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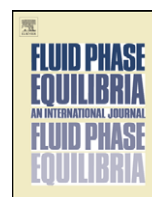
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Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluidLiquid–liquid equilibrium of substituted perfluoro-*n*-octane + *n*-octane systemsFatima R. Varanda^a, Lourdes F. Vega^b, João A.P. Coutinho^a, Isabel M. Marrucho^{a,*}^a CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal^b Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSICs), Campus de la U.A.B., 08193 Bellaterra, Barcelona, Spain

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ABSTRACT

The liquid–liquid phase equilibria of substituted perfluoro-*n*-octane (1Br-perfluoro-*n*-octane, 1H-perfluoro-*n*-octane, 1H,8H-perfluoro-*n*-octane)+*n*-octane were experimentally determined by turbidimetry in the temperature range between 270 K and 330 K and at the vapor pressure of the mixture. The measured equilibrium data were correlated with an equation derived from renormalization group (RG) theory and with soft-SAFT Equation of State. The LLE data of the binary mixtures of *n*-octane + substituted perfluoro-*n*-octane were compared with *n*-octane + perfluoro-*n*-octane data. The results indicate an increasing solubility with 1Br-perfluoro-*n*-octane and show that the introduction of second hydrogen atom has almost no effect on phase equilibrium.

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1. Introduction

The fluorocarbons (FCs) are synthetic compounds defined as saturated fluids, like alkanes, alkenes, ethers or amines, in which the hydrogen atoms are partially or completely substituted by fluorine atoms [1]. When all hydrogen atoms are substituted by fluorine atoms these compounds are called perfluorocarbons (PFCs). PFCs present physical and chemical properties quite different from their corresponding hydrogenated compounds. They have strong intramolecular forces [2] and very weak intermolecular forces, due to fluorine's high ionization potential and low polarizability. These two factors are the main responsible for the uncommon and interesting properties presented by perfluoroalkanes when compared with the corresponding hydrocarbons (HCs).

Although PFCs have a high capacity to solubilize gases like carbon dioxide, oxygen, nitrogen, hydrogen and helium [3,4], they do not mix with common solvents or water [5]. When PFCs are mixed with non-fluorinated solvents, the deviations from ideality are positive and larger than those of nearly all other classes of mixtures containing only non-polar and non-electrolyte substances. The most noticeable consequences of the extent of these deviations are the marked positive azeotropy, liquid–liquid immiscibility [6] and also surface azeotropy [7]. Differences in chain flexibility of the two component molecules and the weak interaction energy inter-

play are, most probably, the main responsible for the occurrence of these phenomena [8].

Siebert et al. [9] measured the excess second virial coefficient for binary mixtures of linear PFC + HC and they found that the proposed correlation was rather insensitive to variations in the Lorentz–Berthelot cross interaction size parameter (σ_{12}), but the interaction energy parameter (ϵ_{12}) differ from the calculated from geometric mean by 10%. These authors considered three main factors to explain the anomalously weak HC–PFC interaction: non-central forces, large differences in ionization potentials between components and large differences in size between components. Mousa et al. [10] also discussed the deviations from the harmonic mean rule for ϵ_{12} . All their results were fitted to an unlike parameter approximately equal to 0.92.

The results of excess molar volumes, VLE and LLE [11,12] and, more recently, the excess and solvation enthalpies [13] of perfluoro-*n*-alkanes + *n*-alkanes mixtures obtained by Matteoli and co-workers indicate, again, that PFCs are very inert molecules that weakly interact with themselves and with HCs. The molecular interaction forces change according to the order F–F < F–H < H–H. The same conclusions were derived by Lo Nostro et al. [14] who published a long list of phase separation in binary mixtures containing linear PFCs.

Freire et al. [5] reported experimental solubility data of water in α -(ω -) substituted perfluoro-*n*-octane systems and it was found that the water solubility increases with the inclusion of heteroatoms according to the sequence F < Br < (Cl)₂ < I < H < (H)₂. The solubility decrease was explained by the increasing electronegativity of the heteroatom that creates a larger dipole, enhancing

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the interaction with polar molecules such as water. The disubstituted fluorocarbons have increased water solubility due to the disubstitution. The same authors performed *ab initio* calculations on these systems and they concluded that there is a specific interaction between the oxygen atom of water and the heteroatom of the fluorocarbon, while for perfluoro-*n*-octane the oxygen atom of water is turned into the interspaces of the perfluorocarbon molecule.

Oxygen solubility in α -substituted perfluoro-*n*-octane has also been reported [4] and it increases in the following order: $(\text{H})_2 < \text{H} < \text{Br} < \text{F}$, which is the reverse order of the water solubility. The authors show that the enthalpies of solution and solvation also vary in this order clearly showing the existence of an interaction between the oxygen and the CF_3 end-groups. These findings are supported by *ab initio* and ^{19}F NMR studies where it is shown that the terminal trifluoromethyl groups have a larger sensitivity to oxygen when compared with the CF_2 groups in molecules as 1Br-perfluoro-*n*-octane, perfluorotripropylamine and perfluorotributylamine [15].

The importance of having a wide and accurate thermophysical database on these compounds which possess unusual properties is very high since most of the correlation and prediction models usually used in engineering present large deviations for these systems. The understanding of their peculiar behavior is thus crucial in order to develop accurate models that will allow the prediction of the relevant thermophysical properties regarding the application of these compounds at the temperature and pressure of interest. In that context and as a continuation of our studies on thermodynamic properties of PFCs [3–5,16–19], this work is another contribution in the effort devoted to the characterization of perfluoroalkanes and their mixtures. The main objective is to complement/validate experimental data available in the literature, to present accurate original experimental data that, besides the practical direct interest, can help to answer/validate the theories and models related to highly fluorinated systems. The experimental data were obtained by a synthetic method, turbidimetry and soft-SAFT EoS (Equation of State) was used to correlate the experimental data of studied systems.

2. Experimental

Liquid–liquid equilibrium of binary mixtures of substituted perfluoro-*n*-octane + *n*-octane were measured using a synthetic method, turbidimetry, at the vapor pressure of mixture. The *n*-octane (CAS No. 111-65-9) was acquired from Fluka (purity 99.5 wt%). The selected substituted perfluoro-*n*-octanes were 1Br-perfluoro-*n*-octane (CAS No. 423-55-2), 1H-perfluoro-*n*-octane (CAS No. 335-65-9) and 1H,8H-perfluoro-*n*-octane (CAS No. 307-99-3) and were all bought from Apollo Scientific with purities of 99.90 wt%, 97.05 wt% and 99.10 wt%, respectively. All the solvents were used without any further purification.

All samples were prepared in ampoules containing a magnetic stirrer. Each compound was rigorously weighted using an analytical balance (± 0.1 mg). The mixture inside the ampoules was immediately frozen in liquid nitrogen, avoiding any changing in composition and sealed under vacuum, in order to minimize the air content inside of the ampoule.

Each sample, with a different composition, was immersed in a thermostatic bath. Cloud points were obtained with a calibrated Pt100 temperature sensor with an uncertainty of ± 0.05 K.

The experimental procedure consisted on heating up the sample until the mixture becomes monophasic. The samples were then slowly cooled (< -0.05 K min^{-1}), so that the error in the cloud point temperature determination is minimized [20], until phase separation was detected by visual observation. The temperature value of

the Pt100 was taken and the procedure was repeated until three independent agreeing values were obtained.

3. Modelling

3.1. Critical point determination

The renormalization group (RG) theory can be used to correlate the liquid–liquid equilibrium of mixtures that have an exact symmetry at the critical point with respect to a proper order parameter (p) [21]. Mole fraction, volume fraction, weight fraction and mass density are some possible order parameters. Experimental data for similar systems [18,19] indicate that the volume fraction representation is more symmetric than other representations, as for example mole fraction, and thus volume fraction was chosen as the order parameter.

The critical exponent β defines the shape of the coexisting curve as $\tau = (T_c - T)/T_c$ approaches zero:

$$\Delta p = B\tau^\beta \quad (1)$$

where Δp is the difference between the order parameters of coexisting phases.

Other terms were added to describe the diameter of coexistence curve over a wide range of temperatures. The relationship that better correlates the experimental data measured in this work is written in the following form:

$$\varphi - \varphi_c = f a \left(\frac{T_c - T}{T_c} \right)^\beta \quad (2)$$

where $f = 1$ for $\varphi > \varphi_c$ and $f = -1$ for $\varphi < \varphi_c$.

3.2. The soft-SAFT EoS

The molecular Equation of State soft-SAFT was also used in this work to describe the measured experimental data. This model has already been successfully used to study vapor–liquid and liquid–liquid equilibria of perfluorocarbons + hydrocarbons and to describe the marked non-ideality that these systems present. Since thorough detailed descriptions of the soft-SAFT model can be found in the literature [22], only a brief overview is presented here.

Within the SAFT context, each non-associating fluid is modeled as a homonuclear chain of tangentially bonded equal spherical segments, which are represented by three parameters: the number of segments (m), the diameter of each segment (σ) and its interaction energy (ε). These parameters are usually obtained by fitting the equation to density and vapor pressure data of the pure compounds. In the present case, the molecular parameters for all the pure compounds used were available in the literature [15,16,23] and are listed in Table 1. Two binary interaction parameters, η and ξ , accounting for differences in size and energy of the segments of the different compounds present in the mixture can be used in the generalized Lorentz–Berthelot combination rules to provide an accurate description of mixture data. When no binary interaction parameter is used, the value of these parameters is unity and the results obtained for the mixture behavior are predictive.

Table 1
Parameters used in soft-SAFT EoS for the compounds present in studied systems

Compound	m	σ (Å)	ε/k_B (K)	Reference
$\text{C}_8\text{F}_{17}\text{Br}$	3.522	4.652	268.9	Dias et al. [16]
$\text{C}_8\text{F}_{17}\text{H}$	3.522	4.492	253.6	Dias et al. [16]
$\text{C}_8\text{F}_{16}\text{H}_2$	3.522	4.456	267.8	Dias et al. [15]
C_8F_{18}	3.522	4.521	245.1	Pàmies et al. [23]
C_8H_{18}	3.522	3.970	264.4	Pàmies et al. [23]

Table 4
Optimized binary parameters used in soft-SAFT EoS for the studied systems

Compound	η_{ij}	ξ_{ij}
$C_8F_{17}Br + C_8H_{18}$	1.000	0.9360
$C_8F_{17}H + C_8H_{18}$	1.000	0.9207
$C_8F_{16}H_2 + C_8H_{18}$	1.000	0.9189
$C_8F_{18} + C_8H_{18}$	1.000	0.9146

these results might be that although the interactions between the 1H,8H-perfluoro-*n*-octane and *n*-octane are more probable than those between 1H-perfluoro-*n*-octane and *n*-octane, the interactions among 1H,8H-perfluoro-*n*-octane itself is also more probable or stronger than those among 1H-perfluoro-*n*-octane itself.

The soft-SAFT model was used to correlate the experimental solubility data results presented here. In a previous work [22], the soft-SAFT equation was used to model the experimental vapor–liquid equilibria and liquid–liquid equilibria of PFCs + HCs and only the unlike energy parameter was treated as adjustable. An optimum value of $\xi = 0.9146$ was found for the correct prediction of the azeotrope of *n*- C_6F_{14} + *n*- C_6H_{14} system at 298.15 K, showing the transferability of the parameter. More recently, we have again used it to successfully describe other PFCs + HCs LLE data [18]. In this work, this parameter was also tested in the prediction of the LLE data for the substituted perfluoro-*n*-octane systems here presented but it did not provide acceptable results. The optimized binary parameters used to describe each system are presented in Table 4. A study on the possibility of using one of these parameters in a transferable manner for the modeling of the other systems was performed but the large deviations were found. The results obtained with the proposed model are depicted in Fig. 2, where it can be seen that the model correctly the solubility order of the studied systems. Despite the flatness of the LLE curve, the model captures the systems behavior qualitatively. Notice that no long range fluctuations are included in the soft-SAFT model used in this work and, hence, the correct description of the critical region should not be expected. Again, it was verified that a fixed size interaction binary parameter ($\eta = 1$) should be used since its fitting does not improve the quality of the modeling.

It is interesting to notice that within the soft-SAFT approach it is possible to use the same energy interaction parameter to describe phase equilibria of PFCs + HCs with different chain lengths and that

it is not possible to use it for substituted perfluorocarbons + HCs. In fact, the transferability of this parameter has been proved to hold also when other of SAFT-type EoS, SAFT-VR, is used [27–31].

From the analysis of the optimal energy interaction parameters from both soft-SAFT and SAFT-VR approaches it is clear that the models overestimate the attractive energy interaction between perfluorocarbons and hydrocarbons in about 8–10%, corroborating the anomalously weak interactions between these two types of molecules described before. As the polarizability of the substituted perfluorocarbons increases, the miscibility window increases also and thus the deviations from the mean geometric rule, given by ξ , usually used for the energy term decreases.

Analyzing Fig. 2, it can be concluded that soft-SAFT can qualitatively capture the nature of the studied mixtures, showing the large solubility gap between the 1Br-perfluoro-*n*-octane and the 1H-perfluoro-*n*-octane and 1H,8H-perfluoro-*n*-octane. More interesting is the description of the systems containing 1H-perfluoro-*n*-octane and 1H,8H-perfluoro-*n*-octane where hardly no distinction is provided by soft-SAFT for them, indicating that it can capture in molecular terms the physical details of both these mixtures. From the theoretical point of view, soft-SAFT provided a successful example on how a molecularly based equation of state can be an important tool in the understanding of the behavior of liquids and liquid mixtures.

List of symbols

EoS	Equation of State
FC	fluorocarbon
HC	hydrocarbon
LLE	liquid–liquid equilibrium
<i>m</i>	chain length
<i>p</i>	order parameter
PFC	perfluorocarbon
RG	Renormalization Group
SAFT	Statistical Associating Fluid Theory
SLE	solid–liquid equilibrium
<i>T</i>	temperature
UCST	upper critical solution temperature
<i>w</i>	weight fraction
<i>x</i>	mole fraction

Greek letters

α	critical exponent
β	critical exponent
ε	segment interaction energy (between Lennard–Jones segments)
η	size parameter of the generalized Lorentz–Berthelot combination rules
ξ	energy parameter of the generalized Lorentz–Berthelot combination rules
ρ	mass density (kg m^{-3})
σ	size parameter of the intermolecular potential/diameter (for Lennard–Jones segments)
τ	reduced temperature
φ	volume fraction

List of indices

<i>c</i>	critical
<i>i</i>	component

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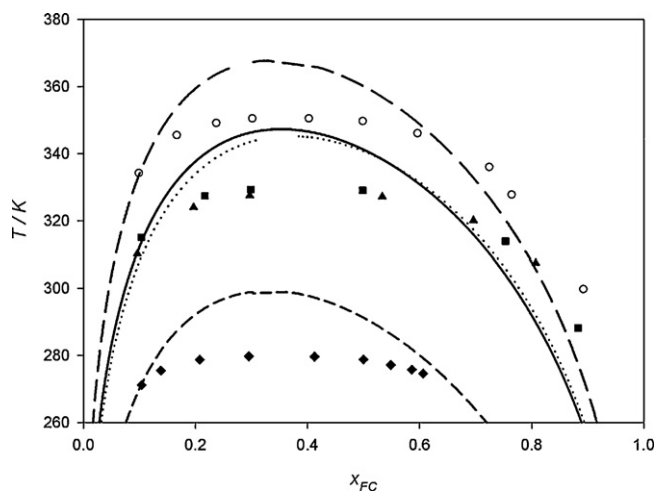


Fig. 2. Soft-SAFT EoS correlation and liquid–liquid data for studied systems in terms of molar fraction of fluorocompound. Symbols: 1Br-perfluoro-*n*-octane + *n*-octane (\blacklozenge , ---), 1H-perfluoro-*n*-octane + *n*-octane (\blacksquare , —), 1H,8H-perfluoro-*n*-octane + *n*-octane (\blacktriangle ,), (\circ , - - -) Represent perfluoro-*n*-octane + *n*-octane data measured by Melo et al. [18]. (X) Represents the critical point for each mixture.

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