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Fluorination effect on the thermodynamic properties of long-chain hydrocarbons and alcohols

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ABSTRACT

Structural and thermodynamic insights are reported for the series of fluorinated alcohols {*o*FTOH; $CF_3(CF_2)_nCH_2OH$, with $n = 5–12$}, with the objective of comparing the phase behaviour of perfluorinated compounds with the analogous linear alkanes and alcohols. As expected the higher vibrational contribution of the $–CF_2–$ groups contributes for the higher heat capacities of the perfluorinated compounds. Concerning the fusion/sublimation equilibria, fluorination of the alcohols decreases ΔH and ΔS of phase transitions. Compared to the regular $–CH_2–$ alkyl chain structure, the less symmetric $–CF_2–$ spiral conformation is characterized by a less efficient molecular alignment in crystal packing, thus explaining the lower ΔH. The lower internal rotational barrier associated with the $–CH_2–$ alkyl chains of *n*-alkanes/alcohols, when compared to $–CF_2–$ chains, contributes to the larger values of ΔS observed. Regarding the vaporization equilibria, fluorination leads to greater values of ΔS, which are explained by the larger translational entropy of the heavier perfluoroalcohols, an effect that is more important in the gas than in the liquid phase.

1. Introduction

Fluorotelomer alcohols (FTOHs) are alcohols with a linear polyfluorinated chain and are subdivided into two main categories: even {FTOH; $CF_3(CF_2)_nCH_2CH_2OH$} and odd {*o*FTOH; $CF_3(CF_2)_nCH_2OH$} fluorotelomer alcohols. The common nomenclature of these compounds is based on the numbers of carbon atoms that are fluorinated and those that are hydrocarbon-based. For example, 11:2 fluorotelomer, an even FTOH, denotes a molecule with 11 fluorinated carbon atoms and 2 $–CH_2–$ groups as in a mono-substituted ethyl alcohol [1–3].

FTOHs are widely used in many commercial products such as fire-fighting foams, detergents, paints, paper treatment agents and electronic equipment, and have a large range of industrial applications [4–6]. The health impact and environmental transformations and occurrence of FTOHs has recently become a subject of special interest in the scientific community [7,8].

These compounds have generally high volatility, are often detected in air and can biodegrade to perfluorinated carboxylic acids (PFCAs), which persist in the environment and are found in the blood serum of populations and wildlife [5,9]. 6:2 FTOH and 8:2 FTOH were found to be estrogenic [10]. Adverse effects of FTOHs on human health might include endocrine toxicity, liver toxicity and reproductive toxicity [11–13]. The United States Environmental Protection Agency (EPA) has asked chemical industries to reduce the amount of residues, which include fluorotelomer alcohols, and is supporting research to better understand the sources, distribution and effects of many perfluorinated compounds (PFCs) in the environment [13,14].

The need for acquiring accurate data on the thermodynamic properties of FTOHs is emphasised by the intense discussion in the recent literature about the environmental impact of this class of substances [15–19]. In previous work, we have performed a phase transition study, including vapour pressure measurements of odd fluorotelomer alcohols, in order to explore the effect of successive introductions of $–CF_2–$ groups on the thermodynamic properties related to phase equilibria [19]. We have observed an odd-even effect on the thermodynamic properties of fusion for the homologous series of *o*FTOHs, which indicate higher crystal packing stability for the members with an odd number of carbon

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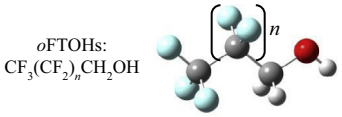

Fig. 1. Structure of the *o*FTOHs studied in this work: 6:1 FTOH ($n = 5$); 7:1 FTOH ($n = 6$); 8:1 FTOH ($n = 7$); 9:1 FTOH ($n = 8$); 10:1 FTOH ($n = 9$); 11:1 FTOH ($n = 10$); 13:1 FTOH ($n = 12$).

atoms. Moreover, when comparing the vaporization of *o*FTOH with the literature data for their alkane analogues, the results showed that liquid fluorotelomer alcohols are more volatile.

In this work, we present a structural, thermodynamic and computational study of two long-chain perfluorinated alcohols belonging to the same series of *o*FTOH: 11:1 FTOH (1H, 1H-perfluorododecan-1-ol) and 13:1 FTOH (1H, 1H-perfluorotetradecan-1-ol). For both solid compounds, the thermodynamic properties of sublimation were measured by two different methods: high temperature Calvet microcalorimeter and Knudsen effusion methodology. The thermodynamic properties of fusion were measured by differential scanning calorimetry. The experimental results were compared with those for the smaller members of the homologous series. Also, we have determined the heat capacities for some members of the *o*FTOH series (from 6:1 FTOH to 13:1 FTOH), with a precise heat capacity drop calorimeter. The structure of the compounds studied is depicted in Fig. 1.

2. Methods

2.1. Purification and characterization of oFTOHs

1H, 1H-perfluoroheptan-1-ol (6:1 FTOH), 1H, 1H-perfluorooctan-1-ol (7:1 FTOH), 1H, 1H-perfluorononan-1-ol (8:1 FTOH), 1H, 1H-perfluorodecan-1-ol (9:1 FTOH), 1H, 1H-perfluoroundecan-1-ol (10:1 FTOH), 1H, 1H-perfluorododecan-1-ol (11:1 FTOH) and 1H, 1H-perfluorotetradecan-1-ol (13:1 FTOH) were purchased from Apollo Scientific Ltd. Prior to their use, the liquid 6:1 FTOH was purified by drying/vacuum treatment and the solids 7:1 FTOH, 8:1 FTOH, 9:1 FTOH, 10:1 FTOH, 11:1 FTOH and 13:1 FTOH were purified by sublimation under reduced pressure (<10 Pa), and the final purity of the samples was verified by gas chromatographic analysis (GC), using an HP 4890 apparatus equipped with a FID detector and an HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane. Mass fraction purity above 0.999 was obtained for all the *o*FTOH studied. Purity details are given in Table 1. The relative atomic masses used in our work are those recommended by the IUPAC Commission in 2007 [20].

2.2. Heat capacity measurements

For the *o*FTOHs studied, the heat capacities of the liquid (6:1 FTOH) or solid phase (7:1 FTOH, 8:1 FTOH, 9:1 FTOH, 10:1 FTOH, 11:1 FTOH, 13:1 FTOH), at $T = 298.15$ K, were measured using a precise heat capacity drop calorimeter, described in detail by Santos et al. [21]. The calorimeter includes a fully automatic setup and data treatment, providing a reliable way for obtaining high-quality heat capacity data for solid or liquid materials.

2.3. Differential scanning calorimetry

The temperatures and the standard molar enthalpies of fusion for 11:1 FTOH and 13:1 FTOH were measured in a heat flux differential scanning calorimeter (NETZSCH, DSC 200 F3) using a heating rate of 0.0333 $K \cdot s^{-1}$, and hermetically sealed aluminium crucibles. A constant flow of nitrogen was applied. The standard molar entropies of fusion for each compound were derived. The temperature and heat flux scales were calibrated by measuring the temperature and the enthalpy of fusion of some reference materials: *o*-terphenyl, benzoic acid, indium, triphenylene, tin, perylene and zinc [22,23]. 11:1 FTOH and 13:1 FTOH were measured with the same experimental methodology used in the calibration runs.

2.4. Calvet microcalorimetry

The standard molar enthalpies of sublimation of 11:1 FTOH and 13:1 FTOH were measured in a high temperature Calvet microcalorimeter, Setaram model HT1000D. The measurement procedure and the description of the apparatus have been described by Santos et al. [24]. Samples of about 4–6 mg were placed into thin capillary tubes, sealed at one end, and dropped, simultaneously with the corresponding blank tube, at $T = 298.15$ K into the hot reaction zone of the calorimeter ($T \approx 396.3$ K). The heating of the sample from room temperature to the calorimeter hot zone temperature, T, is recorded, and after thermostability is reached, the sample is sublimed into the vacuum. The microcalorimeter was calibrated with benzoic acid using the same experimental procedure and conditions of the calibration experiments.

2.5. Vapour pressures measurements

The vapour pressures of 11:1 FTOH and 13:1 FTOH as a function of temperature were measured with the ThinFilmVD system, described by Costa et al. [25,26]. This apparatus was built for the thin film deposition and is also capable of measuring vapour pressures by the Knudsen effusion methodology. The apparatus enables the simultaneous operation of four independent effusion cells. The vapour pressures ($0 < p/\text{Pa} < 1$) of the solid compounds were

Table 1
Source and purity details of 6:1 FTOH, 7:1 FTOH, 8:1 FTOH, 9:1 FTOH, 10:1 FTOH, 11:1 FTOH and 13:1 FTOH.[a]

Chemical name	CAS registry number	Initial/final mass fraction purity	Purification method	Purity analysis method
1H, 1H-perfluoroheptan-1-ol	375-82-6	0.97/0.999	Drying	GC
1H, 1H-perfluorooctan-1-ol	307-30-2	0.98/0.999	Sublimation	GC
1H, 1H-perfluorononan-1-ol	423-56-3	0.98/0.999	Sublimation	GC
1H, 1H-perfluorodecan-1-ol	307-37-9	0.98/0.999	Sublimation	GC
1H, 1H-perfluoroundecan-1-ol	307-46-0	0.95/0.999	Sublimation	GC
1H, 1H-perfluorododecan-1-ol	423-65-4	0.96/0.999	Sublimation	GC
1H, 1H-perfluorotetradecan-1-ol	15622-57-8	0.96/0.999	Sublimation	GC

[a] Compounds purified by sublimation under reduced pressure (<10 Pa).