



## Fluorinated surfactants in solution: Diffusion coefficients of fluorinated alcohols in water



Luís F.G. Martins<sup>a,\*</sup>, Luís A.M. Pereira<sup>a</sup>, Gonçalo M.C. Silva<sup>b</sup>, José R. Ascenso<sup>b</sup>, Pedro Morgado<sup>b</sup>, João P. Prates Ramalho<sup>a</sup>, Eduardo J.M. Filipe<sup>b</sup>

<sup>a</sup> Centro de Química de Évora, Universidade de Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal

<sup>b</sup> Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

### ARTICLE INFO

#### Article history:

Received 7 April 2015

Received in revised form 7 June 2015

Accepted 8 June 2015

Available online 16 June 2015

#### Keywords:

Fluorinated alcohols

Diffusion coefficients

PFG–NMR spin-echo

Molecular dynamics

### ABSTRACT

Intra-diffusion coefficients of three fluorinated alcohols, 2,2,3,3,3-pentafluoropropan-1-ol (PFP), 2,2,3,3,4,4,4-heptafluorobutan-1-ol (HFB) and 2,2,3,3,4,4,5,5,5-nonafluoropentan-1-ol (NFP) in water have been measured by the PFG–NMR spin-echo technique as a function of temperature and composition, focusing on the alcohol dilute region. For comparison, intra-diffusion coefficients of 2,2,2-trifluoroethanol (TFE) and HFB have also been measured in heavy water using the same method and conditions. As far as we know, these are the first experimental measurements of this property for these binary systems. Intra-diffusion coefficients for NFP in water and for TFE and HFB in heavy water have also been obtained by molecular dynamics simulation, complementing those for TFE, PFP and HFB reported in a previous work. The agreement between experimental and simulated results for PFP, HFB and NFP in water is reasonable, although presenting higher deviations than for the TFE/water system. From the dependence of the intra-diffusion coefficients on temperature, diffusion activation energies were estimated for all the solutes in water and heavy water.

© 2015 Elsevier B.V. All rights reserved.

### 1. Introduction

Fluorinated surfactants are fascinating substances that ally a marked surfactant behavior of the hydrophilic/hydrophobic type, to lyophobic behavior towards hydrogenated organic media. Both characteristics result from the presence of the fluorinated chain that simultaneously displays an enhanced hydrophobicity compared to that of hydrogenated chains and a poorly understood antipathy relatively to common hydrogenated solvents.

Due to their many applications, fluorinated surfactants have become important industrial substances. They are used as adjuvant components in fluoropolymer manufacture and processing, aqueous foams for fire extinction, formulations of herbicides, greases and lubricants, paints, polishes and adhesives [1,2].

However it is in biomedical R&D that fluorinated surfactants of different types and natures, have found the most exciting applications, for instance, as emulsifiers for blood substitute formulations [3] and inverse emulsions for drug delivery in liquid ventilation context [4] or as components of the walls of micro-bubbles used for drug delivery and oxygen transport in blood [5].

The stability of all these biphasic nanostructured systems depends critically on the thermodynamic properties of the active substances and the surfactants, namely their surface tension and mobility in the continuous phase given by the diffusion coefficient.

Perfluorinated *n*-alcohols can be considered the simplest fluorosurfactants in terms of chemical structure. Their relative simplicity and the regularity of their thermodynamic properties, makes them the ideal starting point to interpret and predict the thermodynamic properties of fluorinated surfactants in a systematic fashion and to study them in theoretical and modeling terms. On the other hand, the range of industrial and scientific applications of fluorinated alcohols has become wider in the last decades. TFE has long been used in the study of proteins and peptides, as it induces conformational changes, helix formation and folding and stabilizes secondary structures in peptide chains [6]. It is also used as solvent in polymer manufacture and, mixed with water, as working fluid in refrigeration cycles and heat pumps [7]. Fluorinated propanols are used as co-solvents in protein studies, while HFB has potential applications as intermediate for organic synthesis and as surfactant in emulsions for oxygen transport. Both fluorinated propanols and butanols have been tested as co-solvents in supercritical extraction processes [8].

The thermodynamic behavior of aqueous solutions of *n*-fluoroalcohols also presents interesting features, with large

\* Corresponding author. Fax: +351 266744971.

E-mail address: [lfgm@uevora.pt](mailto:lfgm@uevora.pt) (L.F.G. Martins).

negative excess volumes [9], s-shaped but mostly positive excess enthalpies [10,11]. A discontinuity in the compressibility versus composition behavior in dilute solutions of TFE has been recently reported [12]. However, data concerning the dynamic properties of these systems are very scarce, in particular for diffusion coefficients. The work of Harris et al. [13], who measured intra-diffusion coefficients of TFE in water as a function of composition, constitutes a notable exception.

Binary mixtures involving fluorinated and hydrogenated alcohols are also interesting systems from the fundamental point of view, whose behavior has been studied over the last years in our group, hoping to clarify the effect of the combined presence of hydrogen bonding between molecules with mutually phobic segments (hydrogenated and perfluorinated) and how this affects the properties of the liquid mixture and induces organization. In the case of TFE + ethanol mixtures, the evaluation of the importance of the asymmetry in the distribution of hydrogen bonds between the two compounds, as well as the weak fluorinated–hydrogenated interaction, in their thermodynamic properties have been addressed [14].

In a recent paper [15] we have reported intra-diffusion coefficients of TFE in dilute aqueous solutions, extending the composition and temperature ranges of the results available in the literature. Molecular dynamics (MD) simulation results for this system closely reproduced the experimental ones, encouraging us to estimate the diffusion coefficients of aqueous PFP, HFB and the environmentally relevant PFOA and PFOS, by computer simulation.

As an extension of that work, we present here new experimental results of the intra-diffusion coefficients of PFP, HFB and NFP in water as well as intra-diffusion coefficients of TFE and HFB in heavy water (D<sub>2</sub>O), as a function of composition and temperature, in the dilute region. The experimental results are compared with those previously obtained by simulation. New MD simulations were also performed for NFP in water and for the systems involving heavy water.

## 2. Experimental

### 2.1. Materials

2,2,2-trifluoroethanol (99%), supplied by Apollo Scientific, was distilled over potassium sulfate. 2,2,3,3,3-pentafluoropropan-1-ol (Apollo Scientific, 98%), 2,2,3,3,4,4,4-heptafluorobutan-1-ol (Aldrich, 98%) and 2,2,3,3,4,4,5,5,5-nonafluoropentan-1-ol were used as received. All the alcohols were stored in tightly closed bottles and handled under dry nitrogen. Water was purified in a Millipore filtration and ion exchange system to a final resistivity of 18.2 MΩ cm. Deuterium oxide (Aldrich, 99.9%) was also used as received and handled under dry nitrogen.

### 2.2. Experimental methods

Intra-diffusion coefficients were determined by Pulse Field Gradient–Nuclear Magnetic Resonance (PFG–NMR) spin-echo in a NMR Bruker Advance III 500 MHz spectrometer. Two different probes have been used: 5 mm TXI (Triple Resonance) probe for <sup>1</sup>H and a 5 mm BBO (Double Resonance Broad Band) probe tuned to observe both <sup>19</sup>F and <sup>1</sup>H. A bipolar stimulated echo sequence (BPPLIED–Bipolar Pulse Longitudinal Eddy Current Delay) with sine shaped gradients and an eddy current delay *t<sub>e</sub>* of 5 ms was used [16].

The signal intensity (*I*) was monitored as a function of the square of the gradient amplitude (*g*) and the resulting diffusion coefficients (*D*) were calculated according to the Stejskal–Tanner equation

$$I = I_0 \exp \left[ -D(\gamma \delta g)^2 \left( \Delta - \frac{\delta}{3} - \frac{\tau_g}{2} \right) \right] \quad (1)$$

where *I*<sub>0</sub> is the intensity in the absence of gradient pulses,  $\delta$  is the duration of the applied gradient,  $\gamma$  is the gyromagnetic ratio of the nucleus,  $\Delta$  is the diffusion time and  $\tau_g$  is the gradient recovery delay.

**Table 1**

Densities and self-diffusion coefficients of pure compounds obtained by computer simulation in comparison with experimental data and their respective percent deviation.

Heavy water						
T/K	$\rho$ (kg/m <sup>3</sup> )			$D \times 10^9$ (m <sup>2</sup> /s)		
	Simulation	Experiment	Deviation (%)	Simulation	Experiment	Deviation (%)
283.2	1111.7 ± 0.1	1106.7 [33]	0.52	1.28 ± 0.03	1.14 [34]	12.0
					1.22 [35]	4.9
					1.21 [36]	5.8
298.2	1108.5 ± 0.1	1104.5 [33]	0.36	1.91 ± 0.02	1.80 [34]	6.1
					1.78 [35]	7.3
					1.76 [36]	8.5
303.2	1106.7 ± 0.1	1103.3 [33]	0.31			
313.2	1102.8 ± 0.1	1100.0 [33]	0.25	2.60 ± 0.04	2.56 [37]	1.6
					2.50 [35]	4.0
					2.46 [36]	5.7
318.2	1100.4 ± 0.1	1098.0 [33]	0.22			
333.2	1092.0 ± 0.1	1090.6 [33]	0.13			
2,2,3,3,4,4,5,5,5-Nonafluoropentan-1-ol						
T/K	$\rho$ (kg/m <sup>3</sup> )			Deviation (%)		
	Simulation	Experiment	Deviation (%)	Simulation	Experiment	Deviation (%)
283.2	1672 ± 3	1680.2 [38]	−0.5			
298.2	1640 ± 2	1651.3 [38]	−0.7			
313.2	1605 ± 2	1621.2 [38]	−1.0			

Download English Version:

<https://daneshyari.com/en/article/6619619>

Download Persian Version:

<https://daneshyari.com/article/6619619>

[Daneshyari.com](https://daneshyari.com)