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Theoretical investigation of the phase behaviour of model ternary mixtures containing n-alkanes, perfluoro-n-alkanes, and perfluoroalkylalkane diblock surfactants

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RESEARCH ARTICLE

Theoretical investigation of the phase behaviour of model ternary mixtures containing *n*-alkanes, perfluoro-*n*-alkanes, and perfluoroalkylalkane diblock surfactantsMARÍA CAROLINA DOS RAMOS^a and FELIPE J. BLAS^b *^a Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee 37235;^b Departamento de Física Aplicada, Facultad de Ciencias Experimentales, Universidad de Huelva, 21071 Huelva, Spain

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We have used the hetero-SAFT-VR approach developed by McCabe and collaborators [Mol. Phys. **104**, 571 (2006)] to investigate the phase equilibria of a number of binary and ternary mixtures of *n*-alkanes, perfluoro-*n*-alkanes, and perfluoroalkylalkane diblock surfactants. We focussed our work on the understanding of the microscopic conditions that control the phase behaviour of these mixtures, with a particular emphasis of the effect on the liquid-liquid separation and the stabilisation of *n*-alkane + perfluoro-*n*-alkane mixtures when a diblock surfactant is added. We used very simple molecular models for *n*-alkanes, and perfluoro-*n*-alkanes that describe the molecules as chains with tangentially bonded segments with molecular parameters taken from the literature. In the particular case of semifluorinated alkanes or SFA surfactants, we used an hetero-segmented diblock chain model where the parameters for the alkyl and perfluoroalkyl segments taken from the corresponding linear alkanes and perfluoroalkanes, as shown in our previous work [J. Phys. Chem. B **111**, 2856 (2007)]. Our goal was to identify the main effects on the phase behaviour when different perfluoroalkylalkane surfactants are added to mixtures of *n*-alkanes and perfluoro-*n*-alkanes. We selected the *n*-heptane + perfluoromethane binary mixture, and studied the changes on the phase behaviour when a symmetric (same number of alkyl and perfluoroalkyl chemical groups) or an asymmetric (different number of alkyl and perfluoroalkyl chemical groups) diblock surfactants is added to the binary mixture. We have obtained the phase diagrams of a wide range of binary and ternary mixtures at different thermodynamic conditions. We have found a variety of interesting behaviours as we modify the alkyl or/and the perfluoroalkyl chain-length of the diblock surfactants: the usual changes in the vapour-liquid phase separation, changes in the type of phase diagrams (typically from type *I* to type *V* phase behaviour according to the Scott and Konynenburg classification), azeotropy, and Bancroft points. We noted that the main effect of adding a symmetric or an asymmetric surfactant to the *n*-heptane + perfluoromethane mixture is to stabilise the system, i.e., to decrease the two-phase (liquid-liquid) immiscibility region of the ternary diagram as the surfactant concentration is increased. This effect becomes larger as the chain length of the surfactant is increased, which is consistent with a higher number of alkyl-alkyl and perfluoroalkyl-perfluoroalkyl favourable interactions in the mixture.

Keywords: Phase equilibria, semifluorinated alkanes or SFAs, SAFT-VR, alkanes, perfluoroalkanes, binary and ternary mixtures, surfactants.

1. Introduction

The thermodynamic properties of mixtures involving *n*-alkanes and perfluoro-*n*-alkanes are known to exhibit a rich behaviour. From a phenomenological point of view, they show significant deviations from the ideal behaviour, such as large

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1 positive excess functions and extensive regions of liquid-liquid immiscibility [1, 2].
2 Although both types of molecules seem to have a similar structure, since the fluo-
3 rine atoms are just simply replacing the hydrogen atoms in the alkane molecules,
4 the fact is that *n*-alkanes and perfluoro-*n*-alkanes are very different. The rich phase
5 behaviour exhibited by these mixtures is well known since late 1940's [3–6]. How-
6 ever, the origin of the mutual phobicity between alkyl and perfluoroalkyl chemical
7 groups seems to be in an unusual weak hydrocarbon-fluorocarbon interaction. Re-
8 cently, Song and collaborators [7] have reviewed this issue. They concluded that
9 the origins of the weaker-than-expected interactions between perfluoroalkanes and
10 alkanes still remain a mystery. High-level quantum mechanical calculations should
11 provide valuable insights into the problem, but unfortunately, the latest results at
12 this level of electron correlation do not appear to have enough accuracy.

13 Perfluoro-*n*-alkanes are very interesting molecules that have numerous applica-
14 tions in the medical field and the chemical industry due to their unique properties:
15 inertness, biocompatibility, and ability to solubilize high levels of respiratory gases,
16 such as oxygen and carbon dioxide, among other properties [8]. They are also widely
17 used in the chemical industry [9]. For instance, the perfluoroalkyl chemical group
18 is present in most ZONYL intermediate surfactants as a mixture of chain lengths.
19 In addition, short-chain perfluoro-*n*-alkanes, from perfluoro-*n*-hexane to perfluoro-
20 *n*-decane, can be added to colloids or nano-particles to act as stabilisers in the
21 presence of carbon dioxide [10].

22 Although perfluoro-*n*-alkanes are probably the simplest homologous chain-like
23 series of perfluorinated molecules, there exists a great variety of substances and
24 chemical families with even more interesting properties. This is the particular case
25 of the perfluoroalkylalkane or semifluorinated alkanes (SFAs), which have the gen-
26 eral formula $F(CF_2)_i(CH_2)_jH$ or simply named as F_iH_j . They are molecules made
27 up of a hydrogenated segments and a perfluorinated segments covalently bonded
28 to form a single linear chain. The unique properties of perfluoroalkylalkane diblock
29 molecules result from the combined presence of alkyl and perfluoroalkyl chains,
30 which their interactions are mutually phobic. It is relevant at this point to compare
31 the microscopic mechanisms that control the interactions between both chemical
32 groups with those existing in common hydrophilic-hydrophobic surfactants, such
33 as alkyl polyoxyethylene surfactants. The amphiphilicity of perfluoroalkylalkane
34 molecules, and consequently their potential for self-organisation, results from a
35 subtle balance of weak and even weaker dispersion forces, and has led to perfluoro-
36 alkylalkanes sometimes being called *primitive surfactants* due to their ability of
37 self-organise despite of the lack of polar head groups [11–14]. The mutual phobic-
38 ity between both parts of these chains rise innumerable possibilities for the use of
39 semifluorinated molecules as surface-active agents, such as aggregation in solvents
40 selective for one of the blocks, the formation of smectic liquid crystalline phases,
41 and recently, the formation of nanoscale patterns in molecular films of either pure
42 or mixed perfluoroalkylalkanes, among others [11–22].

43 Despite the importance of the SFAs from both experimental and theoretical
44 points of view, there is little experimental information about their thermodynamic
45 behaviour, including the phase equilibria. The main reason for this lack of informa-
46 tion could be mainly due to the high cost in the production of these molecules, since
47 most of them must be synthesised to be studied. Hence, it is highly desirable to
48 have reliable information about the thermodynamic behaviour of these SFAs from
49 alternative routes. The prediction of the thermodynamic properties of chain fluids
50 has experienced an important advance in last decades, the most successful are those
51 based on statistical mechanics. Molecular-based equations of state, such as those
52 derived from the Statistical Associating Fluid Theory or SAFT approach [23, 24],
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1 based on the work of Wertheim [25–28], provide a framework in which the different
2 microscopic effects can be properly estimated and quantified separately, leading
3 to a powerful and reliable equation of state that is applicable to study complex
4 systems. See the excellent reviews on the SAFT approach [29–31].

5 The SAFT approach has been extended to deal with different intermolecular po-
6 tentials, such as the SAFT-VR extension developed by Gil Villegas *et al.* [32, 33]
7 that describes the behaviour of chains formed by spherical segment interacting
8 through a potential of variable range, typically the square-well potential. The
9 SAFT-VR approach, as other versions of SAFT, can be considered as one of the
10 most powerful predicting equations of state nowadays for determining the ther-
11 modynamic properties of systems as complex as chain-like, including the *n*-alkane
12 series, the perfluoro-*n*-alkanes and their mixtures [33–38], systems with refriger-
13 ants [39–41], surfactants [42–46], polymeric [47–50] and aqueous systems [51–53],
14 among others. In recent works [43–46], in a collaboration with other research
15 groups, we have used a modification of the SAFT-VR approach, called hetero-
16 SAFT-VR [54–56], where molecules are composed of different segments, to predict
17 some thermodynamic properties, including the phase equilibrium of two different
18 perfluoroalkylalkane molecules, namely the perfluorohexylhexane and perfluoro-
19 hexyloctane, without the need of experimental data from these surfactants. This
20 is done by assuming that the molecular parameters of the alkyl and perfluoroalkyl
21 groups in the surfactants are the same as those obtained from pure alkanes and
22 perfluoroalkanes, respectively. The same can be done for the unlike interactions
23 between both chemical groups. Using an appropriate rule for the number of chem-
24 ical units in the surfactant molecule, the resulting equation of state is able to
25 predict successfully the saturated liquid density and vapour pressure of several
26 pure perfluoroalkylalkanes without any further fitting [44]. During last three years,
27 several authors have combined the group contribution approaches with the SAFT
28 approach in order to better account for the effects of molecular structure and com-
29 position. Within these works the SAFT- γ approach, developed by Lymperiadis *et*
30 *al.* [57, 58], and the GC-SAFT-VR approach, developed by Peng *et al.* [59], have
31 based their theory on a heteronuclear version of SAFT, which have shown a good
32 predictive capability of the fluid phase behaviour of molecules that were not in-
33 cluded in the determination of the group parameters as well as binary, ternary and
34 polymer systems.

35 In this work, we follow a similar procedure and extend the previous studies to deal
36 with binary and ternary mixtures of SFAs with linear alkanes and perfluoroalkanes.
37 The main goal of this work is to investigate and provide a general picture of the
38 phase behaviour of these mixtures. To this end, we use different sets of reasonable
39 molecular parameters presented previously [43–46] to describe the chemical units
40 of *n*-alkanes, perfluoroalkanes and perfluoroalkylalkanes. It is important to recall
41 that our objective is not to provide a detailed quantitative description of the phase
42 behaviour of these mixtures, but to give an insight of the general features exhibited
43 by these mixtures. In particular, we focus on the effect of the molecular weight of the
44 *n*-alkanes and perfluoroalkanes, as well as in the relative number of the (alkyl and
45 perfluoroalkyl) chemical groups on the surfactant on the type of phase behaviour
46 exhibited by these mixtures. Since the theory has proven to be very successful
47 in predicting the phase behaviour of complex mixtures, we expect to give a good
48 representative model of the phase equilibria of perfluoroalkylalkane + *n*-alkane +
49 perfluoro-*n*-alkane ternary mixtures.

50 The rest of the paper is organised as follows. We describe the molecular model
51 and theory in section 2. The results and discussion are presented in section 3; and
52 the conclusions are discussed in section 4.

2. Molecular Model and Theory

We have considered three different types of homologous series of real molecules that exhibit chain-like molecular behaviour, i.e., n -alkanes, perfluoro- n -alkanes, and perfluoroalkylalkane diblock surfactants. The SFAs or perfluoroalkylalkanes surfactants, F_iH_j , are formed by linear alkane chains bonded to linear perfluoroalkane chains, which can be regarded as semi-flexible copolymers. Following a similar approach used in earlier works [43–46], the diblock surfactant molecules are modelled using a heteronuclear model that considers two homonuclear chains for each branch of the surfactant bonded together. The alkyl branch is also modelled by an united atom approach, where m_A hard-sphere attractive segments of equal diameter σ_{AA} , which are tangentially bonded to form the chain. Similarly, the perfluoroalkyl branch is modelled by an united atom approach where m_B hard-sphere attractive segments of diameter σ_{BB} , which are also tangentially bonded. These two branches are also tangentially bonded to form the diblock surfactants model. σ_{AB} is calculated using the arithmetic Lorentz rule, and represents the bond length between the alkyl and perfluoroalkyl linear chains. The total number of segments forming each surfactant molecule, m_1 , is equal to the sum of the number of alkyl-like and perfluoroalkyl-like segments, i.e. $m_1 = m_A + m_B$.

The other two types of molecules considered here are treated as homonuclear chains. Thus, n -alkanes and perfluoro- n -alkanes are modelled using the same united atom approach for the surfactant branches, where we now consider m_2 and m_3 hard-sphere attractive segments of diameters σ_2 and σ_3 , respectively, which are bonded tangentially to form the corresponding molecules.

The dispersive interactions between two arbitrary segments i and j are described via a square-well (SW) potential given by,

$$u_{ij}^{SW}(r_{ij}) = \begin{cases} +\infty & \text{if } r_{ij} < \sigma_{ij} \\ -\epsilon_{ij} & \text{if } \sigma_{ij} \leq r_{ij} \leq \lambda_{ij}\sigma_{ij} \\ 0 & \text{if } r_{ij} > \lambda_{ij}\sigma_{ij} \end{cases} \quad (1)$$

where r_{ij} is the distance between the two segments, σ_{ij} defines the contact distance between segment type i and segment type j , and λ_{ij} and ϵ_{ij} are the range and depth of the potential well for the i - j interaction, respectively.

The hetero-SAFT-VR approach is used here to deal with mixtures containing surfactant molecules. As any SAFT equation, the theory is written in terms of the contributions to the Helmholtz free energy. In the case of mixtures of non-associating homonuclear and heteronuclear (surfactant) molecules the free energy can be expressed as a sum of three microscopic contributions: an ideal contribution A^{IDEAL} , a monomer term A^{MONO} that takes into account the attractive and repulsive forces between the segments that form the molecules, and a chain contribution A^{CHAIN} that accounts for the connectivity of segments within the molecules. The free energy is then written as,

$$\frac{A}{Nk_B T} = \frac{A^{\text{IDEAL}}}{Nk_B T} + \frac{A^{\text{MONO}}}{Nk_B T} + \frac{A^{\text{CHAIN}}}{Nk_B T} \quad (2)$$

where N is the total number of molecules, T is the temperature, and k_B is the Boltzmann constant. Since the hetero-SAFT-VR theory has already been presented and used to study pure surfactant molecules and mixtures [43–46, 56], here we only give an brief overview of the main expressions.

The ideal free energy a ternary mixture is given by [60],

$$\frac{A^{\text{IDEAL}}}{Nk_B T} = x_1 \ln(\rho_1 \Lambda_1^3) + x_2 (\rho_2 \Lambda_2^3) + x_3 \ln(\rho_3 \Lambda_3^3) - 1 \quad (3)$$

where $\rho_i = N_i/V$ is the number density and Λ_i is the thermal de Broglie wavelength of molecule i , which contains all of the kinetic (translational, rotational, and vibrational) contributions to the partition function of the molecule. The precise form of the function can be obtained from experimental ideal heat capacity. x_1 , x_2 and x_3 are the compositions of each component in the mixture, i.e. $x_1 + x_2 + x_3 = 1$.

The monomer free energy contribution is written in terms of the free energy per segment (a^M), which is in turn given as a second-order high-temperature perturbation expansion [61–63],

$$\begin{aligned} \frac{A^{\text{MONO}}}{Nk_B T} &= \left(\sum_{i=1}^n m_i x_{si} \right) a^M \\ &= \left(\sum_{i=1}^n m_i x_{si} \right) (a^{HS} + \beta a_1 + \beta^2 a_2) \end{aligned} \quad (4)$$

where $\beta = (k_B T)^{-1}$, m_i and x_{si} are the chain length and the molar fraction of segments type i , respectively; n is the number of type of segments in the monomer reference system, which in our case is equal to 4 since the systems under investigation are ternary mixtures composed of two homonuclear chains and one heteronuclear diblock chain (the surfactant). a^{HS} is the residual free energy per segment in a mixture of hard spheres obtained from the expression of Boublík [64] (equivalent to that of Mansoori *et al.* [65]). The mean-attractive energy associated to the first-order perturbation term, a_1 , is treated in the context of the M1Xb mixing rules [32, 33], and the second-order perturbation term a_2 is obtained from a_1 using the local compressibility approximation for mixtures [61–63].

The chain contribution to the free energy takes into account the chain formation of the three different types of molecules, i.e., *n*-alkanes, perfluoro-*n*-alkanes, and perfluoroalkylalkane diblock surfactants. The contribution due to the formation of the surfactant chain molecules is also expressed as a sum of contributions: one contribution term is due to the formation of the alkyl branch (formed by m_A segments), a second contribution term describes the formation of the perfluoroalkyl branch (formed by m_B segments), and the last contribution term represents the bonding of the alkyl and perfluoroalkyl branches to form the surfactant chain. In the case of a ternary mixture formed by homonuclear chains and diblock molecules, the contribution to the free energy is given by,

$$\begin{aligned} \frac{A^{\text{CHAIN}}}{Nk_B T} &= x_1 \left[(1 - m_A) \ln y_{AA}^{\text{SW}}(\sigma_{AA}) + (1 - m_B) \ln y_{BB}^{\text{SW}}(\sigma_{BB}) - \ln y_{AB}^{\text{SW}}(\sigma_{AB}) \right] + \\ & x_2 (1 - m_2) \ln y_{22}^{\text{SW}}(\sigma_{22}) + x_3 (1 - m_3) \ln y_{33}^{\text{SW}}(\sigma_{33}) \end{aligned} \quad (5)$$

where $m_1 = m_A + m_B$ represents the chain length of component 1 (the diblock surfactant), and m_2 and m_3 are the chain lengths of the two homonuclear chains of the mixture (*n*-alkanes and perfluoro-*n*-alkanes). $y_{AA}^{\text{SW}}(\sigma_{AA})$, $y_{BB}^{\text{SW}}(\sigma_{BB})$ and $y_{AB}^{\text{SW}}(\sigma_{AB})$ are the cavity correlation functions of the reference SW fluid mixture between the segments that form the component 1 (the diblock surfactant), and $y_{22}^{\text{SW}}(\sigma_{22})$ and

$y_{33}^{\text{SW}}(\sigma_{33})$ are the cavity correlation functions of the reference SW fluid between the segments that form the second and third components, respectively. All cavity functions can be expressed in terms of the corresponding pair radial distribution functions at the contact value, which within the SAFT-VR framework is given by the high-temperature expansion. For further details see the works of Gil-Villegas *et al.* [32, 33].

The rest of thermodynamic properties, such as the chemical potentials of each component (μ_i), and pressure (P), can be easily obtained from the Helmholtz free energy using standard thermodynamic relations.

The hetero-SAFT-VR approach, as other versions of SAFT, needs a number of molecular parameters to describe the thermodynamic properties of real substances. In this work, each homonuclear molecule (alkane or perfluoroalkane) is characterised by four molecular parameters such as chain length (m_2 or m_3), segment size (σ_{22} or σ_{33}), square-well dispersive energy (ϵ_{22} or ϵ_{33}) and range (λ_{22} or λ_{33}) parameters. For the diblock SFA surfactant molecules, which are formed by two different types of segments, two sets of parameters are needed: one set for the alkyl branch (σ_{AA} , ϵ_{AA} and λ_{AA}) and another set for the perfluoroalkyl branch (σ_{BB} , ϵ_{BB} and λ_{BB}), together with their respective chain-lengths (m_A and m_B) parameters. The potential model parameters σ_{ii} , ϵ_{ii} and λ_{ii} for the n -alkanes and perfluoroalkanes have been obtained in previous works [37, 38, 66]. In this work we used the same values of these molecular parameters (σ_{ii} , ϵ_{ii} and λ_{ii}) to describe the alkyl and perfluoroalkyl parts of the diblock surfactant molecules, respectively. For the n -alkanes and perfluoroalkanes chain-length parameters, we used the simple empirical relationships proposed previously by Jackson and co-workers [67, 68], which relate the number of spherical segments in the model chain to the number of carbon atoms C in the alkyl and perfluoroalkyl molecules. In particular, the expression $m = (1/3)(C - 1) + 1$ for the case of n -alkanes and the expression $m = 0.37(C - 1) + 1$ for the case of perfluoroalkanes are used. For the perfluoroalkylalkanes chain length, we have used an alternative additive scheme presented in our previous works [43–46], which relates the chain length of the perfluoroalkylalkane diblock surfactant model to the total number of carbon atoms. The scheme considers that each branch of the SFA is formed by inner and terminal functional groups, which their only difference is given by their chain length. Then, in the alkyl part each terminal and inner methyl group (CH_3- and $-\text{CH}_2-$) contribute to the chain length by 0.665 and $1/3$ segments, respectively; while in the perfluoroalkyl part each terminal and inner perfluoromethyl group (CF_3- and $-\text{CF}_2-$) contribute to the chain length by 0.685 and 0.37 segments, respectively. Note that this model is a generalisation of the simple empirical rules used for modelling the homonuclear n -alkanes and perfluoroalkanes. Table 1 lists the molecular parameters used in this work to describe each component. For further details we suggest the reader to see our previous works [43–46].

Since we are dealing with mixtures of homonuclear chains and SFA diblock surfactants, a number of cross or unlike parameters need to be specified. The Lorentz combining rule is used for the unlike hard-core diameter,

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (6)$$

while the unlike dispersive energy of the system is defined as,

$$\epsilon_{ij} = \xi_{ij} \sqrt{\epsilon_{ii} \epsilon_{jj}} \quad (7)$$

where ξ_{ij} describes the departure of the attractive interactions between segments i and j from the Berthelot combining rule. A value of $\xi_{ij} < 1$ is usually associated with liquid-liquid immiscibility. The unlike range parameter of the mixtures is obtained from the following equation

$$\lambda_{ij} = \gamma_{ij} \frac{\lambda_{ii}\sigma_{ii} + \lambda_{jj}\sigma_{jj}}{\sigma_{ii} + \sigma_{jj}} \quad (8)$$

where γ_{ij} is a second adjustable parameter which controls the range of the square-well interactions between the alkyl and perfluoroalkyl parts of the molecules.

The unlike interaction parameters ξ_{ij} and γ_{ij} between linear alkanes and perfluoroalkanes have been determined in previous works by different authors. For instance, McCabe *et al.* [34] studied mixtures of perfluoromethane with short n -alkanes (up to n -hexane), and other symmetrical mixtures of n -alkanes and perfluoroalkanes at high-pressure thermodynamic conditions. They found that the values of $\xi_{ij} = 0.9206$ and $\gamma_{ij} = 1$ give the best representation of the continuous high-pressure and high-temperature gas-liquid critical line in the perfluoromethane + n -butane system. However, in order to study binary mixtures with longer chain lengths they also fitted the values $\xi_{ij} = 0.8948$ and $\gamma_{ij} = 1$ to predict the high-pressure critical line of the perfluoromethane + n -heptane mixture. Later, Morgado *et al.* [2] proposed a new set of transferable unlike parameters ($\xi_{ij} = 0.840$ and $\gamma_{ij} = 1.0451$) to predict the upper critical solution temperature and excess volumes for the n -hexane + perfluorohexane binary mixture, which was used in a recent work *et al.* [44] to predict the saturated liquid density values of two different perfluoroalkylalkane diblock surfactants, F_6H_6 and F_6H_8 with an excellent agreement with experimental data. More recently, the authors of the present manuscript investigated the use of these different sets of binary interaction parameters (ξ_{ij} and γ_{ij}) for similar homologous mixtures [43, 46]. In particular, we found that when using the binary interaction parameters proposed by Morgado *et al.* [2] the theory was not able to predict accurately the phase behaviour of asymmetric mixtures of n -alkanes and perfluoroalkanes, and more specific, the theory could not describe the type *III* phase behaviour, according to Scott and van Konynenburg classification (SK) [69, 70], exhibited experimentally by the $F_1 + H_7$ mixture. However, when the binary mixture is more symmetric (components of similar number of carbon atoms) both sets of parameters (those from McCabe *et al.* [34] and from Morgado *et al.* [2]) yield a similar qualitative phase behaviour for the n -alkane + and perfluoroalkane + perfluoroalkylalkane mixtures. Since in this work we are focussed on the description of the high-pressure phase-behaviour of asymmetric mixtures, such as mixtures of perfluoromethane (F_1) and n -heptane (H_7) with different SFAs, we have used the set of unlike interactions $\xi_{ij} = 0.8948$ and $\gamma_{ij} = 1$ for every alkyl-perfluoroalkyl unlike interaction that exist in the different systems considered.

It is important to recall again that our goal is not to provide a detailed account of the phase behaviour of these mixtures, which is completely unknown from the experimental point of view, but only to give a general scenario of the phase equilibria exhibited by these model mixtures.

3. Results and discussion

In this section we present the theoretical predictions of the phase behaviour of our model perfluoroalkylalkane diblock surfactant + perfluoroalkane + n -alkane

ternary mixtures obtained using the hetero-SAFT-VR approach. Since our main goal is to understand the microscopic conditions of the surfactant that control the phase behaviour exhibited by these mixtures, we have fixed two of the three components of the ternary systems of interest. Then, it is relatively simple to study the effect on the phase behaviour exhibited by the mixture due to the different thermodynamic conditions, such as pressure and temperature, as well as the change of the molecular weight of the surfactant. In particular, our work is focussed on mixtures of perfluoromethane (F_1) and n -heptane (H_7) with different perfluoroalkylalkane diblock surfactants. We have chosen $F_1 + H_7$ as prototype binary mixture to carry out our investigation due to several reasons. This mixture is known to exhibit an interesting phase behaviour, the type *III* according to Scott and van Konynenburg classification (SK) [69, 70], which is characterised by large regions of liquid-liquid (LL) immiscibility that exist even at high temperature. This system was previously studied by McCabe *et al.* [34] using the SAFT-VR approach, who were able to describe the LL immiscibility. This LL immiscibility has been explained in terms of the presence of weak unlike dispersive interactions between alkyl and perfluoroalkyl chemical groups, but also in terms of the asymmetry in size of the components in the mixture. This makes the $F_1 + H_7$ system an ideal candidate for studying the macroscopic effect on the phase behaviour, from a molecular perspective, when a diblock SFA surfactant is added to the mixture.

We present our results in the following subsections. We first study the effect of the thermodynamic conditions on the phase behaviour of the ternary mixture of F_1 , H_7 , and a particular SFA, the perfluorohexylhexane (F_6H_6). Later, we consider the phase behaviour of mixtures with perfluoroalkylalkanes of different molecular weights. In particular, we examine the effect of the number of alkyl and perfluoroalkyl groups of the surfactants on the type of phase behaviour exhibited by these mixtures.

3.1. *Effect of the thermodynamic conditions on the $F_6H_6 + F_1 + H_7$ ternary mixture*

We first examine the mixture of perfluorohexylhexane diblock surfactant with perfluoromethane and n -heptane. Perfluorohexylhexane (F_6H_6) has been chosen as a prototype member of the SFA (F_iH_j) series since it has been studied extensively from the experimental [44, 45] and theoretical points of view [43, 46] in previous works. In order to study the phase behaviour of the ternary mixture it is important to know the phase behaviour of the binary mixtures formed from the components of the ternary mixture under consideration. Figure 1 shows the PT projection of the phase diagram of the $F_1 + H_7$ mixture obtained using the hetero-SAFT-VR approach and the molecular parameters presented in Table 1. As can be seen, the mixture exhibits LL immiscibility with the corresponding three-phase liquid-liquid-vapour (LLV) line that runs from low temperatures up to the upper critical end point (UCEP) of the mixture, located at 252.5 K and 7.5 MPa. This phenomenology is associated to mixtures that exhibit a type *III* phase behaviour according to the SK classification [69, 70]. The phase behaviour of this mixture has a vapour-liquid (VL) critical line that connects the UCEP and the critical point of the most volatile component, i.e. F_1 . In addition, there is a second fluid-fluid critical line, running from the critical point of H_7 and extending toward high pressures, passing through a temperature minimum (at ≈ 324 K and 107 MPa), which indicates that the mixture exhibits a *gas-gas immiscibility of second kind* behaviour. It is important to mention that when using the set of optimized parameters shown in Table 1, the theory will over predict the pure component critical points, due to the fact that, as with most engineering equations of state, the hetero-SAFT-VR

equation does not include the long-range density fluctuations that occur near the critical point of real fluids [71–73]. This can be overcome by rescaling the pure component parameters to the experimental values of the critical point, as shown in the work of McCabe *et al.* [34] who showed that the SAFT-VR is able to provide an excellent description of the complete phase diagram of the $F_1 + H_7$ mixture. Since our goal is to understand at a qualitative level the conditions under which diblock SFA surfactants increase the mutual solubilities of these mixtures, we have used non-scaled molecular parameters.

We have also obtained the phase diagrams of the $F_6H_6 + F_1$ and $F_6H_6 + H_7$ binary mixtures, as shown in Figures 2a and 2b. As can be seen, $F_6H_6 + F_1$ and $F_6H_6 + H_7$ binary mixtures exhibit the type *I* and *V* phase behaviour, respectively. The mixture that exhibits a type *I* phase behaviour is characterised by the presence of a VL critical line running continuously from the critical point of one of the components to the other that exhibits a temperature minimum. The $F_6H_6 + H_7$ mixture also exhibits positive azeotropy behaviour, which is a common characteristic feature of mixtures formed by components with similar critical temperatures. The azeotropy line goes from low temperatures up to high temperatures merging with the VL critical line. In the case of the type *V* mixture, the VL critical line is not continuous, but runs from the critical point of the less volatile component to a lower critical end point (LCEP) associated with the corresponding LLV three-phase line. There is also an additional critical line that runs from the critical point of the more volatile component up to the UCEP of a LLV three-phase line. As can be seen in the inset of Figure 2a, the theoretical predictions indicate that the LLV three-phase line lies in a very narrow range of temperatures and pressures, from the LCEP temperature 252 K and pressure 7.5 MPa to the UCEP temperature 253.5 K and pressure 7.8 MPa, approximately.

At this point, it is important to mention, as explained in our previous work [46], that the hetero-SAFT-VR approach is able to predict the existence of LL immiscibility at sufficiently low temperatures for very asymmetric mixtures (see Figure 2a). However, this small three-phase region is located below the melting point of F_6H_6 , which is located at ~ 261 K [15], and therefore, the three-phase line is thermodynamically unstable. This is a direct consequence of the fact that the SAFT approach is a fluid-phase equation of state and does not incorporate the characteristics of the solid phases. Our current results are in agreement with our previous works [43, 46], where we showed that both binary mixtures ($F_6H_6 + F_1$ and $F_6H_6 + H_7$) behave like a type *I* phase behaviour according to the SK classification from temperatures above the melting point of F_6H_6 . This means that no LL immiscibility neither three-phase separation should be observed in these binary mixtures at these conditions.

Once we have characterised the phase behaviour of the binary mixtures forming the ternary system under study, we applied the theory to obtain the phase behaviour of the ternary mixture at different thermodynamic conditions. We first investigate the phase diagram of the mixture at constant temperature (300 K) and several pressures values, ranging from ambient pressure up to 20 MPa, as shown in Figure 3a. At this temperature, the ternary mixture only exhibits a two-phase LV equilibria region due to the fact that 300 K is higher than the UCEP temperature of the $F_1 + H_7$ system (252.5 K) and it is also higher than the UCEP temperature of the $F_6H_6 + F_1$ system (253.5 K). Note that the binary mixture $F_6H_6 + H_7$ does not have a LL immiscibility, as seen in Fig. 2. As can be seen, the mixture shows a large two-phase region with variable size depending on the pressure of the system. The main effect of increasing the pressure on the phase diagram is to reduce the size of the two-phase coexistence region.

1 The phase behaviour exhibited by the ternary system $F_6H_6 + F_1 + H_7$ can be
2 easily understood in terms of the topological structure of the phase diagrams of the
3 binary mixtures that conform the ternary system. At the thermodynamic condi-
4 tions of constant temperature (300 K) and all the pressures considered here (from
5 0.101325 up to 20 MPa), the $F_6H_6 + H_7$ mixture only exhibits one homogenous
6 phase, i.e., no VL exists since the vapour pressure curves of both pure components
7 (F_6H_6 and H_7) are below the lower pressure considered (0.101325 MPa) at 300 K.
8 This explains clearly why none of the coexistence envelopes of the ternary mix-
9 ture cuts the $F_6H_6-H_7$ axis (see Figure 2b for details). In contrast to the $F_6H_6 +$
10 H_7 system, the $F_6H_6 + F_1$ binary mixture at 300 K and $p \lesssim 18$ MPa, exhibits a
11 VL phase separation (note that the VL critical line of the mixtures cuts the 300 K
12 isotherm at $p \approx 18$ MPa), while at higher pressures (including 20 MPa) the mixture
13 is homogenous and no VL phase separation exists (see Figure 2a for details). Hence,
14 it is obvious that only the phase envelope curves at the thermodynamic conditions
15 of temperature of 300 K and pressures 0.101325, 5, 10 and 15 MPa, should cut the
16 $F_6H_6-H_7$ axis at two different points. Finally, the $F_1 + H_7$ binary mixture PT
17 diagram (Figure 1) shows a fluid-fluid separation at 300 K and all the pressures
18 considered. Then, it is expected that the phase envelopes of the ternary system
19 should cut the F_1-H_7 axis at two different points, corresponding to the two-phase
20 coexistence points of the mixture. At the highest pressure considered, the two
21 phases coexistence region cuts only the F_1-H_7 axis, and the phase envelopes meet
22 in the corresponding consolute point. As for the effect of adding the surfactant
23 F_6H_6 to the binary mixture $F_1 + H_7$, we can see that at the lowest pressure the
24 two-phase area covers most of the ternary mixture phase diagram indicating that
25 the addition of surfactant does not make the system more miscible. However, as
26 we increase the pressure, the two phase region becomes smaller moving toward less
27 surfactant composition. Then, it is expected that as we increase the pressure the
28 amount of SFA surfactant needed to make the two fluid phases miscible decreases.

29 We focus now on the effect of the temperature on the phase behaviour of the
30 ternary mixture. We carried out this by keeping constant the pressure at 10 MPa
31 and varying the temperature from 300 up to 550 K. At this pressure, the ternary
32 system phase behaviour is above the critical pressures of all pure components of
33 the ternary mixture. As can be seen in Figure 3b, the theoretical predictions from
34 the hetero-SAFT-VR approach show a complex phase behaviour when the temper-
35 ature is changed. At low temperatures, a two-phase (VL) region divides the
36 phase diagram in two different homogeneous regions: a small vapour phase area
37 located near pure perfluoromethane compositions, and a wider region located at
38 F_1 compositions ranging from 0.25 up to 0.75. As the temperature is increased,
39 from 300 up to 450 K, the liquid and vapour boundaries of the two-phase coexist-
40 ing region move toward higher surfactant and H_7 compositions. Although we note
41 that the displacement of the vapour phase envelope, which can not be seen in the
42 scale of Figure 3b, is much smaller than that of the liquid phase, and hence, the
43 size of the two-phase region increases as the temperature is raised. If the temper-
44 ature is further increased from 450 up to 510 K, the fluid phase envelope rich in
45 the heavier component moves toward the opposite direction as observed from 300
46 up to 450 K, i.e. toward lower surfactant compositions. This behaviour produces a
47 decrease in the size of the two-phase area as the temperature is raised above 450 K.
48 Once again, it is easy to understand the phase behaviour exhibited by this mixture
49 in terms of the phase diagrams of the binary mixtures that form the system. The
50 behaviour exhibited by the $F_1 + H_7$ and $F_6H_6 + H_7$ binary mixtures at higher
51 temperatures ($T \gtrsim 350$ K) is qualitatively the same than that at 300 K, which has
52 been analysed previously. However, the phase behaviour of the $F_6H_6 + F_1$ binary
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1 mixture is more interesting as the temperature changes. From Figure 2a, we can
2 observe that this mixture exhibits a maximum in the VL critical line at ≈ 400 K.
3 We can also note that at 10 MPa, the range of temperatures at which the mixture
4 exhibits two-phase (VL) separation varies from ≈ 260 K up to ≈ 520 K. Then, as
5 we first increase the temperature from 300 up to 400 K the binary system is ex-
6 panding the VL region, while if we keep increasing the temperature up to ≈ 520 K,
7 the VL region is decreasing in size, which explains the behaviour observed in the
8 ternary mixture. At approximately 520 K and 10 MPa, a VL critical point of the
9 binary mixture is located, and due to this, the $F_6H_6 + F_1$ system exhibits only
10 one homogeneous fluid phase at temperatures higher than 520 K. This behaviour
11 is in agreement with the results presented in Figure 3b. When the temperature of
12 the ternary mixture is increased above 520 K (see the phase envelopes at 525 and
13 550 K in the figure 3b), the two-phase region separates from the $F_6H_6 - F_1$ axis.
14 The two-phase boundary curves (at 10 MPa and $\gtrsim 520$ K) cut the F_1-H_7 axis of
15 the triangular phase diagram and exhibits the corresponding consolute point. As
16 the temperature is further increased, the two-phase region decreases in size and
17 moves to higher compositions of H_7 and lower surfactant compositions.
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23 **3.2. Effect of the symmetric surfactant molecular weight on $F_XH_X + F_1 +$** 24 **H_7 ternary mixtures**

25 We now study the effect of the number of perfluoroalkyl and alkyl chemical groups
26 in the SFA on the phase diagram of the $F_XH_X + F_1 + H_7$ ternary mixtures. We
27 first analyse the symmetric case in which we only consider surfactants of the type
28 F_XH_X , i.e., molecules with the same number of perfluoroalkyl and alkyl chemical
29 groups.
30

31 As in the previous section, we start by presenting the phase behaviour of the
32 corresponding binary mixtures. Figure 4a shows the PT projection of the phase
33 diagram of the $F_XH_X + F_1$ binary mixtures, from $X = 3$ (corresponding to the
34 system containing perfluoropropylpropane) up to $X = 10$ (corresponding to the
35 mixture with perfluorodecyldecane). As can be seen, these systems exhibit two
36 different types of phase behaviours depending on the molecular weight of the sur-
37 factant. For short SFA chains, ranging from F_3H_3 to F_5H_5 , the mixtures with
38 perfluoromethane (F_1) show a continuous VL critical line running from the critical
39 point of one component of the mixture to the other. Note that the mixture F_5H_5
40 + F_1 is the last system of the homologous series that exhibits a type *I* phase be-
41 haviour. When the number of alkyl and perfluoroalkyl groups is further increased,
42 the resulting mixtures ($F_6H_6 + F_1$, $F_7H_7 + F_1$, $F_8H_8 + F_1$, $F_9H_9 + F_1$, $F_{10}H_{10}$
43 + F_1) show a type *V* phase behaviour. The LLV three-phase line associated to
44 each mixture cannot be seen in Figure 4a due to the small range of pressures and
45 temperatures at which are located. However, in the inset we show an enlargement
46 of the region near the critical point of pure F_1 . As can be seen, the LLV three-phase
47 line runs in a small range of thermodynamic conditions for all the systems. Specif-
48 ically, the LLVE for the different mixtures runs from 252.1 to 253.5 K and 7.52 to
49 7.78 MPa for the $F_6H_6 + F_1$ mixture, from 245.4 to 251.1 K and 6.44 to 7.44 MPa
50 for the $F_7H_7 + F_1$ mixture, from 241.7 to 250.2 K and 5.89 to 7.30 MPa for the
51 $F_8H_8 + F_1$ mixture, from 237.7 to 249.8 K and 5.32 to 7.25 MPa for the $F_9H_9 +$
52 F_1 mixture, and from 237.2 to 249.6 K and 5.27 to 7.22 MPa for the $F_{10}H_{10} + F_1$.

53 As we mentioned before, care must be taken when a SAFT approach is applied to
54 predict the phase behaviour involving long-chain molecules. Since hetero-SAFT-VR
55 approach does not incorporate the characteristics of solid phases, it is important to
56 check if the predictions at low temperatures are consistent with experimental data
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1 for melting temperatures of the long chain components. In our systems, although
2 SAFT-VR predicts a type *V* phase behaviour for mixtures from $F_6H_6 + F_1$ up to
3 $F_{10}H_{10} + F_1$, the experimental melting temperatures of the surfactants are above
4 the UCEP temperatures of the corresponding mixtures (the F_6H_6 melts at 260 K,
5 while F_8H_8 melts at 300 K, and $F_{10}H_{10}$ melts at 334 K) [15]. In summary, all F_XH_X
6 $+ F_1$ mixtures should experimentally exhibit a type *I* phase behaviour.

7
8 It is important to note how the presence of perfluoroalkyl chemical groups in
9 the surfactant helps to stabilise these mixtures, especially if we take into account
10 that mixtures of F_1 with shorter *n*-alkanes exhibit LL immiscibility. In particular,
11 mixtures of F_1 with *n*-alkanes shorter than H_4 exhibit a type *II* phase behaviour,
12 while the phase behaviour for mixtures with *n*-butane and longer *n*-alkanes shows
13 a type *III* phase behaviour [34]. It is clear that the (favourable) energetic effects
14 dominate over the (unfavourable) steric effects, and hence, determine the phase
15 behaviour for the shortest surfactants. However, as the molecular weight of the
16 diblock SFA molecules increases this effect is inverted. For example, when the
17 number of alkyl plus perfluoroalkyl groups is twelve or greater, the system shows
18 LL immiscibility.

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20 In Figure 4b, we present the phase behaviour of the $F_XH_X + H_7$ binary mix-
21 tures, from F_3H_3 up to $F_{10}H_{10}$. These systems show an interesting and distinctive
22 behaviour as the number of alkyl and perfluoroalkyl chemical groups of the first
23 component is increased, despite of exhibiting a type *I* phase behaviour. The surfac-
24 tants with less than ten carbon atoms (F_3H_3 to F_5H_5) are more volatile than H_7 ,
25 whereas those with twelve or more carbon atoms (F_6H_6 to $F_{10}H_{10}$) are less volatile
26 than H_7 . The mixtures of F_5H_5 and F_6H_6 with H_7 are of particular interest. For the
27 first mixture ($F_5H_5 + H_7$), the vapour pressure curves of the two pure components
28 intersect at a Bancroft point located at 396 K and 0.166 MPa, approximately. The
29 presence of a Bancroft point in a binary mixture is usually related to molecules
30 that are dissimilar in chemical type or in shape but have similar vapour pressure.
31 The existence of a Bancroft point in this system can be understood in the context
32 of varying the number of alkyl and perfluoroalkyl groups in the diblock surfactant
33 molecule. When passing from F_4H_4 to F_5H_5 and to F_6H_6 , the corresponding vapour
34 pressures move from low to high temperature and, eventually, the vapor pressure
35 curve of the SFA crosses the vapour pressure curve of pure H_7 . As a consequence,
36 the H_7 is more volatile than the SFA (this case the F_5H_5) at low temperatures, but
37 less volatile at high temperatures. In addition to the Bancroft point, the mixture
38 also exhibits a positive azeotropy that could be probably associated to the presence
39 of the Bancroft point, which runs near the vapour pressure of pure F_5H_5 until it
40 reaches the vapour-liquid critical line. The other mixture, the $F_6H_6 + H_7$, also
41 exhibits a positive azeotropy but this time the azeotropic line runs near the vapour
42 pressure of pure H_7 , instead of the vapor pressure curve of pure SFA. The rest of
43 the mixtures presented in Figure 4b show a type *I* phase behaviour but without
44 azeotropy, and with the corresponding continuous VL critical line running from
45 the critical of one component to the other, as expected.

46
47 Once described the phase behaviour of the binary mixtures forming the ternary
48 systems, we have studied the ternary phase diagram of the mixture $F_1 + H_7$ with
49 symmetric surfactants (F_XH_X), and examined the effect on the coexistences curves
50 when the number of the chemical groups forming the surfactant is increased. Fig-
51 ure 5 shows the theoretical predictions obtained from the hetero-SAFT-VR ap-
52 proach for mixtures containing F_1 , H_7 , and F_XH_X surfactants, from perfluoro-
53 propylpropane (F_3H_3) up to perfluorodecyldecane ($F_{10}H_{10}$), at 10 MPa and 510 K.
54 The mixture formed by F_1 , H_7 , and the shorter perfluoroalkylalkane considered
55 here (F_3H_3) exhibits a two-phase coexistence region that only cuts the F_1 - H_7 axis
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and the two phase boundaries merge in a consolute point at surfactant composition of approximately 0.25. The presence of the SFA in the mixture helps to stabilise the $F_1 + H_7$ mixture since the composition range of F_1 and H_7 at which the mixture exhibits two-phase coexistence (LL immiscibility) decreases as the surfactant concentration is increased. The phase boundaries seem to be unaffected when the number of alkyl and perfluoroalkyl chemical groups is increased from three up to four or five carbon atom each branch, as can be seen in Figure 5a. However, when the number of alkyl and perfluoroalkyl chemical groups is equal to six or larger than six ($X \geq 6$ for $F_X H_X$ surfactants), the nature of the phase behaviour changes continuously from LL equilibria at low surfactant concentrations to VL equilibria at intermediate and high surfactant concentrations. As a consequence, the phase diagram is divided into two different homogeneous fluid regions that are separated by a two-phase fluid-fluid coexistence region. As the chain length of the surfactant is increased, this two-phase fluid-fluid region becomes wider. It is interesting to note that the phase envelope associated to the high-density one-phase region seems to be unaffected when the molecular weight of the surfactant is increased. Contrary, the phase envelope associated to the perfluoromethane-rich (low-density) one-phase region moves toward higher perfluoromethane concentrations as the chain length of the surfactant is increased.

All the phase diagrams of the mixtures considered in Figure 5 cut the F_1-H_7 axis, as expected since the corresponding binary mixture exhibits LL equilibria at these thermodynamic conditions of pressure and temperature. Conversely, none of the phase envelopes of the ternary mixtures studied cut the $F_X H_X - H_7$ axis, because at the thermodynamic conditions considered (510 K and 10 MPa) the corresponding binary mixtures exhibit only an homogeneous fluid phase since the critical point of the mixture at 510 K lie below 10 MPa. As for the $F_X H_X - F_1$ axis, the phase envelopes of some systems do cross the axis, while for others systems this does not occur. The interesting behaviour shown by the phase envelopes of the ternary mixture can be clearly understood observing the PT projections of the $F_X H_X + F_1$ binary mixtures (Figure 4a). At 510 K and 10 MPa, the binary mixtures containing F_1 and short chain SFA show an homogenous fluid phase, i.e. the corresponding VL critical point of the mixtures at 510 K lies below 10 MPa. However, for the binary mixture of $F_6 H_6 + F_1$, the VL critical point at 510 K lies above 10 MPa, which means that this mixture exhibits VL phase separation at these conditions (see Figure 4a for more details). For longer perfluoroalkylalkane molecules, ($F_X H_X$, with $X \geq 6$), all the mixtures with F_1 at 10 MPa and 510 K are located at the VL phase separation, and therefore the phase envelopes associated to the corresponding ternary mixtures run from the F_1-H_7 axis to the $F_X H_X-F_1$ axis.

3.3. Effect of the asymmetric surfactant molecular weight on $F_6 H_X + F_1 + H_7$ ternary mixtures

We now consider the effect of adding only additional alkyl groups in the surfactant molecule, while keeping constant the number of perfluoroalkyl groups and equal to six. In particular, we study ternary mixtures with the general form of $F_6 H_X + F_1 + H_7$, where X goes from 1 to 6, at the same thermodynamic conditions than the previous systems, i.e. 510 K and 10 MPa.

We first analyse the phase diagrams of the binary mixtures formed by the $F_6 H_X + F_1$ and $+ H_7$. Figure 6a shows the PT projection of the phase diagrams of $F_6 H_X + F_1$ mixtures, from $X = 1$ (corresponding to the mixture with perfluorohexylmethane) up to $X = 6$ (corresponding to perfluorohexylhexane). As can be seen, almost all the mixtures exhibit type *I* phase behaviour, except the heaviest sys-

tem, which shows a type V behaviour (as discussed in section 3.1). Then, it is clear that the effect of increasing the number of alkyl chemical groups in the surfactant molecule is to make more immiscible the binary mixture. When the number of alkyl groups is equal to six or greater, the hetero-SAFT-VR approach predicts the existence of a short three-phase LLV behaviour, as seen in Figure 2a. Let's recall that although the SAFT approach predicts type V , with the corresponding LLV three-phase line, upper and lower critical end-points, this liquid-liquid immiscibility region is probably thermodynamically unstable since the solid phases should appear before the LLV.

We also investigate the phase equilibria of the $F_6H_X + H_7$ binary systems, from perfluorohexylmethane ($X = 1$) up to perfluorohexylhexane ($X = 6$). Figure 6b shows the corresponding PT projections of the phase diagram of these mixtures. Opposite to what happened with the mixtures in Figure 6a, the current systems exhibit a richer phase behaviour when the number of alkyl groups in the SFA is varied. This could be due to the proximity of the critical points of the components of the binary mixtures, and particularly, to the critical temperatures of these pure components. This is true for the current homologous family systems, in which H_7 and all the surfactants have a similar critical temperature. As can be seen, all the mixtures (except that of perfluorohexylmethane with n -heptane) exhibit positive azeotropy. In systems that exhibit this kind of azeotropy, the corresponding azeotropic line is located in the proximity's of the vapour pressure curve of the more volatile component. In Figure 6b, the more volatile component for mixtures with $X \leq 3$ corresponds to the SFA surfactants, whereas for mixtures with $X \geq 5$ the more volatile component is n -heptane. The mixture of $F_6H_4 + n$ -heptane, also has a Bancroft point at 404 K and 0.24 MPa, which means that H_7 is more volatile than F_6H_4 at low temperatures but less volatile at high temperatures. This mixture marks the limit of the azeotropic behaviour, which in general, the azeotropic line is closer to the vapour pressure of the surfactant than to H_7 for short surfactants ($X \leq 4$), but closer to the vapour pressure of n -heptane when $X \geq 5$. The same behaviour has been predicted for mixtures of H_7 with the symmetric surfactants, as discussed in section 3.2.

Figure 7 shows the ternary phase diagram of the mixtures studied. As can be seen, the systems with short alkyl chain in the SFA surfactant exhibit only one single-phase region with a single two-phase separation region, in which the phase envelope ends in a consolute point. This consolute point seems to move toward perfluoromethane richer compositions as we change the surfactant of the system by increasing the alkyl chain branch. Note that the displacement is almost imperceptible when changing the surfactant from F_6H_2 to F_6H_3 in the ternary mixture. The consolute point continues moving until the two phases regions form a two-phase band that connects the F_1-H_7 and $F_6H_X-F_1$ axes, dividing the diagram in three areas: a region of two-phases in coexistence and two regions of one-single phase. We addressed this effect due to the energetic competitions between the chemical groups.

3.4. Effect of the asymmetric surfactant molecular weight on $F_XH_6 + F_1 + H_7$ ternary mixtures

We also analyse the effect of adding additional chemical groups in the surfactant molecule, but now keeping constant the number of alkyl groups (and equal to six), while varying the number of perfluoroalkyl groups. As can be seen in Figure 8a, the $F_XH_6 + F_1$ mixtures exhibit a similar phase behaviour than that corresponding to the mixtures presented in Figure 6a, i.e., all mixtures from $X = 1$ to $X = 5$

1 exhibit a type *I* phase behaviour, and the mixture with $X = 6$ shows type *V*
2 phase behaviour. As the number of perfluoroalkyl chemical groups is increased
3 the mixture becomes less miscible, as expected from the previous results. The *PT*
4 projection of the $F_XH_6 + H_7$ binary mixtures, from $X = 1$ up to $X = 6$, are
5 presented in Figure 8b. These phase diagrams are similar to those presented in
6 Figure 6b, i.e. a type *I* phase behaviour is observed for mixtures from $H_7 + F_1H_6$
7 up to $H_7 + F_3H_6$, while a type *I* with positive azeotropy is obtained for the rest
8 of mixtures, with the binary mixture $H_7 + F_4H_6$ exhibiting a Bancroft point at
9 434 K and 0.475 MPa.

10 Finally, we present the diagrams of the ternary mixtures studied in Figure 9. As
11 can be seen, the systems $F_XH_6 + F_1 + H_7$ exhibit a similar ternary diagram than
12 that corresponding to the $F_6H_X + F_1 + H_7$ mixtures (see Figure 7). This diagram
13 includes the continuous change of the shape of the two-phase coexistence region as
14 the number of perfluoroalkyl chemical groups in the SFA surfactant component is
15 increased. Similar to the previous systems, this behaviour is clearly an effect due
16 to the energetic competition between the alkyl and perfluoroalkyl chemical groups.

21 4. Conclusions

22 We have used the hetero-SAFT-VR approach to predict the phase behaviour of
23 model mixtures of homonuclear chains with diblock surfactants. In particular, we
24 study the phase behaviour of binary and ternary mixtures of model *n*-alkanes,
25 perfluoro-*n*-alkanes and perfluoroalkylalkane surfactants. Since our goal is to un-
26 derstand the effect of different microscopic parameters on the macroscopic phase
27 behaviour of these mixtures, we first considered binary mixtures of selected *n*-
28 alkanes and perfluoro-*n*-alkanes with different diblock surfactants, including sym-
29 metric (F_XH_X) and asymmetric (F_6H_X and F_XH_6) diblock surfactants. In addition
30 to the six sets of different binary mixtures considered, we also analysed the phase
31 behaviour of three different kind of ternary mixtures, namely the $F_1 + H_7 + F_XH_X$,
32 the $F_1 + H_7 + F_6H_X$, and the $F_1 + H_7 + F_XH_6$ systems.

33 We investigated two different types of binary mixtures: (a) mixtures of symmet-
34 ric and asymmetric surfactants with perfluoromethane (F_1) and (b) mixtures of
35 the same surfactants with *n*-heptane (H_7). In the first case, the mixtures of sur-
36 factants $F_XH_X +$, $F_6H_X +$, and $F_XH_6 + F_1$ exhibited a type *I* phase behaviour,
37 according to the SK classification, when $X \leq 5$, i.e. for surfactants formed by less
38 than twelve carbon atoms. However, when the number of carbon atoms is equal or
39 higher than twelve, all the mixtures exhibited a type *V* phase behaviour, although
40 the corresponding LLV three-phase lines associated to each system are probably
41 thermodynamically unstable since the melting points of pure surfactants formed
42 by twelve or more carbon atoms are at higher temperatures than those regions. In
43 the second case, although all the mixtures exhibited type *I* phase behaviour, the
44 phase diagrams of these systems are richer and more complex than the previous one
45 due to the presence of positive azeotropy, especially for mixtures with the heaviest
46 surfactants. For all three homologous mixtures, there is always a particular surfac-
47 tant chainlength for which the presence of a Bancroft point is predicted. The phase
48 behaviour of all the binary mixtures is clearly dominated by two different micro-
49 scopic mechanisms: (a) the energetic balance between favourable strong alkyl-alkyl
50 interactions, the weaker (but still favourable) perfluoroalkyl-perfluoroalkyl inter-
51 actions, and the unfavourable alkyl-perfluoroalkyl interactions; and (b) the difference
52 in size of the components of the mixture. The miscible or immiscible character of
53 a particular mixture is then a consequence of a delicate balance between the dif-
54 ferent interactions of the involved chemical groups, but also due to the difference
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in chainlength of the components of the mixture.

The phase behaviour of the three families of homologous ternary mixtures, i.e., $F_X H_X + F_6 H_X +$, and $F_X H_6 + F_1 + H_7$ systems, is dominated by the behaviour of their binary systems, but also by the balance of the different microscopic effects previously mentioned. In the particular case of the ternary systems containing symmetric surfactants ($F_X H_X + F_1 + H_7$), the mixtures involving short surfactants ($X=3-5$) showed two-phase coexistence regions that only cut the F_1-H_7 axis, and the two-phase boundaries end in a consolute point as the surfactant concentration increases. The LL immiscibility of the $F_1 + H_7$ mixture decreases as the symmetric surfactant is added, indicating that the presence of favourable interactions between alkyl and perfluoroalkyl chemical groups of the surfactants and F_1 and H_7 help to stabilise the system. Similar results were obtained for the phase diagrams containing the asymmetric surfactant. As is our previous work [43-46], we believe that the hetero-SAFT-VR approach was able to predict the most important qualitative trends exhibited by mixtures involving n -alkanes, perfluoro- n -alkanes, and perfluoroalkylalkane surfactants.

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Table 1. Optimised intermolecular potential parameters for the *n*-alkanes and perfluoroalkanes series using the hetero-SAFT-VR approach.

Substance	<i>m</i>	λ	σ (Å)	ϵ/k_B (K)
C ₁ H ₄ ^a	1.00	1.444	3.670	168.8
C ₂ H ₆ ^a	1.33	1.449	3.788	241.8
C ₃ H ₈ ^a	1.67	1.452	3.873	261.9
<i>n</i> -C ₄ H ₁₀ ^a	2.00	1.501	3.887	256.3
<i>n</i> -C ₅ H ₁₂ ^a	2.33	1.505	3.931	265.0
<i>n</i> -C ₆ H ₁₄ ^a	2.67	1.552	3.920	250.4
<i>n</i> -C ₇ H ₁₆ ^a	3.00	1.563	3.933	251.3
<i>n</i> -C ₈ H ₁₈ ^a	3.33	1.574	3.945	250.3
<i>n</i> -C ₉ H ₂₀ ^a	3.67	1.602	3.938	241.3
<i>n</i> -C ₁₀ H ₂₂ ^a	4.00	1.621	3.959	227.3
C ₁ F ₄ ^b	1.00	1.287	4.346	278.6
C ₂ F ₆ ^b	1.37	1.339	4.436	289.0
C ₃ F ₈ ^b	1.74	1.359	4.474	298.8
<i>n</i> -C ₄ F ₁₀ ^b	2.11	1.406	4.452	284.2
<i>n</i> -C ₅ F ₁₂ ^c	2.48	1.421	4.469	282.0
<i>n</i> -C ₆ F ₁₄ ^d	2.85	1.432	4.456	283.1
<i>n</i> -C ₇ F ₁₆ ^e	3.22	1.436	4.464	285.3
<i>n</i> -C ₈ F ₁₈ ^c	3.59	1.462	4.472	274.0
<i>n</i> -C ₉ F ₂₀ ^f	3.96	1.460	4.475	279.3
<i>n</i> -C ₁₀ F ₂₂ ^f	4.33	1.465	4.477	278.9

^a[37], ^b[32], ^c[2], ^d[66], ^e[38], and ^f[43].

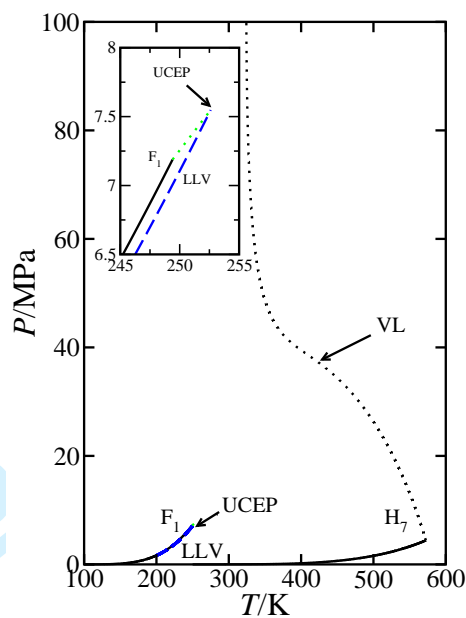


Figure 1. Theoretical predictions of the PT projection of the phase behaviour for the perfluoromethane (F_1) + n -heptane (H_7) binary mixture using the hetero-SAFT-VR approach. Solid lines describe the vapour-pressure curves of pure components, dotted curves are the gas-liquid critical lines ($(L - V)_1$ (black) and $(L - V)_2$ (green)), and dashed line (blue) is the three phase line ($L - L - V$).

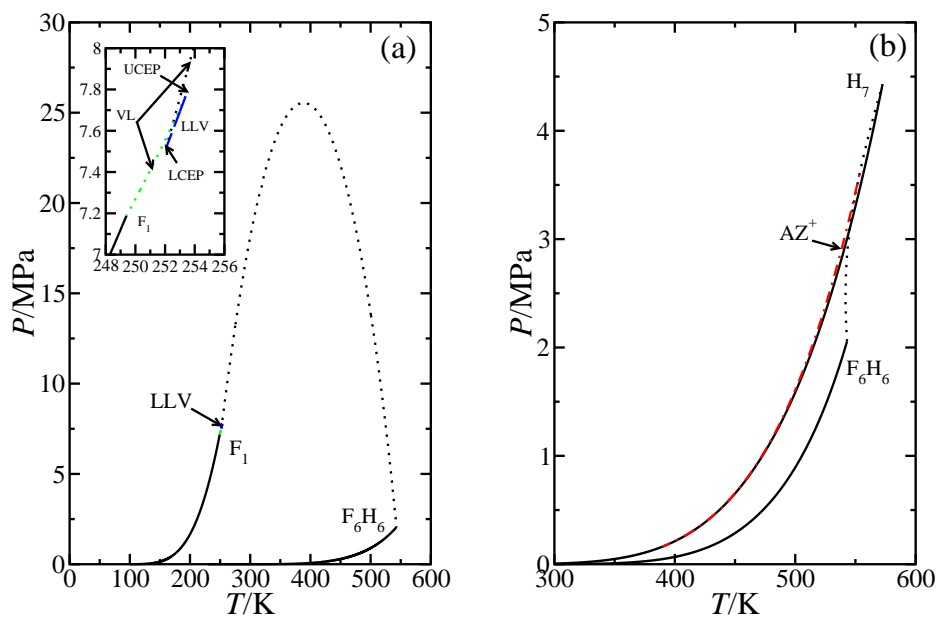
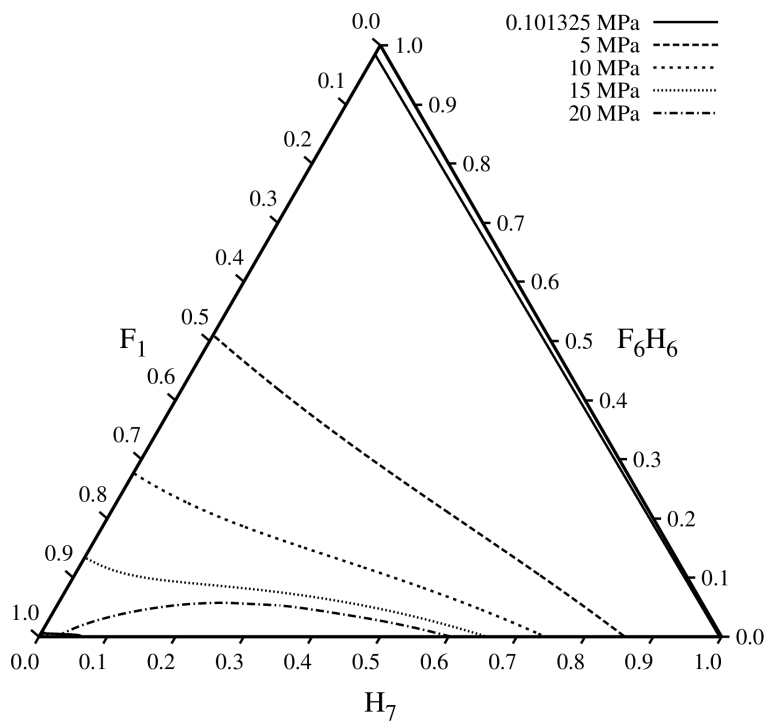


Figure 2. Theoretical predictions of the PT projection of the phase behaviour for the binary mixtures (a) perfluoromethane (F_1) + perfluorohexylhexane (F_6H_6) and (b) n -heptane (H_7) + perfluorohexylhexane (F_6H_6) using the hetero-SAFT-VR approach. Solid lines describe the vapour-pressure curves of pure components, dotted curves are the gas-liquid critical lines ($(L-V)_1$ (black) and $(L-V)_2$ (green)), dashed line (blue) is the three phase line ($L-L-V$) and dashed-dot line (red) describe the azeotropic line (AZ^+).

(a)



(b)

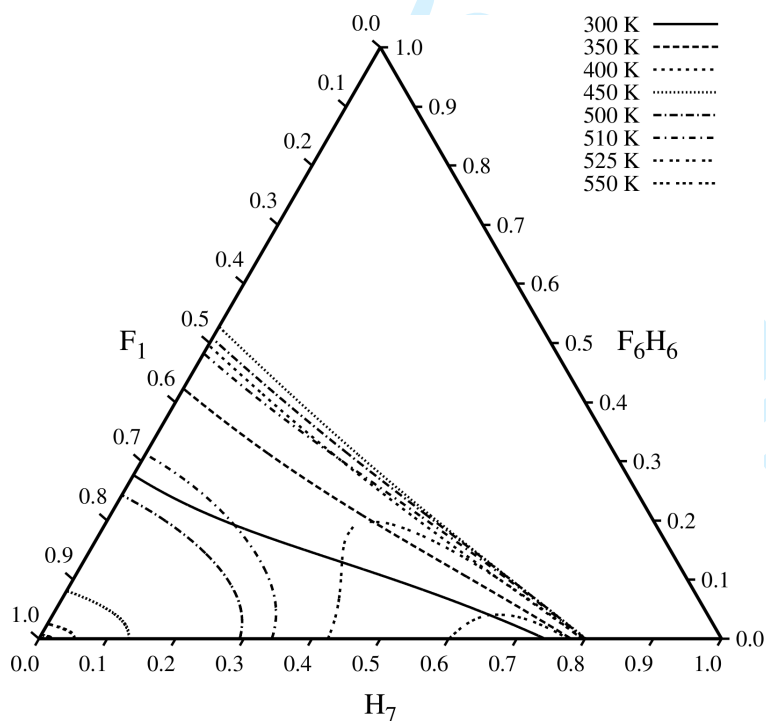


Figure 3. Ternary phase diagram for the mixture F_6H_6 (1) + F_1 (2) + H_7 (3) using the hetero-SAFT-VR approach. Part (a): high-pressure effect on the ternary diagram at 300 K, where lines correspond to the theoretical predictions at different pressure values from 0.101325 MPa up to $P=20$ MPa. Part (b): temperature effect on the ternary diagram for the mixture at 10 MPa, where lines correspond to the theoretical predictions at different temperature values values from $T=300$ K to $T=550$ K.

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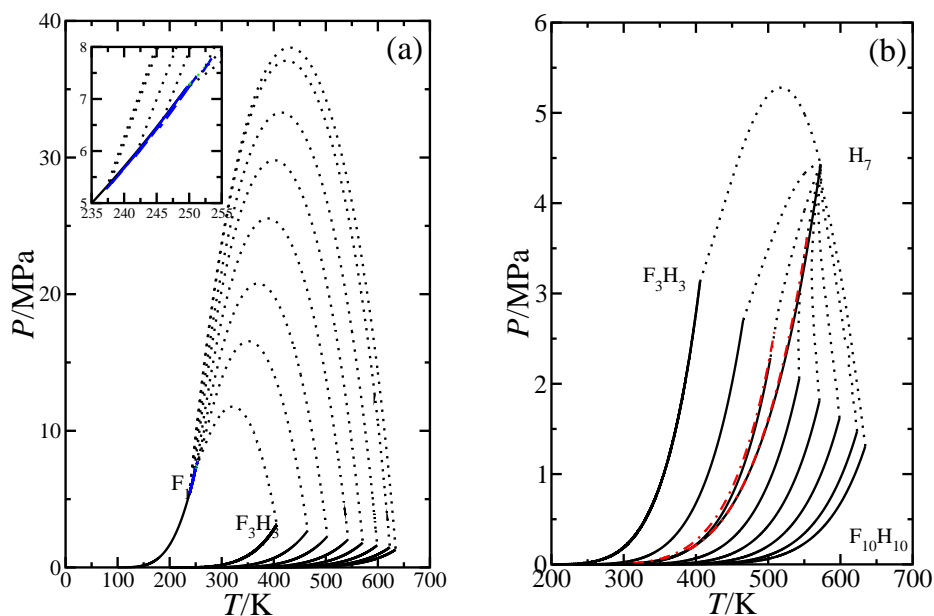


Figure 4. Theoretical predictions of the PT projection of the phase behaviour for the binary mixtures (a) perfluoromethane (F_1) + symmetric surfactant (F_XH_X) and (b) n -heptane (H_7) + symmetric surfactant (F_XH_X) using the hetero-SAFT-VR approach. Solid lines describe the vapour-pressure curves of pure components, dotted curves are the gas-liquid critical lines ($(L - V)_1$ (black) and $(L - V)_2$ (green)), dashed line (blue) is the three phase line ($L - L - V$) and dashed-dot line (red) describe the azeotropic lines (AZ).

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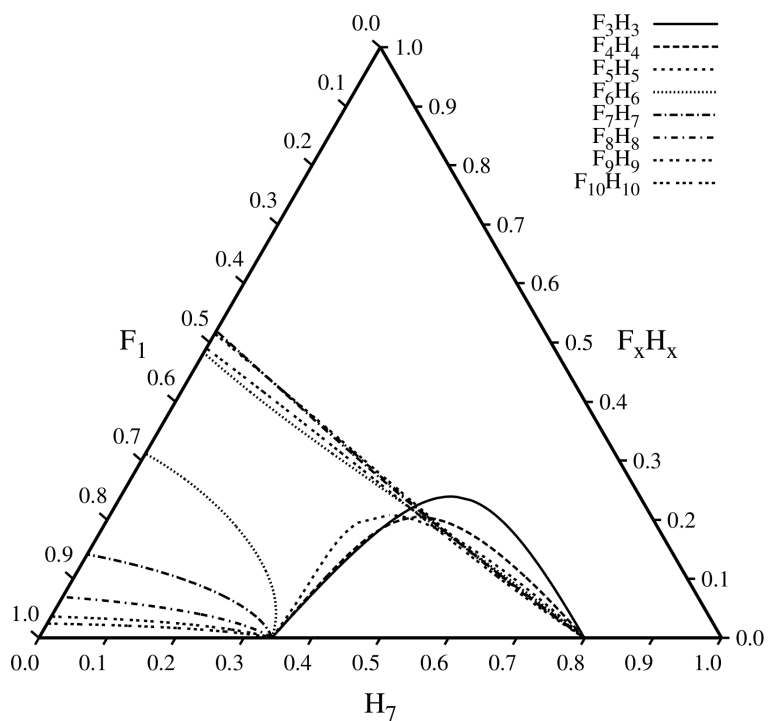


Figure 5. Effect of the symmetric surfactant chainlength on the liquid-liquid phase separation for the $F_X H_X$ (1) + F_1 (2) + H_7 (3) ternary mixtures at 510 K and 10 MPa using the hetero-SAFT-VR approach.

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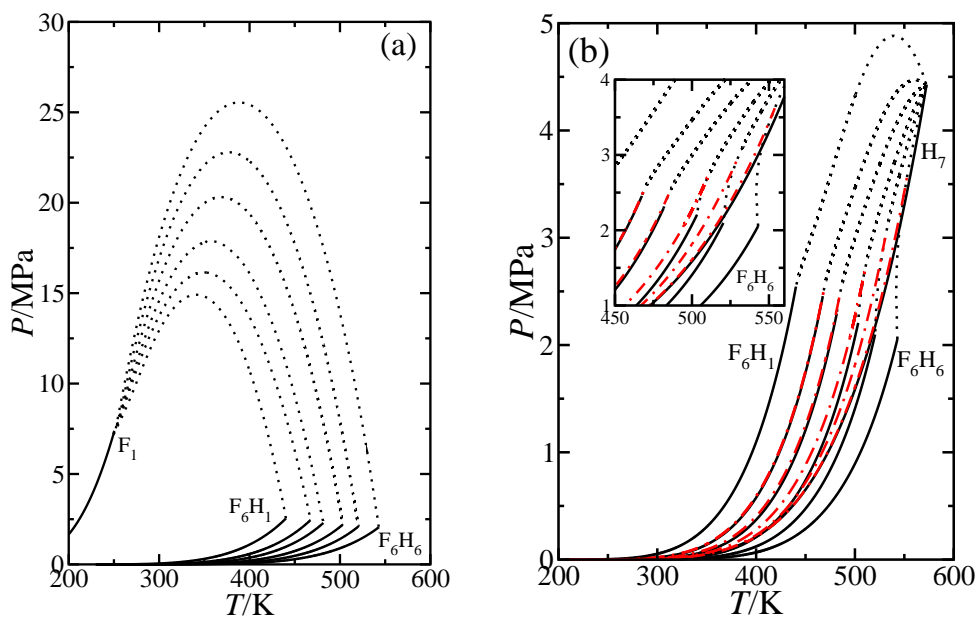


Figure 6. Theoretical predictions of the PT projection of the phase behaviour for the binary mixtures (a) perfluoromethane (F_1) + asymmetric surfactant (F_6H_X) and (b) n -heptane (H_7) + asymmetric surfactant (F_6H_X) using the hetero-SAFT-VR approach. Solid lines describe the vapour-pressure curves of pure components, dotted curves are the gas-liquid critical lines ((L - V) (black)), dashed line (blue) is the three phase line (L - L - V) and dashed-dot line (red) describe the azeotropic line (AZ).

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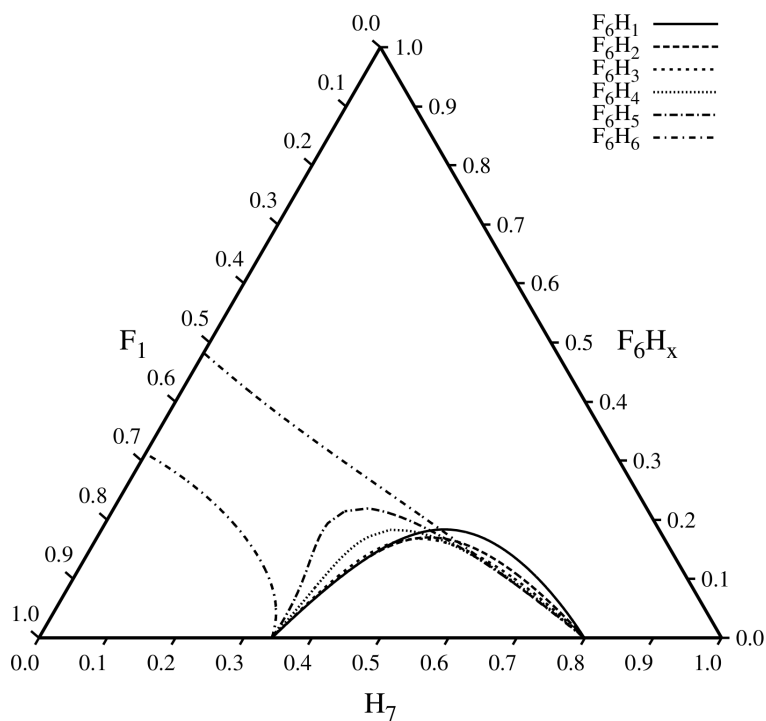


Figure 7. Effect of the alkyl chainlength of the asymmetric surfactant of the type F_6H_X on the liquid-liquid phase separation of the ternary mixtures composed of F_6H_X (1) + F_1 (2) + H_7 (3) at 510 K and 10 MPa using the hetero-SAFT-VR approach.

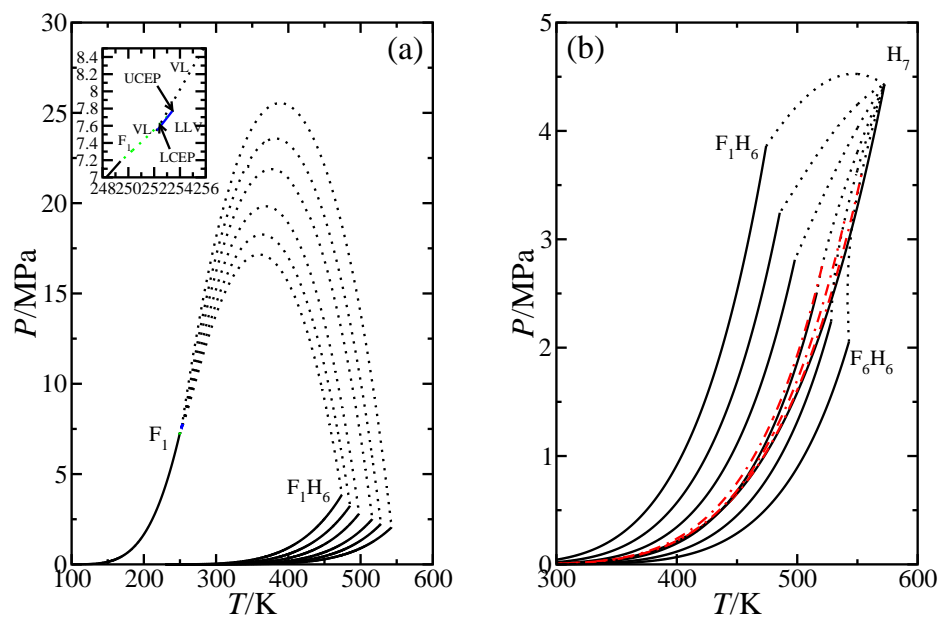


Figure 8. Theoretical predictions of the PT projection of the phase behaviour for the binary mixtures (a) perfluoromethane (F_1) + asymmetric surfactant (F_XH_6) and (b) n -heptane (H_7) + asymmetric surfactant (F_XH_6) using the hetero-SAFT-VR approach. Solid lines describe the vapour-pressure curves of pure components, dotted curves are the gas-liquid critical lines ($(L-V)_1$ (black) and $(L-V)_2$ (green)), dashed line (blue) is the three phase line ($L-L-V$) and dashed-dot line (red) describe the azeotropic line (AZ).

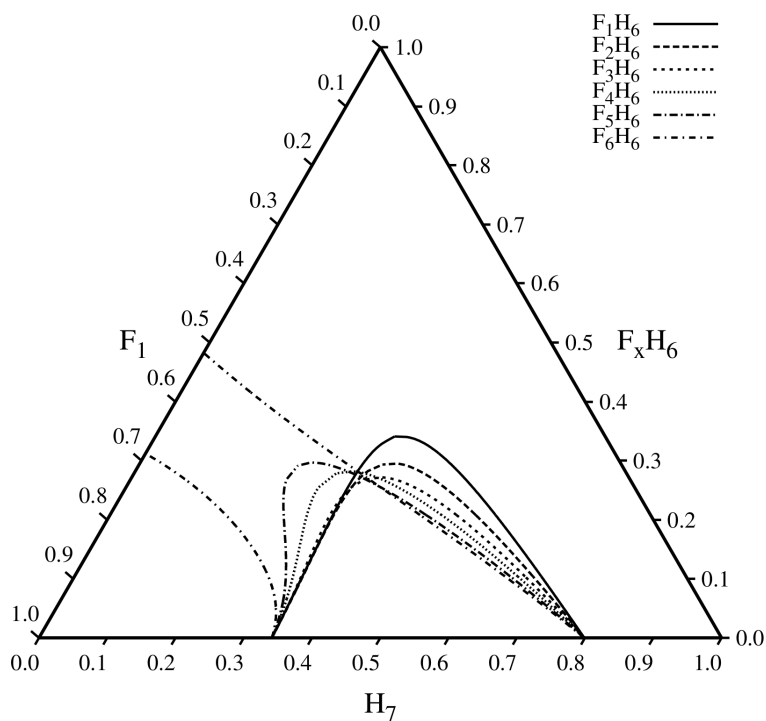


Figure 9. Effect of the perfluoroalkyl chainlength of the asymmetric surfactant of the type F_xH_6 on the liquid-liquid phase separation of the ternary mixtures F_xH_6 (1) + F_1 (2) + H_7 (3) at 510 K and 10 MPa using the hetero-SAFT-VR approach.