

From nano-emulsions to phase separation: Evidence of nano-segregation in (Alkane + Perfluoroalkane) mixtures using ^{129}Xe NMR Spectroscopy.

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Supplementary information

S1. Magnetic Susceptibility

The molar magnetic susceptibilities of the studied perfluoroalkanes were determined in this work according to the method of Frei and Bernstein,ⁱ as presented (in a modified form) by Hatada and Kitayama.ⁱⁱ The samples of unknown susceptibility were placed inside a glass capillary-sphere microcell (Wilmad 529-A), which consists of a small hollow sphere connected to a cylindrical capillary. This microcell was coaxially placed inside a 10mm NMR tube, with a reference solvent of known susceptibility filling the space around the microcell. The ¹⁹F NMR spectra of the samples were then obtained using a broadband 10mm probe and, due to the difference in geometry between the sample in the cylindrical part of the assembly and in the spherical bulb,ⁱⁱⁱ the spectra showed two peaks for each resonance. It can be shown that the separation between these peaks is proportional to the difference between the volume susceptibility of the sample χ_s and of the reference solvent χ_r according to

$$\Delta\delta = \frac{4}{3}\pi(\chi_s - \chi_r) \quad (1)$$

In this work, deuterated chloroform ($\chi_v = -0.738 \times 10^{-6}$ at 298.15K) was used as a reference solvent, with its deuterium signal used for frequency locking. Since perfluoroalkanes have more than one ¹⁹F NMR resonance, the peaks were assigned and the average of the separations was taken for each sample. The validity and accuracy of the method was verified, using their ¹H NMR signals, with two substances of known susceptibility, water and benzene, and the determined susceptibilities reproduced the literature values^{Error! Bookmark not defined.} within experimental uncertainty. The determined molar magnetic susceptibilities are presented in Table S1. Following standard practice, and maintaining consistency with equation 1, the values are presented in units appropriate to the c.g.s. system (should be multiplied by 4π to obtain values for use in SI equations). The combined precision and accuracy of the results are expected to be better than $0.4 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. The conversion between molar and volumetric susceptibility of the studied PFA was done using the density results determined in previous work.^{iv} The molar susceptibility values show a linear increase with the number of carbon atoms of the perfluoroalkane, as is also observed for the n-alkanes.^v This allows the establishment of a simple additive scheme, with $-\chi_m(\text{CF}_2) = 17.6 \times 10^{-6}$ and $-\chi_m(\text{CF}_3) = 31.3 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

Table S1: Molar magnetic susceptibilities of the perfluoroalkanes studied.

| Compound | $-\chi_m/10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ |
|------------------|---|
| perfluoropentane | 117.0 |
| perfluorohexane | 129.8 |
| perfluorooctane | 170.3 |
| perfluorononane | 184.5 |

In this work, simulations have thus been performed optimizing both the energy (ϵ) and size (σ) parameters of the cross Hydrogen - Fluorine interaction to simultaneously match the experimental excess enthalpy and volume. The carbon - hydrogen and carbon - fluorine cross parameters were kept at their original OPLS-AA values (geometric mean). We found that a 20% reduction of $\epsilon_{\text{H-F}}$ and a 4% increase of $\sigma_{\text{H-F}}$ (relatively to their corresponding geometric mean values) are needed to bring simultaneous agreement between the simulated and experimental excess enthalpy and volume (see figure S1). As can be seen, the simulations now quantitatively reproduce the excess volumes, including their temperature dependence. Good agreement with the experimental excess enthalpies is also achieved. In order to test transferability, simulations were also performed for the *n*-butane + perfluorobutane equimolar mixture at 260K. The obtained excess volume ($4.5 \text{ cm}^3 \cdot \text{mol}^{-1}$) and excess enthalpy ($1.6 \text{ kJ} \cdot \text{mol}^{-1}$) also compare favourably with the experimental results of Simons and Mausteller^{vi} ($4.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $2.1 \text{ kJ} \cdot \text{mol}^{-1}$, respectively).

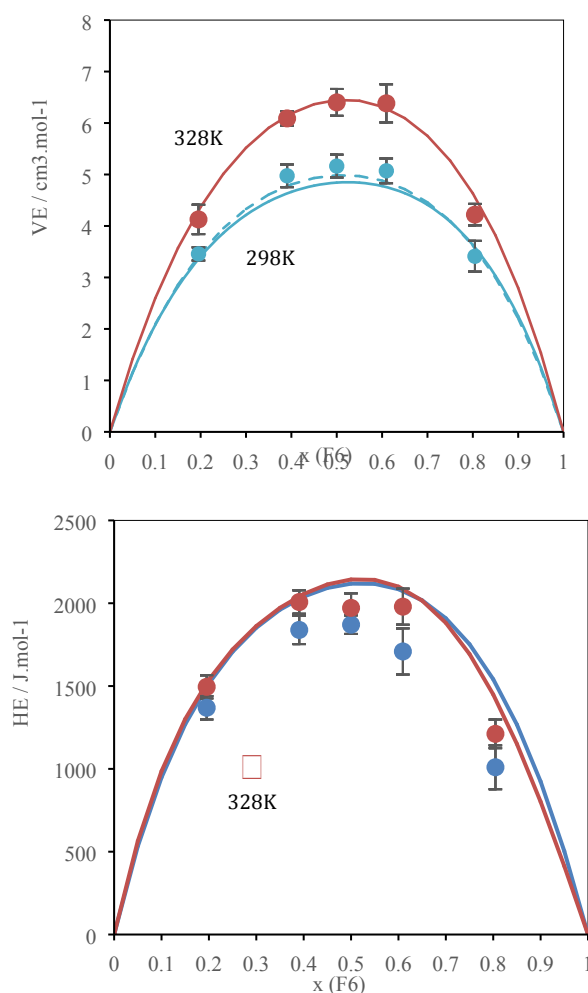


Figure S1: Simulation results for the excess properties of the (hexane + perfluorohexane) mixture: (left) Excess volume; (right) Excess enthalpy. Lines are literature data from refs 36 and 40.

S2. ^{129}Xe NMR spectra

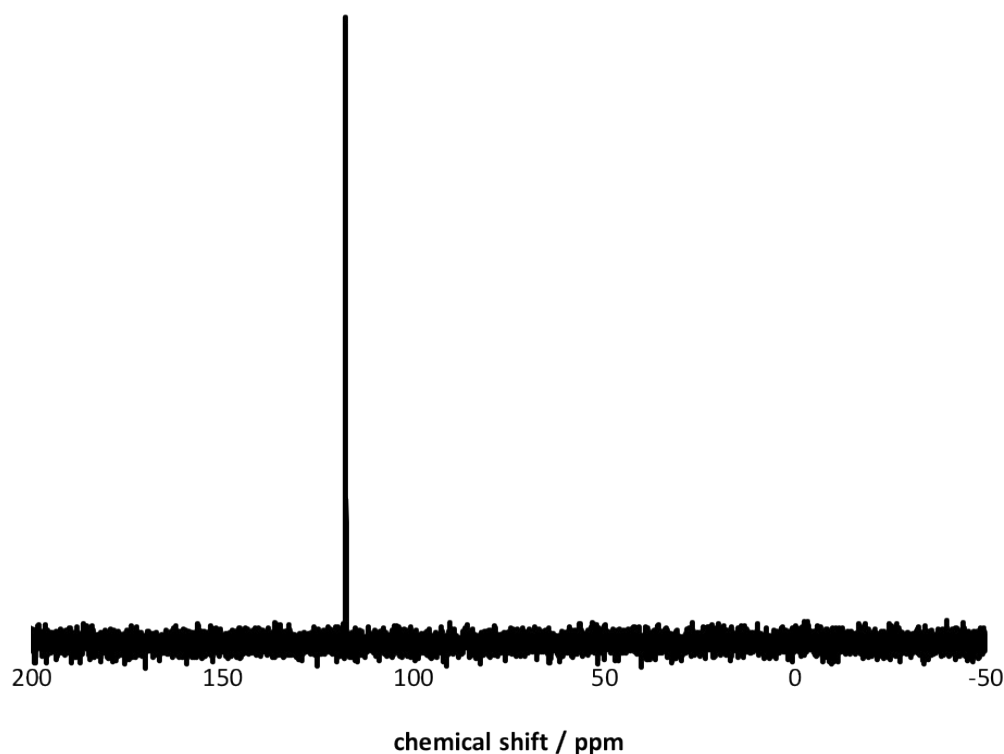


Figure S2. Typical ^{129}Xe NMR spectrum in (hexane + perfluorohexane) mixtures above the UCST. The presented spectrum was obtained for $x(\text{perfluorohexane}) = 0.37$ at 22°C .

ⁱ Frei, K., Bernstein, H.J., *J. Chem. Phys.*, **37**, 1891-1892 (1962)

ⁱⁱ Hatada, K., Kitayama, T., *NMR Spectroscopy of Polymers*, Springer, Berlin Heidelberg (2004)

ⁱⁱⁱ Gil, V.M.S., Geraldes, C.F.G.C., *Ressonância Magnética Nuclear - Fundamentos, Métodos e Aplicações*, Fundação Calouste Gulbenkian, Lisboa (1987)

^{iv} Morgado, P.; Lewis, J. B.; Laginhas, C. M. C.; Martins, L. F. G.; McCabe, C.; Blas, F. J.; Filipe, E. J. M. Systems Involving Hydrogenated and Fluorinated Chains: Volumetric Properties of Perfluoroalkanes and Perfluoroalkylalkane Surfactants. *J. Phys. Chem. B* **2011**, *115*, 15013–15023.

^v Lide, D.L., ed., *CRC Handbook of Chemistry and Physics (87th Edition)*, Taylor and Francis, Boca Raton, FL (2007)

^{vi} Simons, J. H.; Mausteller, J. W. The Properties of N-Butforane and Its Mixtures with N-Butane. *J. Chem. Phys.* **1952**, *20*, 1516–1519.