Complex Interfacial Behaviour of Mixtures of Fluorinated and Hydrogenated Alcohols

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1.Abstract

The interfacial behaviour of mixtures of fluorinated and hydrogenated alcohols was studied.

The surface tension of trifluoroethanol (TFE)and mixtures of TFE with ethanol, 1-propanol, 1-butanol and tert-butanol was measured. All mixtures display minima. The excess molar volumes of the mixtures were also measured and found to be positive, increasing with the chain length of hydrogenated alcohol. The mixtures display a complex behaviour that indicate high cohesion in the bulk and low cohesive forces at the interface.

Langmuir films of 1H,1H-Perfluoro-1-tetradecanol (14F), 1H,1H,-Perfluoro-1-octadecanol (18F) and 1-Octadecanol (18H) and their mixtures were prepared, transferred to the surface of silicon wafers and analysed by AFM. Films of pure 18F display starry-hexagonal domains that form spontaneously at room temperature and low surface density. The domains are compatible with 2D crystals and seem to melt at higher temperature forming circular domains. Films of pure 14F at room temperature display a "lacy" pattern that seem to crystalize at low temperature. Mixtures of 14F and 18F display a combination of the "lacy" patterns and hexagonal domains characteristic of the pure alcohols. Molecular dynamics simulations of the pure Langmuir films seem to confirm the tendency of fluorinated species to crystalize at the surface of water, while hydrogenated species form liquid-like domains.

Langmuir-Blodgett films of a mixture of 18H and 18F display circular and hexagonal domains suggesting that the two alcohols phase separate in 2D. Simulations showed no evidence of phase separation within the time scale of the simulation.

Key words: Langmuir films; Fluorinated alcohols; AFM; Surface tension; aneotropy

1.   Introduction

Binary mixtures of alkanes and perfluoroalkanes are highly non-ideal in spite of the apparent similarity between these substances. They exhibit large regions of liquid–liquid immiscibility, large positive deviations from Raoult's law and large positive excess properties (such as the excess enthalpy and volume), a clear indication of weak unlike interactions. Since the late 40s the potential application of these systems as refrigerant mixtures or as immiscible solvents has motivated their study. However in recent years, perfluoroalkanes have become key fluids in a wide range of fields due to their chemical inertness, biocompatibility and peculiar physical properties [1,2]. For example, from medical applications, where they find use as oxygen carriers in blood substitute formulations [3] or as fluids in eye surgery, to technological applications as solvents for biphasic synthesis, fire-extinguishers or lubricants. As a result, considerable work has been done on the theoretical and computational modelling of n-alkane + n-perfluoroalkane mixtures [4,5,6,7,8,9,10,11,12,13,14]. In particular, special attention has been given to understanding the unlike molecular interactions [5,6,14]. These studies concluded that the usual Lorentz–Berthelot combining rules for the crossed intermolecular potential parameters fail to give satisfactory results, because of an unusually weak hydrocarbon–fluorocarbon attractive interaction.

Structurally, the substitution of hydrogens for the larger and heavier fluorine atoms results in a larger cross-sectional area for fluorinated chains (0.283 nm^2 compared to 0.185 nm^2) and consequently higher densities and molar volumes for n-perfluoroalkanes when compared with n-alkanes of the same number of carbon atoms.

Another important difference between fluorinated and hydrogenated chains is conformational. For the n-alkanes, the value of the dihedral angle at the energy minimum of a "trans" C-C bond is exactly 180⁰, so that the chains tend to be in their all-trans planar form. For the n-perfluoroalkanes, the dihedral angle at minimum energy is not exactly 180⁰, and as a consequence, perfluorinated chains display a helical conformation and rigidity, which contrasts with the flexible character of hydrogenated chains. It is believed that one of the consequences of chain stiffness in liquid fluorocarbons is less efficient molecular packing and the existence of "holes" in the liquid. This can explain (at least in part) the enhanced solubility of simple gases (e.g., oxygen, nitrogen, etc.) in liquid perfluoroalkanes.

The key idea of this project is to study the peculiar properties of mixtures of fluorinated and hydrogenated species at interfaces. In particular, the possibility of occurring phase separation at the interface will be investigated. Ultimately, the aim is to understand and control the resulting formation of domains/patterns.

Hydrogenated and fluorinated alcohols were chosen for this study. The presence of the OH group is useful to guarantee an adequate orientation and anchoring of the molecules at the interface. The possibility of strong interactions between the two types of alcohols through hydrogen bonding adds an extra interesting challenge to the investigation.

The interfacial behaviour of mixtures of hydrogenated and fluorinated alcohols, that simultaneously interact through strong hydrogen bonding, was thus inspected. In the case of short chain alcohols (trifluoroethanol, ethanol, 1-propanol, 1-butanol and tert-butanol) which are liquids at room temperature and soluble in water, surface tensions as a function of composition were measured as well as liquid densities. For long chain alcohols (1H,1H-Perfluoro-1-tetradecanol (14F), 1H,1H,-Perfluoro-1-octadecanol (18F) and 1-Octadecanol (18H)) which are solids and insoluble in water, Langmuir films at the surface of water

were prepared, transferred to the surface of silicon wafers and analysed by atomic force microscopy (AFM). All films were studied by molecular dynamics computer simulation.

Excess volumes for mixtures of TFE with short chain hydrogenated alcohols have been reported in the literature and in the case of TFE + ethanol, vapour-liquid equilibrium data and excess enthalpies are also found [15]. As for surface properties, no studies could be found in the literature.

Mixtures of TFE with short chain hydrogenated alcohols display a very complex behaviour when compared with mixtures of hydrogenated alcohols or with mixtures of alkanes and perfluoroalkanes: large and positive excess molar volumes are observed (unlike those of mixtures of hydrogenated alcohols with similar chain length, which are very small), as well as large and negative excess enthalpies (unlike those of mixtures of alkanes and perfluoroalkanes which are large and positive)[4-14]. In a recent work [15] it was shown that the large negative excess enthalpy found for TFE + ethanol mixtures, result from a preferential hydrogen bond between the two alcohols. These mixtures thus have very complex bulk properties and it would be interesting to understand how they behave at the interface. Since there is a lack in literature of surface properties this work intends to fill this void.

Surface tensions of mixtures of alkanes and perfluoroalkanes have been described in the work of Mukerjee *et al.* [16] and Handa *et al.* [17] where a minimum in the surface tension of hexane and perfluorohexane mixture is reported. The minimum in the surface tension (aneotrop) of this mixture cannot be fully explained by simple models and is qualitatively interpreted as a consequence of week cross interactions in the bulk.

Qaqish et al. [18] studied the phase separation of long chain fluorinated and hydrogenated acids at the air-water interface. No information could be found in the literature concerning mixtures of long chain alcohols. In the work of Qaqish *et al.* domains are observed for mixtures of arachidic acid ($C_{19}H_{39}COOH$) and perfluorotetradecanoic acid ($C_{13}F_{27}COOH$). The observed structures are composed mainly of arachidic acid and the continuous phase is essentially the perfluorinated acid. Increasing temperature and time increase the size of the hexagonal domains. It was also found that shaking the spreading solutions prior to deposition may change the observed domains which is very intriguing. The mechanism proposed to explain the growth of the hexagonal domains is the 2D Ostwald ripening mechanism as an alternative to pure nucleation-and-growth mechanism [19].

2. Experimental Section

1-Octadecanol was obtained from Sigma-Aldrich (99%), both 1H,1H-Perfluoro-1-Octadecanol and 1H,1H-Perfluoro-1-tetradecanol were obtained from Fluorochem (95%). Ethanol was obtained from Pacreac (99.5%), Propan-1-ol was obtained from Lab Scan (99.5%), both 1-Butanol and Tert-Butanol were obtained from Sigma Aldrich (99.7%) and 2,2,2-Trifluoroethanol was obtained from Apollo (99%).

Short chain hydrogenated alcohols were kept in molecular sieves with 0.3nm pores. Fluorinated alcohols were used as received. The water content of TFE was regularly checked using a Karl-Fischer coulometer. TFE was used under a dried nitrogen flux. It was found to decompose when kept in molecular sieves. All mixtures were prepared gravimetrically in an analytical balance (resolution of 1×10^{-5} g).

The solid alcohols were dissolved in a convenient spreading solvent. The fluorinated alcohols were dissolved in a mixture of 1,1,2-Trichlorotrifluoroethane (99.9+% Aldrich) and perfluorohexane (99% Aldrich) 9:1 (V:V). Hydrogenated alcohols were dissolved in Hexane (Merck). Concentrations on the order of 0.2 to 1 mg/mL were prepared, followed by at least 10min of ultrasonication. Perfluorohexane and hexane were kept in molecular sieves with 0.3nm pores. 1,1,2-trichlorotrifluoroethane was distilled and kept under nitrogen atmosphere. It was found to decompose when kept in molecular sieves. Solid compounds were kept in a closed glass vessel in a dry atmosphere.

The water used in cleaning or as the subphase was purified using Milli-Q system (Milipore). The solutions were spread with gas-tight Hamilton syringes (100 to 250μL).

The surface tension of short chain alcohols was measured by an optical tensiometer using the pendant drop method. Using ADSA analysis method, axisymmetric drop shape analysis [20]. The software used in this work was developed by Neumann *et al.* [21].

The densities were measured in a vibrating-tube Anton Paar DMA 5000 densimeter. The DMA 5000 has a built-in temperature control system, based on Peltier units, which is stable at ±0.001K. This densimeter was calibrated with water (distilled, deionized in a Milli-Q 185 Plus water purification system and freshly boiled) and at air at 20.000ºC, taking into account atmospheric pressure. The calibration was checked with water over the whole range of operating temperatures, and the maximum deviation from literature values was found to be less than 2×10^{-5} g cm^{-3}. The cleanliness of the measurement cell was verified at the beginning of each series of measurements by checking the measure of the density of air.

Langmuir films were produced on a NIMA trough type 601. A submerged platinum thermometer was used to register the temperature of the subphase. The surface tension was measured with a Wilhelmy plate sensor using a filter paper plate.

The desired quantity of the film-forming substance solution is spread drop by drop at the subphase surface with the help of a syringe. After waiting at least 10 minutes for solvent evaporation, the film can be compressed. The solutions are prepared before the deposition by weighting a certain amount of the long chain alcohol with a precision of 1×10^{-5} g in a calibrated flask of 25mL. The solutions of mixtures of alcohols are prepared by mixing solutions of pure compounds.

Langmuir-Blodgett films were prepared by placing a silicon wafer (8 cm²) vertically in the water before the solution spread. Once the solution was spread and the solvent evaporated, the film was compressed up to the desired surface pressure / surface density. Silicon wafer was chosen due to its hydrophilic properties after proper treatment [22]. The silicon wafers were scrubbed with an aqueous solution of detergent and rinsed with Milipore water. The wafer was then submersed in chromic mixture for at least 30 minutes and rinsed with Milipore water. Throughout this work it is assumed that the film extraction process does not change the structure produced at the surface of water.

The compression speed ranged from 5 to 30 cm²/min. Langmuir-Blodgett film were extracted at 3 mm/min. The temperature was kept constant at ±1K during experiments.

There are several AFM techniques to scan the surface of samples. Due to the softness of the studied films, the scans were made using tapping mode. Attempts made to scan the samples in contact mode proved to be unsuccessful. Images from 100 μm to 3 μm width were made with a NANOSENSOR PPP-NCLAuD tip (resonance frequency204-497 kHz), PID control parameters of P-2000, I-1000, D-0 and 256 lines per image and 256 points per line. Image treatments were performed using WSxM 5.0 software developed by Horcas et al.[23] and consisted in Plane, Flatten, Equalize and line removal.

All simulations were performed using the *DL_POLY Classic* software. The raw data was analysed using the software integrated in *DL_POLY* package, as well as additional programs developed in our laboratory.

Alcohol molecules were modelled with the OPLS-AA force Field[24]. Water was modelled with the three site spc-e rigid body model[25]. Trajectories were visualised using the VMD software, developed by Humphrey et al.[26].

To quantitatively analyse the organization of the monolayer at the surface of water an order parameter was calculated, defined as follows. The orientation of each alcohol molecule was defined by calculating a normalized vector with origin at the oxygen atom and ending at the carbon atom of the terminal group. The order parameter, calculated for each time step, is defined as the average of the scalar product of the orientation vectors for each molecule pair,

$$O_u = \langle \vec{u}_i . \vec{u}_j \rangle_{i \neq j}, \tag{6}$$

The order parameter can display values between -1 to 1. 1 indicates that all molecules are parallel to each other in the same direction. 0 represents a disordered monolayer.

3. Results and Discussion
Short chain Alcohols

The surface tension of pure TFE was studied in a temperature range of 266.15K to 308.15K. The results are reported plotted in Figure 1.

In Figure 1, our measurements are also compared with those of Kim et al.[27]. As can be seen, although the temperature dependence is very similar for both sets of results, our data are systematically lower (~5%). It should be mentioned that the results of Kim et al. were obtained using a different experimental method (Wilhelmy plate) and that their TFE was used as received, without further purification. Since TFE is highly hygroscopic, a small amount of absorbed water can easily explain the difference in surface tension.

Mixtures of TFE with ethanol, propanol, 1-butanol and tert-butanol were studied as a function of composition at 293.15K. The results are plotted Figure 2.

As expected the surface tension of hydrogenated alcohols increases with chain length. The measured values are in agreement with those reported in the literature [28-29]. Tert-Butanol is the only hydrogenated alcohol that does not follow this tendency.

All systems display minima in surface tension, more pronounced as the difference of surface tension between pure compounds decreases.

Mixtures richer in hydrogenated alcohols display a typical adsorption behaviour. The component with the lower surface tension (TFE) migrates to the surface in order to minimize the surface tension of the mixture.

Mixtures richer in TFE behave in a different way from what could be expected. Since TFE has the lowest surface tension it could be expected that these molecules would have the tendency to completely cover the surface, driving those of the hydrogenated alcohol to migrate from the surface to the bulk (due to its higher surface tension), remaining the surface tension of the mixture nearly constant. The experimental results show, however, that the presence of hydrogenated alcohol decreases the surface tension of the mixtures to values lower than either pure compound.

The liquid densities of the mixtures of fluorinated and hydrogenated alcohols were also measured at 293.15K and atmospheric pressure. The corresponding excess molar volumes of the mixtures were calculated. The results are plotted in Figure 3.

As can be seen, the excess molar volumes of all mixtures are positive and increase as the chain length of the hydrogenated alcohol increases. Mixtures of TFE with Ethanol, 1-Propanol and 1-Butanol have been studied by Atik et al.[30,31]. Their results although obtained at a different temperature, 298.15K, (V_m^E ½ ethanol = 0.8172 cm^3 mol^{-1}, V_m^E ½ 1-Propanoll = 1.0192 cm^3 mol^{-1} and V_m^E ½ 1-butanol = 1.0421 cm^3 mol^{-1}) seem to agree with those obtained in this work.
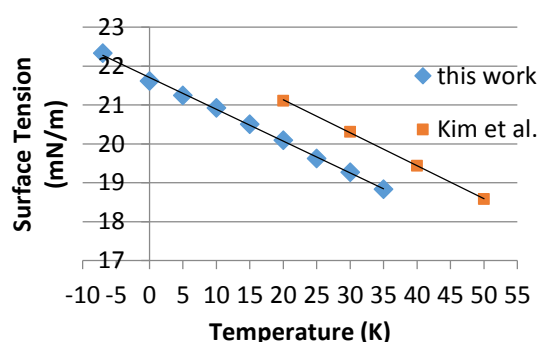

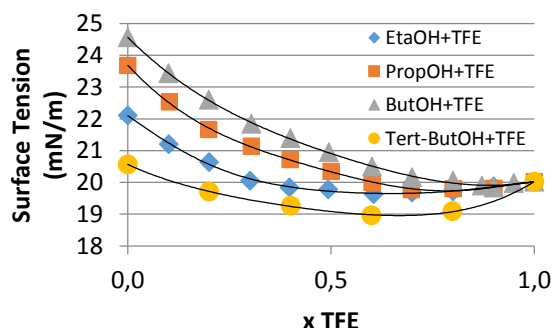Figure 1 - Surface Tension of TFE as a function of temperature.

Figure 2 - Surface Tension of mixtures of hydrocarbon and fluorinated alcohols as a function of composition at 293.15K.
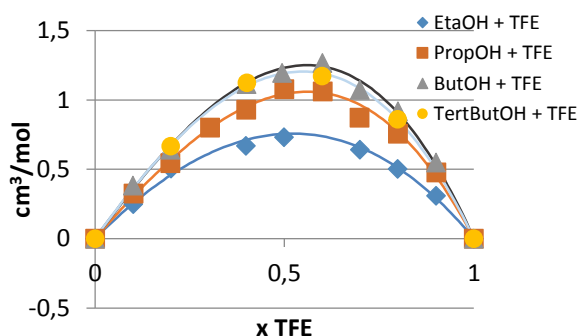

Figure 3 – Excess molar volume of hydrogenated alcohols and TFE mixtures. Points represent experimental results and the solid lines the Redlich-Kister equation.

As previously explained, one of the objectives of this work is to understand the effect of mixing fluorinated and hydrogenated molecules that simultaneously associate through hydrogen bonding.

Due to its fundamental and technologic importance, mixtures of ethanol and TFE have been studied by a number of authors. Minamihonoki et al.[32] measured the excess molar volumes and excess molar enthalpies. The former were found to be positive ($V_m^E{}_{1/2}$ = 0.8 cm^3 mol^{-1}) and the later negative ($H_m^E{}_{1/2}$ = -700 J mol^{-1}). Smith et al.[33] studied the vapour-liquid equilibrium of this system at 298.15K and found negative deviations to Raoults law and a negative azeotrope at $x_{(TFE)}$ = 0.4. The simultaneous existence of a large positive excess molar volume and a large negative excess molar enthalpy (negative deviations to Raoult's law and a negative azeotrope) of mixing is a clear indication of the complexity of this binary mixture.

For comparison, it should be mentioned that mixtures of primary alcohols display positive excess molar volumes and enthalpies, which are very small when the alcohols have similar chain length and increase with the difference in chain length. Thus, the mixture of ethanol and TFE displays an opposite behaviour relatively to mixtures of hydrogenated alcohols. On the other hand, mixtures of alkanes and perfluoroalkanes exhibit large positive excess molar volumes and enthalpies[15]. The negative excess enthalpy of the ethanol + TFE mixture is an indication of stronger cross interaction between the hydrogenated and fluorinated alcohols. The positive excess molar volume can be either a sign of less efficient packing or weaker interaction between the hydrogenated and fluorinated segments, as found for mixtures of alkanes and perfluoroalkanes.

The surface tension as a function of composition of all studied mixtures displays a minimum. Minima in surface tension or aneotropes, denote a complex behaviour in the mixture, are relatively unusual and can be interpreted as an indication of low cohesion in the liquid-vapour interface. Nevertheless, aneotropes have been reported in the literature. Mclure et al. [17] and Handa et al.[17] reported aneotropes for mixtures of alkanes and perfluoroalkanes and Mejia et al. [34] reported aneotropes for binary mixtures of ethanol with alkanes.

Aneotropes cannot be explained by the Gibbs adsorption equation (4). At the aneotrope, the concentration of both the bulk and surface, must be equal [34]. Aneotropes are also frequently related with the proximity of an upper critical solution temperature (UCST) [17,35]. Furthermore, in all systems reported in the literature displaying aneotropes, these can be interpreted as resulting from weak interactions between the two types of molecules in the bulk.

In the case of mixtures of hydrogenated and fluorinated alcohols, however, the interactions between the two components are rather strong as shown by their negative excess enthalpies. Moreover, all mixtures studied in this work demonstrated no sign of phase separation when cooled up to 193.15K or upon heating to 373.15K. In the bulk, hydrogen bonding dominates over the weak dispersion forces between hydrogenated and fluorinated chains [16]. The existence of minima in the surface tension curves must be then related to weak surface cohesion. This suggests that the unfavourable coexistence of alkyl and perfluoroalkyl segments, conditioned by the geometry of the interface, is not compensated by hydrogen bonding.

Long chain Alcohols

Langmuir fims of 18H, 14F, 18F and their mixtures

The behaviour of Langmuir films at the air-water interface of 18H, 18F, 14F and their mixtures was studied. The films were transferred to the surface of silicon wafers using the Langmuir-Blodgett technique and analysed by Atomic Force Microscopy (AFM). MD simulations were performed to obtain molecular level insight of the behaviour of the films of both pure species and mixtures.

Langmuir isotherms of 18H, 18F and their mixtures were obtained at 293.15K and are shown in Figure 4.

The results obtained for 18H has consistent with those from the literature [36]. There are three regions characterizing the 18H isotherm. A vapour-liquid expanded equilibrium plateau where π remains practically zero. A condensed tilted phase where the surface pressure starts to increase and the solid untilted phase after the inflection at 12mN/m.

18F displays a different behaviour in which only two regions are observed: a) a plateau at low π generally interpreted as a region of liquid-vapour equilibrium; b) a region of high surface density corresponding to a condensed monolayer, generally described as a hexatic phase.

The major difference, between 18H and 18F is the presence of a clear kink in the former, distinguishing the transition from a tilted to an untilted monolayer. Another important difference is the difference in the extrapolated areas to π=0 mN/m. While 18H has an area of 21.5 Å^2/molecule, 18F has an area of 28.5 Å^2/molecule. These results are coincident with the literature and with the cross section of hydrogenated and fluorinated chains.

As could be expected, the Langmuir isotherms of the mixtures are located between those of the pure alcohols. It should be noted that isotherms corresponding to an ideal 2D mixture and to a mixture that separates in two completely immiscibility phases will display exactly the same areas per molecule.
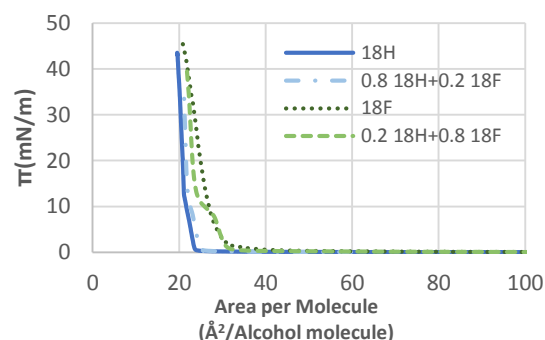

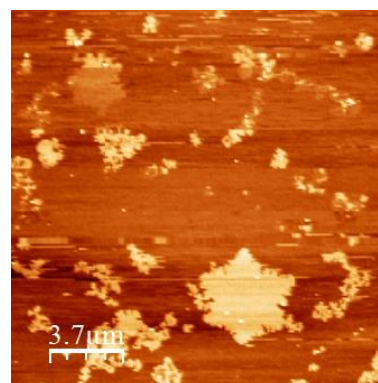Figure 4 - Langmuir Isotherms of 18F and 18H, pure and mixtures, at 293.15K.

Figure 5– AFM scan of mixture between 18F and 18H (0.8-0.2) at 70Å^2/molecule - topography contrast

In order to obtain a deeper understanding of the structure of the Langmuir films, these were transferred to the surface of silicon wafers and analysed using Atomic Force Microscopy (AFM).

Figure 5 shows an AFM scan of a mixture richer in 18F (80%mol). It shows several hexagonal domains, the largest having between 2μm and 5μm width. Height profiles indicate that the average thickness of the film ranges between 1.7nm and 2.2nm, which is compatible with a monolayer. Small clusters with heights comparable with those of the hexagonal domains are also seen.

Figure 6 shows the AFM image of a mixture richer in 18H (80%mol). In addition to the hexagonal domains, it also displays several circular domains between them. Hexagonal domains now have from 1μm to 3.5μm width. The height of the hexagonal domains are similar to those found on the 18F richer mixture.

Circular domains are commonly related to the presence of 2D liquids in Langmuir Films. Hydrogenated alcohols are known to form 2D liquids at room temperature. The images show an additional interesting characteristic. The liquid circular domains seem to be surrounded by hexagonal domains, as if they were preventing them to coalesce.

The AFM scans clearly shows evidence of phase separation. Phase separation cannot be inferred by the Langmuir isotherms.

Langmuir-Blodgett films of the pure alcohols were also produced and analysed by AFM. This was done to obtain a basis of comparison as no evidence of crystallization was expected in the pure films.

The AFM scan of Langmuir-Blodgett film of pure 18H, shows a flat surface, suggesting that the coalescence of 18H 2D liquid domains produces a homogeneous surface. Several unsuccessful attempts were made in order to demonstrate the presence of circular domains at low pressure, at the vapour-liquid equilibrium region.

In Figure 7, the AFM scan of a Langmuir-Blodgett film of pure 18F deposited at 85Å^2/molecule and π=0mN/m, is shown. The figure shows the existence of hexagonal / star shaped domains as well as smaller irregular shaped clusters, with height similar to those previously found. The largest hexagonal domain has 5.5μm width. This result clearly shows that the hexagonal domains form spontaneously in the film of pure fluorinated alcohol at π=0mN/m and that the presence of the hydrogenated alcohols (18H) is not needed to induce the nucleation of hexagonal domains. It also suggest that the composition of the hexagonal domains observed in the mixtures should be predominantly composed by 18F.

In order to obtain a deeper understanding of the 2D crystallization of pure fluorinated alcohols, Langmuir films of a fluorinated alcohol with a shorter chain were studied. It is interesting to note that this is equivalent to increasing the reduced temperature.

The Langmuir isotherms of 14F, 18F and a x(18F)=0.8 mixture of the two alcohols, are shown in Figure 8. The isotherm of pure 14F is more expanded than that of 18F, which is consistent with literature results [36]. The isotherm of the mixture is very close to that of pure 18F.

In Figure 9 the AFM scan of Langmuir-Blodgett film of pure 14F is shown. As can be seen, it displays a completely different type of pattern from what has been observed until now. These "lacy" type structures are approximately 2nm high. The open structure of the domains and the absence of regular shapes suggests lower tendency to accrete or crystalize.

Figure 10 shows the AFM scan of a Langmuir-Blodgett film of a mixture of 18F and 14F alcohols.

As can be seen the image shows an intricate structure that seems to combine the domains observed in the films of pure 18F and 14F. Hexagonal domains are clearly seen, having attached strands that could be considered reminiscent of the "lacy" structures found in the films of pure 14F. The height of both types of structures is similar to those observed before (1.5-2.2nm).
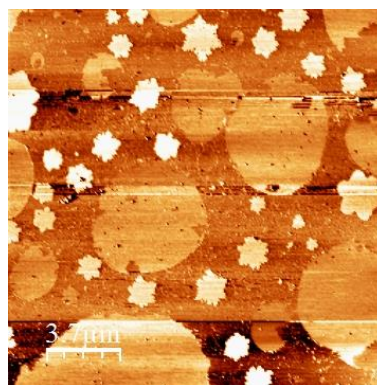

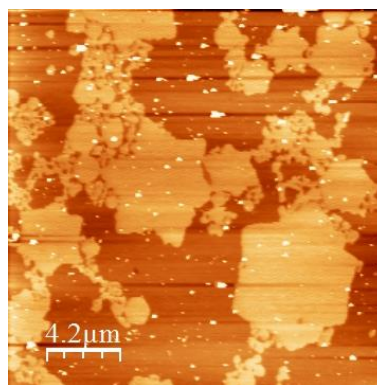Figure 6– AFM scan of a mixture between 18F and 18H (0.2-0.8) at 70Å^2/molecule. phase contrast.

Figure 7 – AFM scan of pure 18F at 85Å^2/molecule - topography contrast.
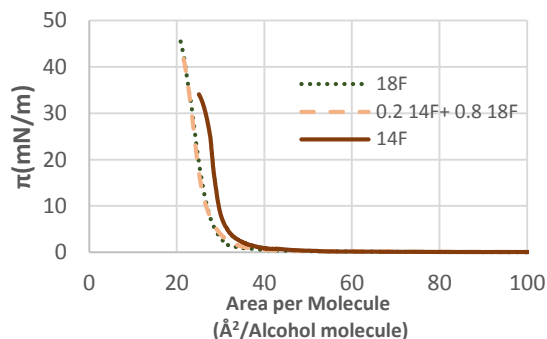

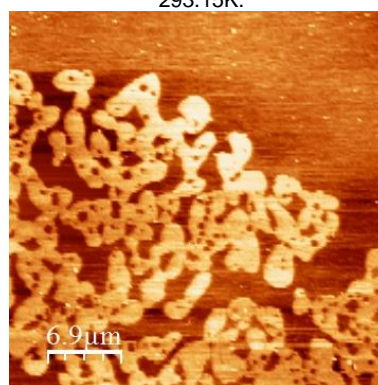Figure 8 - Langmuir balance Isotherm of 18F and 14F, pure and mixtures, at 293.15K.

Figure 9 - AFM scan of pure 14F at 70Å^2/molecule – topography contrast.

Temperature Influence on 18F and 14F

Langmuir and Langmuir-Blodgett films of 14F and 18F were studied as a function of temperature (278.15K and 308.15K).

In Figure 12 the AFM image of a Langmuir-Blodgett film of pure 18F obtained at 308.15K is shown. The system displays predominantly circular domains, very polydisperse. The larger domains are 2.5 μm width and are still hexagonal although displaying much smoother edges than the hexagonal domains found at 293.15K. The height of the domains was found to be similar to those found at lower temperatures (1.5-2nm).

The AFM image of a Langmuir-Blodgett film of pure 18F obtained at 278.15K is shown in Figure 11. As can be seen, at this temperature the domains are star-shaped, with sharp edges, with a maximum width of 1.5μm.

It was noticed that the Langmuir isotherms are displaced to larger areas as the temperature decreases. This seems to be consistent with what is observed in Figure 12 and Figure 11: at the same surface pressure, the free area increases at lower temperatures. In fact, in Figure 12 the hexagonal domains are very close to each other, touching by edges, while in Figure 11 the hexagonal domains are well separated from each other, touching by the vertices. These findings deserve further confirmation.

Finally, in Figure 14 the AFM image of a Langmuir-Blodgett film of pure 14F obtained at 278.15K is shown. As can be seen, at this temperature the "lacy" structures observed at 293.15K (Figure 9) transformed into well individualized geometric domains, almost hexagonal.

Evaporation Casting of pure 18F on silicon

Figure 13 shows the AFM image of a film of pure 18F produced with a different procedure. The film was obtained by spreading drops of the 18F solution directly on the surface of the dry hydrophilic silicon substrate. The amount of 18F deposited was consistent with the formation of a close-packed monolayer. The picture shows a highly dense pattern of hexagonal shapes with a regular size and distribution.

Molecular Dynamics Simulations

MD simulations of Langmuir films of 18H, 18F and 14F and their mixtures were performed as a function of temperature (278.15K – 308.15K).

The purpose of performing these simulations was to obtain molecular level insight into the studied systems, in particular, to obtain arguments in favour of a particular type of organization at the surface of water. It is important to stress that the simulation results were not used to obtain quantitative estimations of the properties of the system, as much larger systems and simulation runs, would probably be required.

The simulations were conducted with the purpose of finding answers to three specific aspects experimentally found:

1- Do fluorinated alcohols have an enhanced tendency, as compared to their hydrogenated analogues, to spontaneously form highly organized aggregates (2D crystals) at the surface of water, even at very low surface coverage?
2- How does this tendency depends on chain length and temperature?
3- Do mixtures of fluorinated and hydrogenated alcohols tend to spontaneously phase separate at the surface of water?

To answer question 1, MD simulations of Langmuir films of 18F and 18H were performed. These simulations started with initial configurations formed by an array of regularly distributed parallel 18F and 18H molecules parallel to each other, placed over a 3.2nm layer of equilibrated water molecules (4000 molecules). The average density of alcohol molecules was quite low, approximately 93Å^2/molecule.
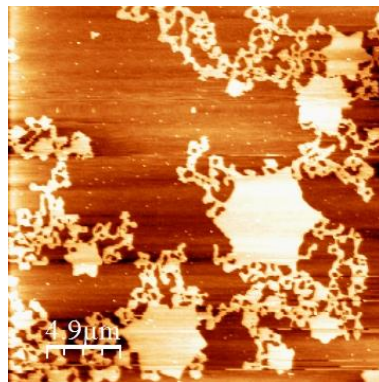
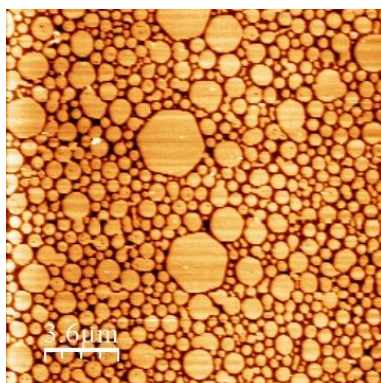Figure 10 - AFM scan of mixture between 18F and 14F (0.8-0.2) at 80Å^2/molecule – topography contrast.

Figure 12 - AFM scan of pure 18F at 30Å^2/molecule and 5mN/m and 308.15K – topography contrast.

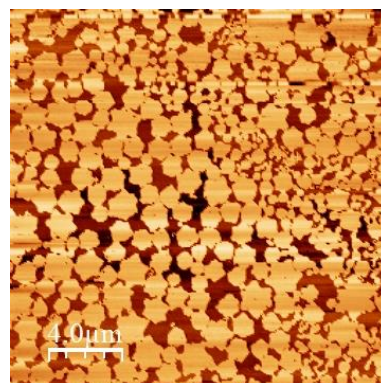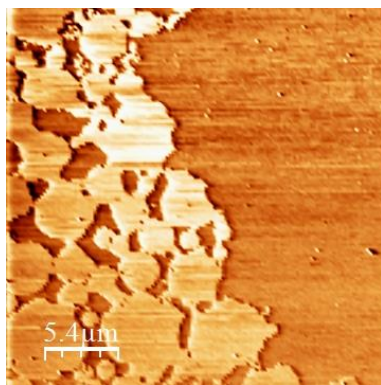Figure 11 - AFM scan of pure 18F at 35Å^2/molecule and 5mN/m and 278.15K – topography contrast.

Figure 14 - AFM scan of pure 14F at 32Å^2/molecule and 5mN/m 278.15K – phase contrast.
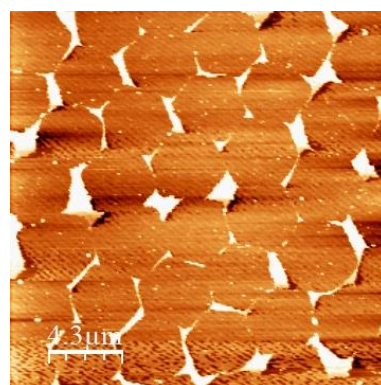
Figure 13 - AFM scan of pure 18F by evaporation casting – phase contrast.

In Figure 15, a snapshot is shown of the simulation boxes of 18F and 18H at 25ps simulation time. As can be seen, both 18F and 18H molecules have clustered together and float at the surface with their OH groups in contact with water and the hydrophobic chains perpendicular to the surface. However, already at this short simulation time, the two systems display very different structures in terms of organization. 18F chains seem to be in a strait conformation, essentially parallel to each other, forming a highly organized structure. The hydrogenated chains of 18H on the contrary, seem to be much disorganized relatively to each other, many of them parallel to the surface and displaying numerous bend conformations. These findings agree with the known flexibility of hydrogenated chains as opposed to the rigidity of fluorinated chains.
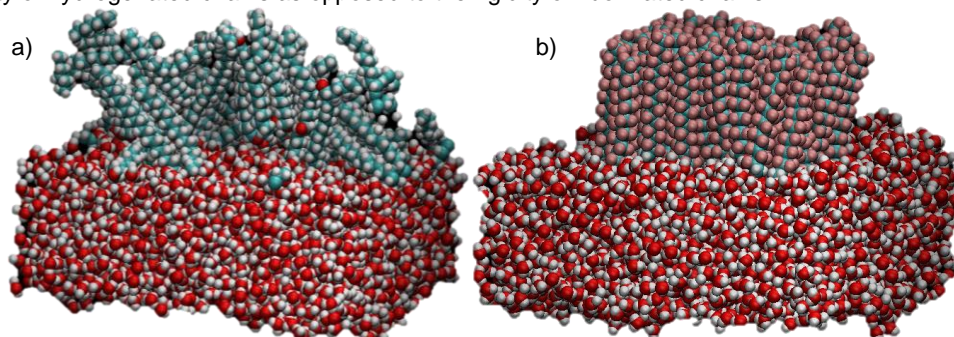

Figure 15 – a) 18H and b) 18F, above water after 25ps of simulation time.

The total simulation time is 5ns, but the overall structure of the films seems not to change after 1-2ns.

The hydrogenated chains of 18H form what seems to be a disorganized liquid like domain. Most chains lie parallel to the surface and display numerous bend conformations.

As previously described, 18F molecules immediately form a highly ordered structure, with almost all molecules parallel to each other and essentially perpendicular to the surface of water. After that, the film moves and tilts at the surface of water but the overall organization of the film seems to remain essentially intact throughout the simulation.

18F presents a hexatic molecular arrangement that can be examined in more detail in Figure 16. Two planes can be devised, one containing all OH groups and the other containing the carbon atoms of terminal CH3 groups (CT). Both planes are parallel and this alignment persists during the simulation. In the vertical projection the hexagonal structure of 18F film is clearly seen. Each molecule is surrounded by six molecules and this order extends throughout the structure. This structure is maintained during the simulation and can be related with the macroscopic hexagonal shapes of 18F, described before.
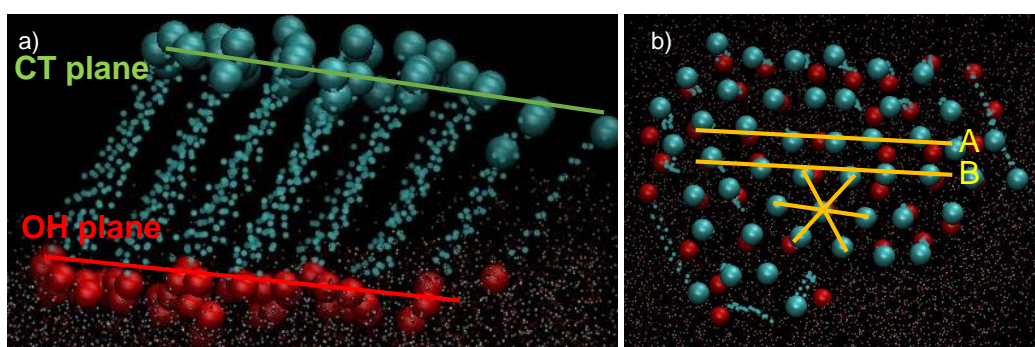

Figure 16 – a) Lateral and b) vertical projections of 18F. Red spheres represent oxygen atoms of OH groups. Blue spheres represent the carbon atoms terminal CH3 groups.

In conclusion, the simulations seem to provide evidence of the tendency of long chain fluorinated alcohols to spontaneously form highly organized aggregates at the surface of water in agreement with the experimental observations. In order to evaluate the influence of chain length on the formation of these aggregates, equivalent MD simulations of 14F films were also performed.

The overall behaviour of the 14F film can be considered very similar to that of 18F just described, but there are differences that are noteworthy. Although each molecule is still locally surrounded by six other molecules, the longer range ordering is less apparent than in the case of 18F.

In Figure 17 the average order parameter of all studied films is shown as a function of simulation time. The order parameter is a measure of how parallel the molecules are to each other within the film and was calculated as explained before.
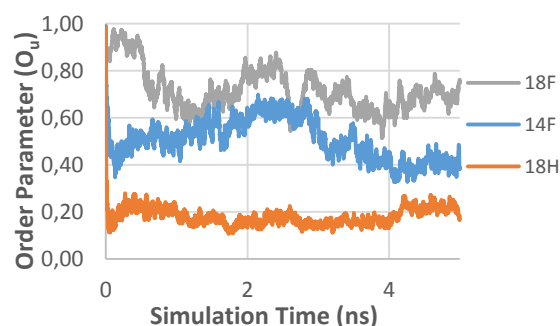

Figure 17 – Evolution of order parameter of Alcohols (18F, 14F, 18H) molecules in time.

The results shown in Figure 17 clearly show that the films formed by fluorinated chains are considerably more organized than that formed by hydrogenated chains. It is also seen that the longer the fluorinated chain the higher the order. These results are likely to be related to the tendency of 18F to form solid-like domains at the surface of water.

An attempt was made to assess the influence of temperature on the organization of the films of pure fluorinated alcohols. Simulations, of 14F and 18F were performed at different temperatures (278.15K, 293.15K and 308.15K). The results are shown in Figure 18 and Figure 19, where the order parameter of the films at each temperature is plotted as function of simulation time. As can be seen, no significant differences were found, i.e., the order parameter doesn't change with temperature in the simulation conditions. Temperatures were not changed more significantly due to water evaporation and freezing.

Finally, equimolar mixtures of fluorinated and hydrogenated alcohols were simulated in order to assess their tendency to spontaneously phase separate at the surface of water. Equimolar mixtures of the two fluorinated alcohols, 14F and 18F, were also simulated, as experimentally it is found that the two substances crystalize separately. Additionally, this could also provide insight about the mutual diffusion of the molecules within the film.

In the initial configuration of the mixture (Figure 20), molecules were positioned in a checkerboard pattern in order to make the mixture as homogenous as possible, although this may not be entropically the most favourable configuration.

For the 18F and 14F mixture, the initial configuration (checkerboard) is only partially maintained. This seems to result from distortion of the planes of each alcohol, rather than from diffusion of the individual molecules. In Figure 21 the order parameter of this mixture is represented. As can be seen, it is practically identical to that of the pure 18F film. This is an indication that the network of 18F molecules is able to "absorb" a similar number of 14F molecules and maintain most of their characteristic order. The molecules remain parallel to each other, independently of the differences in chain length and in spite of the reduction in chain cohesion.

In the case of the mixture of 18F + 18H, the distortion of the initial configuration is much more pronounced. The initial planes of each type of alcohol are now difficult to identify. Nevertheless, the disordered liquid-like structure characteristic of the pure hydrogenated alcohol is completely absent as shown by the order parameter plotted in Figure 21. As can be seen, this very similar to that of pure 18F, suggesting that the fluorinated molecules are supporting the hydrogenated molecules. Within the simulation time, no evidence was found to the formation of segregated fluorinated and hydrogenated domains. It is likely that a much larger system would be necessary, as well as a quantitative criterion to identify the segregated domains.

One of the most important results of this work has been the observation of hexagonal domains in films of 18F at low surface density. Given their regular geometric shape, it is likely to assume that these domains are 2D crystals. The domains were observed at virtually zero surface pressure and very low surface density. It is thus reasonable to assume that, at this stage, the film is at a solid-vapour equilibrium region. These observations seem to indicate that long chain fluorinated alcohols tend to spontaneously crystalize at the surface of water.

Contrarily to what is observed in the isotherms of long chain hydrogenated alcohols (e.g. 18H), in which a sharp "kink" signals the transition from a condensed to a solid phase, in the isotherm of 18F there is a gradual increase of surface pressure that should correspond to the compression of solid domains against each other.

The influence of temperature on structure of the films corroborates what has been proposed. At a higher temperature, 18F films displays predominantly circular domains, very polydisperse, and the remaining hexagonal domains show much smoother edges than those found at
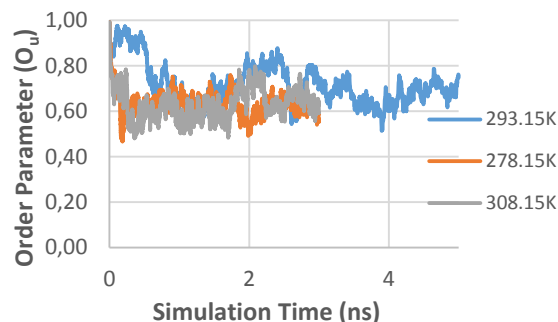

Figure 18 - Evolution of the order parameter of 18F at different temperatures in time, 278.15K, 293.15K, 308.15K.
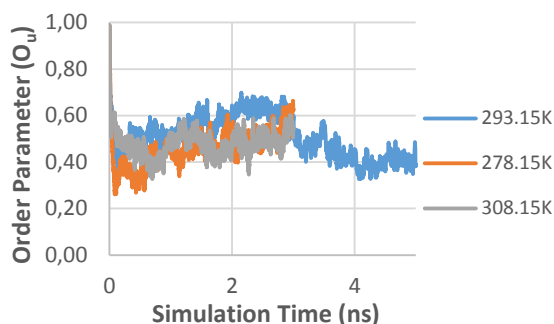

Figure 19 - Evolution of the order parameter of 14F at different temperatures in time, 278.15K, 293.15K, 308.15K.
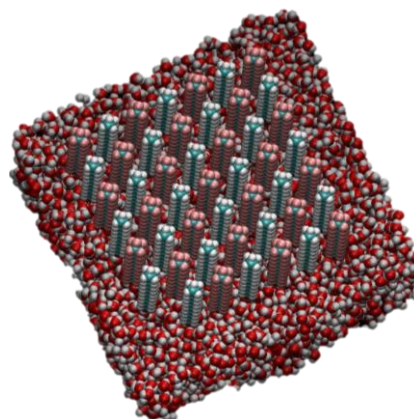

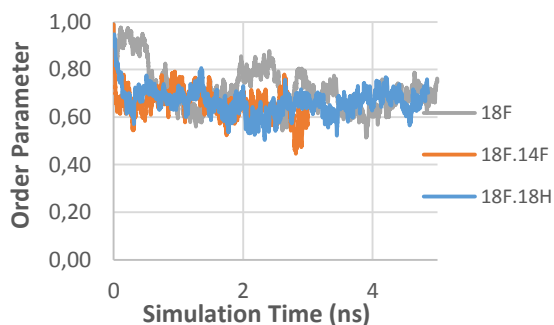Figure 20 –Initial configuration of 18F + 18H mixture.

Figure 21 – Order Parameter as a function of time for both mixtures, 18F-14F and 18F-18H.

293.15K. The film is now at a liquid-vapour boundary. At lower temperature the domains are again predominantly star-shaped, as seen in Figure 11. The existence of a 2D triple point is inferred.

Studies involving a fluorinated alcohol with a smaller chain length (14F) attested and reinforced previous arguments. It is important to stress that smaller chains imply less cohesive energy within the film and thus higher reduced temperature.

At room temperature and low surface density, 14F films do not exhibit the geometric shaped domains that identify the solid-vapour equilibrium. Although the displayed "lacy" structure is difficult to ascertain to a liquid phase, at lower temperature it transforms into distinct solid like hexagonal domains. It is thus reasonable to conclude that at low temperature the 14F films is at a solid-vapour equilibrium region, while at higher temperature it is probably at or near to liquid-vapour boundary.

Figure 22 – Hexagonal Lattice.

A closer analysis of the distribution of sizes and shapes of the observed domains can be useful to provide information about the possible mechanisms of domain growth.

It is known that crystalline structures grow more rapidly along the most compact directions. As shown in Figure 22, directions a_1, a_2 and their family $-a_1$, $-a_2$, $-a_1+a_2$ and a_1-a_2, are the most compact directions in a hexagonal lattice. This explains the existence of star shaped domains, as observed in the films of 18F. At low temperatures, as diffusion is slower, the difference in growth speed along more compact and less compact directions becomes more pronounced and star shaped domains are favoured, as can be seen in Figure 11. At higher temperature, growth becomes faster in all directions and the domains are hexagonal (Figure 12).
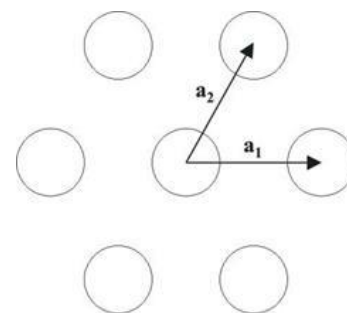
An alternative mechanism to the pure nucleation-and-growth is a 2D Ostwald ripening process [19]. This mechanism is driven by the minimization of the phase boundary area and consists on the dissolution of the smaller domains in favour of the growth of the larger. This effect may be the reason for the large differences in domain size found in 18F films at high and low temperatures. At low temperature the size of domains is fairly constant. At high temperature the film is composed by a large number of small clusters and few large domains. Since mobility is larger at higher temperatures, the 2D Ostwald ripening process may be more pronounced. These evidences suggest that at the beginning the mechanism of crystallization may be controlled by typical 2D nucleation and growth and for longer times may be controlled by 2D Ostwald ripening process.

4. Conclusions

The surface tension of TFE (from 266.15K to 308.15K)

mixtures of TFE with ethanol, 1-propanol, 1-butanol and tert-butanol was measured at 293.15K. All mixtures display minima. The excess molar volume of mixtures of TFE and ethanol, 1-propanol, 1-butanol and tert-butanol was also measured at 293.15K. The excess molar volumes are all positive increasing with the chain length of hydrocarbon alcohol.

The mixtures display a very complex behaviour when compared with mixtures of hydrogenated alcohols and mixtures of alkanes and perfluoroalkanes, showing signs of high cohesion in the bulk and low cohesive forces at the surface.

Langmuir films of 18H, 14F, 18F and their mixtures were prepared on a Langmuir trough at several temperatures and transferred to the surface of silicon wafers. The Langmuir-Blodgett films were analysed by AFM.

Langmuir-Blodgett films of pure 18F display starry-hexagonal domains that form spontaneously at room temperature and low surface density. The domains are compatible with 2D crystals and seem to melt at higher temperature forming circular domains.

Langmuir-Blodgett films of pure 14F at room temperature display a "lacy" pattern that seem to crystalize at lower temperature forming starry-hexagonal domains.

Langmuir-Blodgett films of a mixture of 14F and 18F display a combination of the "lacy" patterns and hexagonal domains characteristic of the pure alcohols.

Langmuir-Blodgett films of a mixture of 18H and 18F display a combination of circular and hexagonal domains characteristic of the pure alcohols suggesting that the two alcohols phase separate in 2D.

Molecular dynamics simulations of the pure 18F Langmuir films seems to confirm the tendency of fluorinated species to spontaneously crystalize at the surface of water, as opposed to hydrogenated species that form liquid-like domains.

Molecular dynamics simulations of a mixture of 18H and 18F indicates that the fluorinated molecules are able to accommodate the hydrogenated molecules and partially maintain the ordered structure of the pure fluorinated film. The simulation results showed no evidence of phase separation within the time scale of the simulation.

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