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Theory of phase equilibria for model mixtures of n-alkanes, perfluoroalkanes and perfluoroalkylalkane diblock surfactants

MARÍA CAROLINA DOS RAMOS and FELIPE J. BLAS*

Departamento de Física Aplicada, Facultad de Ciencias Experimentales, Universidad de Huelva, 21071 Huelva, Spain

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An extension of the SAFT-VR equation of state, the so-called hetero-SAFT approach [*Mol. Phys.* **104**, 571 (2006)], is used to examine the phase equilibria exhibited by a number of model binary mixtures of n-alkanes, perfluoroalkanes and perfluoroalkylalkane diblock surfactants. Despite the increasing interest in last years by semifluorinated alkanes (or perfluoroalkylalkane diblock molecules), the phase behaviour of mixtures involving these molecules with n-alkanes or perfluoroalkanes is practically unknown from the experimental point of view. In this work we use simple molecular models for n-alkanes, perfluoroalkanes and perfluoroalkylalkane diblock molecules to predict, from a molecular perspective, the phase behaviour of selected model mixtures of perfluoroalkylalkanes with n-alkanes and perfluoroalkanes. In particular, we focus our interest on the understanding of the microscopic conditions that control the liquid-liquid separation and the stabilisation of these mixtures. n-Alkanes and perfluoroalkanes are modelled as tangentially bonded monomer segments with molecular parameters taken from the literature. The perfluoroalkylalkane diblock molecules are modelled as heterosegmented diblock chains, with parameters for the alkyl and perfluoroalkyl segments developed in earlier work. This simple approach, which has been proposed in a previous work [*J. Phys. Chem. B*, in press (2006)], is now extended to describe model n-alkane + and perfluoroalkane + perfluroalkylalkanes binary mixtures. We have obtained the phase behaviour of different kind of mixtures and studied the effect of the molecular weight of n-alkanes and perfluoroalkanes on the type of phase behaviour observed in these mixtures. In addition, we have analyzed the effect of the number of the alkyl and perfluoroalkyl chemical groups in the surfactant molecule on the phase behaviour. As well as the usual vapour-liquid phase separation, liquid-liquid, positive azeotropes, and Bancroft points are found for different mixtures. This rich phase behaviour is a consequence of a delicate balance between the alkyl-alkyl, perfluoroalkyl-perfluoroalkyl, and alkyl-perfluoroalkyl interactions in different molecules. We have used the SAFT-VR microscopic description of chainlike systems to analyse the conditions that the n-alkane + and perfluoroalkane + perfluoroalkyalkane mixtures should posses in order to exhibit complete liquid miscibility. Although the model proposed here is chosen to reproduce most of the quantitative features of the phase equilibria of some pure perfluoroalkylalkane diblock surfactants and their mixtures with n-alkanes, this is the first time the SAFT approach is used to predict the phase behaviour of the mixtures considered here. The lack of experimental data for these systems does not allow to test the accuracy our theoretical predictions directly. However, since SAFT has proven to be an excellent approach to predict the phase behaviour of complex mixtures, we expect that the theory will reproduce the most important qualitative trends exhibited by the real mixtures.

1 Introduction

The thermodynamic properties of semifluorinated alkanes or perfluoroalkylalkanes, which have the general formula $F(CF_2)_i(CH_2)_jH$ or simply F_iH_j, have attracted considerable interest in recent years due to their unique properties, such as inertness, biocompatibility and its ability to solubilize high levels of respiratory gases characteristics of fluorinated solvents, among other properties [1]. But perhaps the most important feature exhibited by this class of substances is their tendency to autoorganize in different media and interfaces. This makes perfluoroalkylalkanes very interesting for different industrial and technical applications [2–12].

The use of semifluorinated molecules as surface active agents has been recently discovered and applied in different fields. Alkanes and perfluoroalkanes, in spite of the apparent similarity between them, exhibit large regions of liquid-liquid immiscibility, large positive deviations from Raoult's law and large positive excess properties, indicating weak unlike interactions [13]. This fact is very well known since late 40s, when these substances were intensively studied for their potential use as refrigerant mixtures or immiscible solvents. Due to the mutual phobicity exhibited by alkanes and perfluoroalkanes, perfluoroalkylalkane

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*Corresponding author. Email: felipe@uhu.es

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diblock surfactants can be viewed as potential agents for stabilizing those mixtures and a great number of possible applications are appearing in the literature [14, 15]. But the origin of this increasingly interest in semifluorinated compounds may probably be found in the unusual affinity of perfluorinated groups toward carbon dioxide (CO_2). During last years there have been a great number of studies in which perfluorinated molecules have been used as solvents to improve the solubility of chemicals in supercritical reaction or extraction media in CO_2 [16–20].

Despite the importance of these substances from both experimental and theoretical points of view, there is little experimental information about its thermodynamic behaviour, including phase equilibria. The reason for this lack of information may be due to the high cost in the production of these molecules, which most of them must be synthesized to be studied. Due to this, it will be desirable to have reliable information about its thermodynamic behaviour from alternative routes. The prediction of the thermodynamic properties of chain fluids has experienced an important advance in last decades, the most successful based in statistical mechanics. Molecular-based equations of state, such as those derived from the SAFT [21, 22] approach (following the seminal work of Wertheim [23–26]), provide a framework in which the different microscopic effects can be properly estimated and quantified separately, leading to a predicting, powerful and reliable equation of state applicable to complex systems. See the excellent reviews of Müller and Gubbins [27, 28].

The SAFT-VR approach, as other versions of SAFT, can be considered as one of the most powerful predicting equations of state nowadays for determining the thermodynamic properties of systems as complex as chainlike molecules, surfactants and polymeric systems among others. In a recent work [29], in collaboration with other groups, we have used the modification of the SAFT-VR approach, the so called hetero-SAFT-VR, to predict some thermodynamic properties, including the phase equilibria, of two different perfluoroalkylalkane molecules (perfluorohexylhexane and perfluorohexyloctane) from a truly manner. This is done by assuming that the molecular parameters of the alkyl and perfluoroalkyl groups in the surfactants are the same as those in pure alkanes and perfluoroalkanes. The same can be done for the unlike interactions between both chemical groups. Using an appropriate rule for the number of chemical units in the surfactant molecule, the resulting equation of state is able to predict sucessfully, without any further fitting, the saturated liquid density and vapour pressure of several perfluoroalkylalkanes [29].

In this work we follow a similar procedure and extend the previous work to deal with mixtures of perfluoroalkylalkanes with n-alkanes and linear perfluoroalkanes. The main goal of this work is to investigate and provide a general picture of the phase behaviour of these mixtures. To this end, we use different sets of reasonable parameters obtained in previous works to describe the chemical units of n-alkanes, perfluoroalkanes and perfluoroalkylalkanes. It is important to recall that our objective is not to provide a detailed description of the phase behaviour of these mixtures, but to give an insight of the general features exhibited by these mixtures. In particular, we focus in the effect of the molecular weight of the n-alkanes and perfluoroalkanes, as well as in the relative number of the (alkyl and perfluoroalkyl) chemical groups on the type of phase behaviour exhibited by these mixtures. Since the theory has proven to be very sucessful in predicting the behaviour of complex mixtures, we expect to give a representative picture of the phase equilibria of n-alkane + and perfluoroalkane + perfluoroalkylalkane surfactant model binary mixtures.

The rest of the paper is organised as follows. We present the molecular model and theory in section 2, where we also highlight the most relevant features of the molecular parameters used in this work. The results and discussion are presented in section 3; and the conclusions are made in section 4.

2 Molecular Model and Theory

Semifluorinated alkanes of perfluoroalkanes, F_iH_j, considered in this work are formed by linear alkane chains bonded to linear perfluoroalkane chains. These molecules can be regarded as semi-flexible copolymers of linear alkanes and perfluoroalkanes. Following a similar approach used in earlier work [29], the surfactant molecules are modelled with a simple united atom approach, in which m_{A} hard-sphere attractive segments of equal diameter σ_{AA} are bonded tangentially to form its alkyl part, m_{B} hard-sphere attractive segments of diameter σ_{BB} are also bonded tangentially to form its perfluoroalkyl part, and finally both parts are also tangentially bonded to form the diblock surfactants.

Attractive interactions between two segments i and j are described *via* an square-well potential, which is given by,

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

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

In this work we use the SAFT-VR approach to deal with mixtures containing surfactant molecules. Since this theory has already been presented [30–32], here we only give an overview of the main expressions, and the equations corresponding to the extension of the formalism to deal with linear surfactant molecules. The equation is written in terms of the Helmholtz free energy. In the case of non-associating 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}, which takes into account the attractive and repulsive forces between the segments that form the molecules, and a chain contribution A^{CHAIN}, which accounts for the connectivity of the molecules. The free energy is then written as

$$\frac{A}{Nk_{\text{B}}T} = \frac{A^{\text{IDEAL}}}{Nk_{\text{B}}T} + \frac{A^{\text{MONO}}}{Nk_{\text{B}}T} + \frac{A^{\text{CHAIN}}}{Nk_{\text{B}}T} \tag{2}$$

where N is the total number of molecules, T is the temperature, and k_{B} is the Boltzmann constant.

The monomer free energy is written as a second-order high temperature perturbation expansion:

$$\frac{A^{\text{MONO}}}{Nk_{\text{B}}T} = \left(\sum_{i=1}^{n} m_i x_{si}\right) \frac{A^{\text{M}}}{N_s k_{\text{B}}T} = \left(\sum_{i=1}^{n} m_i x_{si}\right) (a^{\text{HS}} + \beta a_1 + \beta^2 a_2) \tag{3}$$

where $\beta = (k_{\text{B}}T)^{-1}$, m_i and x_{si} are the number of segments and the molar fractions of segments type i, respectively, a^{HS} is the residual free energy per segment in a mixture of hard spheres, and a_1 and a_2 are the first- and second-order perturbation terms associated with the attractive interactions $u_{ij}(r)$ given by Eq. (1). The residual free energy per segment of the reference hard-sphere mixture is obtained from the expression of Boublík [33] (equivalent to that of Mansoori *et al.* [34]), the mean-attractive energy associated with the first-order perturbation term a_1 is treated in the context of the M1Xb mixing rules, [30, 31] and the second-order perturbation term a_2 is obtained using the local compressibility approximation.

The chain contribution to the free energy can be written in the usual way, although care must be taken with the contribution due to the surfactant formation. This contribution is now written as a sum of three terms, the formation of the subchain type 1, the formation of the subchain type 2, and the contribution to the free energy due to the bond of both parts. In particular, we use here the so-called hetero-SAFT version of the SAFT-VR [29, 35–37]. In the case of a binary mixture formed by homonuclear chains and diblock molecules, the contribution to the free energy is written as:

$$\frac{A^{\text{CHAIN}}}{Nk_{\text{B}}T} = x_1(1-m_1)\ln y_{11}^{\text{SW}}(\sigma_{11}) + x_2\left[(1-m_{\text{A}})\ln y_{\text{AA}}^{\text{SW}}(\sigma_{\text{AA}}) + (1-m_{\text{B}})\ln y_{\text{BB}}^{\text{SW}}(\sigma_{\text{BB}}) - \ln y_{\text{AB}}^{\text{SW}}(\sigma_{\text{AB}})\right] \tag{4}$$

where x_1 and x_2 are the compositions of the mixture, m_1 represents the chain length of component 1 (the homonuclear chain) and $(m_{\text{A}} + m_{\text{B}})$ is the chain length of the component 2 (the diblock surfactant). $y_{11}^{\text{SW}}(\sigma_{11})$ is the cavity correlation function of the reference SW fluid mixture between the segments that form the component 1 (the homonuclear chain), and $y_{\text{AA}}^{\text{SW}}(\sigma_{\text{AA}})$, $y_{\text{BB}}^{\text{SW}}(\sigma_{\text{BB}})$ and $y_{\text{AB}}^{\text{SW}}(\sigma_{\text{AB}})$ those between the segments forming the second component. The cavity function can be easily written in terms of the pair radial distribution function at contact. In the SAFT-VR context this function is given by the high-temperature expansion. For further details see the seminal works of Jackson and co-workers [30, 31]. The rest of thermodynamic properties, such as the chemical potential μ and compressibility factor Z, can be easily obtained from the Helmholtz free energy using standard thermodynamic relations.

The SAFT-VR approach, as other versions of SAFT, needs a number of molecular parameters to describe the thermodynamic properties of real substances. In this particular case, each homonuclear molecule is characterised by four molecular parameters, the segment size (σ_{11}), the square-well dispersive energy parameter (ϵ_{11}), the range of the attractive interactions (λ_{11}), and the chain length (m_1). In the case of diblock surfactant molecules formed by two different types of segments, two sets of parameters (one for the alkyl part and another for the perfluoroalkyl part) are needed. The potential model parameters σ_{ii}, ϵ_{ii} and λ_{ii} for the n-alkanes and perfluoroalkanes have been obtained from previous works [38–40]. In this work we use these values for describing the alkyl and perfluoroalkyl parts of the diblock surfactant molecules, respectively. For the n-alkanes and perfluoroalkanes, the simple empirical relationships proposed previously in the literature [41, 42], which relate the number of spherical segments in the model chain with the number of carbon atoms C in the alkyl and perfluoroalkyl molecules, are used here. In particular, $m = (1/3)(C - 1) + 1$ for the case of pure n-alkanes and $m = 0.37(C - 1) + 1$ for the case of pure perfluoroalkanes. Following our previous work [29], we use an alternative additive scheme to relate the chain length of the perfluoroalkylalkane diblock surfactant model and the total number of carbon atoms. For the alkyl part, each terminal and inner methyl group (CH_3– and –CH_2–) are modelled by 0.665 and 1/3 segments, respectively. For the perfluoroalkyl part, each terminal and inner perfluoromethyl group (CF_3– and –CF_2–) are modelled by 0.685 and 0.37 segments, respectively. This model is a generalisation of the simple empirical rules used for modelling pure n-alkanes and perfluoroalkanes. Table 1 lists the parameters used in this work to describe the pure components. For further details see our previous work [29, 32].

Since we are dealing with mixtures, and the diblock surfactants are formed by two different types of segments, a number of cross or unlike parameters need to be specified. The Lorentz combining rule is used for the unlike hard-core diameter

$$\sigma_{12} = \frac{\sigma_{11} + \sigma_{22}}{2} \tag{5}$$

while the unlike dispersive energy of the system is defined as

$$\epsilon_{12} = \xi_{12}(\epsilon_{11}\epsilon_{22})^{1/2} \tag{6}$$

where ξ_{12} describes the departure of the system from the Berthelot combining rule. A value of $\xi_{12} < 1$ is usually associated with liquid-liquid immiscibility. The unlike range parameter of the mixtures is obtained from the following equation

$$\lambda_{12} = \gamma_{12}\frac{\lambda_{11}\sigma_{11} + \lambda_{22}\sigma_{22}}{\sigma_{11} + \sigma_{22}} \tag{7}$$

where γ_{12} 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_{12} and γ_{12} have been determined in previous works by different authors. McCabe *et al.* [43] have studied mixtures of perfluoromethane with short n-alkanes (up to n-hexane), and some symmetrical mixtures of n-alkanes and perfluoroalkanes at high-pressure conditions. Their values ($\xi_{12} = 0.9206$ and $\gamma_{12} = 1$) were adjusted to give the best representation of the continuous high-pressure and high-temperature gas-liquid critical line in the perfluoromethane + n-butane system. In order to study binary mixtures with longer chain lengths these authors proposed the values $\xi_{12} = 0.8948$ and $\gamma_{12} = 1$ to predict the high-pressure critical line of the perfluoromethane + n-heptane mixture (see the work of McCabe *et al.* for further details [43]). More recently, Morgado *et al.* [13] have proposed a new set of transferable unlike parameters ($\xi_{12} = 0.840$ and $\gamma_{12} = 1.0451$) which enable the accurate prediction of the upper critical solution temperature and excess volumes for the n-hexane + perfluorohexane binary mixture. With these parameters they are able to predict, without any further adjustment, the vapour-liquid equilibria, LL immiscibility, and excess volumes of similar homologous mixtures (formed by molecules with between 5 and 8 carbon atoms in both components). The advantage of this set of parameters is that able to predict, from a truly manner, the saturated liquid density of two different perfluoroalkylalkane diblock surfactants, F_6H_6 and F_6H_8, in excellent agreement with experiment [29].

The use of several binary interaction parameter values for similar homologous mixtures or even the same molecules at different thermodynamic conditions is not fully justified from a theoretical point of view. This is a consequence of the approximations made in the theory and the use of effective intermolecular potential models. In the particular description of the n-alkane + and perfluoroalkane + perfluoroalkylalkane binary mixtures care must be taken when using the binary interaction parameters proposed by Morgado *et al.* [13] for describing mixtures of n-alkanes and perfluoroalkanes with arbitrary chain lengths. Although they are able to accurately describe the phase behaviour (liquid-liquid equilibria) and excess properties of n-alkanes and perfluoroalkanes of intermediate chain lengths (between 5 and 8 carbon atoms in both components) and at moderate temperatures and pressures, we have checked that the set of parameters proposed by Morgado *et al.* [13] can not predict accurately the phase behaviour of asymmetric mixtures of n-alkanes and perfluoroalkanes. In particular, these unlike binary parameters are not able to predict the type III phase behaviour exhibited by the $F_1 + H_7$ mixtures. We have also checked that both sets of parameters (those from McCabe *et al.* [43] and from Morgado *et al.* [13]) yield a similar qualitative phase behaviour for the n-alkane + and perfluoroalkane + perfluoroalkylalkane mixtures when the number of alkyl and perfluoroalkyl groups is 4 or greater (obviously, although different parameter values give different particular values of critical points, three-phase lines, critical lines, etc., they provide the same type of phase behaviour). To recap, in this work we use the original set of parameters of McCabe *et al.* [43] when the n-alkane and/or the perfluoroalkane has less than four carbon atoms. We also use the same parameters when the alkyl and/or the perfluoroalkyl part of the surfactant contains less than 4 carbon atoms. Otherwise, both sets of parameters (McCabe *et al.* [43] and Morgado *et al.* [13]) give essentially the same phase behaviour. **In particular, we have used the $\xi_{12} = 0.8948$ and $\gamma_{12} = 1$ in all the calculations presented in this work**.

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

In this section we present the main predictions we have obtained using the SAFT-VR approach for describing model mixtures of n-alkanes with perfluoroalkylalkanes and perfluoroalkanes with perfluoroalkylalkane diblock surfactants. We first concentrate on mixtures with a particular perfluoroalkylalkane surfactant and study the effect of the molecular weight of the n-alkanes and perfluoroalkanes on the phase behaviour of a selection of model binary mixtures. In the following sections we focus on the phase behaviour of mixtures with perfluoroalkylalkanes of different molecular weights. In particular, we study 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 *Mixtures of perfluorohexylhexane with n-alkanes and perfluoroalkanes*

We first consider mixtures of perfluorohexylhexane diblock surfactant with n-alkanes formed by up to 10 carbon atoms. Perfluorohexylhexane (F_6H_6) has been choosen as a prototype member of the perfluoroalkylalkane (F_iH_j) homologous series of surfactants since has been extensively studied by us (in collaboration with other groups) from both experimental and theoretical points of view [29].

We use the theory presented in section 2, in combination with the molecular parameters and unlike interaction parameters described previously, to obtain a general picture of the phase behaviour exhibited by mixtures of perfluorohexylhexane (F_6H_6) with n-alkanes (H_i). The predictions from our calculations are shown in Fig. 1. As can be seen, all mixtures considered here (from $H_1 + F_6H_6$ to $H_{10} + F_6H_6$) exhibit type I phase behaviour according to the Scott and Konynenburg (SK) classification [44, 45]. A more detailed picture of the critical region corresponding to mixtures of the surfactant with the longest n-alkanes (from n-hexane up to n-decane) is shown in the inset of the figure. Although it is difficult to distinguish from this figure, the binary mixtures of the surfactant with n-alkanes formed up to 7 carbon atoms exhibit no azeotropy, whereas the rest of the homologous mixtures (from n-octane to n-decane) exhibit positive azeotropy. It is interesting to note that although we are considering long molecules, no liquid-liquid phase separation is found in any case.

It is interesting to compare the phase behaviour of this series with that of methane + n-alkane ($H_1 + H_i$) binary mixtures. It is well known that the $H_1 + H_6$ mixture exhibits type V phase behaviour, and that the SAFT approach is able to predict it [46, 47]. In our current case, we have a mixture more asymmetric ($H_1 + F_6H_6$) and with intermolecular interactions (alkyl-perfluoroalkyl) which are clearly unfavourable (the tendency to demix of n-alkanes and perfluoroalkanes is well known). Why then our SAFT-VR results predict type I phase behaviour for this mixture? The answer to this question is directly related with another one: Why the $H_1 + H_6$ system is the only mixture of the $H_1 + H_i$ series that exhibits type V phase behaviour? The answer is that the melting point of the longer component (H_i) is located well above the critical point of the lighter component (methane), and the LL region is thermodynamically metastable. This is an example of how immiscibility is preempted by the appearance of the solid phases. In our particular case, the melting point of F_6H_6 is located at 261K approximately [9], clearly above the critical point of methane (190K approximately, although our theory predicts 204K approximately due to its classical character). But the question still remains: does the SAFT-VR predict the existence of LL immiscibility at sufficiently low temperatures? The answer is yes. This mixture exhibits LL immiscibility of type V well below the melting point of F_6H_6. In particular, we have found a three-phase line running from a Lower Critical End-Point (LCEP), located at $155.22\,$K and $1.30\,$MPa, to an Upper Critical End-Point (UCEP), located at $204.66\,$K and $6.78\,$MPa, near to the predicted critical point of pure methane ($204.20\,$K and $6.71\,$MPa). Note that we are using a classical equation of state and the critical properties are overestimated. This is in agreement with the fact that the SAFT approach predicts the existence of LL immiscibility, provided the temperature is low enough. It is also interesting to note that the result is expected since the segment size and dispersive energy values between the alkyl and perfluoroalkyl groups are more dissimilar than those corresponding to the alkyl-alkyl interactions. In summary, the $H_i + F_6H_6$ binary mixtures do not exhibit LL immiscibility, and only show type I phase behaviour.

We have also studied the phase behaviour of the perfluoroalkane + perfluorohexylhexane binary mixtures. In particular, we have considered mixtures of perfluoroalkanes with different number of carbon atoms (from 1 to 10 carbon atoms). The predictions from the hetero-SAFT-VR approach are presented in Fig. 2, where the pressure-temperature phase diagram is shown. All mixtures considered here show type I phase behaviour according to the SK classification, similarly to those studied in Fig. 1. In the current case only the mixture with the longest perfluoroalkane is seen to exhibit azeotropy.

Although we only present here results for binary mixtures of perfluorohexylhexane with n-alkanes or perfluoroalkanes, we have also determined the phase behaviour of similar mixtures containing perfluorohexyloctane (F_6H_8). In all cases we have found type I phase behaviour with absence of (liquid-liquid) immiscibility.

3.2 *Binary mixtures of n-hexane with perfluorohexylalkanes*

We now turn on the investigation of the phase behaviour of the homologous binary mixtures n-hexane + perfluorohexylalkane (H_6 + F_6H_i). The n-hexane + perfluorohexane (H_6 + F_6) binary mixture could be considered the first member of the series, in which the number of alkyl groups in the surfactant molecule is equal to zero (H_6 + F_6H_0). We change continuously the phase behaviour of the n-hexane + surfactant binary mixtures by increasing the number of alkyl groups in the F_6H_i molecule and compare their phase behaviour with that of the mixture H_6 + F_6.

The first mixture considered here is the n-hexane + perfluorohexylmethane (H_6 + F_6H_1) binary mixture, which can be viewed as a mixture of n-hexane + perfluorohexane in which a methyl group (CH_3) has been added to the perfluorohexane. The PT projection of the phase diagram is shown in Fig. 3. We also show the PT diagram corresponding to the H_6 + F_6 binary mixture (see part (a) of Fig. 3). The H_6 + F_6H_1 mixture is seen to exhibit type II^{A} phase behaviour according to the SK classification. As can be seen, the mixture exhibits vapour-liquid (VL) phase equilibria at high temperatures, azeotropy, and liquid-liquid (LL) immiscibility at low temperatures. Since F_6H_1 is more volatile than perfluorohexane, the vapor pressure curve of the surfactant is seen to displace toward lower temperatures and pressures ($T_\mathrm{c} \approx 440\,\mathrm{K}$ and $P_\mathrm{c} \approx 2.52\,\mathrm{MPa}$) with respect to that corresponding to pure perfluorohexane ($T_\mathrm{c} \approx 472\,\mathrm{K}$ and $P_\mathrm{c} \approx 2.88\,\mathrm{MPa}$). The critical temperature of the F_6H_i chemical family decreases first when passing from F_6 to the surfactant (F_6H_1), an opposite behaviour of the expected when increasing the molecular weight (see the vapour pressures of longer F_6H_i molecules). At this level of description and without experimental data to check our predictions, it is difficult to asses if this behaviour can be adscribed to the real behaviour of the F_6H_i homologous surfactants or simply an effect of the anomalous parameter values of the terminal CH_3 group in F_6H_1. In addition, the liquid-liquid critical line of the mixture with the surfactant is located at lower temperatures than those corresponding to the H_6 + F_6 mixture, indicating that the range of temperatures at which the mixture is immiscible decreases. In fact, the associated Upper Critical End Point (UCEP) of the mixture occurs at 350 K, a smaller value compared with that corresponding to the n-hexane + perfluorohexane binary mixture (380 K). This effect should be addressed to the presence of an alkyl group in the second component which stabilises the mixture. It is important to note that we are using a set of optimized parameters to the VL phase behaviour, which obviously overestimate the critical points, as well as the UCEPs of the mixture. As can be seen, the UCEP moves not only to lower temperatures, but also to lower pressures. As a consequence of this, the LL critical line associated to the UCEP is displaced toward lower temperatures, which can be understood as an stabilisation effect over the mixture when alkyl groups are added to the perfluoroalkane molecule.

A selected number of Tx slices of the PTx surface are given in Fig. 4 at different pressures for the H_6 + F_6 and H_6 + F_6H_1 binary mixtures. Parts (a) and (b) show the Tx slices at $p = 0.5\,\mathrm{MPa}$ for both mixtures. This pressure lies between the UCEP pressures of both mixture. According to the results shown in parts (a) and (b), and in agreement with our previous calculations, both mixtures exhibit type II^{A} phase behaviour. At this thermodynamic conditions, the H_6 + F_6H_1 mixture exhibits a region of complete liquid miscibility between the UCEP and the minimum of the VL azeotropy. We have also considered the Tx slices of both mixtures at a higher pressure ($P = 1.789\,\mathrm{MPa}$), as shown in parts (c) and (d) of the figure. At these conditions both mixtures exhibit LL phase separation at low temperatures and VL equilibria at high temperatures. A wider region of complete miscibility between both zones (VL and LL) is seen in the H_6 + F_6H_1 mixture, as expected from our previous results.

The next system we examine is the n-hexane + perfluorohexylethane (H_6 + F_6H_2) binary mixture, which can be viewed as the next member of the homologous series considered in this section. The phase equilibria and critical lines of this mixture are depicted in Fig. 5a. The PT projection of the phase diagram shows that this mixture exhibits a similar behaviour than the previous mixture (type II^{A} phase behaviour according to the SK classification). However, a number of differences can be seen. The vapour pressure curves of the two components 1 and 2 cross at a Bancroft poinf of $T \approx 320\,\mathrm{K}$ and $P \approx 0.045\,\mathrm{MPa}$. The presence of a Bancroft point in a binary mixture is usually related with molecules that are dissimilar in chemical type or in shape but have similar vapour pressure. This is indeed the particular case of the homologous H_6 + F_6H_i binary mixtures considered in this work. The existence of a Bancroft point in this system can be understood in the context of varying the number of alkyl groups in the diblock surfactant molecule. When passing from perfluorohexylmethane to perfluorohexylethane, the vapour pressure curve moves from low to high temperatures and eventually, it crosses the vapour pressure curve of pure n-hexane.

Similarly to the previous mixture, the system exhibits VL equilibria at high temperatures. As can be seen in Fig. 5a, the critical locus extends through a temperature minimum ($T \approx 470\,\mathrm{K}$), at which the pressure is $P \approx 2.8\,\mathrm{MPa}$. This behaviour is associated with the occurrence of a positive azeotrope extending up to the critical line. The azeotropic line is seen to finish tangentially to the projection of the critical locus, but does not meet it at the temperature minimum. This means that azeotropy can only be found at temperatures and pressures below 470 K and 2.8 MPa, respectively. The projection of the azeotropic line along the Tx plane of the phase diagram is seen to exhibit positive slope in the whole range of temperatures considered. A region of LL immiscibility is also found and the corresponding critical line, which has a positive slope, meets the three-phase line at an UCEP located approximately at 310 K and 0.05 MPa. This is expected since the system exhibits type II phase behaviour with the presence of azeotropy.

The UCEP of the mixture is seen to move toward lower temperatures and pressures as the number of alkyl groups is increased in the surfactant molecule. In particular, the UCEP temperature of the mixture $H_6 + F_6H_2$ is located at 310 K, 40 K approximately bellow than the corresponding UCEP temperature of the $H_6 + F_6H_1$ binary mixture (350 K). As a consequence of this behaviour, the critical line associated to the UCEP is displaced toward lower temperatures. This means that the range of temperatures at which the mixture of H_6 and F_6H_2 exhibits an homogeneous liquid phase raises when is compared with that corresponding to the $H_6 + F_6H_1$ binary mixture. This behaviour is not surprising since an increase of the number of alkyl groups in the surfactant favours the interactions between the alkyl groups in the H_6 and the surfactant molecule, and consequently, the miscibility between the components of the mixture.

The results for the mixture of n-hexane and perfluorohexylpropane ($H_6 + F_6H_3$) are presented in Fig. 5b. The general features of the phase behaviour for this system can be seen in the corresponding PT projection. This mixture still exhibits type II^{A} phase behaviour with an azeotropic line. The vapour-pressure curve of the pure perfluorohexylpropane has moved toward higher temperatures and lower pressures due to the increasing of the surfactant length, making it less volatile than F_6H_2 (the critical temperature and pressure of the diblock surfactant are now approximately 480 K and 2.4 MPa, respectively) in a wide range of conditions. As in the previous mixture, the $H_6 + F_6H_3$ system exhibits a Bancroft point, but now at a much higher temperature and pressure (475 K and 1.8 MPa approximately). The corresponding VL equilibria at high temperatures also exhibits azeotropic behaviour at temperatures and pressures below approximately 485 K and 3 MPa, respectively. At these coordinates, the azeotropic line finishes tangentially to the projection of the critical line along the PT projection. At low pressures the mixture exhibits the corresponding UCEP at approximately 285 K and 0.012 MPa. The main effect of increasing the length of the surfactant molecule (by passing from perfluorohexylethane to perfluorohexylpropane) is to decrease the pressure and temperature of the UCEP with respect to that of the previous system, making the mixture more miscible. As can be seen in Fig. 5b, the corresponding LL immiscibility region is smaller as a consequence of the increment of the number of alkyl groups in the diblock surfactant molecule.

We have also considered a number of Tx projections of the PTx phase diagram in Fig. 6. Parts (a) and (b) correspond to the Tx slices of the $H_6 + F_6H_2$ and $+ F_6H_3$ binary mixtures at 0.5 MPa, and parts (c) and (d) at 1.789 MPa. As can be seen, all four slices show LL equilibria at low temperatures and VL behaviour with azeotropy at high temperatures, in agreement with results presented in Fig. 5. Since the thermodynamic conditions selected in Figs. 4 and 6 are the same (Tx slices at 0.5 and 1.789 MPa), it is possible to analize the changes in the phase diagram of the mixtures for a wide range of surfactant molecules. The inspection of both figures shows that the increase of the number of alkyl groups in the surfactant molecules is seen to raise the temperature gap between the azeotropic minimum associated to the VL equilibria of the mixture and the UCST associated to the LL behaviour. It is worthy to note that the increase of this gap is mainly due to the lowering of the UCST of the mixture, since according to our calculations, the VL phase envelope is rather insensitive to the presence of additional alkyl groups in the surfactant molecule.

The phase equilibria of mixtures of n-hexane with longer perfluoroalkylalkanes has also been examined. Fig. 7 shows the PT projection of the phase diagram corresponding to mixtures from n-hexane + perfluorohexylbutane up to n-hexane + perfluorohexyloctane. All the mixtures considered exhibit type I phase behaviour without azeotropy. It is important to note at this point that no LL immiscibility is observed in these systems above 250 K. **We should recall here that the melting points of these surfactants are around this temperature, and LL immiscibility regions can not exist, in a truly thermodynamic sense, at temperatures around this value.** However, as it is common in all versions of fluid-phase equations of state (including SAFT), SAFT-VR would probably predicts the existence of LL immiscibility (characteristics of type II class) in all systems, provided the temperature is low enough; this is a direct consequence of the fact that the current version of SAFT is a fluid-phase equation of state and does not incorporate the characteristics of the solid phases. Apart from this fact, the main conclusion from Fig. 7 is that the diblock perfluorohexylalkane molecules mixed with n-hexane form a completely (liquid) miscible phase at all proportions if the number of alkyl groups in the diblock molecules is four or higher.

The effect of increasing the length of the diblock surfactant molecule (by adding more alkyl groups) on the *PT* projection of the phase diagram is to displace the critical temperature and pressure of the pure surfactant toward higher and lower values, respectively. As a consequence of this, the continuous gas-liquid critical line (which goes from component 1 to component 2) moves toward higher temperatures. The temperature minimum exhibited by the critical line of the mixtures with the shortest diblock surfactants (F_6H_4 and F_6H_5) is seen to move not only to higher temperatures but also to higher pressures. The critical line at the minimum in the $H_6 + F_6H_4$ mixture reaches a pressure equal to 3 MPa, whereas in the $H_6 + F_6H_5$ system the pressure at which the critical line exhibits a minimum in temperature is approximately 4 MPa (note that for mixtures of n-hexane with shorter diblock surfactants the corresponding value of the pressure lies below 3 MPa).

To recap, the hetero-SAFT-VR formalism describes continuously the changes in phase behaviour of model mixtures containing n-hexane and perfluorohexylalkane surfactant molecules. Mixtures that contain a small number of alkyl groups exhibit type II^{A} phase behaviour, with a decreasing of the existing LL immiscibility region as the surfactant becomes larger. Mixtures with longer surfactants show type I phase behaviour and complete (LL) miscibility at all thermodynamic conditions.

3.3 *Binary mixtures of perfluorohexane with perfluoroalkylhexanes*

We finally consider similar homologous mixtures containing perfluoroalkylhexane surfactant molecules with perfluorohexane. Fig. 8 shows the *PT* projection of the phase diagram corresponding to the $F_6 + F_1H_6$ (part a) and $F_6 + F_2H_6$ (part b) binary mixtures. Note that we are considering the 'symmetrical' systems studied in Figs. 3b and 5a (system of Fig. 3 can be recovered from the current one by swapping the identity of the alkyl and perfluoroalkyl chemical groups). In the current case we 'add' additional perfluoroalkyl groups to the n-hexane molecule and consider the phase behaviour of the resulting diblock surfactant molecules. n-Hexane, H_6, can be viewed as the first member, F_0H_6, of the homologous chemical family of the perfluoroalkylhexane surfactants. Obviously, the other component of the mixture is necessarily perfluorohexane in order to keep the symmetry in our study. Note that now we are interested in changes of the phase behaviour of $F_6 + H_6$ when different number of perfluoroalkyl groups are added to the second component of the mixture. As can be seen in the Fig. 8a, the $F_6 + F_1H_6$ binary mixture exhibits type II^{A} phase behaviour according to the SK classification. The continuous gas-liquid critical line extends from component 1 to component 2 and exhibits a minimum in temperature, characteristic of mixtures with positive azeotropy. The corresponding azeotropic line extends from the low temperature region (for pressures higher than those corresponding to the vapour pressure curves of the pure components at each temperature) up to the high temperature region, where finishes tangentially to the projection of the critical locus. The corresponding UCEP of the mixture is seen to occur at low temperatures ($T_{\mathrm{UCEP}} \approx 265\,\mathrm{K}$). The LL critical line associated to the UCEP extends toward the high-pressure region nearly vertically, as expected for a binary mixture that exhibits type II^{A} phase behaviour. This mixture shows a similar behaviour than that of the 'symmetrical' binary mixture considered in Fig. 3b (in fact, both systems show type II^{A} phase behaviour), although an important quantitative difference can be observed. The effect of including an additional perfluoroalkyl group in the n-hexane molecule is seen to decrease the UCEP temperature associated to the corresponding LL critical line. But, why the UCEP temperature of the $F_6 + F_1H_6$ binary mixture decreases nearly 115 K with respect to that of the $F_6 + H_6$ mixture, which represents nearly four times more than the corresponding decrease in the system of Fig. 3b. It is difficult to provide an ‘exact’ answer to this question since it depends on fine molecular details, compositions of the mixtures, etc., but we can give a qualitative description of the scenario and understand why the lowering in temperature of the UCEP in the current mixture is higher than that corresponding to the previous one.

LL immiscibility appears in these mixtures due to the presence of unfavourable interactions between the chemical groups in different components of the mixture. If one adds chemical groups of, for instance, alkyl type in perfluoroalkane molecules, the immiscibility decreases since favourable interactions appear in the system that help to stabilise homogeneous liquid phases. The same is true if one adds perfluoroalkyl chemical groups in alkane chains of the mixture. Both mixtures, $H_6 + F_6H_1$ and $F_6 + F_1H_6$ are symmetrical and ‘constructed’ from the same original mixture $H_6 + F_6$. In the first case, a methyl group is added in the second component, and in the second one a perfluoromethyl group is added. The different (macroscopic) thermodynamic behaviour observed in both mixtures (Figs. 3 and 8) should be adscribed to the presence of these two different chemical groups. Methyl and perfluoromethyl groups are very different. In terms of SAFT-VR parameters, the segment size value of the perfluoromethyl group is approximately a 18% higher than that corresponding to the methyl group ($\sigma_{\mathrm{CF}_3}/\sigma_{\mathrm{CH}_3} \approx 1.18$). But perhaps more important is the fact that the dispersive energy value associated to the perfluotomethyl group is a 65% higher than that corresponding to the methyl group ($\epsilon_{\mathrm{CF}_3}/\epsilon_{\mathrm{CH}_3} \approx 1.65$). This is a huge increment, especially in the case of the dispersive energy of the chemical groups.

The effect of passing from this mixture to the $H_6 + F_6H_1$ binary mixture is the presence of new alkyl-perfluoroalkyl and alkyl-alkyl interactions in the system: the new methyl groups interact with the perfluoroalkyl groups of the surfactant molecules (in the same molecules), and with the alkyl groups of the n-alkane molecules. In the same way, the effect of passing from the original mixture to the $F_6 + F_1H_6$ is the presence of new alkyl-perfluoroalkyl and perfluoroalkyl-perfluoroalkyl interactions. Due to the symmetry of the mixtures, the only difference between both systems ($H_6 + F_6H_1$ and $F_6 + F_1H_6$) are the new alkyl-alkyl and perfluoroalkyl-perfluoroalkyl interactions, respectively. Note that the alkyl-perfluoroalkyl interactions are identical in both systems. Both, alkyl-alkyl interactions in $H_6 + F_6H_1$ and perfluoroalkyl-perfluoroalkyl interactions in $F_6 + F_1H_6$ help to stabilise the free energy of the mixtures. This includes the lowering of the UCEP temperature and LL critical line, which increases the temperature range at which mixtures exhibit single homogeneous liquid phases. However, due to the difference in energy and size between the alkyl-alkyl and perfluoroalkyl-perfluoroalkyl interactions ($\sigma_{\mathrm{CF}_3-\mathrm{CF}_2}/k_\mathrm{B} \approx 4.4\,\mathrm{\AA}$ and $\epsilon_{\mathrm{CF}_3-\mathrm{CF}_2}/k_\mathrm{B} \approx 281\,\mathrm{K}$, and $\sigma_{\mathrm{CF}_3-\mathrm{CF}_2}/k_\mathrm{B} \approx 3.8\,\mathrm{\AA}$ and $\epsilon_{\mathrm{CH}_3-\mathrm{CH}_2}/k_\mathrm{B} \approx 206\,\mathrm{K}$), one can expect with a degree of confidence that the effect of adding a perfluoromethyl group in the n-hexane molecule will stabilise more effectively the F_6H_6 mixture than the symmetrical change. Obviously, this is not a definitive proof of our hypothesis, but provides a plausible explanation from microscopic arguments of the differences observed in the systems presented in Fig. 3 and 8. These conclusions can be useful for searching the optimal surfactant which can stablise a given n-alkane + perfluoroalkane mixture, especially if we take into account the complete lack of experimental information for these systems.

Similarly to the $H_6 + F_6H_i$ binary mixtures, we also consider here a selection of Tx slices of the PTx phase diagram of mixtures of perfluorohexane with perfluoromethylhexane and perfluoroethylhexane. Fig. 9 shows the Tx slices at two different pressures, 0.5 and 1.789 MPa. Note that these two pressures are the same as those considered previously in section 3.2. Parts (a) and (b) indicate that mixtures show VL equilibria at high temperatures and (LL) immiscibility at low temperatures, in agreement with the results presented in Fig. 8. It is interesting to compare the change in the Tx slice corresponding to the $H_6 + F_6$ binary mixture when an alkyl group is added to the perfluorohexane molecule (Fig. 4b) and when a perfluoroalkyl group is added to the n-hexane molecule (Fig. 9a). The effect in the later case is much more important since the LL immiscibility region is seen to move toward much lower temperatures than in the case shown in Fig. 4b. In fact, the UCST is seen to displace 100 K below more than in the other case. A further decrease of the UCST is observed when a new perfluoroalkyl group is added, as shown in Fig. 9b. The presence of this additional group in the surfactant molecule greatly modifies the stability of the liquid mixture. The same behaviour is observed at further higher pressures (1.789 MPa). As in the previous case, the addition of perfluoroalkyl groups to the surfactant molecule makes the $F_6 + F_iH_6$ binary mixture more miscible. As can be seen in parts (c) and (d), the temperature gap between the VL and the LL regions is approximately 200 K, which is 50 K larger than that corresponding to the symmetrical mixtures (H_6 + F_6H_1 and + F_6H_2). These results confirm the microscopic hypothesis formulated above.

Finally, we consider mixtures of perfluorohexane with longer homologous surfactants, from perfluoropropylhexane up to perfluorooctylhexane. Fig. 10 shows the corresponding PT projection of the phase diagram of these mixtures. As can be seen, the critical lines of the mixtures are continuous, going from the gas-liquid critical point of one component to the other one. This behaviour clearly indicates that all mixtures exhibit type I phase behaviour according to the SK classification, and consequently, perfluorohexane and the surfactants considered are completely miscible for all compositions (no LL immiscibility is observed). This expected behaviour is in agreement with the scenario proposed before: the presence of additional perfluoroalkyl groups in the surfactant molecule helps to stabilise the interactions with the perfluorohexane molecule. As the number of chemical groups increases the favorable interactions are more dominant and the homogenous liquid phase becomes stable.

4 Conclusions

We have used an extension of the SAFT-VR approach recently proposed (the so-called hetero-SAFT) [29, 36] to predict the phase behaviour of model mixtures of homonuclear chains with diblock surfactants. In order to gain a comprehensive understanding of the phase behaviour of the systems studied here we have considered model n-alkane + and perfluoroalkane + perfluoroalkylalkane binary mixtures. In particular, we consider four different types of mixtures: (a) H_i + F_6H_6, (b) F_i + F_6H_6, (c) H_6 + F_6H_i , and (d) F_6 + $F_\mathrm{i}H_6$. In the two first cases (a and b), we study the effect of the molecular weight of n-alkanes and perfluoroalkanes when are mixed with a typical diblock surfactant of the chemical family considered here as F_6H_6. The predictions from the theory indicate that all mixtures exhibit type I phase behaviour, with absence of (LL) immiscibility, due to the favorable interactions between the similar chemical units in both components. The last two types of systems considered (c and d) allow us to gain an understanding in the effect of the relative number of alkyl and perfluoroalkyl groups in the diblock molecules on the phase behaviour with n-alkanes and perfluoroalkanes. The results lead to a number of interesting conclusions: type II phase behaviour, i.e., LL immiscibility (at low temperatures) and VL equilibria (at high temperatures) for mixtures H_6 + F_6H_i ($i \leq 4$) and F_6 + F_iH_6 ($i \leq 2$) due to the weak alkyl-perfluoroalkyl interactions; complete miscibility in the systems as the number of similar chemical groups increases (alkyl and perfluoroalkyl groups in the H_6 + F_6H_i and F_6 + F_iH_6 mixtures, respectively); stronger effect on the phase behaviour when additional perfluoroalkyl groups are added to the surfactant molecules instead of alkyl groups.

The change in the phase behaviour of the H_6 + F_6H_i and F_6 + $F_\mathrm{i}H_6$ binary mixtures has been analysed from the molecular perspective of the SAFT-VR equation of state. The addition of extra alkyl and perfluoroalkyl groups in the mixtures promotes the stabilisation of the systems due to the presence of favourable (alkyl-alkyl and perfluoroalkyl-perfluoroalkyl) interactions between chemical groups located at different components. The stronger effect observed on the phase behaviour of mixtures F_6 + $F_\mathrm{i}H_6$ when perfluoroalkyl groups are added to the second component compared with that corresponding to the H_6 + F_6H_i binary mixtures has been interpreted in terms of the relative strength of the alkyl and perfluoroalkyl groups. Due to the symmetry of the mixtures, the stability of liquid phases is mainly governed by the number of alkyl and perfluoroalkyl groups in the surfactant molecules and by the alkyl-alkyl and perfluoroalkyl-perfluoroalkyl interaction parameters. In particular, the observed phase behaviour is a direct consequence of the large segment size and dispersive energy values of the perfluoroalkyl groups compared with those corresponding to the alkyl groups.

Although the potential parameters of the molecules were choosen to reproduce the quantitative features of the phase behaviour of some pure surfactants recently studied [29] and their mixtures with n-alkanes, [48] this is the first time we use this theory to predict the high-pressure phase equilibria of these mixtures. We think the most important qualitative trends exhibited by these systems have been predicted by the SAFT-VR approach. In fact, our goal is not to provide an exact description of these mixtures, since no experimental data is available at the moment. We hope this work will promote the research (from an experimental point of view) of this kind of systems in the future. The study of the phase equilibria of model ternary mixtures of n-alkanes, perfluoroalkanes and perfluoroalkylalkanes is continued in subsequent work [49].

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

Substance	m	λ	σ (Å)	ϵ/k_B (K)
C_1H_4 [a]	1.00	1.444	3.670	168.8
C_2H_6 [a]	1.33	1.449	3.788	241.8
C_3H_8 [a]	1.67	1.452	3.873	261.9
$n-C_4H_{10}$ [a]	2.00	1.501	3.887	256.3
$n-C_5H_{12}$ [a]	2.33	1.505	3.931	265.0
$n-C_6H_{14}$ [a]	2.67	1.552	3.920	250.4
$n-C_7H_{16}$ [a]	3.00	1.563	3.933	251.3
$n-C_8H_{18}$ [a]	3.33	1.574	3.945	250.3
$n-C_9H_{20}$ [a]	3.67	1.602	3.938	241.3
$n-C_{10}H_{22}$ [a]	4.00	1.621	3.959	227.3
C_1F_4 [b]	1.00	1.287	4.346	278.6
C_2F_6 [b]	1.37	1.339	4.436	289.0
C_3F_8 [b]	1.74	1.359	4.474	298.8
$n-C_4F_{10}$ [b]	2.11	1.406	4.452	284.2
$n-C_5F_{12}$ [c]	2.48	1.421	4.469	282.0
$n-C_6F_{14}$ [d]	2.85	1.432	4.456	283.1
$n-C_7F_{16}$ [e]	3.22	1.436	4.464	285.3
$n-C_8F_{18}$ [c]	3.59	1.462	4.472	274.0
$n-C_9F_{20}$ [f]	3.96	1.460	4.475	279.3
$n-C_{10}F_{22}$ [f]	4.33	1.465	4.477	278.9

[a] [40], [b] [30], [c] [13], [d] [39], [e] [38], and [f] [32].

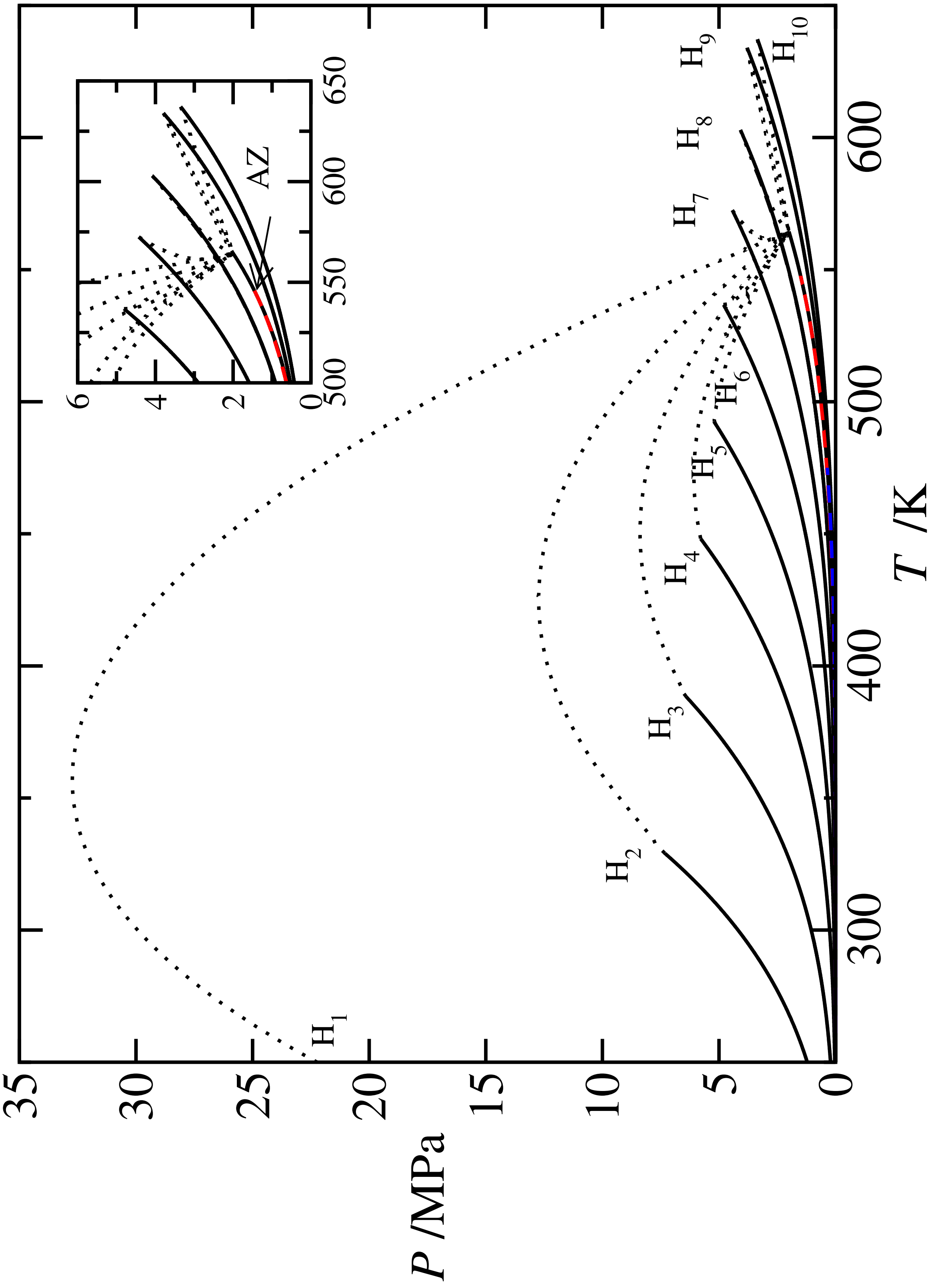

Figure 1. *PT* projections for the homologous binary mixtures $H_i + F_6H_6$, with i = 1 to 10, predicted by the theory. The solid curves correspond to the vapour pressures of pure components, the dotted curves are the gas-liquid critical lines for all the binary mixtures, and the dashed curves are the azeotropic lines for the mixtures of F_6H_6 with the three longest n-alkanes. Note that the vapour-pressure curve corresponding to methane is not visible since is out of the range of the scale shown in the figure. The near critical region of the perfluorohexylhexane can be seen clearly in the inset.

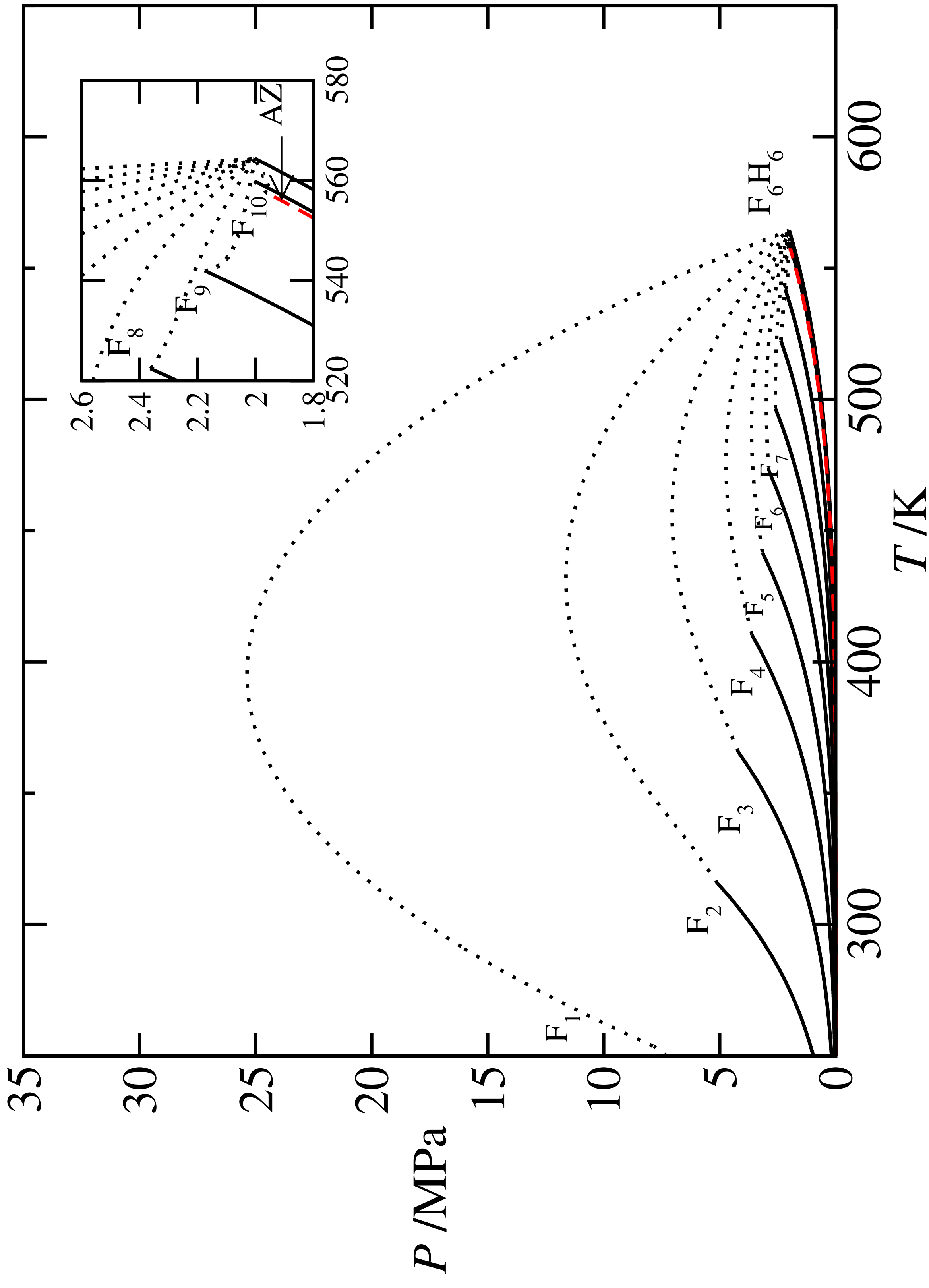

Figure 2. PT projections for the homologous binary mixtures F_i + F_6H_6, with i = 1 to 10, predicted by the theory. The legends are the same as in Fig. 1. The dashed curve in this case represents the azeotropic line of the F_6H_6 + F_{10} binary mixture. Note that the vapour-pressure curve corresponding to perfluoromethane is not visible since is out of the range of the scale shown in the figure. The near critical region of the perfluorohexylhexane can be seen clearly in the inset.

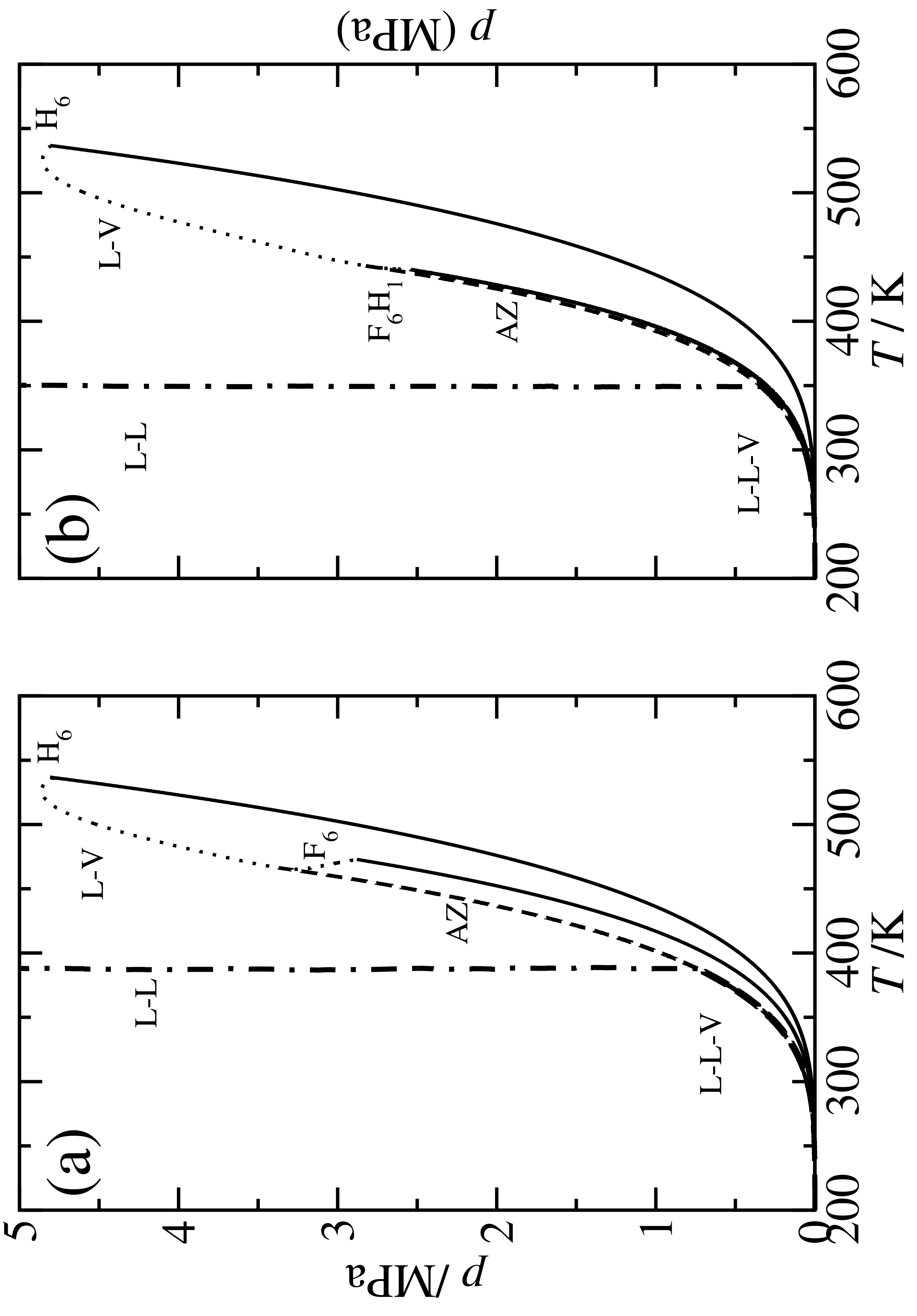

Figure 3. *PT* projections for the binary mixtures (a) H_6 + F_6 and (b) H_6 + F_6H_1 predicted by the theory. The solid surves represent the vapour pressures of the pure components, the dotted curves are the gas-liquid critical lines (LV), the dot-dashed curves are the liquid-liquid critical lines (LL), the dashed curves are the azeotropic lines (AZ), and the long-dashed curves are the three-phase liquid-liquid-vapour lines (LLV).

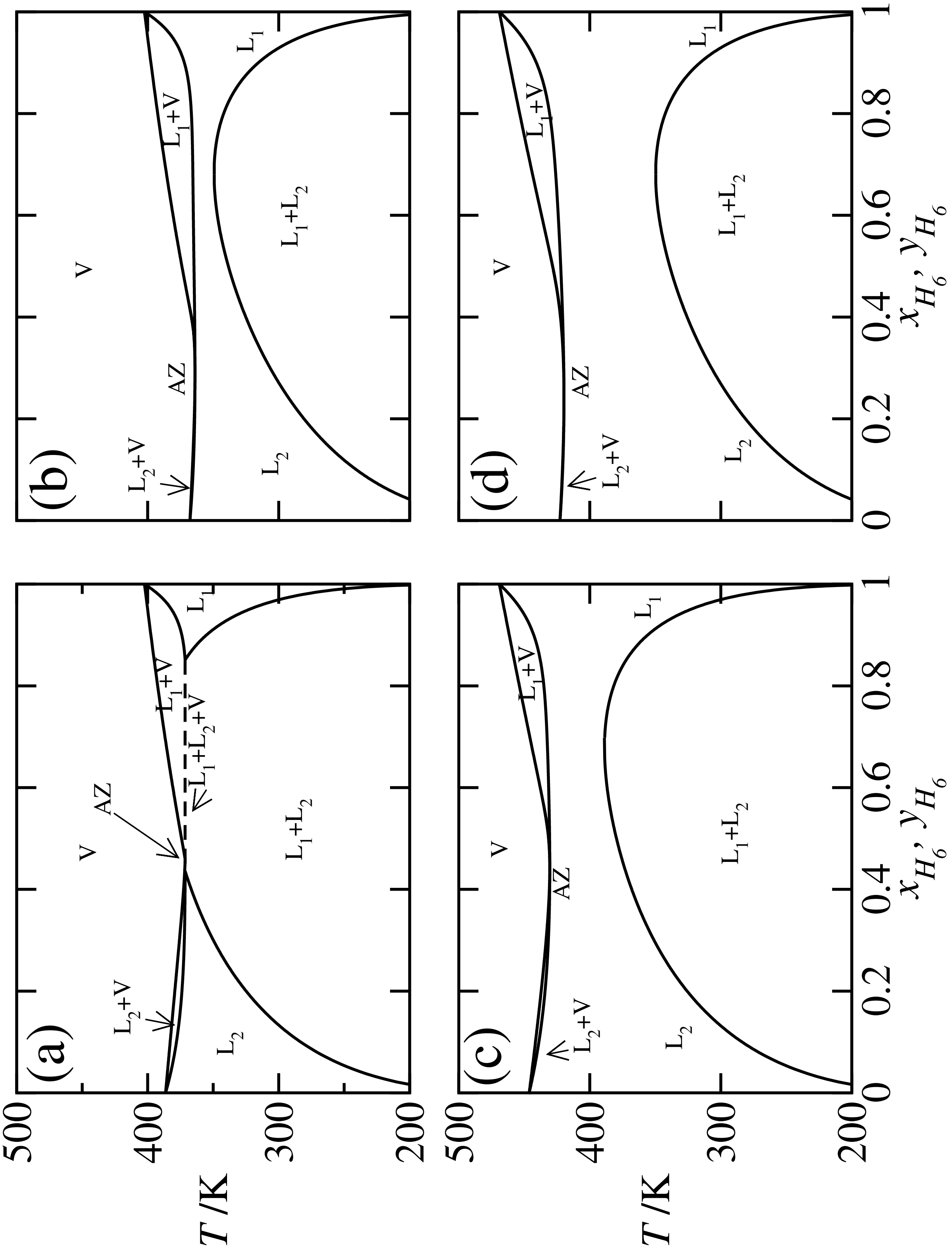

Figure 4. Tx constant-pressure slices predicted by the theory for the two systems considered in the previous figure at different pressures: (a) H_6 + F_6 at $P = 0.5\,\mathrm{MPa}$, (b) H_6 + F_6H_1 at $P = 0.5\,\mathrm{MPa}$, (c) H_6 + F_6 at $P = 1.789\,\mathrm{MPa}$, and (d) H_6 + F_6H_1 at $P = 1.789\,\mathrm{MPa}$. The solid curves correspond to the two-phase boundaries and the dashed line represents the three-phase liquid-liquid-vapour coexistence (L_1L_2V).

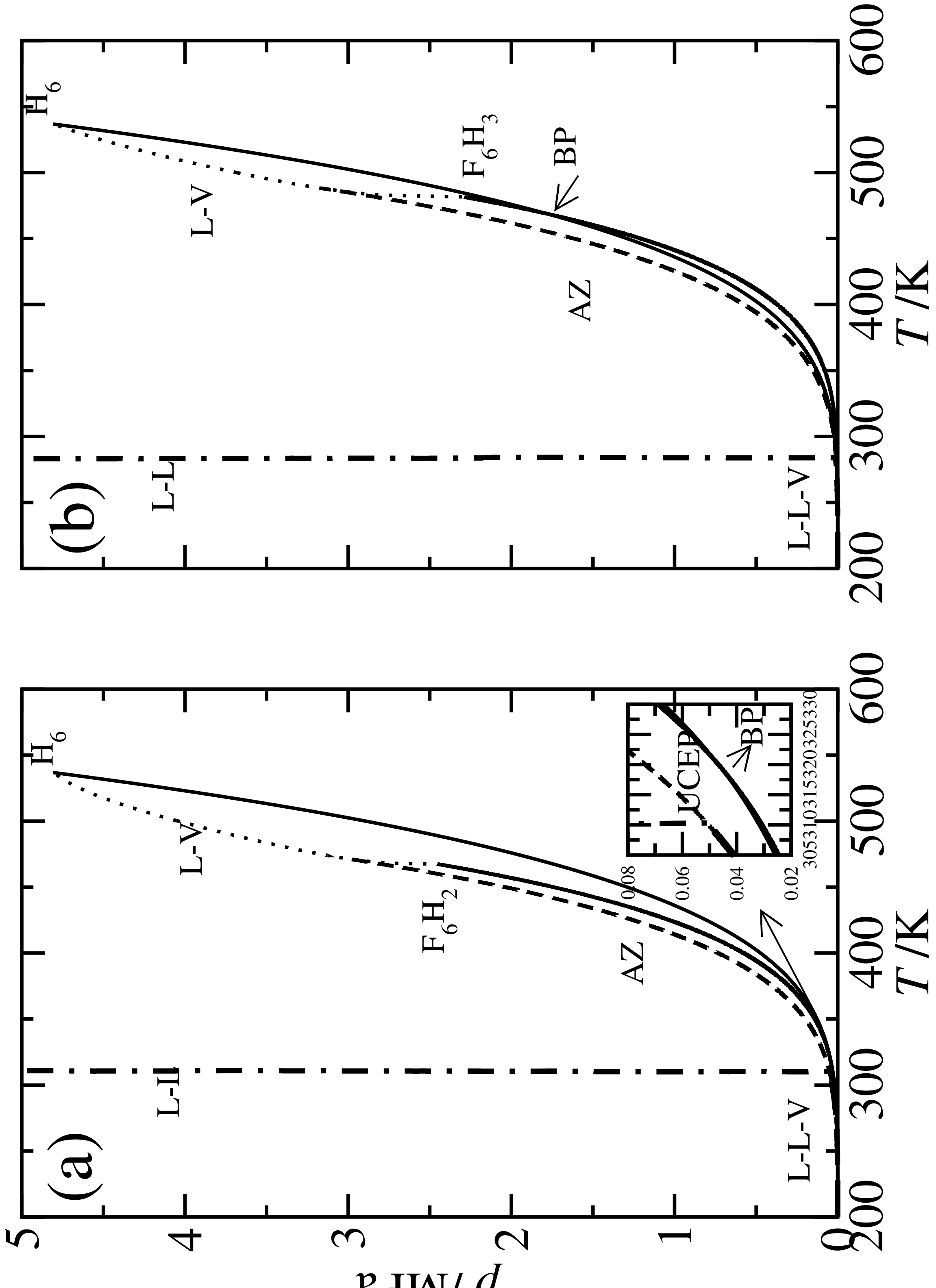

Figure 5. *PT* projections for the binary mixtures (a) H_6 + F_6H_2 and (b) H_6 + F_6H_3 predicted by the theory. The legends are the same as in Fig. 3. The Bancroft point and the UCEP for the H_6 + F_6H_2 binary mixture can be seen clearly in the inset of part (a) of the figure.

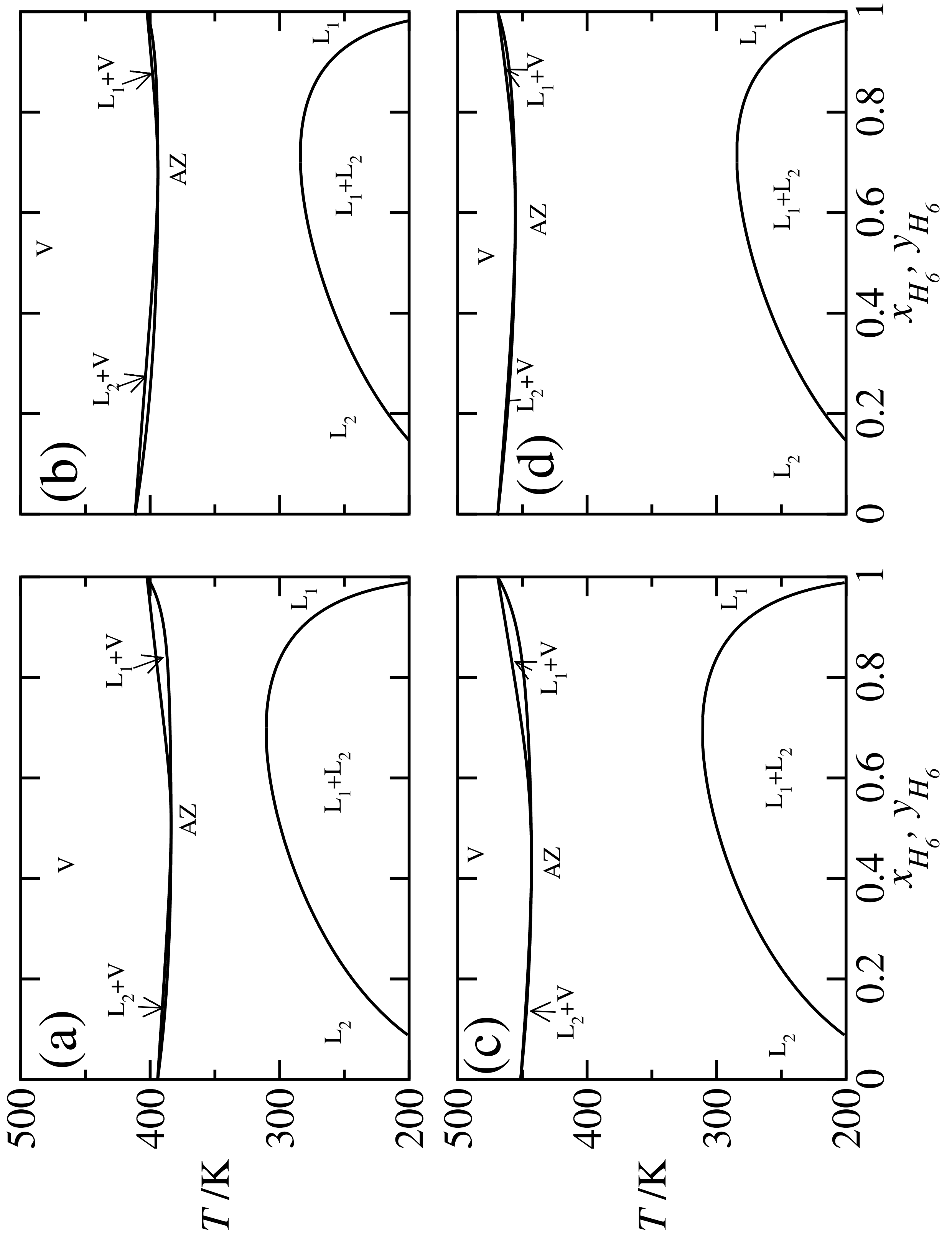

Figure 6. Tx constant-pressure slices predicted by the theory for the two systems considered in the previous figure at different pressures: (a) H_6 + F_6H_2 at $P = 0.5\,\mathrm{MPa}$, (b) H_6 + F_6H_3 at $P = 0.5\,\mathrm{MPa}$, (c) H_6 + F_6H_2 at $P = 1.789\,\mathrm{MPa}$, and (d) H_6 + F_6H_3 at $P = 1.789\,\mathrm{MPa}$. The legends are the same as in Fig. 4. Note the absence of three-phase liquid-liquid-vapour coexistence in the current system.

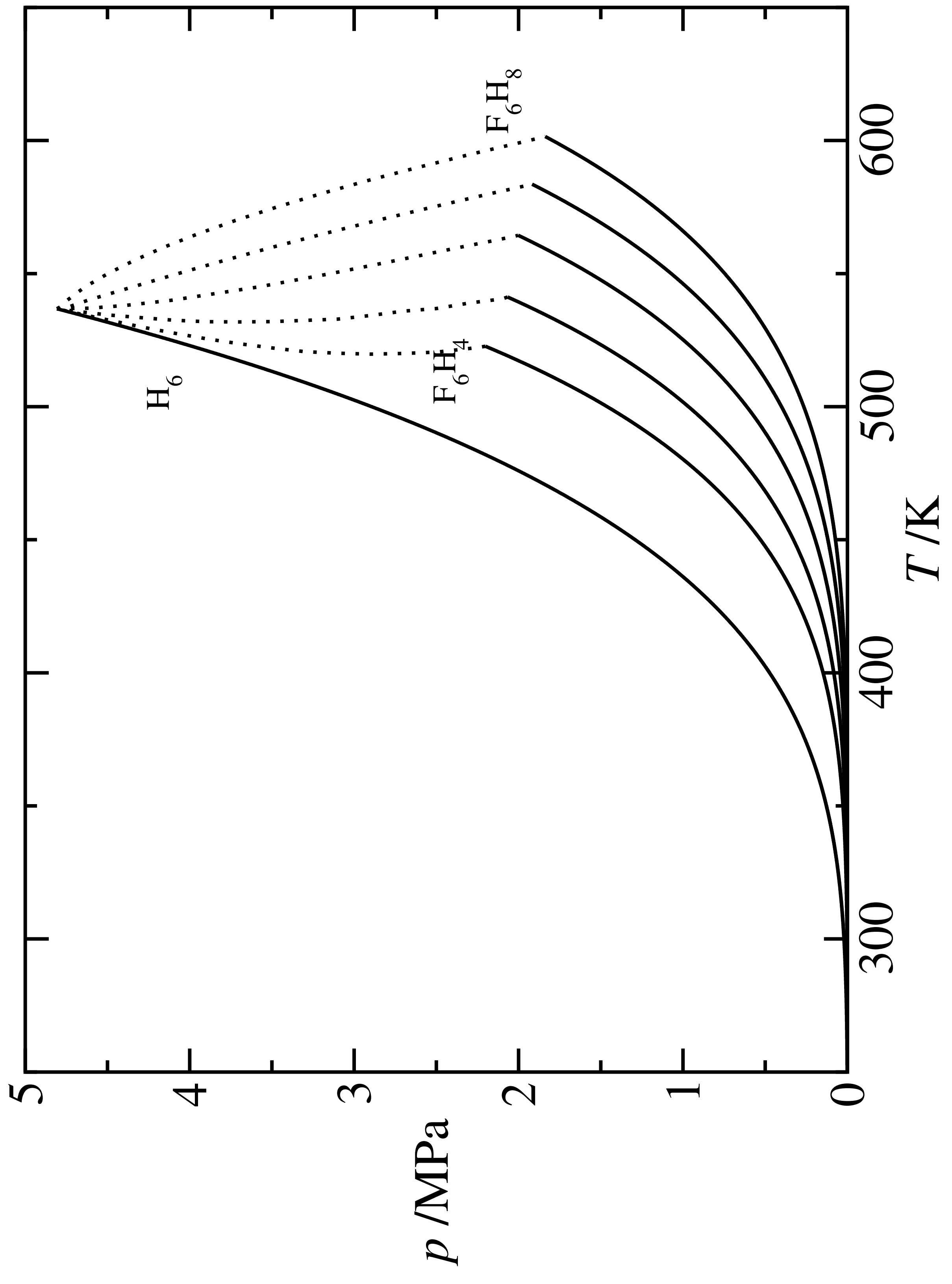

Figure 7. PT projections for the binary mixtures H_6 + F_6H_4, + F_6H_5, + F_6H_6, + F_6H_7, and + F_6H_8 predicted by the theory. The solid curves correspond to the vapour-pressure of pure components, and the dotted curves to the gas-liquid critical lines.

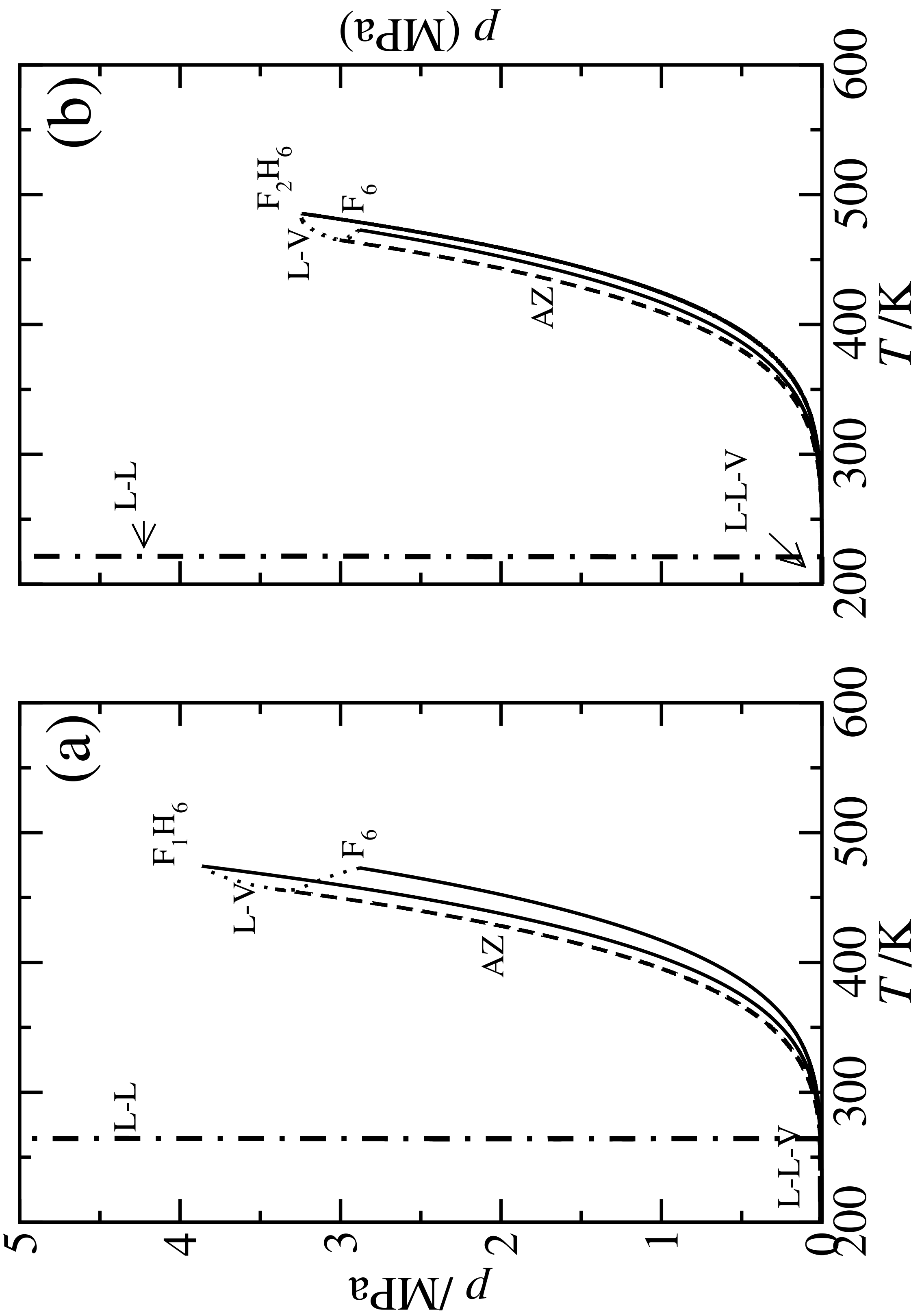

Figure 8. *PT* projections for the binary mixtures (a) F_6 + F_1H_6 and (b) F_6 + F_2H_6 predicted by the theory. The legends are the same as in Fig. 3.

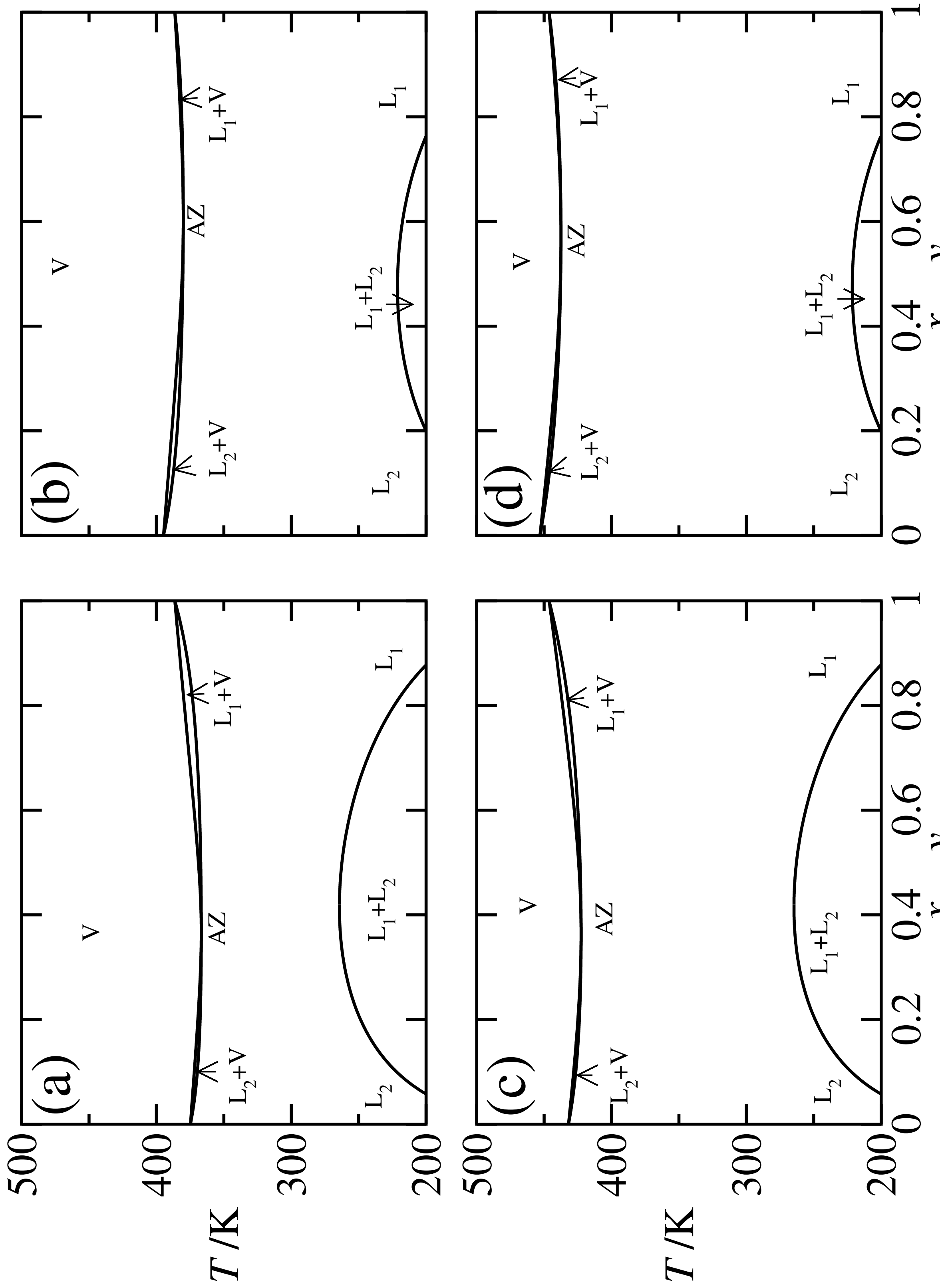

Figure 9. Tx constant-pressure slices predicted by the theory for the two systems considered in the previous figure at different pressures: (a) $F_6 + F_1H_6$ at $P = 0.5$ MPa, (b) $F_6 + F_2H_6$ at $P = 0.5$ MPa, (c) $F_6 + F_1H_6$ at $P = 1.789$ MPa, and (d) $F_6 + F_2H_6$ at $P = 1.789$ MPa. The legends are the same as in Fig. 4.

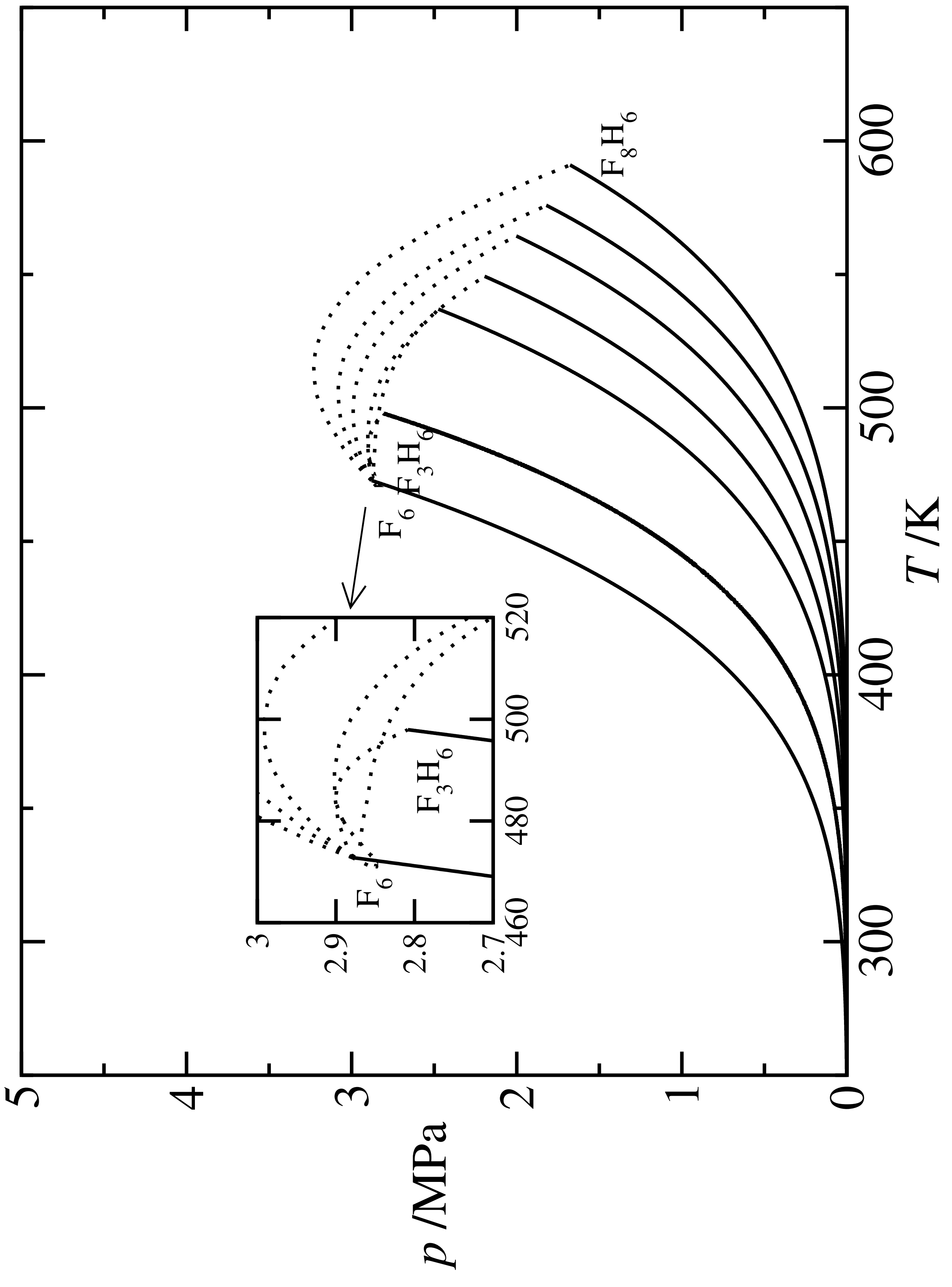

Figure 10. *PT* projections for the binary mixtures F_6 + F_3H_6, + F_4H_6, + F_5H_6, + F_6H_6, + F_7H_6, and + F_8H_6 predicted by the theory. The legends are the same as in Fig. 7. The near critical region of the perfluorohexane can be seen clearly in the inset.