Viscosity of liquid systems involving hydrogenated and fluorinated substances: Liquid mixtures of (hexane + perfluorohexane)

Pedro Morgado [a], Jana Black [b], J. Ben Lewis [b], Christopher R. Iacovella [b], Clare McCabe [b,c], Luís F.G. Martins [d], Eduardo J.M. Filipe [a,*]

[a] Centro de Química Estrutural, Instituto Superior Técnico, Universidade Técnica de Lisboa, 1049-001 Lisboa, Portugal
[b] Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN 37235, USA
[c] Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA
[d] Centro de Química de Évora, Universidade de Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal

ARTICLE INFO

ABSTRACT

The viscosity of (hexane + perfluorohexane) mixtures has been measured at 298 K, 303 K and 308 K, over the whole composition range. The results show large negative deviations from the arithmetic mean of the viscosities of the pure components, reaching −17% at x(perfluorohexane) = 0.7. To obtain molecular level insight into the behaviour of the system, all-atom molecular dynamics simulations have been performed and used to calculate the viscosities, radial distribution functions, and rotational relaxation times of the studied (hexane + perfluorohexane) mixtures. This is the first effort to assess the effect of mixing hydrogenated and fluorinated molecules in the viscosity.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

It is well known that alkane + perfluoroalkane mixtures display large deviations from ideal behaviour (liquid–liquid immiscibility, large positive excess volumes and enthalpies, positive deviations to Raoult's law, etc.). In the case of transport properties, even though the concept of ideality is not clearly defined, atypical behaviour could also be expected due to the alleged weak cross interactions between hydrogenated and perfluorinated chains. However, despite its obvious importance, the subject has not been addressed in the literature. The only measurements of viscosity reported for mixtures of alkanes and perfluoroalkanes are those of McLure and Clements [1], who focused on the discontinuity in viscosity near a liquid–liquid critical temperature. The authors measured the viscosity of a single (hexane (H6) + perfluorohexane (F6)) mixture, at the critical composition (x(F6) = 0.370), at several temperatures above the liquid–liquid upper critical solution temperature (UCST). Below the UCST, the viscosity of both phases in equilibrium was also measured at several temperatures.

The knowledge of the viscosity behaviour of alkane + perfluoroalkane mixtures is of special importance in the field of biphasic synthesis and catalysis known as "fluorous chemistry", since the solvents used are (partially miscible) mixtures of hydro- and fluorocarbons. Additionally, this knowledge is of great benefit to the interpretation of perfluoroalkylalkane (PFAA) viscosities, recently measured [2] in our group. PFAA are diblock compounds made of alkyl and perfluoroalkyl segments covalently bonded to form a single chain. They can be pictured as chemical mixtures of two mutually phobic segments that in most cases would otherwise phase separate.

Structurally, the substitution of hydrogen for the larger and heavier fluorine atom results in a larger cross-sectional area for perfluorinated chains [3] (0.283 nm^2 compared to 0.185 nm^2 for n-alkanes) and also in higher densities and molar volumes for n-perfluoroalkanes, when compared to n-alkanes with the same number of carbon atoms. Consequently, in a mixture of a n-alkane with the corresponding perfluoroalkane, the volume fraction of perfluoroalkane is always considerably higher than its mole fraction and a probe immersed in such a mixture would "experience" a much more fluorinated environment than expected from the molar composition. Another important difference between fluorinated and hydrogenated chains is conformational. While the n-alkanes tend to be in an all-trans planar form, n-perfluoroalkanes display a helical conformation [4]; also, the flexible character of hydrogenated chains contrasts with the rigidity of their perfluorinated counterparts. It is believed that one of the consequences of chain

---

* Corresponding author. Tel.: +351 218419261.
 E-mail address: efilipe@ist.utl.pt (E.J.M. Filipe).

stiffness in liquid fluorocarbons is a 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 (oxygen, nitrogen, etc.) in liquid perfluoroalkanes. On the other hand, perfluoroalkanes tend to be more volatile than the corresponding *n*-alkanes due to their weaker cohesive forces, showing however higher viscosity, which can also be attributed to the known rigidity of their molecular structure.

Considerable changes in volume occur when hydrogenated chains are mixed with fluorinated chains. We have recently reported partial molar volumes at infinite dilution for a series of *n*-perfluoroalkanes in *n*-octane [5,6]. For example, when a molecule of F6 is immersed in *n*-octane, at infinite dilution, its molar volume increases from 202.4 cm^3 mol^{-1} to 229.3 cm^3 mol^{-1}, i.e., 13%. Literally, a layer of empty space is created around the F6 molecule. The effect is even more pronounced when *n*-alkanes are dissolved in *n*-perfluoroalkanes: their molar volumes increase by 20% [7]! It should be emphasized that these are infinite dilution data, i.e., no packing effects are included that at higher concentrations would contribute to the excess volume. In view of these results, it can be anticipated that the viscosity of mixtures of alkanes and perfluoroalkanes might be lower than that expected from the viscosity of the pure components.

In this work we have measured the viscosity of mixtures of (H6 + F6) at three temperatures, over the whole composition range. Additionally, all-atom molecular dynamics simulations have been performed and used to calculate viscosity and rotational relaxation times for the studied mixtures, as well as to examine the molecular level structure via radial distribution functions. We believe this is the first study of the transport properties of alkane + perfluoroalkane mixtures.

2. Experimental

H6 and F6, both with 99% claimed purity, were purchased from Sigma–Aldrich and used as received. The mixtures were prepared by weight in 20 ml screw-cap vials. To ensure internal consistency of the results, the viscosity of H6 was measured in the same experimental conditions as the mixtures. The viscosity of F6 was recently measured by our group [2] using the same method, briefly outlined below.

The viscosities were measured using a Schott-Geräte Type 545–00/0 Ubbelohde viscometer, with the AVS 440 measuring unit. This automatic system comprises a viscometer stand (AVS/S) with optical sensors, an automatic pumping system and a control and recording unit; the viscometer stand is immersed in a thermostatic bath, with temperature stability better than 0.01 K. Each viscosity reported is obtained from the average of five independent measurements of flow time, with a scattering of less than 0.2%; the uncertainty of each flow time measurement using this unit is 0.01 s. The temperature of the thermostatic bath was measured with a calibrated platinum resistance probe connected to a 5 ½ digital multimeter (Keithley 191), with an accuracy of 0.05 K and a precision of 0.01 K.

The density of all samples was measured with an Anton Paar DMA 5000 vibrating-tube densimeter, for the determination of the dynamic viscosity. This instrument was calibrated with water (distilled, deionized in a Milli-Q 185 Plus water purification system and freshly boiled) and air at 20.000 °C, taking into account atmospheric pressure; its internal temperature control system is stable at ± 0.001 K. The density of the liquid mixtures was determined before and after the viscosity measurements, in order to estimate any composition change due to differential evaporation during the measuring process. The viscosities were measured at 298 K, 303 K and 308 K, and the measurement at 298 K was repeated at the end

Table 1
Density, relative volume and simulated rotational relaxation times at T = 298 K as a function of F6 molar fraction.

x(F6)	Density (g cm^{-3})	Volume relative to pure H6	τ H6 (ps)	τ F6 (ps)
0	0.655	1.000	12	–
0.25	0.956	1.111	11	17
0.50	1.207	1.194	12	19
0.75	1.457	1.266	13	23
1.0	1.672	1.333	–	27

of the series to further assess the effect of eventual evaporation. When the two measurements, composition and/or viscosity, were different the average value was taken. The changes in composition were estimated to be always less than 0.015 mole fraction.

Even though the temperature was constant within ± 0.01 K, it was not possible to stabilize the temperature at exactly the same value for all the studied compositions. Hence, reported temperatures correspond to an average value of ± 0.1 K. The combined uncertainty of the measured mixture viscosities is estimated to be less than 1.5%.

3. Simulations

To compare with experiment, atomistic molecular dynamics (MD) simulations have been performed. The optimized potentials for liquid simulations all-atom (OPLS-AA) force field, originally developed for alkanes [8] and extended to perfluoroalkanes [9], was used to model the molecules studied. The OPLS-AA force field was developed to accurately reproduce experimental properties of liquids, and recent studies [2,10] demonstrate excellent agreement with experiment for pressure vs. density isotherms of PFAA alkanes. Simulations were performed using the LAMMPS simulation engine [11], carried out in the *NVT* ensemble (constant number of atoms, temperature, and volume) at a temperature of 298 K to match experiment. Temperature was controlled via the Nosé–Hoover thermostat; the rRESPA multi-timestep algorithm was used with time steps of 0.1 fs for bond, angle, and dihedral interactions and time steps of 1.0 fs for the non-bonded interactions and electrostatic interactions, which are computed using the particle–particle, particle–mesh algorithm (PPPM). Simulations were conducted for systems composed of 256 molecules. While system size N is conserved as the molar ratio of alkanes to perfluoroalkanes was changed, the system volume was adjusted to the experimental density reported by Bedford and Dunlap [12]; the density and system volume ratios used are reported in Table 1.

The rotational relaxation time of the individual H6 and F6 molecules was calculated for each composition. The rotational relaxation time of each molecule was estimated using the auto-correlation function of the dot product of the end-to-end vector of the molecule:

$$C(t) = \left\langle \frac{1}{N} \sum_{i=1}^{N} \widehat{u_i}.\widehat{u_j} \right\rangle \tag{1}$$

where N is the total number of molecules in the system and $\hat{u}_i$ is the director of molecule i. To obtain the relaxation time, τ, $C(t)$ is fit using the Kohlrausch–Williams–Watts function [13]:

$$C(t) = \alpha \exp\left(-\left[\frac{t}{\tau}\right]^{\beta}\right) \tag{2}$$

where t corresponds to the time and α and β are fitting parameters. Fitted rotational relaxation times at 298 K, rounded to the nearest picosecond, are reported in Table 1 for each composition. Using the criteria proposed by Mondello and Grest [14] that simulations should be run for between 100 and 200 times the
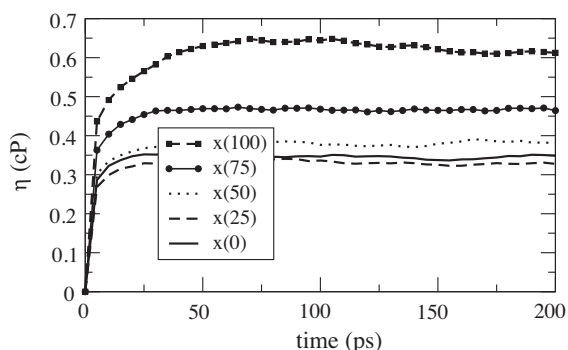
Fig. 1. Average viscosity calculated as a function of time from simulation at $T = 298$ K for the range of F6 concentrations.

Table 2
Experimental dynamic viscosity of H6.

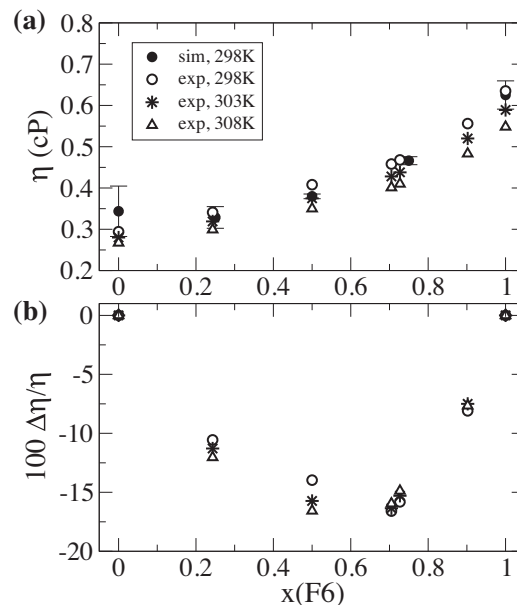| T/K	η/mPa.s
298.20	0.2937
303.16	0.2798
308.13	0.2669

Uncertainty in viscosity less than 0.8%.

Fig. 2. (a) Experimental and simulated viscosity of (H6 + F6) mixtures, η. (b) Relative viscosity deviations from the arithmetic mean of the pure component viscosities, $\triangle\eta/\eta$, from experiment and simulation; for clarity this has been expanded by a factor of 100 to give percent deviation. The legend applies to both panels.

rotational relaxation time of the molecule in order to obtain 10% statistical uncertainty in viscosity calculations, this data suggests a minimum of 5.4 ns simulation time is needed. Simulations at each composition were conducted in excess of 60 ns (in 3 independent simulations for each composition), well beyond this minimum time and of sufficient length to capture fluctuations in the spatial arrangement of molecules in the mixtures.

The zero shear viscosity was calculated using the Green–Kubo relation:

$$\eta = \frac{V}{k_B T} \int_0^\infty \left\langle P_{ij}(0) P_{ij}(t) \right\rangle dt \tag{3}$$

In this equation, V is the volume of the system, k_B is the Boltzmann constant, T is temperature, and t is time. The quantity P_{ij} corresponds to the ij off-diagonal component of the pressure tensor. The average autocorrelation function of the pressure tensor is calculated within a 200 ps window; since this quantity depends on the relative time difference (i.e., $t-t_0$), the average autocorrelation function was constructed via time shifting of the origin, with a correlation offset of 10 fs. In general, the viscosity as a function of time plateaus by ~50 ps into this window (see Fig. 1); the average viscosity reported in this work was calculated from 20 evenly spaced data points from 100 to 200 ps within this plateaued region. To provide an estimate of the error in these measurements, each of the three 20 ns simulation trajectories are considered independently and the standard deviation of these three viscosity measurements is reported as the error.

4. Results

The experimentally measured dynamic viscosity of H6 is presented in Table 2. The results compare favourably with literature data [15] (deviations are less than 0.5%). Table 3 reports the experimental viscosities of the H6 + F6 mixtures, as well as the calculated

deviations from the arithmetic mean of pure component viscosities:

$$\Delta\eta = \eta_{\exp} - (\eta_{F6} x_{F6} + \eta_{H6} x_{H6}) \tag{4}$$

The experimental viscosity of the pure compounds at each temperature was interpolated using the Andrade equation [17]. Fig. 2a plots the viscosities calculated from experiment.

Relative viscosity deviations, $\triangle\eta/\eta$, are plotted in Fig. 2b. Although the absolute deviations shown in Table 3 decrease with increasing temperature, this is not the case for the relative values plotted in Fig. 2b. The temperature dependence of the relative viscosity deviations is probably within the estimated experimental uncertainty. Measurements in a closed viscometer (without evaporation) would allow a larger range of temperatures to be studied. As can be seen, the highest relative viscosity deviation has a value of about -17% and is located between $x(F6) = 0.5$ and $x(F6) = 0.7$.

Table 3
Experimental dynamic viscosity of (H6 + F6) mixtures, η and deviations from the arithmetic mean of pure component viscosities (Eq. (4)), $\triangle\eta$.

$x(F6)$	298.0 K		303.0 K		308.0 K	
	η/mPa.s	$\triangle\eta$/mPa.s	η/mPa.s	$\triangle\eta$/mPa.s	η/mPa.s	$\triangle\eta$/mPa.s
0.000	0.294	–	0.280	–	0.267	–
0.243	0.341	−0.036	0.319	−0.036	0.299	−0.036
0.500	0.408	−0.057	0.375	−0.059	0.350	−0.058
0.500	0.407	−0.057	–	–	0.352	−0.056
0.705	0.458	−0.076	0.428	−0.070	0.401	−0.064
0.727	0.468	−0.074	0.438	−0.067	0.410	−0.061
0.902	0.556	−0.045	0.520	−0.039	0.483	−0.037
1.000	0.635	–	0.589	–	0.548	–

Uncertainty in viscosity less than 1%.

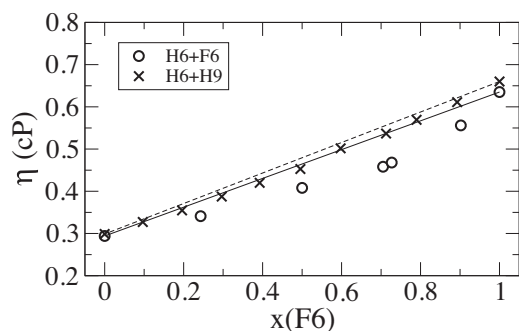**Fig. 3.** Viscosity of H6 + F6 (298.0 K) and H6 + H9 (298.15 K) mixtures. The lines represent the arithmetical mean of pure component viscosities.

Table 4
Simulated dynamic viscosity of the H6 + F6 system at 298.0 K and the calculated viscosity deviations $\triangle \eta$.

x(F6)	η/mPa.s	$\triangle \eta$/mPa.s
0.000	0.344 ± 0.061	–
0.250	0.329 ± 0.026	−0.085
0.500	0.380 ± 0.006	−0.105
0.750	0.466 ± 0.010	−0.089
1.000	0.625 ± 0.034	–

Fig. 2a also includes viscosities calculated from the molecular dynamics simulations, which are additionally summarized in Table 4. The values calculated from the simulations demonstrate close agreement with experiment. As previously mentioned, the simulations were done at the experimental density. It is known from previous work [16] that the force field used is unable to reproduce the experimental positive excess volume, even when the H–F cross interaction is reduced by 25%, which is sufficient to bring agreement between the experimental and simulated excess enthalpy. It is interesting to note that simulations run at the experimental density produce viscosities that agree closely with experiment. We also note that the relatively large uncertainty in the reported viscosity for pure H6 makes it difficult to provide a meaningful comparison of the relative viscosity deviations, although the absolute viscosity deviations show similar behaviour to that seen experimentally.

5. Discussion

It is known that binary mixtures often show negative viscosity deviations, as defined in Eq. (4). Hence, most predictive methods for the viscosity of mixtures propose the use of equations similar to Eq. (4), but in terms of the logarithm of viscosity, using subsequent adjustable parameters which are fitted to each binary mixture [17].

To provide additional insight into the mixing behaviour, Fig. 3 compares the experimental viscosities of H6 + F6 mixtures at 298 K with literature results [18] for H6 + nonane (H6 + H9) at 298.15 K. This latter mixture was chosen because the viscosity of nonane (0.66 mPa.s) is close to that of F6 (0.635 mPa.s) and because both components have, in this case, very similar intermolecular interactions, i.e., dispersion forces between hydrogenated chains exclusively. As can be seen from Fig. 3, the (H6 + H9) system has negative deviations from the linear behaviour, which reach a maximum of 5.5% at the equimolar composition. However, as previously shown, the alkane + perfluoroalkane system shows a much larger negative viscosity deviation with a maximum of 17%. The difference in these otherwise similar systems is likely related to (i) the significant volume increase associated with H6 + F6 mixtures; (ii) the rigidity of the fluorinated molecule; (iii) the weakness of the cross interaction between alkylic and fluorinated chains. As previously discussed, the molar volume of perfluoroalkanes infinitely diluted in n-alkanes increases by 13%, whereas the molar volume of n-alkanes dissolved in n-perfluoroalkanes increases by 20%; also recall that the volume of pure F6 is larger than the volume of pure H6 by a factor of 1.33.

To further explore the effect of volume of these systems at the molecular level, the radial distribution function (RDF) has been calculated from the simulation trajectories; the first peaks, corresponding to the nearest neighbour distances, are highlighted in Fig. 4. The RDF is calculated between the carbon atoms in the molecule backbone (excluding distances between atoms on the same chain) as a function of molecular species. Fig. 4a–c show the RDFs for H6–H6, H6–F6, and F6–F6, respectively. There is a significant increase in the width and the intensity of the first peak of the H6–H6 RDF as F6 is added to the system (Fig. 4a), whereas both the peak width and the peak intensity remain relatively unchanged in the other two cases. In the H6–H6 RDF, as the F6 mole fraction is increased from 0 to 0.75, the peak width, as estimated from the location of the first minimum, increases by ~1 Å. This suggests that the volume accessible to a H6 molecule that is in contact with other H6 molecules increases as F6 is added to the system. Recall that the excess volume for this system is positive and large, ~5 cm³ mol⁻¹, and that the simulations were performed at the experimental density. The simulation results seem to indicate that a portion of this increased volume is more efficiently taken by H6, probably aided by its higher flexibility relatively to F6 (e.g., in the equimolar mixture, the average end-to-end distance of the carbon backbone is 6.10 ± 0.04 Å for H6 and 6.38 ± 0.03 Å for F6). Thus, as F6 is added to the system the effective density of the H6 fraction decreases, which should result in a reduction in the contribution to the total viscosity of the mixture. These findings are compatible with the increase of molar
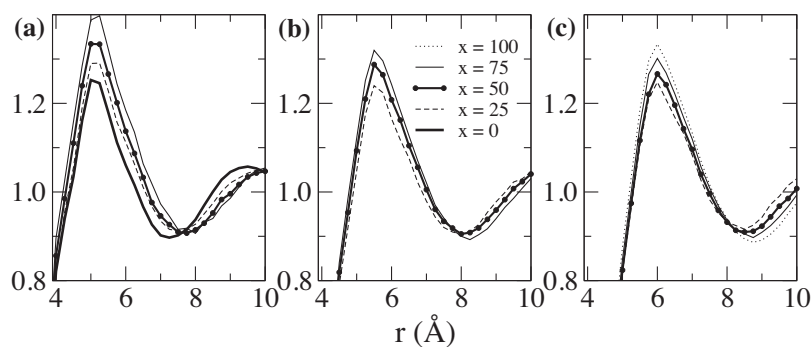

Fig. 4. Radial distribution function (RDF) calculated between the carbon atoms of the compounds as a function of F6 concentration, x, for: (a) H6–H6 (b) H6–F6, and (c) F6–F6. The legend in (b) applies to all panels. Note the RDF only includes atoms on separate chains.

volume at infinite dilution of H6 when dissolved in F6. However, the simulations show no direct explanation for the increase of partial molar volume at infinite dilution of F6 when dissolved in alkanes. This could indicate the presence of a more subtle effect, solvophobic in origin. The increase of the width and intensity of the first peak of the H6–H6 RDF as F6 is added to the system could also be the sign of an incipient segregation between the two substances and the corresponding formation of alkane and perfluoroalkane rich domains. This hypothesis will be investigated in future work.

Re-examination of the rotational relaxation times reported in Table 1 provides additional insight into the role of molecular rigidity. While the rotational relaxation of H6 is relatively unchanged at all statepoints, the rotational relaxation time of F6 increases significantly as the F6 concentration is increased. Statepoints with shorter rotational relaxation times should exhibit increased rotational freedom; with less encumbered molecular motion, it would be expected that the viscosity should be reduced, reducing the contribution to the total viscosity of the mixture. This, in combination with the increased accessible volume of H6 as F6 is added to the system, is likely the cause of the significant deviations seen in both experiment and simulation.

6. Conclusions

The effect of mixing hydrogenated and fluorinated molecules on the viscosity of the mixture has been assessed for the first time. The viscosity of H6 + F6 has been measured over the whole composition range, at three temperatures and shows large negative deviations from the arithmetic mean of the viscosities of the pure components, reaching -17% at $x(F6) = 0.7$. The results obtained from molecular dynamics simulations follow the trend exhibited by the experiments, and give additional insight into the molecular level behaviour. Specifically, it is seen that the volume accessible to H6 molecules increases as F6 is added and the rotational relaxation time of F6 is significantly reduced as H6 concentration increases; these two factors likely contribute for the strong non-linear mixing behaviour seen in both experiment and simulation. These results correlate with the recently reported volume expansions observed in alkane + perfluoroalkane mixtures.

Acknowledgements

References

[1] I.A. McLure, P.J. Clements, Shear viscosity of hexane + tetradecafluorohexane near the upper critical endpoint, Ber. Bunsenges. Phys. Chem. 101 (1997) 114–119.

[2] P. Morgado, C.M.C. Laginhas, J.B. Lewis, C. McCabe, L.F.G. Martins, E.J.M. Filipe, Viscosity of liquid perfluoroalkanes and perfluoroalkylalkane surfactants, J. Phys. Chem. B 115 (2011) 9130–9139.

[3] P. Kirsch, Modern Fluoroorganic Chemistry, Wiley-VCH, Weinheim, 2004.

[4] S.S. Jang, M. Blanco, W.A. Goddard, G. Caldwell, R.B. Ross, The source of helicity in perfluorinated n-alkanes, Macromolecules 36 (2003) 5331–5341.

[5] P. Morgado, R. Tomás, H. Zhao, M.C. dos Ramos, F.J. Blas, C. McCabe, E.J.M. Filipe, Solution behavior of perfluoroalkanes and perfluoroalkylalkane surfactants in n-octane, J. Phys. Chem. C 111 (2007) 15962–15968.

[6] P. Morgado, H. Rodrigues, F.J. Blas, C. McCabe, E.J.M. Filipe, Perfluoroalkanes and perfluoroalkylalkane surfactants in solution: partial molar volumes in n-octane and hetero-SAFT-VR modelling, Fluid Phase Equilib. 306 (2011) 76–81.

[7] L. Lepori, E. Matteoli, A. Spanedda, C. Duce, M.R. Tiné, Volume changes on mixing perfluoroalkanes with alkanes or ethers at 298.15 K, Fluid Phase Equilib. 201 (2002) 119–134.

[8] W.L. Jorgensen, D.S. Maxwell, J. Tirado Rives, Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids, J. Am. Chem. Soc. 118 (1996) 11225–11236.

[9] E.K. Watkins, W.L. Jorgensen, Perfluoroalkanes: conformational analysis and liquid-state properties from ab initio and Monte Carlo calculations, J. Phys. Chem. A 105 (2001) 4118–4125.

[10] P. Morgado, J.B. Lewis, C.M.C. Laginhas, L.F.G. Martins, C. McCabe, F.J. Blas, E.J.M. Filipe, Systems involving hydrogenated and fluorinated chains: volumetric properties of perfluoroalkanes and perfluoroalkylalkane surfactants, J. Phys. Chem. B 115 (2011) 15013–15023.

[11] S. Plimpton, Fast parallel algorithms for short-range molecular-dynamics, J. Comput. Phys. 117 (1995) 1–19.

[12] R.G. Bedford, R.D. Dunlap, Solubilities and volume changes attending mixing for the system: perfluoro-n-hexane-n-Hexane, J. Am. Chem. Soc. 80–2 (1958) 282–285.

[13] G. Williams, D.C. Watts, Non-symmetrical dielectric relaxation behaviour arising from a simple empirical decay function, Trans. Faraday Soc. (1970) 80–86, 66-565P.

[14] M. Mondello, G.S. Grest, Viscosity calculations of n-alkanes by equilibrium molecular dynamics, J. Chem. Phys. 106 (1997) 9327–9336.

[15] P.J. Linstrom, W.G. Mallard (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov, (retrieved 20.07.11).

[16] W. Song, P.J. Rossky, M. Maroncelli, Modeling alkane + perfluoroalkane interactions using all-atom potentials: failure of the usual combining rules, J. Chem. Phys. 119 (2003) 9145–9162.

[17] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, The Properties of Gases and Liquids, 5th ed., McGraw-Hill, New York, 2001.

[18] A. Aucejo, M.C. Burguet, R. Munoz, J.L. Marques, Densities, viscosities, and refractive indices of some n-alkane binary liquid systems at 298.15 K, J. Chem. Eng. Data. 40 (1995) 141–147.