Transport properties of fluorinated surfactants: viscosity and diffusion of mixtures involving fluorinated alcohols

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Abstract: This work will focus on studying thermodynamic properties of fluorotelomer alcohols, which are linear highly fluorinated molecules with a terminal OH group. Recently, experimental densities and viscosities of ($CF_3(CF_2)_3(CH_2)OH$ + Butanol) and ($CF_3(CF_2)_5(CH_2)OH$ + Hexanol) were reported and revealed large positive excess volumes and large negative excess viscosities.

This work consists on a computational methods namely, Molecular Dynamics simulations focused on studying the significant deviations to ideal behaviour of the transport properties of this mixtures and the possible existence of nano structures. It was concluded that this behaviour results from the unfavourable dispersion forces between the hydrogenated and fluorinated chains.

Molecular dynamics simulations were also used to calculate densities and excess volumes for three different systems, namely, (BuOH + HFB), (HexOH + UFH) and, (DOH + PFO). Also, diffusion coefficients were calculated for the (BuOH + HFB) mixture and the (HexOH + UFH) mixture.

Experimental data for the viscosity of 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-ol as a function of temperature between 283.15 K and 353.15 K was also reported.

Keywords: Viscosity, Molecular Dynamics, Fluorotelomer Alcohols, Segregation

1. Introduction

Fluorinated surfactants are fluorocarbon based surfactants that match the typical hydrophilic/hydrophobic surfactant behaviour to lyophobic behaviour towards hydrogenated organic medium. Inside this class of surfactants, fluorotelomer alcohols, are linear highly fluorinated molecules with a terminal OH group, described by the general formula, $CF_3(CF_2)_n(CH_2)_mOH$ (n+1:m FTOH).

It is well known that mixtures of hydrogenated and fluorinated chains display significant non-ideal behaviour, reflected on a tendency for phase separation, large positive deviations from Raoult's law, and, large positive excess properties, due to weak dispersion forces. However, the addition of a polar alcoholic group to both these mutually phobic segments provides the existence of associative interactions between these molecules. As a result, this mixtures have been reported to create an $O \cdots HO$ network of hydrogen bonds and, simultaneously, segregate into hydrogenated and fluorinated domains to achieve the best packing possible for the phobic segments.[8][9]

Mixtures of alcohols and fluorotelomer alcohols have also been shown to present large non-ideal behaviour but the role possible molecular structural arrangements and molecular interactions has on the thermodynamic properties of such mixtures has not been thoroughly analysed. In addition, experimental data of this mixtures is rather scarce.

Recently, experimental densities and viscosities of (2,2,3,3,4,4,4-heptafluorobutan-1-ol + Butanol) and (2,2,3,3,4,4,5,5,6,6,6-undecafluorohexan-1-ol + Hexanol) were reported which revealed large positive excess volumes and large negative excess viscosities[9][4]. In this work, molecular dynamics simulations were performed, mainly, to understand the reason beyond the significant deviations to ideal behaviour of the transport properties of this mixtures. Nonetheless, other properties such as densities and excess volumes were calculated and compared with literature data for three different systems, namely, (BuOH + HFB), (HexOH + UFH) and, (DOH + PFO).

2. Computational Chemistry and Molecular Simulations

2.1. Molecular Dynamics Simulations

Molecular simulations provide a better understanding experimental observations and allow the identification of underlying mechanisms by providing a insight of the system at a molecular level.

In Molecular Dynamics simulations, a simulation engine numerically integrates Newtons laws of motion to move particles through time. This allows the observation of the system evolution during time and the calculation of its transport properties. Therefore, MD simulations were the chosen method to conduct this computational study over Monte Carlo simulations.

2.2. Force Field - OPLS

A force field is a mathematical expression chosen to describe the intra- and inter-molecular potential energy of a collection of atoms, and the corresponding parameters that will determine the energy of a given ensemble.[2]

A force field requires the definition of intermolecular interactions, non-bonded parameters, and intra-molecular interactions, bonded parameters, existent in a system.

The intra-molecular or local contributions to the total energy include bond stretching, angle bending and dihedral torsions.

$$U = \sum_{bonds} \frac{1}{2} k_b (r - r_0)^2 + \sum_{angles} \frac{1}{2} k_a (\theta - \theta_0)^2 + \sum_{torsions} \frac{Vn}{2} [1 + \cos(n\Phi - \delta)] \quad (1)$$

where r_0 and k_b are stretching and bending constants, respectively; k_a is the equilibrium bond length and θ_0 is the equilibrium angle. Torsional energy is usually represented by a cosine function, where Φ is the torsional angle, δ is the phase, n defines the number of minima or maxima between 0 and 2π (also called multiplicity) and, V_n determines the height of the potential barrier.

Regarding the non-bonded terms, Van der Waals interactions arise from the balance between repulsive and attractive forces. The 12-6 Lennard-Jones (LJ) potential is very often used to represent these interactions:

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2}$$

in which the first term represents the repulsive part of the potential while the second is the attractive term. The ϵ is depth of the potential well, σ is the finite distance at which the inter-particle potential is zero and, r is the distance between particles. The final term of the non-bonded parameters serves to describe the electrostatic interactions. The electrostatic interaction arises due to the unequal distribution of charge in a molecule. This interaction between these point charges is generally modelled by a Coulomb potential:

$$V(r) = \sum_{i}\sum_{j\neq i}\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \tag{3}$$

where ϵ_0 is the permittivity of free space, q are atomic charges and, r_{ij} is the distance between nuclei i and j.

3. Experimental Procedure

The 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-ol (6:1 FTOH, CAS number: 375-82-6) was purchased from Apollo Scientific, for which was claimed a 97% purity. Prior to experimental measurements, the 6:1 FTOH was dried with VWR Prolabo 4A molecular sieves to a maximum water content of 200 ppm (analysed by Karl-Fischer coulometry).

The viscosity of 6:1 FTOH was measured in the temperature range of 283.15 K and 253.15 K at atmospheric pressure using an automated SVM 3000 Anton Paar rotational Stabinger viscosimeter-densimeter. The temperature uncertainty is ±0.02 K from 288.15 to 378.15 K. The precision of the dynamic viscosity measurements is ±0.5%.

4. Simulation procedure and details

Molecular dynamics simulations were performed by applying models based on the atomistic optimized potential for liquid simulations all-atom (OPLS-AA) force field.[7] The necessary potential parameters for Butanol were published in the original OPLS-AA papers[7][13], while for Hexanol and Decanol the parameters are published in the L-OPLS-AA papers, namely the extension for alcohols.[11]

To describe the fluorinated alcohols, 3:1 FTOH, 5:1 FTOH and 7:1 FTOH, the model used in this work was built by using the force-field parameters of the $(-CF_2 - CH_2 - OH)$ segment from the model of Trifluoroethanol developed by Duffy [3] and for the perfluoroalkyl “tail” $(-CF_3 - CF_2-)$ from the OPLS-AA work on perfluoroalkanes.[13] The remaining dihedral torsion parameters were taken from the work of Padua[10], and the partial charge of the carbon atom in the first $-CF_2$ group was adjusted to give the molecule a net zero.

According to the OPLS parametrization, the non-bonded Lennard-Jones interactions between different types of sites were calculated using the geometrical mean rule for both size and energy. For the cross-interaction energy and the cross-interaction diameter between alkyl hydrogen atoms and perfluoroalkyl fluorine atoms, in order to capture the weak unlike interactions between hydrogenated and fluorinated chains, it it was introduced corrections to the energy and size binary interaction parameters, $\xi = 0.80$ and $\upsilon = 1.035$, for (BuOH + HFB) as suggested by Morgado for the OPLS-AA force field [9] and $\xi = 0.77$ and $\upsilon = 1.035$ for (HexOH + UFH) in the L-OPLS-AA force field.

All MD simulations were carried out with the open-source package GROMACS (version 2018)[1][12], in cubic boxes with periodic boundary conditions imposed in all directions and a time step of 2 fs. All bonds involving Hydrogen atoms were constrained to their equilibrium lengths, using the LINCS algorithm.[6] Simulations were conducted for systems composed of 300 molecules for (HexOH + UFH) and (DOH + PFO) and, 500 molecules for (BuOH + HFB) with the system size being conserved as the molar ratio of alcohol to fluorinated alcohol was changed. The general simulation scheme was the following: Initially, the molecules were placed randomly in the box and were allowed to equilibrate in the NPT ensemble for 2.5 ns, during this period, the density of the system converged to mean values, then a 2.5 ns long production run is performed. Afterwards, 2 ns long equilibration runs were performed in the NVT emsemble at densities obtained from NPT simulations at atmospheric pressure which are followed with NVT production runs from 5 to 50 ns long.

5. Densities and Excess Volumes

From the simulations performed, the systems densities were collected directly from the average values of the box volume in the NPT production runs. The densities were calculated for (BuOH + HFB), (HexOH + UFH) and (DOH + PFO) at 298.15 K. The calculated densities showed good agreement with experimental data.

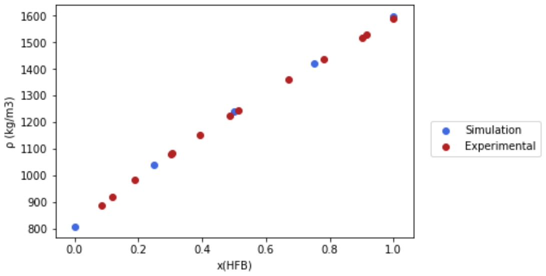


Figure 1: Densities of (BuOH + HFB) at 298.15 K

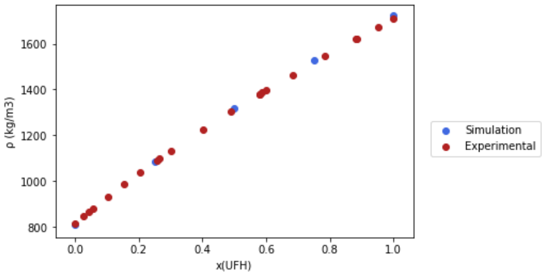


Figure 2: Densities of (HexOH + UFH)at 298.15 K

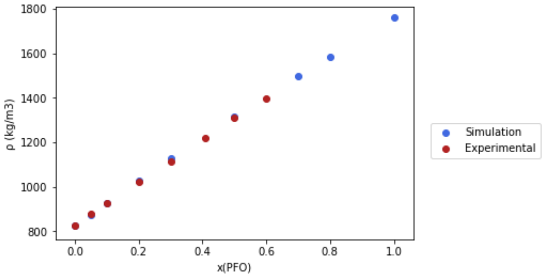


Figure 3: Densities of the mixture (PFO + Decanol) at 298.15 K

Subsequently, the related excess volumes were calculated and plotted in figures 4 and 5. For the (BuOH + HFB) the values were compared with the experimental data published by Morgado[9] while the (HexOH + UFH) system were compared with experimental measurements performed by research collaborator Mariana Leitão.

$$V_m^E = \frac{x_1M_1 + x_2M_2}{\rho_{12}} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \quad (4)$$

To model the unlike $H - F$ interaction, the corrections on size and energy parameters proposed by Morgado[9], $\xi = 0.8$ and $\upsilon = 1.035$, were introduced in the forcefield for the (BuOH + HFB) mixture. The values calculated for excess volume from MD simulations for this system demonstrate a good agreement with the experimental data.

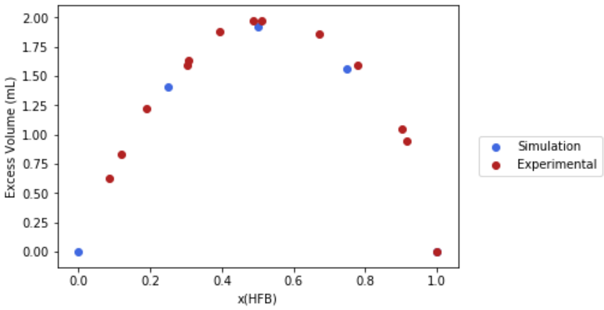


Figure 4: Excess Volumes of (BuOH + HFB)

However, when the parameters modelled for (Hexane + Perfluorohexane) in the L-OPLS force field, $\eta = 1.035$ and $\upsilon = 0.77$, were applied to the mixture of (HexOH + UFH), the calculated excess volumes are significantly lower than the ones experimentally obtained. Accordingly, simulations were ran to parametrize the best correction for the (HexOH + UFH) which is $\eta = 0.77$ and $\upsilon = 1.039$.

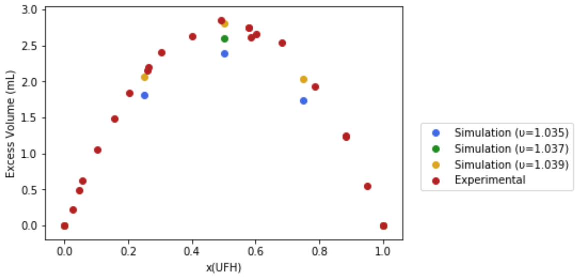


Figure 5: Excess Volumes of (HexOH + UFH)

This correction was kept for the (DOH + PFO) system. For this system, instead of comparing excess volumes, calculated and experimental molar volumes were compared, figure 6.

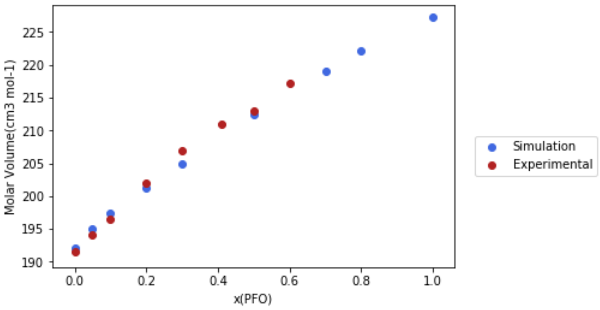


Figure 6: Molar Volume of the mixture (PFO + Decanol) at 298.15 K

6. Viscosities and Excess Viscosity

6.1. Pure compounds

The experimental measurements of the viscosity of 6:1 FTOH as function of temperature are plotted in the figure 7, alongside other different fluorotelomer alcohols. As expected, the viscosities of fluorotelomer alcohols increase with the increase in chain length. As far as known, this are the first reported viscosities for 6:1 FTOH. Moreover, the viscosities of FTOH were compared with the viscosity of different types of compounds.

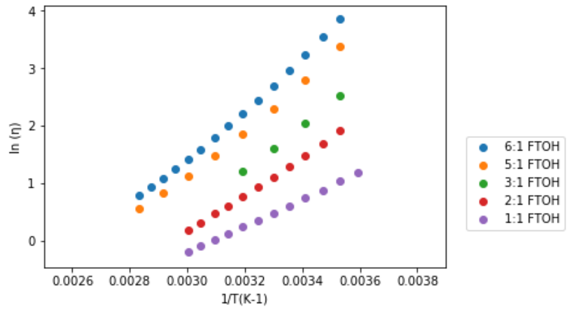


Figure 7: Experimental viscosities of fluorotelomer alcohols as a function of temperature

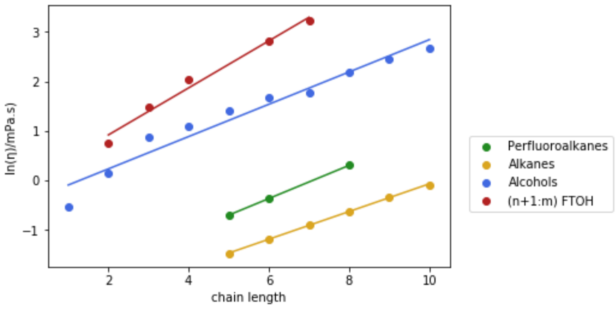


Figure 8: Experimental viscosities at 293.15 K

The measurements executed for 6:1 FTOH show good agreement with previous reported viscosities for other fluorotelomer alcohols. Also, FTOH have an higher viscosity than the remaining types of compounds due to the existence of hydrogen bonds combined with the higher molecular weight of Fluorine.[5]

6.2. Mixtures

Due to its simplicity, the Green-Kubo relation based equilibrium molecular dynamics (MD) simulations is perhaps the most widely used method to calculate viscosities. In this approach, the shear viscosity is calculated from the integral over time of the pressure tensor autocorrelation function

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{\alpha\beta}(t) \cdot P_{\alpha\beta}(0) \rangle dt \qquad (5)$$

where V is the system volume, k_B is the Boltzmann constant, T is temperature, $P_{\alpha\beta}$ denotes the off-diagonal elements of the pressure tensor, and the angle bracket indicates the average ensemble. To obtain the viscosities from the MD simulations, the methodology proposed by Zhang was used.[14]

The calculated viscosities for the (BuOH + HFB) mixture , at 293.15 K were compared with viscosities experimentally measured by Costa. [4].

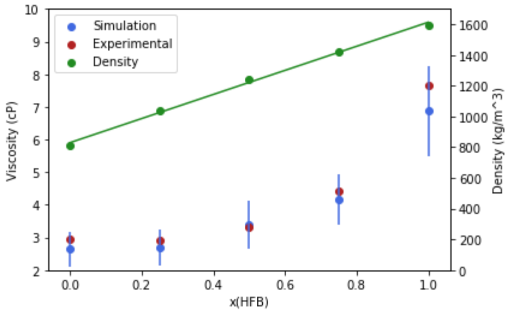


Figure 9: Experimental and simulated viscosities of (BuOH + HFB) and simulated densities at 293.15 K

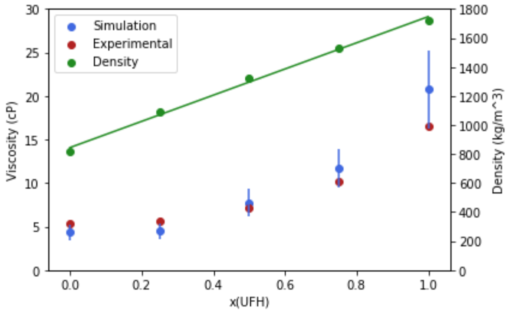


Figure 10: Experimental and simulated viscosities of (HexOH + UFH) and simulated densities at 293.15 K

The simulations are capable of predicting the singular excess behaviour of viscosity in this mixtures, showing results close to the experimental and revealing large negative deviations.

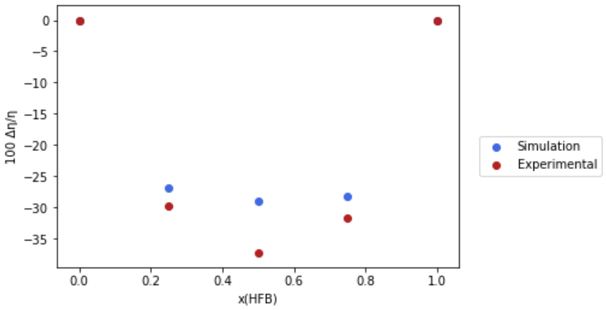


Figure 11: Experimental and simulated excess viscosities for (BuOH + HFB)

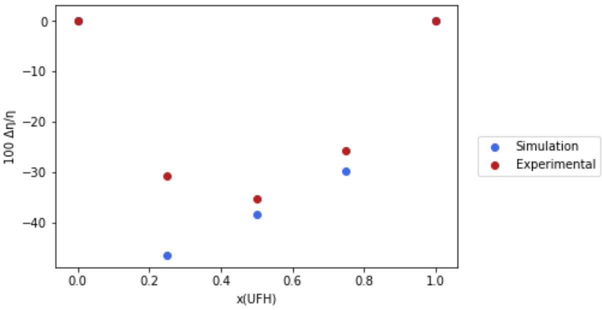


Figure 12: Experimental and simulated excess viscosities for (HexOH + UFH)

7. Diffusion Coefficients and Hydrodynamic Radii

The diffusion coefficients of different mixtures were calculated from the linear part of the mean square displacement of the center of mass of the solute molecules according to the Einstein equation:

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} < [r_i(t) - r_i(0)]^2 > \quad (6)$$

where $[r_i(t) - r_i(0)]^2$ is the mean square displacement of the solute and the brackets stand for average over time. The summation extends to all solute molecules in the simulation. The final value of diffusion coefficient was obtained from the average of 5 values obtained independently.

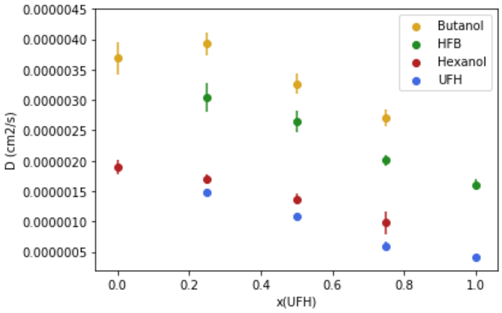


Figure 13: Diffusion coefficients at 293.15 K for (BuOH + HFB) and (UFH + Hexanol)

To further understand the molecules motion in this mixtures the effective radius was calculated. By cancelling the effect different viscosities have on molecules movement, the effective radius allows a better evaluation of the molecules motion. Therefore, a higher effective radius means the motion of the molecule in the mixture is more difficult.

The translational motion of a solute in a fluid solution at infinite dilution can be described by the Stokes-Einstein relation.

$$D = \frac{k_B T}{C \pi \eta r} \quad (7)$$

where D is the diffusion coefficient, k_B is the Boltzmann constant, T is the absolute temperature, and C is equal to 6 for the case of “stick” boundary conditions. Furthermore, because the calculated viscosities from MD simulations have an high of uncertainty, these hydrodynamic radii were calculated using experimental viscosities reported by Costa.[4]

Simulations of HexOH and UFH at infinite dilution in UFH and HexOH, respectively, were also performed and the corresponding diffusion coefficients and effective radii calculated. These are included in figure 14. Figure **??** consisted of a single molecule of hexane and a single molecule of perfluorohexane inserted in pure hexanol, pure UFH and an equimolar mixture. This allows understanding the influence of the weak interactions between hydrogenated and fluorinated chains have on the flow in the absence of hydrogen bonding. This study was conducted at 343.15 K to speed up the molecular dynamics of the (HexOH + UFH) system, making the samplings faster.

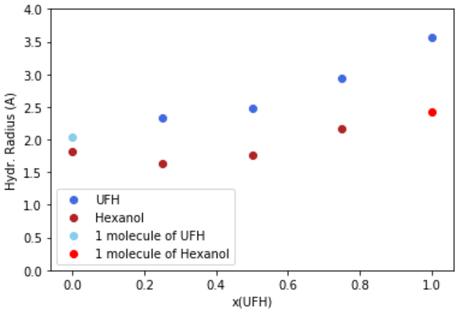


Figure 14: Hydrodynamic radius of HexOH and UFH at 343.15 K with experimental viscosities

Figure 14 suggests that when diluted in Hexanol, molecules of UFH tend to have a higher motion than when pure as shown by the clear tendency of decreasing its hydrodynamic radii when the concentration on Hexanol increases. Regarding Hexanol, the change of effective radius is much smaller. Nevertheless, the results seem to indicate that there is an initial slight decrease of the effective radius of Hexanol in the mixtures, increasing afterwards.

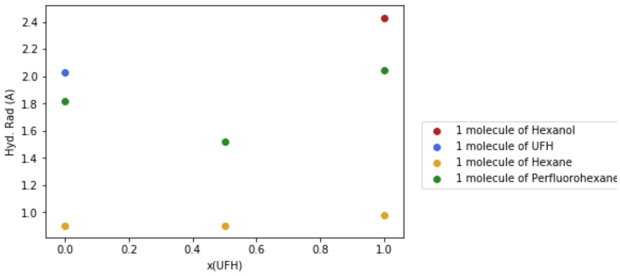


Figure 15: Hydrodynamic radius at 343.15 K with experimental viscosities

The Perfluorohexane molecule decreases slightly its effective radius when infinitely diluted in Hexanol and even more significantly when in the equimolar mixture. This overall decrease could indicate that the weak dispersion interactions between hydrogenated and fluorinated chains can "help" the movement of the fluorinated chain.

8. Liquid Structure

Intermolecular radial distribution functions (rdfs) provide a measure of the local structure in liquids. They were calculated from the simulation trajectories for the the fluorinated chain of UFH and PFO and, the hydrogenated chain of Hexanol and Decanol excluding the Hydrogens bonded to Carbon-1 and, the Oxygen and Hydroxyl group, not only for pure like interactions but also for cross-interactions.

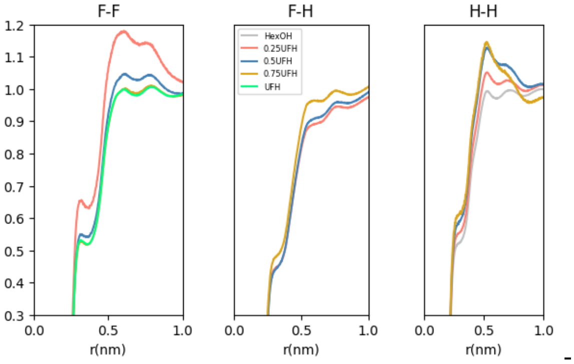


Figure 16: Intermolecular rdfs between the Hydrogen and Fluorine atoms (H or F) for (HexOH + UFH) mixtures at different compositions, from molecular dynamics simulations.

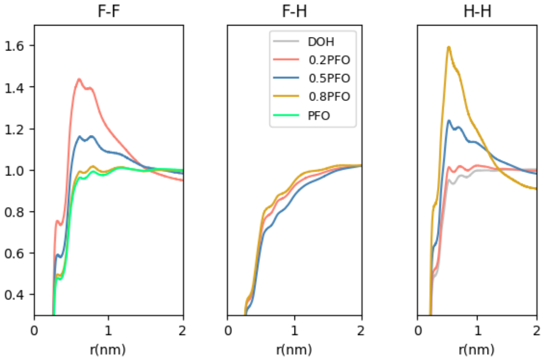
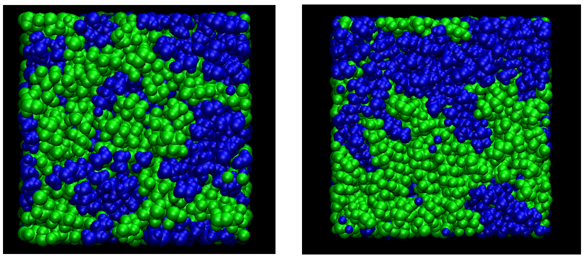


Figure 17: Intermolecular rdfs between the Hydrogen and Fluorine atoms (H or F) for (DOH + PFO) mixtures at different compositions, from molecular dynamics simulations.

Radial distribution functions generated for $H-H$ and $F-F$ group, increase notably with the increase in concentration of the second component. This a strong indication of segregation between hydrogenated and fluorinated segments and supports the conclusion of the presence of different clusters of fluorinated and hydrogenated chains in the mixture.



(a) HexOH + UFH

(b) DOH + PFO

Figure 18: Snapshot of a MD simulation box consisting of an equimolar mixture. Alcohols (HexOH and DOH) are the blue chains and, fluorinated alcohols (UFH and PFO) are the green chains

Intermolecular rdfs between the oxygen and hydroxyl hydrogen atoms for the (HexOH + UFH) system show that the addition of the different alcohol also increases the variety of H-bonds formed upon mixing. Even so, the new established cross-interaction are stronger than the intersections between identical molecules with the curve corresponding to hydrogen bonding between the Oxygen atom in HexOH, highest negative partial charge, and the Hydrogen atom, highest positive partial charge, in UFH being much more intense than the others, which follows the difference of the partial charges assigned to the interacting atoms.

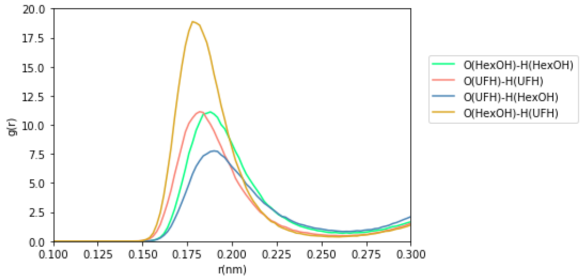


Figure 19: Intermolecular rdfs between the oxygen and hydroxyl hydrogen atoms for the (HexOH + UFH) at equimolar mixture.

The analysis of the rdfs indicate that similar to what was previously seen by Morgado[9] for the (BuOH + HFB) system, mixtures of (HexOH + UFH) can be regarded as nanostructured. This nanostructure consists of a $O \cdots H$ network of hydrogen bonds formed between the hydroxyl headgroups, surrounded by the carbon chain tails, which, in turn, segregate into hydrogenated and fluorinated domains. Figure 20, is a molecular dynamics simulation snapshot obtained for an equimolar mixture of (HexOH + UFH) which illustrates such structure.

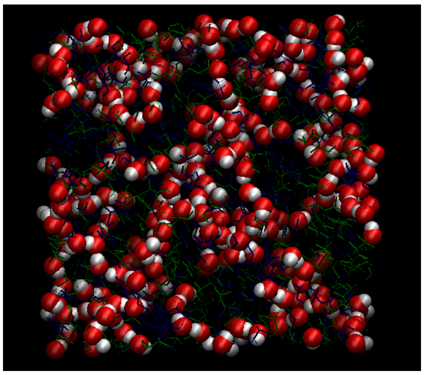


Figure 20: Snapshot of the $O \cdots H$ network in a MD simulation box consisting of an equimolar mixture of HexOH (blue chains) and UFH (green chains); coloured red are the Oxygen's of both molecules and white are the Hydrogen's

9. Conclusions and Future Work

The molecular dynamics simulations performed indicate that the large negative excess viscosities of mixtures of (BuOH + HFB) and (HexOH + UFH) results from an enhanced motion of fluorinated segments when in contact with hydrogenated alcohols due to the unfavourable dispersion forces.

The existence of mutual segregation between fluorinated and hydrogenated chains was identified using radial distribution functions. Also, the existence of a nano structure composed by a $O \cdots HO$ network was identified for the (HexOH + UFH) mixture.

The comparison of the reported viscosities for 2,2,3,3,4,4,5,5,6,6,7,7,7-

tridecafluoroheptan-1-ol with other fluorotelomer alcohols, present in literature, shows a good agreement with viscosities reported for other fluorotelomer alcohols.

Acronyms

BuOH - Butanol
HexOH - Hexanol
DOH - Decanol
HFB - 2,2,3,3,4,4,4-heptafluorobutan-1-ol
UFH - 2,2,3,3,4,4,5,5,6,6,6-undecafluorohexan-1-ol
PFO - 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctan-1-ol
FTOH - Fluorotelomer alcohol
MD - Molecular Dynamics
OPLS - Optimized Potential for Liquid Simulation
AA - All Atom
H-Bonds - Hydrogen Bonds
rdf - Radial Distribution Function

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