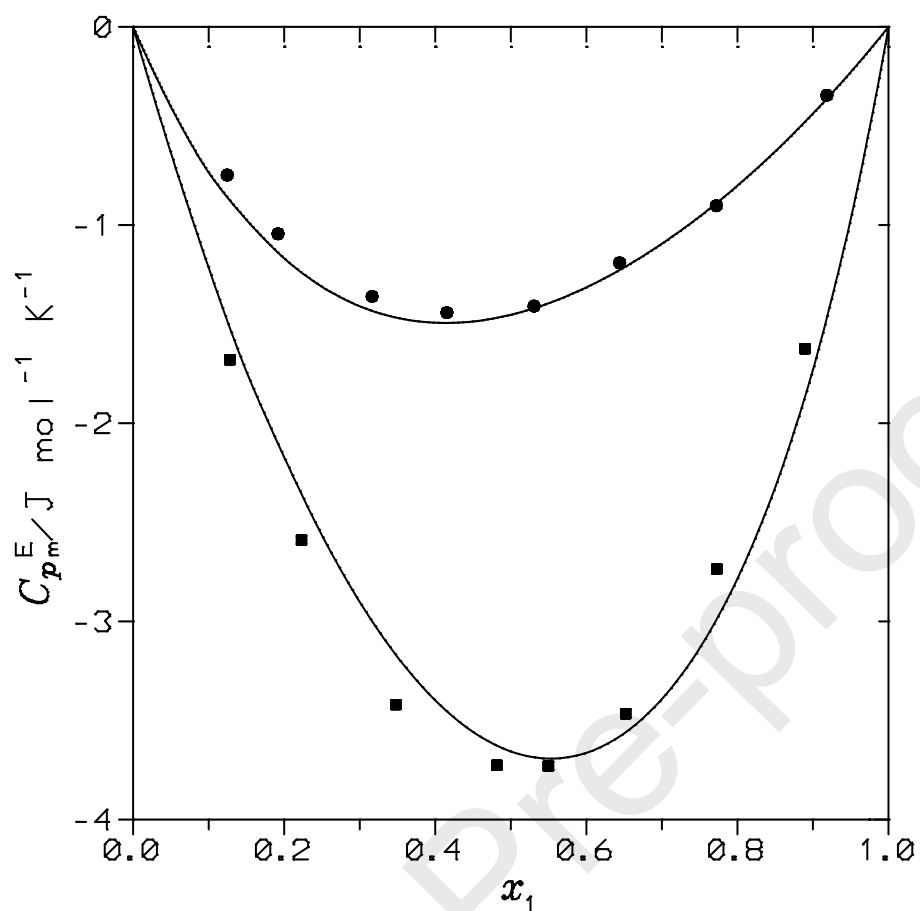
Figure 2. H_m^E of fluorobenzene(1) + *n*-alkane(2) mixtures at 298.15 K. Points, experimental results [17]: (●), heptane; (■), tetradecane. Solid lines, DISQUAC calculation
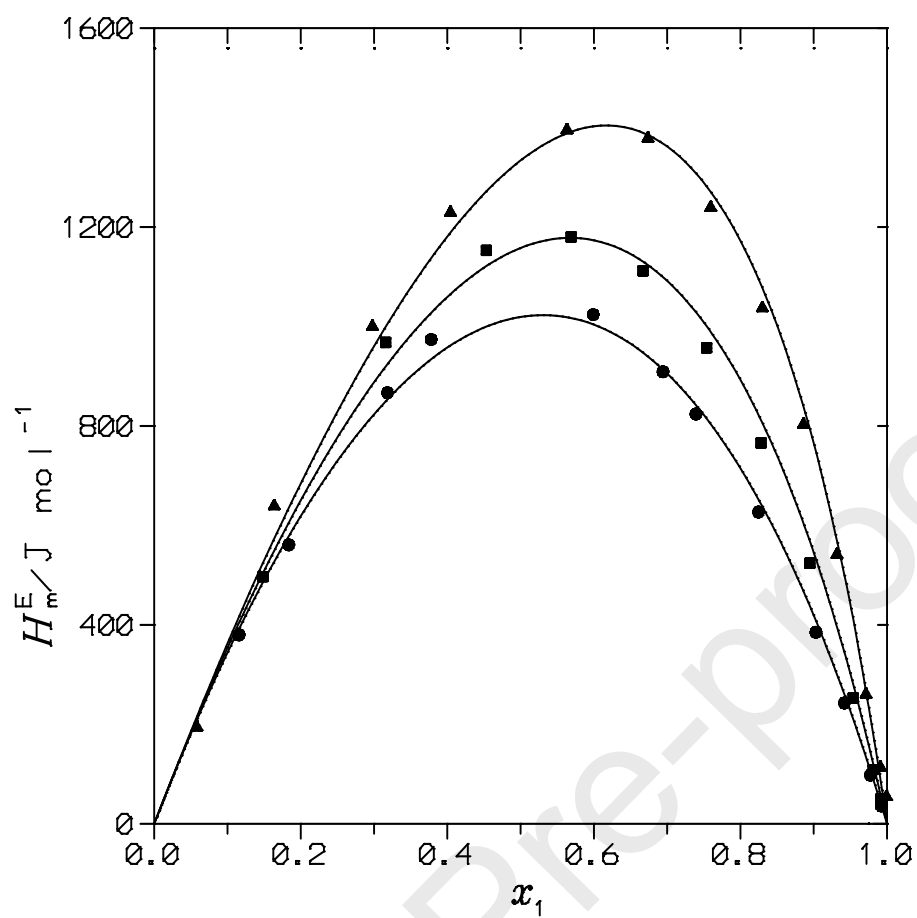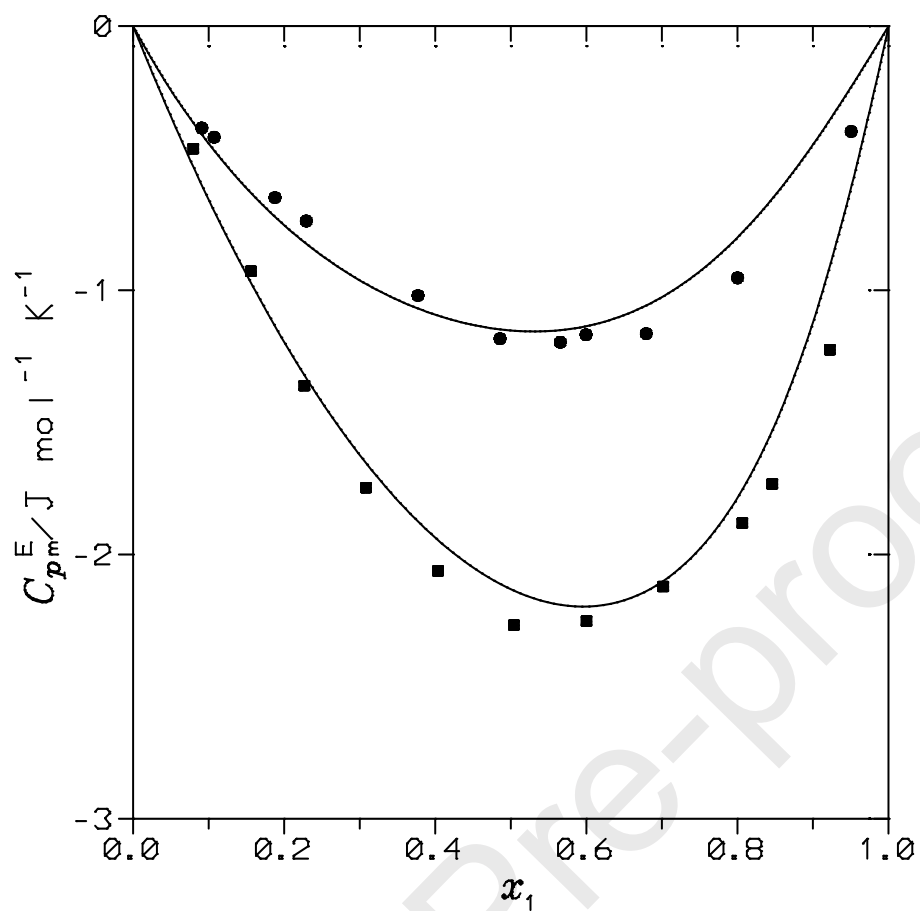
Figure 3. $H_{\mathrm{m}}^{\mathrm{E}}$ of 1,4-difluorobenzene(1) + n-alkane(2) mixtures at 298.15 K. Points, experimental results [15]: (●), heptane; (■), decane; (▲), tetradecane. Solid lines, DISQUAC calculations.
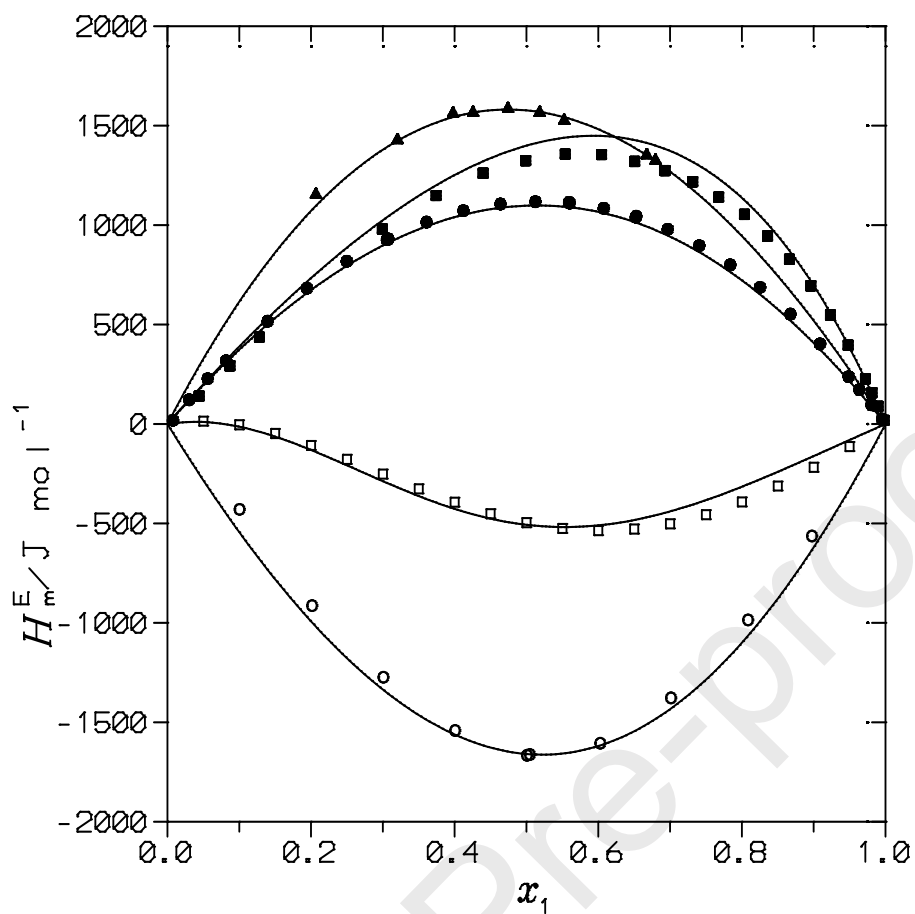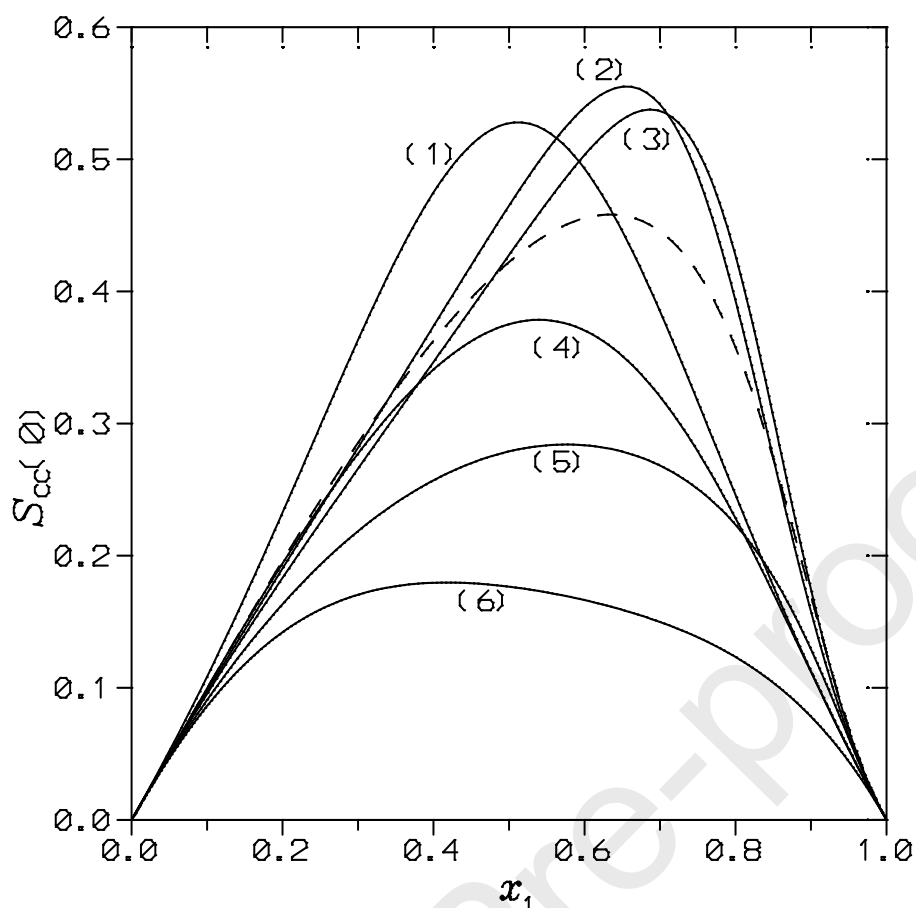
Figure 4. H_m^E of hexafluorobenzene(1) + hydrocarbon(2) mixtures. Points, experimental results: (●), heptane [15]; (■), tetradecane [15]; (▲), cyclohexane [27]; (□), benzene [27] (T = 298.15 K); (O), 1,4-dimethylbenzene [27] (T = 313.15 K). Solid lines, DISQUAC calculations.

Figure 5. C_{pm}^{E} of fluorobenzene(1) + *n*-alkane(2) mixtures at 298.15 K. Points, experimental results [17]: (●), heptane; (■), tetradecane. Solid lines, DISQUAC calculations.

Figure 6. C_{pm}^{E} of hexafluorobenzene(1) + *n*-alkane(2) mixtures at 298.15 K. Points, experimental results [15]: (●), octane; (■), tetradecane. Solid lines, DISQUAC calculations.

Figure 7. $S_{CC}(0)$ of fluorobenzene(1), or hexafluorobenzene(1) + hydrocarbon(2) mixtures at 298.15 K. Solid lines, DISQUAC calculations: (1) hexafluorobenzene(1) + heptane(2); (2), hexafluorobenzene(1) + tetradecane(2); (3), hexafluorobenzene(1) + hexadecane(2); (4), fluorobenzene(1)+ hexadecane(2); (5) fluorobenzene(1) + heptane(2); (6), hexafluorobenzene(1) + benzene(2). Dashed line, experimental results for hexafluorobenzene(1) + hexadecane(2) [63].

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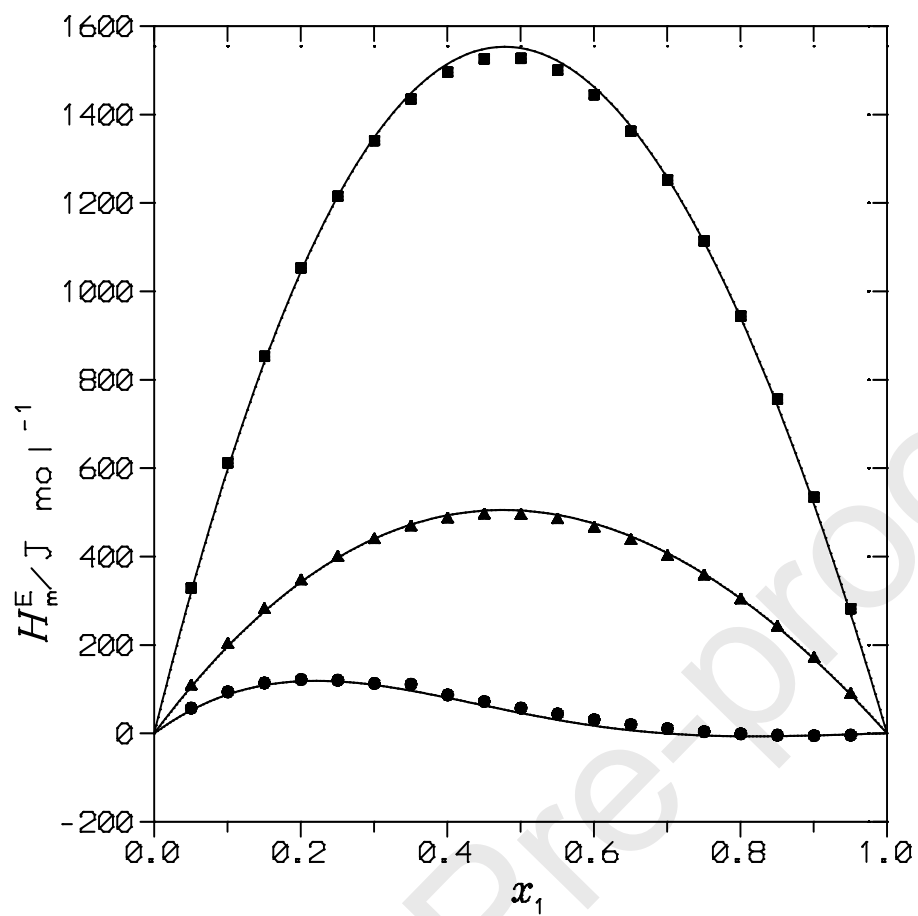
Figure 8. H_m^E of fluorinated benzene(1) + hydrocarbon(2) mixtures at 298.15 K. Points, experimental results: (●), C_6HF_5 + benzene [26]; (▲), 1,3,5-trifluorobenzene + benzene [26]; (■), C_6HF_5 + cyclohexane [83]. Solid lines, DISQUAC calculations with interaction parameters from Table S2.

CRediT authorship contribution statement

J.A. González, Conceptualization, Formal Analysis, Methology, Review and Editing. L.F. Sanz, Conceptualization, Software, Validation, Original Draft. I. García de la Fuente, Investigation, Supervision, Original Draft, Funding. J.C. Cobos, Methodology, Investigation, Supervision, Validation, Funding . F. Hevia, Formal Analysis, Investigation, Validation, Writing

Highlights

→DISQUAC, UNIFAC and $S_{CC}(0)$ are applied to C_6H_5F, $1,4\text{-}C_6H_4F_2$, C_6F_6 + hydrocarbon systems

→Alkane mixtures are characterized by dispersive interactions and don't show Patterson's effect

→The contribution from structural effects on H_m^E is examined using $U_{V,m}^E$

→For systems with a given *n*-alkane, H_m^E changes as: C_6F_6 >$1,4\text{-}C_6H_4F_2$> C_6H_5F, and $U_{V,m}^E$ changes as: $1,4\text{-}C_6H_4F_2$> C_6H_5F > C_6F_6

→Homocoordination is dominant in alkane systems; mixtures with aromatic hydrocarbons show heterocoordination

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: