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Evidence of an odd–even effect on the thermodynamic parameters of odd fluorotelomer alcohols

José C.S. Costa^a, Michal Fulem^b, Bernd Schröder^c, João A.P. Coutinho^c, Manuel J.S. Monte^a,
Luís M.N.B.F. Santos^{a,*}

^a Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

^b Department of Physical Chemistry, Institute of Chemical Technology, Technická 5, CZ-166 28 Prague 6, Czech Republic

^c CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

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ABSTRACT

A phase transition study, including vapour pressure determinations of odd fluorotelomer alcohols {oFTOH; $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{OH}$, with $n = 5$ to 9), is reported in order to explore the effect of the successive introduction of $-\text{CF}_2-$ groups into the molecule on the thermodynamic properties related to (solid + liquid, solid + gas, and liquid + gas) equilibria. An odd–even effect on the thermodynamic parameters of fusion and sublimation was observed in the homologous series of odd fluorotelomer alcohols indicating an increase of the stability in the crystal packing for the members with an odd number of carbon atoms. The vaporization parameters of o-FTOH were compared with the literature data for their alkane analogues and the results showed a higher volatility of liquid fluorotelomer alcohols than their congeners. The higher molecular conformation restriction of perfluorinated alcohols and/or the higher molar mass seems to contribute to their higher entropy of vaporization which drives the volatility of the 1H,1H-perfluorinated alcohols.

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1. Introduction

Fluorotelomer alcohols (FTOHs) are linear chain polyfluorinated organic compounds with an alcohol functional group used in numerous commercial products such as fire-fighting foams, textile protection agents, floor polishers, detergents, paints, paper treatment agents, electronic equipment and as precursor compounds in the production of fluorotelomer polymers [1–6]. Fluorotelomer alcohols are also precursors of perfluorinated carboxylic acids (PFCAs) such as perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) [7–9]. There are two major groups of these compounds: even fluorotelomer alcohols {FTOH; $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ } and odd fluorotelomer alcohols {oFTOH; $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{OH}$ }. Commonly, an individual fluorotelomer alcohol molecule is named by the number of carbon atoms that are fluorinated *versus* the number that are hydrocarbon-based. For example, 6:2 fluorotelomer alco-

hol would represent a molecule with 6 fluorinated carbon atoms and a 2 carbon atoms in ethyl alcohol group. FTOHs are volatile and widely detected in air, but the precise degree of FTOH volatility has been subjected to some dispute [10–13]; nevertheless, the volatility and solubility properties of FTOHs present a potential for these compounds to volatilize and/or leach from consumer products and be subjected to a long-range transport in the environment. Given the capabilities of consumer products to act as sources of FTOHs, and their physical–chemical properties contributing to the high atmospheric mobility, some studies have been carried out to determine the extent to which FTOHs and other perfluorinated compounds have been distributed in the environment [14–22]. Even-fluorotelomer alcohols such as 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH have been identified as residuals in consumer products such as stain repellents and windshield wash, among others [21]. Fluorotelomer alcohols can biodegrade to PFCAs that persist in the environment and are found in the blood serum of populations and wildlife. The United States Environmental Protection Agency (EPA) has asked chemical

* Corresponding author. Tel.: +351 220402536; fax: +351 220402520.

E-mail address: lbsantos@fc.up.pt (L.M.N.B.F. Santos).

companies to reduce the amount of residuals, including fluorotelomer alcohols, from products, and is supporting research to better define the sources, distribution and effects of numerous perfluorinated compounds (PFCs) in the environment. In 2006, EPA created the 2010/15 PFOA Stewardship Program, in which companies committed to reduce global facility emissions and product content of PFOA and related chemicals by 95% by 2010, and to work toward eliminating emissions and product content by 2015. Recently, the environmental impact of FTOHs became the subject of intense discussion in the literature, revealing the need of acquiring accurate thermodynamic property data, including determinations of vapour pressures. In this context, this work is included in a project related to the accurate measurement and prediction of thermophysical properties of perfluorinated compounds [23–29]. The vapour pressures of some fluorotelomer alcohols can be found in the literature [30–35]. In this work, a phase transition study including vapour pressure determinations of odd fluorotelomer alcohols (with $n = 5$ to 9) is presented. The most stable conformer of 9:1 FTOH and 10:1 FTOH obtained using Gaussian calculations are shown in figure 1.

This work aims to explore the origins of energetic and entropic differentiation in the condensed phases of odd fluorinated alcohols caused by insertion of a $-CF_2-$ group in the linear chain. The trends in the standard molar enthalpies, entropies, and Gibbs free energies of fusion, sublimation and vaporization were studied and analysed for this series of compounds. The volatilities of the liquid odd fluorotelomer alcohols were compared altogether with the literature data values (C6–C12 series) for their alkane analogues [36–39].

2. Experimental

2.1. Purification and characterization of odd fluorotelomer alcohols

1H,1H-perfluoroheptan-1-ol (6:1 FTOH, CAS Registry Number 375-82-6), 1H,1H-perfluorooctan-1-ol (7:1 FTOH, CAS Registry Number 307-30-2), 1H,1H-perfluorononan-1-ol (8:1 FTOH, CAS Registry Number 423-56-3), 1H,1H-perfluorodecan-1-ol (9:1 FTOH, CAS Registry Number 307-37-9) and 1H,1H-perfluoroundecan-1-ol (10:1 FTOH, CAS Registry Number 307-46-0) were purchased from Apollo Scientific Ltd. Prior to their use, the compounds 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. The following mass fraction purity was obtained for all the oFTOH studied: 0.999. Purity details are given in table 1.

The relative atomic masses used in our work were those recommended by the IUPAC Commission in 2007 [40].

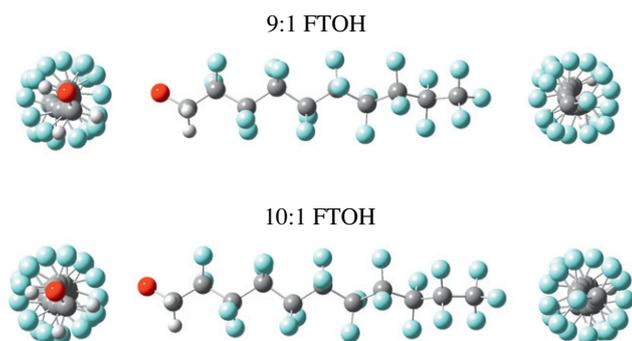


FIGURE 1. Schematic representation of the most stable conformer of 1H,1H-perfluorodecan-1-ol (9:1 FTOH) and 1H,1H-perfluoroundecan-1-ol (10:1 FTOH).

2.2. Differential scanning calorimetry

The temperatures and the standard molar enthalpies of fusion for 7:1 FTOH, 8:1 FTOH, 9:1 FTOH and 10:1 FTOH were measured in a power compensation differential scanning calorimeter, SETARAM model DSC 141, using a heating rate of $0.0333 \text{ K} \cdot \text{s}^{-1}$, 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 [41]: *o*-terphenyl (CAS Registry Number 84-15-1), benzoic acid (CAS Registry Number 65-85-0), indium (CAS Registry Number 7440-74-6), 4-methoxy benzoic acid (CAS Registry Number 100-09-4), tin (CAS Registry Number 7440-31-5), and lead (CAS Registry Number 7439-92-1). At least five experiments for each reference compound were performed. The compounds studied were measured with the same experimental procedure used in the calibration runs.

2.3. Vapour pressure measurements

The vapour pressures of the *o*-FTOH were measured at different temperatures in solid (for 7:1 FTOH, 8:1 FTOH, 9:1 FTOH and 10:1 FTOH) and liquid (for 6:1 FTOH, 7:1 FTOH and 8:1 FTOH) phases using the static apparatus based on a MKS Baratron 631A01TBEH pressure gauge, capable of measuring in the pressure range of (0.4 to 133) Pa and in the temperature range of (253 to 413) K, and on a MKS Baratron 631A11TBFP pressure gauge, capable of measuring in the pressure range of (3 to 1330) Pa and in the temperature range of (253 to 463) K. The apparatus was previously described in detail in the literature by Monte *et al.* [42]. To avoid condensation of the sample, the temperature of the vacuum line was maintained 20 K above the sample temperature. The vapour pressures of the compounds studied were measured at different temperature intervals: 6:1 FTOH, (275 to 313) K; 7:1 FTOH, (268 to 340) K; 8:1 FTOH, (275 to 352) K; 9:1 FTOH, (303 to 359) K; 10:1 FTOH, (310 to 348) K.

2.4. Computational thermochemistry

Quantum chemical calculations were performed with the Gaussian 03 software package [43]. The optimization of the geometries as well as the fundamental vibrational frequency calculations were performed for the compounds using the B3LYP/6-311++G(d,p) level of theory [44,45]. The frequencies were scaled using the scaling factors of 0.9688 and 1.0161 for the fundamental vibrational frequencies when applied to the calculation of heat capacity and entropy, respectively [46]. These calculations were used for the determination of gas phase heat capacities and entropies for all species at $T = 298.15$ K.

3. Results

3.1. Thermodynamic parameters of fusion

For 7:1 FTOH, 8:1 FTOH, 9:1 FTOH, and 10:1 FTOH, the experimental fusion temperatures, T_{fus} , and standard molar enthalpies of fusion at T_{fus} , $\Delta_{\text{cr}}^{\text{f}} H_{\text{m}}^{\circ}(T_{\text{fus}})$, were measured in a power compensation differential scanning calorimeter, SETARAM model DSC 141. The detailed experimental results concerning the fusion are given as Supporting Information. For each compound, the hypothetical molar enthalpy of fusion, at $T = 298.15$ K, was calculated according to equation (1):

$$\Delta_{\text{cr}}^{\text{f}} H_{\text{m}}^{\circ}(T) = \Delta_{\text{cr}}^{\text{f}} H_{\text{m}}^{\circ}(T_{\text{fus}}) + \Delta_{\text{cr}}^{\text{f}} C_{p,\text{m}}^{\circ} \cdot (T - T_{\text{fus}}). \quad (1)$$

TABLE 1

Provenance and purity details of 6:1 FTOH, 7:1 FTOH, 8:1 FTOH, 9:1 FTOH, and 10:1 FTOH.

Chemical name	CAS Registry Number	Provenance	Initial mass fraction purity	Purification method	Final mass fraction purity	Purity analysis method
1H,1H-perfluoroheptan-1-ol	375-82-6	Apollo Scientific Ltd.	0.97	Drying	0.999	GC
1H,1H-perfluorooctan-1-ol	307-30-2	Apollo Scientific Ltd.	0.98	Sublimation	0.999	GC
1H,1H-perfluorononan-1-ol	423-56-3	Apollo Scientific Ltd.	0.98	Sublimation	0.999	GC
1H,1H-perfluorodecan-1-ol	307-37-9	Apollo Scientific Ltd.	0.98	Sublimation	0.999	GC
1H,1H-perfluoroundecan-1-ol	307-46-0	Apollo Scientific Ltd.	0.95	Sublimation	0.999	GC

The hypothetical molar entropy of fusion, at $T = 298.15$ K, was calculated according to equation (2):

$$\Delta_{\text{cr}}^{\text{l}} S_{\text{m}}^{\circ}(T) = \Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^{\circ}(T_{\text{fus}})/T_{\text{fus}} + \Delta_{\text{cr}}^{\text{l}} C_{\text{p,m}}^{\circ} \cdot \ln(T/T_{\text{fus}}). \quad (2)$$

The hypothetical molar Gibbs free energy of fusion, at $T = 298.15$ K, was calculated according to equation (3):

$$\Delta_{\text{cr}}^{\text{l}} G_{\text{m}}^{\circ}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^{\circ}(298.15 \text{ K}) - 298.15 \cdot \Delta_{\text{cr}}^{\text{l}} S_{\text{m}}^{\circ}(298.15 \text{ K}). \quad (3)$$

Table 2 shows the experimental fusion temperatures, and the values for the standard molar enthalpies and entropies of fusion at the fusion temperature for the solid *o*-FTOH studied.

3.2. Vapour pressures and thermodynamic parameters of sublimation and vaporization

Table 3 presents the vapour pressures at several temperatures, obtained using the static apparatus, for the solids 7:1 FTOH, 8:1 FTOH, 9:1 FTOH, and 10:1 FTOH and for the liquids 6:1 FTOH, 7:1 FTOH, and 8:1 FTOH.

The standard molar enthalpies of sublimation/vaporization at the mean temperature of the sublimation/vaporization experiments, $\langle T \rangle$, were derived for the *o*-FTOH studied, using the integrated form of the Clausius–Clapeyron according to equation (4):

$$\ln(p/\text{Pa}) = a - b \cdot [(1/T)/\text{K}^{-1}], \quad (4)$$

where a is a constant and $b = \Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/R$. The plots of $\ln p = f(1/T)$ for 6:1 FTOH, 7:1 FTOH, 8:1 FTOH, 9:1 FTOH, and 10:1 FTOH are shown in figure 2. The values of the triple points are also depicted.

Table 4 presents the parameters of the Clausius–Clapeyron equation, the calculated standard deviations, and the standard molar enthalpies and entropies of sublimation/vaporization at the mean temperature, $\langle T \rangle$. The standard molar enthalpies of sublimation/vaporization at the mean temperature were determined by the parameter b , of the Clausius–Clapeyron equation, and the molar entropies of sublimation/vaporization at $\langle T \rangle$ and $p(\langle T \rangle)$, $\Delta_{\text{cr,l}}^{\text{g}} S_{\text{m}}^{\circ}(\langle T \rangle, p(\langle T \rangle))$, were calculated by equation (5):

$$\Delta_{\text{cr,l}}^{\text{g}} S_{\text{m}}^{\circ}(\langle T \rangle, p(\langle T \rangle)) = \Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/\langle T \rangle. \quad (5)$$

TABLE 2

Experimental fusion temperatures, standard molar enthalpies, and standard molar entropies of fusion, for 7:1 FTOH, 8:1 FTOH, 9:1 FTOH, and 10:1 FTOH.

Compound	$T_{\text{onset}}/\text{K}$	$\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^{\circ}(T_{\text{fus}})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr}}^{\text{l}} S_{\text{m}}^{\circ}(T_{\text{fus}})/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
7:1 FTOH	318.2 ± 0.5	11.9 ± 1.1	37.4 ± 3.5
8:1 FTOH	342.2 ± 0.4	16.6 ± 0.2	48.4 ± 0.6
9:1 FTOH	358.5 ± 0.5	15.9 ± 0.9	44.5 ± 2.6
10:1 FTOH	374.0 ± 0.4	22.4 ± 0.3	60.0 ± 0.6

The uncertainties of the experimental results were assigned based on independent experiments as $t \cdot s/(n)^{1/2}$, including the calibration uncertainty, where t is obtained from student's t -distribution, s is the standard deviation and n is the number of independent experiments.

The standard molar enthalpies of sublimation/vaporization, at $T = 298.15$ K, $\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K})$, were determined by equation (6):

$$\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\circ}(T) = \Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle) + (T - \langle T \rangle) \cdot \Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\circ}. \quad (6)$$

The standard molar entropies of sublimation/vaporization, at $T = 298.15$ K, $\Delta_{\text{cr,l}}^{\text{g}} S_{\text{m}}^{\circ}(298.15 \text{ K})$, were calculated using the equation (7):

$$\Delta_{\text{cr,l}}^{\text{g}} S_{\text{m}}^{\circ}(T) = \Delta_{\text{cr,l}}^{\text{g}} S_{\text{m}}^{\circ}(\langle T \rangle, p(\langle T \rangle)) + \Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\circ}(T) \cdot \ln(T/\langle T \rangle) - R \cdot \ln(p^{\circ}/p(\langle T \rangle)), \quad (7)$$

where $p^{\circ} = 10^5$ Pa. $\Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\circ}$ is the heat capacity of sublimation or vaporization, at $T = 298.15$ K, calculated as $\Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\circ} = C_{\text{p,m}}^{\circ}(\text{g}) - C_{\text{p,m}}^{\circ}(\text{cr,l})$. For each compound, $C_{\text{p,m}}^{\circ}(\text{g})$ was calculated using DFT

TABLE 3

Experimental data of vapour pressures for 6:1 FTOH, 7:1 FTOH, 8:1 FTOH, 9:1 FTOH, and 10:1 FTOH.

T/K	p/Pa	T/K	p/Pa	T/K	p/Pa
6:1 FTOH (l)					
275.55	17.86	290.46	78.37	305.40	293.97
278.02	23.08	292.95	99.12	307.91	363.18
280.53	30.01	295.45	124.73	310.39	434.44
282.99	38.04	297.97	158.70	312.88	533.90
285.49	48.58	300.43	194.63	315.35	624.75
287.97	62.27	302.94	243.08	317.87	755.26
7:1 FTOH (cr)					
268.27	1.04	295.64	30.33	308.10	111.31
273.24	2.01	298.14	39.11	310.56	141.25
278.21	3.88	300.61	51.77	313.08	181.52
283.17	7.14	303.13	66.48	315.52	228.80
288.15	12.72	305.62	87.24	318.05	293.58
293.15	22.73				
7:1 FTOH (l)					
320.52	361.50	328.01	623.58	335.47	1048.20
323.01	435.13	330.49	745.70	337.97	1232.70
325.52	524.00	332.97	871.04	339.44	1359.20
8:1 FTOH (cr)					
275.71	0.48	293.14	4.77	313.09	47.67
278.17	0.67	298.11	8.66	318.06	79.33
283.16	1.28	303.13	15.68	323.03	130.00
288.15	2.50	308.10	27.27		
8:1 FTOH (l)					
342.99	801.75	345.48	944.70	350.45	1299.96
344.00	857.10	347.97	1110.16	351.45	1382.92
9:1 FTOH (cr)					
303.92	4.52	327.88	64.57	347.71	414.00
308.00	7.55	332.84	104.50	352.65	624.70
312.98	13.15	337.79	171.40	355.65	800.80
318.07	22.89	342.75	267.70	358.15	970.00
323.07	37.65				
10:1 FTOH (cr)					
310.53	2.19	325.47	13.21	337.85	49.77
313.02	2.99	327.95	17.24	340.35	64.15
315.51	4.02	330.42	22.07	342.81	82.75
318.00	5.37	332.87	29.09	345.30	106.38
320.48	7.15	335.42	38.15	347.80	136.13
323.00	9.68				

Uncertainties: $\sigma(T/\text{K}) = 0.01$; $\sigma(p/\text{Pa}) = 0.01 + 0.0025 \cdot (p/\text{Pa})$ [42].

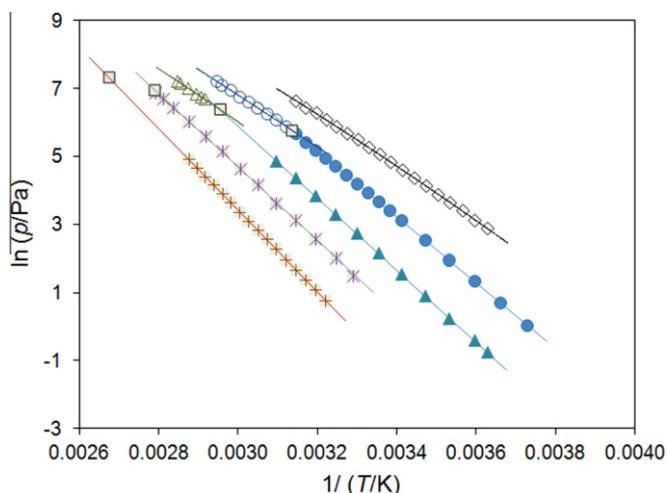


FIGURE 2. Plots of $\ln p$ versus $1/T$ for the odd fluorotelomer alcohols studied: \diamond liquid 6:1 FTOH; \bullet solid 7:1 FTOH; \circ liquid 7:1 FTOH; \blacktriangle solid 8:1 FTOH; \triangle liquid 8:1 FTOH; $*$ solid 9:1 FTOH; $+$ solid 10:1 FTOH; and \square triple points coordinates.

with B3LYP/6-311++G(d,p) level of theory, and for each respective minimum energy conformation of 6:1 FTOH, 7:1 FTOH, 8:1 FTOH, 9:1 FTOH and 10:1 FTOH, yielding for $C_{p,m}^{\circ}(g)$ the values (314.4, 358.4, 402.5, 446.5, and 490.0) $J \cdot K^{-1} \cdot mol^{-1}$, respectively. The uncertainty in $C_{p,m}^{\circ}(g)$ was considered to be $\pm 5 J \cdot K^{-1} \cdot mol^{-1}$. For the liquid 6:1 FTOH and the solid 7:1 FTOH, the heat capacity of the condensed phase, at $T = 298.15$ K, was measured in this work, using a precise heat capacity drop calorimeter; for 6:1 FTOH and 7:1 FTOH, the values of $C_{p,m}^{\circ}(l) = (476.8 \pm 0.3) J \cdot K^{-1} \cdot mol^{-1}$, and $C_{p,m}^{\circ}(cr) = (468.6 \pm 1.1) J \cdot K^{-1} \cdot mol^{-1}$ were obtained, respectively. The measurement procedure and the description of the apparatus have been described in detail elsewhere by Santos *et al.* [47], and the additional information concerning the experimental calibration procedure of the apparatus is available as Supporting Information. From the previous data, $\Delta_f^{\circ} C_{p,m}^{\circ} = -(162 \pm 5) J \cdot K^{-1} \cdot mol^{-1}$ and $\Delta_{cr}^{\circ} C_{p,m}^{\circ} = -(110 \pm 5) J \cdot K^{-1} \cdot mol^{-1}$ were derived for 6:1 FTOH and 7:1 FTOH. Based on these results, $\Delta_{cr}^{\circ} C_{p,m}^{\circ} = -(110 \pm 20) J \cdot K^{-1} \cdot mol^{-1}$ and $\Delta_f^{\circ} C_{p,m}^{\circ} = -(160 \pm 20) J \cdot K^{-1} \cdot mol^{-1}$, were considered for the remaining odd fluorotelomer alcohols, and consequently, a typical value of $\Delta_{cr}^{\circ} C_{p,m}^{\circ} = (50 \pm 20) J \cdot K^{-1} \cdot mol^{-1}$ for the difference in heat capacity between the solid and liquid phases, which is in good agreement with the value of $54.4 J \cdot K^{-1} \cdot mol^{-1}$ proposed by Sidgwick [48] and recommended by Chickos [49]. The standard molar Gibbs free energies of sublimation were calculated through equation (8), where the parameters are referenced to $T = 298.15$ K:

$$\Delta_{cr,l}^{\circ} G_m^{\circ}(T) = \Delta_{cr,l}^{\circ} H_m^{\circ}(T) - T \cdot \Delta_{cr,l}^{\circ} S_m^{\circ}(T). \quad (8)$$

The vapour pressures, at $T = 298.15$ K, were derived through equation (9):

$$p(T) = p^{\circ} \cdot e\left(-\frac{\Delta_{cr,l}^{\circ} G_m^{\circ}(T)}{R \cdot T}\right), \quad (9)$$

where $p^{\circ} = 10^5$ Pa. Table 5 lists the derived standard ($p^{\circ} = 10^5$ Pa) molar enthalpies, entropies, and Gibbs free energies of sublimation/vaporization and the vapour pressures, at $T = 298.15$ K, for 6:1 FTOH, 7:1 FTOH, 8:1 FTOH, 9:1 FTOH, and 10:1 FTOH.

Table 6 lists the fusion and triple point temperatures, the triple point vapour pressure and the standard ($p^{\circ} = 10^5$ Pa) molar enthalpies, entropies, and Gibbs energies of fusion, at $T = 298.15$ K, for the compounds studied, derived from the combined results for the sublimation and vaporization, using equations (10) and (11):

$$\Delta_{cr}^{\circ} H_m^{\circ}(T) = \Delta_{cr}^{\circ} H_m^{\circ}(T) - \Delta_f^{\circ} H_m^{\circ}(T), \quad (10)$$

$$\Delta_{cr}^{\circ} S_m^{\circ}(T) = \Delta_{cr}^{\circ} S_m^{\circ}(T) - \Delta_f^{\circ} S_m^{\circ}(T), \quad (11)$$

The values of the thermodynamic parameters of fusion derived from DSC experiments were calculated (equations (1)–(3)). Table 7 presents the molar entropies in the solid, liquid and gas phases, at $T = 298.15$ K, for the compounds studied. Total gas phase entropies were estimated from the data derived from quantum chemical calculations, and entropies in the condensed phases were derived from the sublimation and vaporization results using equations (12) and (13), respectively

$$S_m^{\circ}(cr,T) = S_m^{\circ}(g,T) - \Delta_{cr}^{\circ} S_m^{\circ}(T), \quad (12)$$

$$S_m^{\circ}(l,T) = S_m^{\circ}(g,T) - \Delta_f^{\circ} S_m^{\circ}(T). \quad (13)$$

4. Discussion

An entropic and enthalpic differentiation along the odd fluorotelomer alcohols series was observed, which strongly supports the existence of an odd–even effect on the thermodynamic parameters of fusion and sublimation. This effect was already observed in some thermodynamic properties of different kinds of compounds, such as paraffins [50], alcohols [51], fatty acids [52], and furthermore, in certain liquid crystals [53] and long-chain amphiphiles [54]. Recently, the same effect was observed in the thermodynamic parameters of a series of oligothiophenes [55]. Concerning the odd fluorotelomer alcohols, a regular odd–even alternation is evidenced in the enthalpies and entropies of sublimation and fusion wherein terms with odd number of carbon atoms show higher values than even terms reflecting the denser packing arrangement of odd-numbered *o*-FTOH. Interactions due to dispersion forces between molecules have attracted increasing attention since the emergence and rapid development of supramolecular chemistry and molecular recognition [56–59]. These intermolecular forces whose energetic and geometric properties are less well understood than those of chemical bonds between atoms in individual molecules support the odd–even effect verified in some properties of other families of compounds [60–68]. Although those interactions

TABLE 4 Experimental sublimation and vaporization results obtained for the odd fluorotelomer alcohols studied, where a and b are from the Clausius–Clapeyron equation, $\ln(p/Pa) = a - b \cdot [(1/T)/K^{-1}]$, and $b = \Delta_{cr,l}^{\circ} H_m^{\circ}(T)/R$; $R = 8.3144621 J \cdot K^{-1} \cdot mol^{-1}$.

Compound	A	b/K	r ²	(T)/K	p((T))/Pa	$\Delta_{cr,l}^{\circ} H_m^{\circ}((T))/(kJ \cdot mol^{-1})$	$\Delta_{cr,l}^{\circ} S_m^{\circ}((T), p((T)))/(J \cdot K^{-1} \cdot mol^{-1})$
7:1 FTOH (cr)	36.04 ± 0.06	9653 ± 19	0.99995	297.04	34.65	80.3 ± 0.2	270.2 ± 1.3
8:1 FTOH (cr)	37.69 ± 0.09	10596 ± 26	0.99995	298.35	8.83	88.1 ± 0.2	295.3 ± 1.5
9:1 FTOH (cr)	37.02 ± 0.14	10781 ± 46	0.9998	332.42	98.35	89.6 ± 0.4	269.6 ± 1.9
10:1 FTOH (cr)	39.35 ± 0.07	11978 ± 24	0.99995	329.17	19.46	99.6 ± 0.2	302.5 ± 1.3
6:1 FTOH (l)	31.20 ± 0.12	7796 ± 36	0.9997	296.70	137.21	64.8 ± 0.3	218.5 ± 1.8
7:1 FTOH (l)	29.61 ± 0.09	7601 ± 30	0.99989	330.38	735.74	63.2 ± 0.2	191.3 ± 1.5
8:1 FTOH (l)	29.34 ± 0.03	7771 ± 12	0.999991	347.06	1046.06	64.6 ± 0.1	186.2 ± 0.9

TABLE 5

Values of the standard ($p^\circ = 0.1$ MPa) molar enthalpies, $\Delta_{\text{cr,l}}^{\text{g}}H_{\text{m}}^\circ$, entropies, $\Delta_{\text{cr,l}}^{\text{g}}S_{\text{m}}^\circ$, and Gibbs free energies, $\Delta_{\text{cr,l}}^{\text{g}}G_{\text{m}}^\circ$, of sublimation and vaporization, and vapour pressures, at $T = 298.15$ K, for the odd fluorotelomer alcohols studied.

Compound	$\Delta_{\text{cr,l}}^{\text{g}}H_{\text{m}}^\circ /$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$\Delta_{\text{cr,l}}^{\text{g}}S_{\text{m}}^\circ /$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	$\Delta_{\text{cr,l}}^{\text{g}}G_{\text{m}}^\circ /$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$p(\text{cr}, T = 298.15 \text{ K}) /$ (Pa)	$\Delta_{\text{cr,l}}^{\text{g}}H_{\text{m}}^\circ /$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$\Delta_{\text{cr,l}}^{\text{g}}S_{\text{m}}^\circ /$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	$\Delta_{\text{cr,l}}^{\text{g}}G_{\text{m}}^\circ /$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$p(\text{l}, T = 298.15 \text{ K}) /$ (Pa)
6:1 FTOH					64.6 ± 0.3	162.9 ± 1.8	16.0 ± 0.6	156.0
7:1 FTOH	80.1 ± 0.2	203.5 ± 1.3	19.5 ± 0.4	39.1	68.4 ± 0.7	166.9 ± 2.5	18.6 ± 1.0	55.1
8:1 FTOH	88.1 ± 0.2	217.8 ± 1.5	23.2 ± 0.5	8.6	72.4 ± 1.0	172.6 ± 3.2	21.0 ± 1.4	21.0
9:1 FTOH	93.4 ± 0.8	224.0 ± 2.9	26.6 ± 1.2	2.2	80.5 ± 0.8	188.8 ± 2.9	24.2 ± 1.2	5.7
10:1 FTOH	103.0 ± 0.7	242.4 ± 2.4	30.7 ± 1.0	0.4	84.4 ± 0.7	193.7 ± 2.4	26.6 ± 1.0	2.2

The values for the thermodynamic parameters of vaporization for 9:1 FTOH and 10:1 FTOH were derived from the combination of the thermodynamic parameters of sublimation (table 5) and fusion (table 6) by equations 10 and 11.

TABLE 6

Fusion temperatures, T_{fus} , values of the temperature, T_{Tp} , and pressure, p_{Tp} , of the triple point and derived hypothetical molar enthalpies, $\Delta_{\text{cr,l}}^{\text{l}}H_{\text{m}}^\circ$, entropies, $\Delta_{\text{cr,l}}^{\text{l}}S_{\text{m}}^\circ$, and Gibbs free energies, $\Delta_{\text{cr,l}}^{\text{l}}G_{\text{m}}^\circ$, of fusion, at $T = 298.15$ K, for the odd fluorotelomer alcohols studied.

Compound	$T_{\text{fus}} / (\text{K})$		$T_{\text{Tp}} / (\text{K})$	$p_{\text{Tp}} / (\text{Pa})$	$\Delta_{\text{cr,l}}^{\text{l}}H_{\text{m}}^\circ / (\text{kJ} \cdot \text{mol}^{-1})$		$\Delta_{\text{cr,l}}^{\text{l}}S_{\text{m}}^\circ / (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$		$\Delta_{\text{cr,l}}^{\text{l}}G_{\text{m}}^\circ / (\text{kJ} \cdot \text{mol}^{-1})$		
	DSC	#			DSC	Δ	#	DSC	Δ	#	DSC
7:1 FTOH	318.2	318.9	321.3	11.8 ± 0.7	10.9 ± 1.2	-0.9 ± 1.1	36.7 ± 2.9	34.1 ± 3.7	-2.5 ± 4.0	0.8 ± 1.1	0.7 ± 1.6
8:1 FTOH	342.2	338.3	587.3	15.7 ± 1.0	14.4 ± 0.9	-1.3 ± 1.8	45.2 ± 3.5	41.5 ± 2.8	-3.7 ± 5.7	2.2 ± 1.5	2.0 ± 1.2
9:1 FTOH	358.5		1040.9		12.9 ± 1.5			35.3 ± 4.5			2.4 ± 2.0
10:1 FTOH	374.0		1524.4		18.6 ± 1.5			48.7 ± 4.6			4.1 ± 2.1

Calculated by the combination of the sublimation and vaporization parameters by equations (10) and (11); Δ – difference between the calculated and the derived values by DSC (differential scanning calorimetry). The values of the triple point temperature for 9:1 FTOH and 10:1 FTOH were assumed as the fusion temperatures measured by DSC and corresponding vapour pressures were obtained by extrapolation to the fusion temperature.

TABLE 7

Values of the entropies in crystalline, $S_{\text{m}}^\circ(\text{cr})$, liquid, $S_{\text{m}}^\circ(\text{l})$, and gas, $S_{\text{m}}^\circ(\text{g})$, phases, at $T = 298.15$ K, for the odd fluorotelomer alcohols studied.

Compound	$S_{\text{m}}^\circ(\text{cr}) /$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	$S_{\text{m}}^\circ(\text{l}) /$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	$S_{\text{m}}^\circ(\text{g}) /$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)
6:1 FTOH		458.8 ± 8.3	622
7:1 FTOH	476.5 ± 5.2	513.0 ± 5.9	680
8:1 FTOH	519.2 ± 5.2	564.6 ± 6.3	737
9:1 FTOH	573.0 ± 5.8	608.4 ± 7.3	797
10:1 FTOH	609.6 ± 5.5	658.4 ± 7.2	852

The $S_{\text{m}}^\circ(\text{g})$ uncertainty was estimated as $\pm 5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

can be related with the alternation verified in some thermodynamic parameters respecting the odd and even 1H,1H-perfluorinated alcohols, we do not found any other support in the literature relating evidences of the odd–even effect in this type of compounds.

4.1. Sublimation and vaporization equilibria

In figure 3, the trends of $\Delta_{\text{cr,l}}^{\text{g}}H_{\text{m}}^\circ$ (298.15 K), $\Delta_{\text{cr,l}}^{\text{g}}S_{\text{m}}^\circ$ (298.15 K), and $\Delta_{\text{cr,l}}^{\text{g}}G_{\text{m}}^\circ$ (298.15 K) for the *o*-FTOHs studied are presented. For the sublimation results, enthalpic and entropic differentiations are observed for these compounds with a visible an odd–even effect showing higher values of $\Delta_{\text{cr,l}}^{\text{g}}H_{\text{m}}^\circ$ (298.15 K), $\Delta_{\text{cr,l}}^{\text{g}}S_{\text{m}}^\circ$ (298.15 K), and $\Delta_{\text{cr,l}}^{\text{g}}G_{\text{m}}^\circ$ (298.15 K) for the members with an odd number of carbon atoms. The members with odd number of carbon atoms are characterized by a slightly increased stability in the crystal packing which leads to their lower volatility. For the vaporization results, the enthalpic and entropic differentiations are not so evidenced. The thermodynamic parameters of vaporization for 9:1 FTOH and 10:1 FTOH were derived by the combination of the thermodynamic parameters of sublimation and fusion equilibria and may be affected by uncertainties of the corresponding heat capacity corrections. The enthalpic and entropic differentiations seem to be more pronounced for these two compounds than for the rest of

the series. The odd–even effect is less evident in the thermodynamic parameters of vaporization suggesting that the volatilities of the liquid *o*-FTOHs changes linearly with the carbon atoms in molecule, *i.e.* there is no distinct difference in the behaviour of odd and even members of the homologous series.

4.2. Fusion equilibria

In figure 4, the trends of T_{Tp} and $\ln(p_{\text{Tp}})$ for the *o*-FTOH studied are presented. The parameters of the triple point for the 6:1 FTOH or other compounds of this family can be estimated by extrapolation. A similar trend is found for the triple point temperatures and for their corresponding pressures, suggesting a subtle but not distinctive trend change from 9:1 FTOH onwards, because of the limited number of the members of the series. The triple point temperatures are approximately equal to the fusion temperatures at these pressures. This analysis becomes important for comparison of the phase stability of different perfluoroalcohols because the fusion temperatures are related to enthalpic and entropic contributions, as indicated by the relation $T_{\text{fus}} = \Delta_{\text{cr,l}}^{\text{l}}H_{\text{m}}^\circ(T_{\text{fus}}) / \Delta_{\text{cr,l}}^{\text{l}}S_{\text{m}}^\circ(T_{\text{fus}})$.

In figure 5, the trends of $\Delta_{\text{cr,l}}^{\text{l}}H_{\text{m}}^\circ$ (298.15 K), $\Delta_{\text{cr,l}}^{\text{l}}S_{\text{m}}^\circ$ (298.15 K), $\Delta_{\text{cr,l}}^{\text{l}}G_{\text{m}}^\circ$ (298.15 K) and S_{m}° for the *o*-FTOH studied are presented. The thermodynamic parameters of fusion refer to the hypothetical values corrected to $T = 298.15$ K, thus allowing a direct comparison of the fusion parameters along this series. As can be seen, enthalpic and entropic differentiations along with an odd–even effect are observed with higher values of $\Delta_{\text{cr,l}}^{\text{l}}H_{\text{m}}^\circ$ (298.15 K), $\Delta_{\text{cr,l}}^{\text{l}}S_{\text{m}}^\circ$ (298.15 K), and $\Delta_{\text{cr,l}}^{\text{l}}G_{\text{m}}^\circ$ (298.15 K) for the compounds with an odd number of carbon atoms. This effect corroborates the results observed for sublimation equilibrium, supporting the idea that the members with an odd number of carbon atoms are characterized by a stability increase in the respective crystal packing. This is further supported by comparison of the entropies in the solid, liquid and gas phases. The odd–even alternation is clearly noted for the entropy of the solid phase while the entropy of gas and liquid phases shows a linear dependence on a number of carbon atoms. Higher values of the

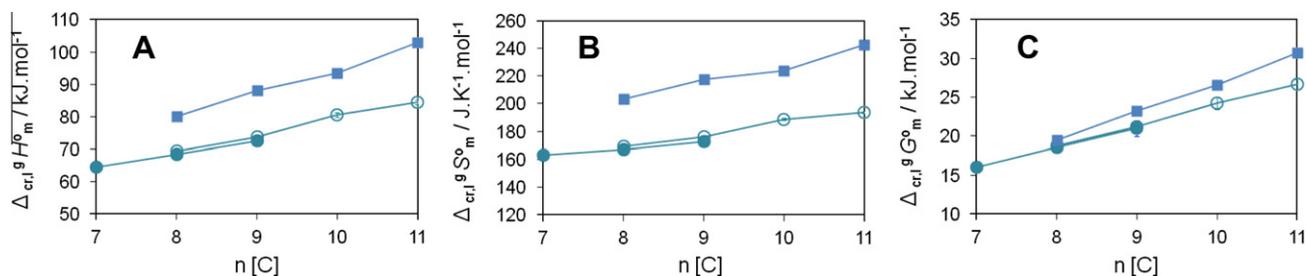


FIGURE 3. Trends of $\Delta_{\text{cr,l}}^{\text{g}}H_{\text{m}}^{\text{o}}$ (A), $\Delta_{\text{cr,l}}^{\text{g}}S_{\text{m}}^{\text{o}}$ (B), and $\Delta_{\text{cr,l}}^{\text{g}}G_{\text{m}}^{\text{o}}$ (C), at $T = 298.15$ K, for the odd FTOH series: thermodynamic parameters of sublimation (■); thermodynamic parameters of vaporization derived from the vapour pressures (●); and derived by the combined fusion and sublimation equilibrium (○).

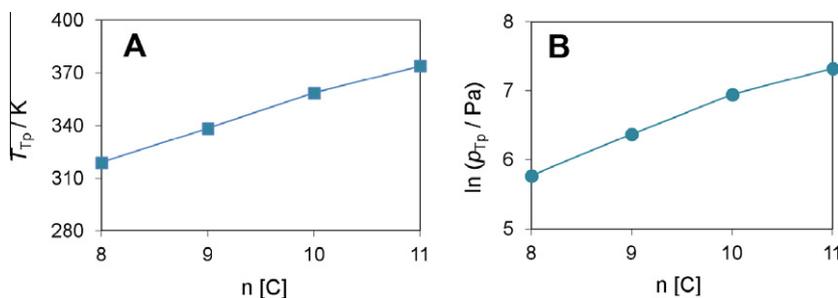


FIGURE 4. Trends of T_{Tp} (A) and $\ln(p_{\text{Tp}})$ (B) for the odd FTOH series.

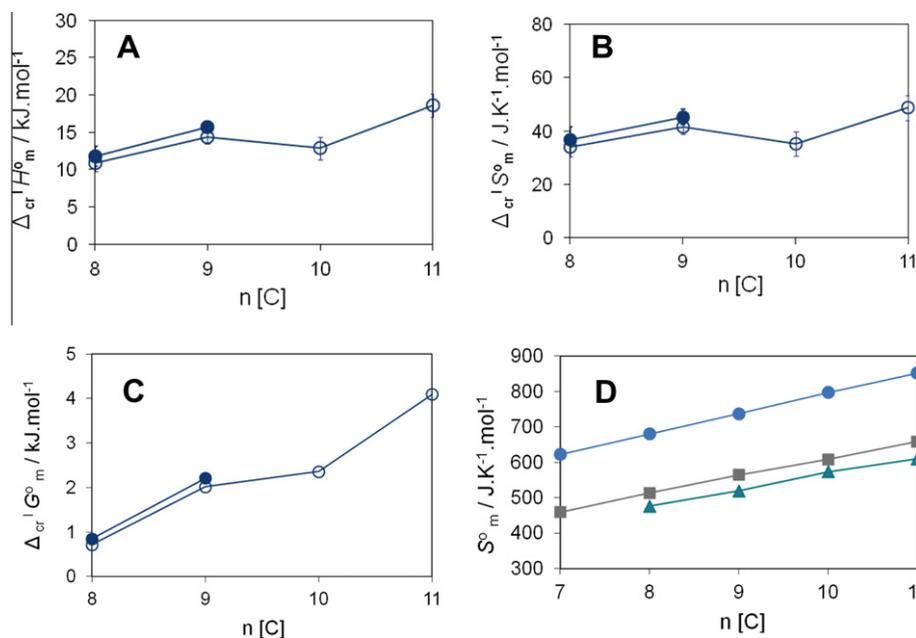


FIGURE 5. Trends of $\Delta_{\text{cr,l}}^{\text{l}}H_{\text{m}}^{\text{o}}$ (A), $\Delta_{\text{cr,l}}^{\text{l}}S_{\text{m}}^{\text{o}}$ (B), and $\Delta_{\text{cr,l}}^{\text{l}}G_{\text{m}}^{\text{o}}$ (C), at $T = 298.15$ K, for the odd FTOH series: values derived by the combined sublimation and fusion equilibria (●); values derived by DSC (○), and derived absolute entropies, S_{m}^{o} (D), for the crystal (▲), liquid (■), and gas (●) phases.

entropy of the solid phase for the members with an even number of carbon atoms suggest looser packing arrangements in the crystalline phase and lower cohesive energies as compared to the odd members.

4.3. Liquid odd fluorotelomer alcohols and their alkane analogues

The thermodynamic parameters of vaporization of the *o*-FTOH compounds were compared with the literature data values for the *n*-alcohols to verify the enthalpic and entropic differentiations and the corresponding different volatilities between these families of compounds. Table 8 summarizes the enthalpies, entropies and

Gibbs energies of vaporization for the polyfluorinated compounds series studied in this work and for their alkane analogues from the hexan-1-ol to dodecan-1-ol (C6–C12 series). In figure 6, the trends of $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\text{o}}$, $\Delta_{\text{l}}^{\text{g}}S_{\text{m}}^{\text{o}}$, and $\Delta_{\text{l}}^{\text{g}}G_{\text{m}}^{\text{o}}$ for the *o*-FTOHs and related *n*-alcohols are presented.

The results show a higher volatility for liquid fluorotelomer alcohols than for their alkane analogues, which is easily verified by analysis of the $\Delta_{\text{l}}^{\text{g}}G_{\text{m}}^{\text{o}}$ trends representation. The differences in Gibbs energy values between *n*-alcohols and *o*-FTOHs, from C7 onwards, amounts to a constant value of $3.9 \text{ kJ} \cdot \text{mol}^{-1}$ allowing the estimation of the volatilities of the higher liquid *o*-FTOH from the volatilities of the *n*-alcohols. The enthalpies of vaporization

TABLE 8

Values of the standard ($p^\circ = 0.1$ MPa) molar enthalpies, $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^\circ$, entropies, $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^\circ$, and Gibbs free energies, $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ$, of vaporization, at $T = 298.15$ K, for n -alcohols and odd fluorotelomer alcohols.

Compound	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^\circ / (\text{kJ} \cdot \text{mol}^{-1})$		$\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^\circ / (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$		$\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ / (\text{kJ} \cdot \text{mol}^{-1})$		$\Delta(\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ) / (\text{kJ} \cdot \text{mol}^{-1})$
	n -alcohols	o -FTOH	n -alcohols	o -FTOH	n -alcohols	o -FTOH	
C6	61.0 ± 0.1		147.1 ± 0.7		17.2 ± 0.2		
C7	66.9 ± 0.1	64.6 ± 0.3	157.5 ± 0.8	162.9 ± 1.8	19.9 ± 0.2	16.0 ± 0.6	3.9
C8	70.2 ± 0.1	68.4 ± 0.7	159.6 ± 0.7	166.9 ± 2.5	22.6 ± 0.2	18.6 ± 1.0	4.0
C9	73.6 ± 1.4	72.4 ± 1.0	163.5 ± 3.9	172.6 ± 3.2	24.9 ± 1.8	21.0 ± 1.4	3.9
C10	81.3 ± 0.1	80.5 ± 0.8	178.8 ± 0.8	188.8 ± 2.9	28.0 ± 0.3	24.2 ± 1.2	3.8
C11	84.9 ± 0.4	84.4 ± 0.7	182.4 ± 1.3	193.7 ± 2.4	30.5 ± 0.5	26.6 ± 1.0	3.9
C12	90.1 ± 0.3		190.5 ± 1.1		33.3 ± 0.4		

The enthalpies and entropies of vaporization for C6:C12 n -alcohols were derived from vapour pressure data [36–39]. The correction for $T = 298.15$ K was made using the $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ$ calculated values of (–90, –100, –110, –120, –130, –140, and –150) $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, respectively, and considering an uncertainty of $\pm 10 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

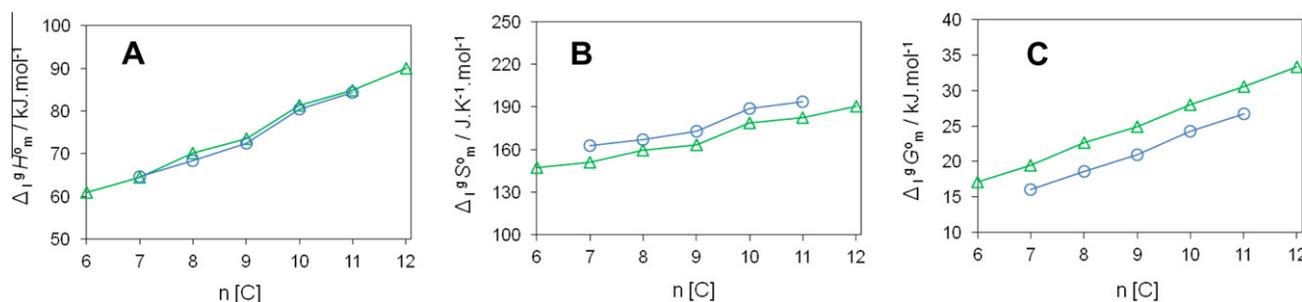


FIGURE 6. Trends of $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^\circ$ (A), $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^\circ$ (B), and $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ$ (C), at $T = 298.15$ K, for n -alcohols (Δ) and odd FTOHs (\circ) series.

of 6:1 FTOH, 7:1 FTOH, 8:1 FTOH, 9:1 FTOH, and 10:1 FTOH are similar to those observed for the n -alcohols but the entropies of vaporization are clearly higher, which corresponds to the observed difference in volatility ($\approx ca. 4 \text{ kJ} \cdot \text{mol}^{-1}$) between n -alcohols and o -FTOHs. The higher volatility of liquid odd fluorotelomer alcohols when compared to their alkane analogues is entropically driven due to the higher molecular conformation restriction and/or the higher molecular weight of liquid polyfluorinated alcohols.

5. Conclusions

A phase transition study of odd fluorotelomer alcohols evidenced a distinctive odd–even effect in the thermodynamic parameters of sublimation and fusion indicating an increase of the stability in the crystal packing for the members with an odd number of carbon atoms. The odd–even effect was verified through the results derived for $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^\circ$, $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^\circ$, $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ$, $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^\circ$, $\Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^\circ$, and $\Delta_{\text{cr}}^{\text{l}}G_{\text{m}}^\circ$. The thermodynamic parameters of vaporization for the o -FTOH series studied were compared with the literature results for their alkane analogues, showing a higher volatility of liquid fluorotelomer alcohols (a constant difference of $\approx ca. 4 \text{ kJ} \cdot \text{mol}^{-1}$ in $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ$), which is entropically driven and could be attributed to the higher molecular conformation restriction and/or the higher molecular weight of liquid polyfluorinated alcohols.

The environmental impact of FTOHs became a recent subject of intense discussion in the literature, and the measurements of vapour pressures performed in this work contribute to the efforts of acquiring accurate thermodynamic property data for this family of compounds.

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Appendix A. Supplementary data

Tables showing the experimental results of fusion, heat capacities determinations, and gas phase optimized geometries are available. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.micromeso.2007.04.043>.

References

- [1] D.A. Ellis, J.W. Martin, S.A. Mabury, Environ. Sci. Technol. 37 (2003) 3816–3820.
- [2] D.A. Ellis, J.W. Martin, A.O. Silva, S.A. Mabury, M.D. Hurley, M.P.S. Andersen, T.J. Wallington, Environ. Sci. Technol. 38 (2004) 3316–3321.
- [3] J.J. Ellington, J.W. Washington, J.J. Evans, T.M. Jenkins, S.C. Hafner, M.P. Neill, J. Chrom. J. Chrom. A 1216 (2009) 5347–5354.
- [4] H. Yoo, J.W. Washington, J.J. Ellington, T.M. Jenkins, M.P. Neill, Environ. Sci. Technol. 44 (2010) 8397–8402.
- [5] Z. Wang, A.U. Daula, S. Fiedler, K.W. Schramm, Environ. Sci. Pollut. Res. 17 (2010) 154–164.
- [6] M. Shoeb, T. Harner, G.M. Webster, S.C. Lee, Environ. Sci. Technol. 45 (2011) 7999–8005.
- [7] G. Yarwood, S.K. Cook, M. Keinath, R.L. Waterland, S.H. Korzeniowski, R.C. Buck, M.H. Russel, S.T. Washburn, Environ. Sci. Technol. 41 (2007) 5756–5762.
- [8] C. Eschauzier, J. Haftka, P.J. Stuyfzand, P. Voogt, Environ. Sci. Technol. 44 (2010) 7450–7455.
- [9] C.E. Müller, A.C. Gerecke, A.C. Alder, M. Scheringer, K. Hungerbühler, Environ. Pollut. 159 (2011) 1419–1426.
- [10] N.L. Stock, D.A. Ellis, L. Deleebeeck, D.C. Muir, S.A. Mabury, Environ. Sci. Technol. 38 (2004) 1693–1699.
- [11] P.J. Krusic, A.A. Marchione, F. Davidson, M.A. Kaiser, C.P. Kao, R.E. Richardson, M. Botelho, R.L. Waterland, R.C. Buck, J. Phys. Chem. A 109 (2005) 6232–6241.
- [12] K.-U. Goss, G. Bronner, T. Harner, M. Hertel, T.C. Schmidt, Environ. Sci. Technol. 40 (2006) 3572–3577.
- [13] H.P.H. Arp, C. Niederer, K.-U. Goss, Environ. Sci. Technol. 40 (2006) 7298–7304.
- [14] G.T. Tomy, W. Budakowski, T. Hallderson, P.A. Helm, G.A. Stern, K. Friesen, K. Pepper, S.A. Tittlemier, A.T. Fisk, Environ. Sci. Technol. 38 (2004) 6475–6481.

- [15] H.J. Lehmler, *Chemosphere* 58 (2005) 1471–1496.
- [16] J. Liu, L.S. Lee, *Environ. Sci. Technol.* 41 (2007) 5357–5362.
- [17] C.J. Young, D.J. Donaldson, *J. Phys. Chem. A* 111 (2007) 13466–13471.
- [18] C.M. Butt, U. Berger, R. Bossi, G.T. Tomy, *Sci. Total Environ.* 408 (2010) 2936–2965.
- [19] M.D. Sedlak, D.J. Greig, *J. Environ. Monit.* 14 (2012) 146–154.
- [20] M.J. Strynar, A.B. Lindstrom, S.F. Nakayama, P.P. Egeghy, L.J. Helfan, *Chemosphere* 86 (2012) 252–257.
- [21] R. Renner, T. Eichenseher, L. Thrall, *Environ. Sci. Technol.* 40 (2006) 1376–1380.
- [22] M. Joyce, A. Dinglasan, Y. Ye, E.A. Edwards, S.A. Mabury, *Environ. Sci. Technol.* 38 (2004) 2857–2864.
- [23] A.M.A. Dias, A.I. Caco, J.A.P. Coutinho, L.M.N.B.F. Santos, M.M. Piñeiro, L.F. Vega, M.F. Costa Gomes, I.M. Marrucho, *Fluid Phase Equilib.* 225 (2004) 39–47.
- [24] A.M.A. Dias, C.M.B. Gonçalves, A.I. Caço, L.M.N.B.F. Santos, M.M. Piñeiro, L.F. Vega, J.A.P. Coutinho, I.M. Marrucho, *J. Chem. Eng. Data* 50 (2005) 1328–1333.
- [25] M.G. Freire, L. Gomes, L.M.N.B.F. Santos, I.M. Marrucho, J.A.P. Coutinho, *J. Phys. Chem. B* 110 (2006) 22923–22929.
- [26] J.R. Trindade, A.M.A. Dias, M. Blesic, N. Pedrosa, L.P.N. Rebelo, L.F. Vega, J.A.P. Coutinho, I.M. Marrucho, *Fluid Phase Equilib.* 251 (2007) 33–40.
- [27] M.G. Freire, P.J. Carvalho, L.M.N.B.F. Santos, L.R. Gomes, I.M. Marrucho, J.A.P. Coutinho, *J. Chem. Thermodyn.* 42 (2010) 213–219.
- [28] L.R. Schröder, L.M.N.B.F. Santos, M.B. Oliveira, I.M. Marrucho, J.A.P. Coutinho, *Chemosphere* 84 (2011) 415–422.
- [29] A.C. Meeks, I.J. Goldfarb, *J. Chem. Eng. Data* 12 (1967) 196.
- [30] N.L. Stock, D.A. Ellis, L. Deleebecck, D.C.G. Muir, S.A. Mabury, *Environ. Sci. Technol.* 38 (2004) 1693–1699.
- [31] P.J. Krusic, A.A. Marchione, F. Davidson, M.A. Kaiser, C.P.C. Kao, R.E. Richardson, M. Botelho, R.L. Waterland, R.C. Buck, *J. Phys. Chem. A* 109 (2005) 6232–6241.
- [32] D.P. Cobranchi, M. Botelho, L.W. Buxton, R.C. Buck, M.A. Kaiser, *J. Chrom. A* 1108 (2006) 248–251.
- [33] D. Ambrose, C. Tsonopoulos, E.D. Nikitin, *J. Chem. Eng. Data* 54 (2009) 669–689.
- [34] J. Dykji, J. Svoboda, R.C. Wilhoit, M. Frenkel, K.R. Hall, K.R. Hall (ed.), *Springer Materials – The Landolt-Börnstein Database*. <<http://www.springermaterials.com>>, http://dx.doi.org/10.1007/10680373_19.
- [35] V. Majer, V. Svoboda, *Enthalpies of Vapourization of Organic Compounds: A Critical Review and Data Compilation*, Blackwell Scientific Publications, Oxford, 1985, p. 300.
- [36] D. Kulikov, S.P. Verevkin, A. Heintz, *Fluid Phase Equilib.* 192 (2001) 187–207.
- [37] G.N. Roganov, P.N. Pisarev, V.N. Emel'yanenko, S.P. Verevkin, *J. Chem. Eng. Data* 50 (2005) 1114–1124.
- [38] K. Nasirzadeh, R. Neueder, W. Kunz, *J. Chem. Eng. Data* 51 (2006) 7–10.
- [39] M. Wieser, M. Berglund, *Pure Appl. Chem.* 81 (2009) 2131–2156.
- [40] R. Sabbah, A. Xu-wu, J.S. Chickos, M.L. Leitão, M.V. Roux, L.A. Torres, *Thermochim. Acta* 33 (1999) 193–204.
- [41] M.J.S. Monte, L.M.N.B.F. Santos, M. Fulem, J.M.S. Fonseca, C.A.D. Sousa, *J. Chem. Eng. Data* 51 (2006) 757–766.
- [42] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian03, Revision C.02*, Gaussian Inc., Pittsburgh, PA, 2004.
- [43] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098–3100.
- [44] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648–5652.
- [45] J. Merrick, D. Moran, L. Radom, *J. Phys. Chem. A* 111 (2007) 11683–11700.
- [46] L.M.N.B.F. Santos, M.A.A. Rocha, A.S.M.C. Rodrigues, V. Štefja, M. Fulem, M. Bastos, *J. Chem. Thermodyn.* 43 (2011) 1818–1823.
- [47] N.V. Sidgwick, *The Covalent Link in Chemistry*, Cornell University Press, Ithaca, New York, 1933, p. 104.
- [48] J.S. Chickos, *Thermochim. Acta* 313 (1998) 19–26.
- [49] G.L. Somayajulu, *Int. J. Thermophys.* 11 (1990) 555–572.
- [50] H. Izumi, S. Yamagami, S. Futamura, L.A. Nafie, R.K. Dukor, *J. Am. Chem. Soc.* 126 (2004) 194–198.
- [51] D. Yablou, D. Wintgens, W. Flynn, *J. Phys. Chem. B* 106 (2002) 5470–5475.
- [52] M.I. Capar, E. Cebe, *J. Theor. Comput. Chem.* 28 (2007) 2140–2146.
- [53] T. Kobayashi, T. Seki, *Langmuir* 19 (2003) 9297–9304.
- [54] J.C.S. Costa, C.F.R.A.C. Lima, L.R. Gomes, B. Schröder, L.M.N.B.F. Santos, *J. Phys. Chem. C* 115 (2011) 23543–23551.
- [55] M.S. Searle, D.H. Williams, *J. Am. Chem. Soc.* 114 (1992) 10690–10697.
- [56] R. Boese, H.-C. Weiss, D. Bläser, *Angew. Chem., Int. Ed.* 38 (1999) 988–992.
- [57] A.K. Tewari, R. Dubey, *Bioorg. Med. Chem.* 16 (2008) 126–143.
- [58] J.A.A.W. Elemans, S. Lei, S.D. Feyter, *Angew. Chem., Int. Ed.* 48 (2009) 7298–7332.
- [59] W.A. Caspari, *J. Chem. Soc.* (1928) 3235.
- [60] S.C. Khetarpal, L. Krishan, H.L. Bhatnagar, *Indian J. Chem.* 19A (1980) 516.
- [61] Y. Tao, P.H. McMurry, *Environ. Sci. Technol.* 23 (1989) 1519–1523.
- [62] P. Saxena, L.M. Hildemann, *J. Atmos. Chem.* 24 (1996) 57–60.
- [63] R. Boese, H.C. Weiss, D. Bläser, *Angew. Chem., Int. Ed. Engl.* 38 (1999) 988–992.
- [64] V.R. Thalladi, R. Boese, H.C. Weiss, *J. Am. Chem. Soc.* 122 (2000) 1186–1190.
- [65] M. Bilde, S. Svenningsson, J. Mønster, T. Rosenørn, *Environ. Sci. Technol.* 37 (2003) 1371–1378.
- [66] R. Azumi, M. Goto, K. Honda, M. Matsumoto, *Bull. Chem. Soc. Jpn.* 76 (2003) 1561–1567.
- [67] K. Kim, K.E. Plass, A.J. Matzger, *J. Am. Chem. Soc.* 127 (2005) 4879–4887.

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