Vapor pressure and liquid density of fluorinated alcohols: Experimental, simulation and GC–SAFT-VR predictions

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ABSTRACT

The vapor pressure of four liquid 1H,1H-perfluoroalcohols ($CF_3(CF_2)_n(CH_2)OH$, n = 1, 2, 3, 4), often called odd-fluorotelomer alcohols, was measured as a function of temperature between 278 K and 328 K. Liquid densities were also measured for a temperature range between 278 K and 353 K. Molar enthalpies of vaporization were calculated from the experimental data. The results are compared with data from the literature for other perfluoroalcohols as well as with the equivalent hydrogenated alcohols. The results were modeled and interpreted using molecular dynamics simulations and the GC–SAFT-VR equation of state.

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1. Introduction

Highly fluorinated compounds have become important substances, both from an industrial and fundamental point of view. Fluorinated alcohols in particular, find application in numerous commercial products from textile protection agents and fire-fighting foams, to detergents, paints, and as precursors in the production of fluorinated polymers [1].

Fluorotelomer alcohols are linear highly fluorinated molecules possessing a terminal OH group, with the general formula, $CF_3(CF_2)_n(CH_2)_mOH$ that is often summarized as n+1:m FTOH. This molecular structure results in an enhanced amphiphilic character compared to hydrogenated alcohols, as fluorinated chains are known to be more hydrophobic than their hydrogenated analogues. Fluorotelomers can be divided into two major groups: odd FTOH with m = 1 and even FTOH when m = 2. In an effort to understand and model these molecules, experimental properties such as vapor pressure and densities were measured and enthalpies of vaporization calculated.

This work is part of a project in which experimental measurements, molecular simulation techniques and theoretical calculations have been simultaneously used to elucidate the properties of fluorinated substances and their mixtures. Using this approach, we have recently reported diffusion coefficients of fluorinated alcohols in aqueous solutions [2]. The behaviour of mixtures of fluorinated and hydrogenated alcohols has also been studied [3]. These mixtures display a very complex behaviour when compared with mixtures of hydrogenated alcohols and mixtures of alkanes and perfluoroalkanes. The excess volumes are large and positive (unlike those of mixtures of hydrogenated alcohols [4]) while the excess enthalpies are large and negative (contrasting with those of mixtures of alkanes and perfluoroalkanes [5]). This peculiar behaviour results from a delicate balance between the weak dispersion forces between the hydrogenated and fluorinated groups and a preferential hydrogen bond between the hydrogenated and the fluorinated alcohols.

Following this line of work, we now present new experimental data for the vapor pressures and liquid densities of four liquid 1H,1H-perfluoroalcohols ($CF_3(CF_2)_nCH_2OH$, n = 1, 2, 3, 4) as a function of temperature. Molar enthalpies of vaporization were calculated from the experimental data and the results compared

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with data from the literature for other perfluoroalcohols as well as their equivalent hydrogenated alcohols. Vapor pressure measurements were previously reported for the longer chained $(CF_3(CF_2)_nCH_2OH$, n = 5—9) odd fluorotelomers [6], but for the short chains studied in this work, experimental data has not been reported or is of insufficient accuracy. Molecular dynamics simulations were also performed and provide molecular level insight into the experimental results. Experimental molar enthalpies of vaporization and densities were used to validate the force field used in the molecular dynamics simulations. Additionally, the GC-SAFT-VR equation was used to predict the experimental results. Excellent agreement has been found between the theoretical predictions and the experimental results.

2. Experimental and simulation techniques

2.1. Purification and characterization

1H,1H-perfluoropropan-1-ol (2:1 FTOH, CAS number:422-05-9), 1H,1H-perfluorobutan-1-ol (3:1 FTOH, CAS number:375-01-9), 1H,1H-perfluoropentan-1-ol (4:1 FTOH, CAS number:355-28-2) and 1H,1H-perfluorohexan-1-ol (5:1 FTOH, CAS number:423-46-1) were purchased from Apollo Scientific Ltd; a 98% purity was indicated for all the alcohols except perfluoropentanol, for which a 97% purity was claimed. Prior to their use, the compounds were dried with VWR Prolabo 4A molecular sieves to a maximum water content of 500 ppm (analysed by Karl-Fischer coulometry) and their purity was confirmed by ^1H NMR spectroscopy (See Table 1).

2.2. Vapor pressure measurements

The vapor pressure of the fluoroalcohols was measured in the 278—328 K temperature range, with the exception of the 3:1 FTOH that was measured from 298 to 328 K. The measurements were made using a static apparatus previously described [7], which consists of a spherical glass cell connected to a vacuum line and to a pressure transducer. The cell is immersed in a thermostatic water bath controlled by a Hart Scientific 2100 PID temperature controller. The temperature of the liquid was measured using a calibrated Pt100 temperature sensor connected to a Keithley 2000 6½ digital multimeter, with an absolute uncertainty of 0.05 K. The temperature stability and uniformity during a measurement is estimated to be better than 0.01 K. The pressure was measured with a Paroscientific Series 1000 quartz absolute pressure transducer connected to a Paroscientific model 715 display unit. The pressure sensor is capable of measuring up to 100 psia (0.69 MPa), with a resolution of 0.0001% of the full scale and has an integrated temperature compensation system. While measuring, the connecting line between the glass cell and the pressure transducer was kept at a higher temperature than the bath's in order to avoid condensation of the vapor.

The liquids were submitted to freezing in liquid nitrogen, vacuum pumping and melting cycles to degas them. The samples were further purged to the vacuum line for a few seconds while agitating the liquid. The latter procedure was repeated until the measured vapor pressure was reproducible, confirming that no other volatile species were present. The temperature was then changed and the pressure recorded after stabilization. Measurements were made in paths of increasing and decreasing temperature, in order to reduce the possibilities of systematic error.

2.3. Density measurements

The liquid densities of the fluoroalcohols were measured in an Anton Paar DMA 5000 vibrating-tube densimeter. The instrument was calibrated with water (distilled, purified with a Mili-Q 185 plus water purification system, and freshly boiled) and air at 20.000 °C, 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 0.00002 g cm^{-3}. The density of air was verified at the beginning of each series of measurements to ensure the cleanliness of the measurement cell.

2.4. Molecular dynamics simulations

Molecular dynamics simulations were carried out to obtain molecular-level information on the behaviour of the studied systems, using an all atom force field based on OPLS all atom force field (OPLS-AA) [8]. For the perfluoroalkyl segments of the molecules, the OPLS-AA parameters from Watkins and Jorgensen [9] were used, while the $-CF_2CH_2OH$ segment was modeled with the parameters developed by Duffy for trifluoroethanol [10,11], adjusting the partial charge of the fluorinated carbon to maintain the neutrality of the molecule. The missing dihedral torsion parameters, for the fluorinated-hydrogenated junction, were taken from the work of Pádua [12]. The simulations were performed using the DL_POLY [13] simulation engine, in the NpT ensemble at 1 atm and 298.15 K. All bonds involving hydrogen atoms were constrained to their equilibrium lengths, using the SHAKE algorithm. Pressure and temperature were kept constant using the Nosé-Hoover barostat and thermostat, with relaxation times of 2 and 0.5 ps, respectively. A total of 20 ns were simulated with a 2 fs time step for the liquid phases. In the gas phases, for each compound, 20 independent simulations of a single molecule system, started from different initial configurations, were performed for 20 ns each with a 1 fs time step. A cut-off of 14 Å was used for the Lennard-Jones and Coulomb potentials, with analytic tail corrections applied for the former and the Ewald sum method incorporated to calculate the long-range interactions for the latter.

The system densities were obtained directly from the average values of the system volume in the NpT simulations and the enthalpies of vaporization calculated using Equation (1).

$$\Delta H_{vap.calcd} = E_{config.g} - E_{config.l} + RT \tag{1}$$

where $E_{config.g}$ and $E_{config.l}$ are the configurational molar energies of the liquid and gas phases and RT corresponds to the PV-work term for an ideal gas. The work term for the liquid phase is considered negligible. Gas and liquid phase simulations were performed to obtain the configurational energies.

The average number of hydrogen bonds in the liquid

Table 1
Sample Provenance and purity for 2:1, 3:1, 4:1 and 5:1 FTOH.

Compound	Source	Claimed purity	Purification method	Analysis methods	Water content
2,2,3,3,3-Pentafluoro-1-propanol (2:1 FTOH)	Apollo Scientific Ltd.	0.98	Drying in molecular sieves	-	—
2,2,3,3,4,4,4-Heptafluoro-1-butanol (3:1 FTOH)	Apollo Scientific Ltd.	0.98	Drying in molecular sieves	KF Coulometry	472 ppm
2,2,3,3,4,4,5,5,5-Nonafluoro-1-pentanol (4:1 FTOH)	Apollo Scientific Ltd.	0.97	Drying in molecular sieves	—	—
2,2,3,3,4,4,5,5,6,6,6-Undecafluoro-1-hexanol (5:1 FTOH)	Apollo Scientific Ltd.	0.98	Drying in molecular sieves	KF Coulometry	316 ppm