Supporting Information

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, Prague, Technická 5, CZ-166 28 Prague 6, Czech Republic

[c] CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal.

Tables

TABLE S1: Experimental results obtained for the study of the solid-liquid equilibrium of 7:1 FTOH in a power compensation DSC (SETARAM model 141).

m / mg	T_{onset} / K	φ / μV·s·mg^{-1}	ΔT_{corr} / K	T_{corr} / K	K / μV·s·mJ^{-1}	$\Delta_{fus}H^o$ / kJ·mol^{-1}
18.4962	318.18	277.2	-0.184	318.36	8.593	12.91
21.0784	319.03	269.2	-0.151	319.18	8.600	12.52
20.5180	318.46	233.7	-0.173	318.63	8.596	10.88
25.6394	318.10	261.6	-0.188	318.29	8.593	12.18
9.4917	318.00	238.1	-0.192	318.19	8.592	11.09
21.4234	316.57	243.4	-0.248	316.82	8.580	11.35
	T_{fus} / K	318.2		$\Delta_{fus}H^o$ / kJ·mol^{-1}	11.9	

Note:

$\Delta T_{corr} = -0.0000284 \times (T_{onset})^2 + 0.0578 \times T_{onset} + (-15.70)$

$T_{corr} = T_{onset} - \Delta T_{corr}$

$K = -0.0000346 \times (T_{corr})^2 + 0.0303 \times T_{corr} + 2.45$

The temperature and heat flux scales were calibrated by measuring the temperature and the heat of fusion of some reference materials for calorimetry and differential thermal analysis: o-terphenyl, benzoic acid, indium, 4-methoxy-benzoic acid, tin, lead and zinc.

The uncertainties of the experimental results were assigned based on independent experiments as $t \times s/\sqrt{n}$, 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.

Uncertainty in T_{fus} = 0.5 K
Uncertainty in $\Delta_{fus}H^o$ = 1.1 kJ·mol^{-1}

TABLE S2: Experimental results obtained for the study of the solid-liquid equilibrium of 8:1 FTOH in a power compensation DSC (SETARAM model 141).

m / mg	T_{onset} / K	φ / μV·s·mg^{-1}	ΔT_{corr} / K	T_{corr} / K	K / μV·s·mJ^{-1}	$\Delta_{fus}H^o$ / kJ·mol^{-1}
29.078	343.16	327.7	0.790	342.37	8.772	16.81
22.2358	343.11	322.1	0.788	342.32	8.772	16.53
18.3242	342.45	324.3	0.763	341.69	8.768	16.65
18.4449	343.15	320.5	0.790	342.36	8.772	16.45
20.9890	342.88	319.1	0.780	342.10	8.770	16.38
	T_{fus} / K	342.2		$\Delta_{fus}H^o$ / kJ·mol^{-1}	16.6	

Note:

$\Delta T_{corr} = -0.0000284 \times (T_{onset})^2 + 0.0578 \times T_{onset} + (-15.70)$

$T_{corr} = T_{onset} - \Delta T_{corr}$

$K = -0.0000346 \times (T_{corr})^2 + 0.0303 \times T_{corr} + 2.45$

The temperature and heat flux scales were calibrated by measuring the temperature and the heat of fusion of some reference materials for calorimetry and differential thermal analysis: o-terphenyl, benzoic acid, indium, 4-methoxy-benzoic acid, tin, lead and zinc.

The uncertainties of the experimental results were assigned based on independent experiments as $t \times s/\sqrt{n}$, 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.

Uncertainty in T_{fus} = 0.4 K
Uncertainty in $\Delta_{fus}H^o$ = 0.2 kJ·mol^{-1}

TABLE S3: Experimental results obtained for the study of the solid-liquid equilibrium of 9:1 FTOH in a power compensation DSC (SETARAM model 141).

m / mg	T_{onset} / K	φ / $\mu V \cdot s \cdot mg^{-1}$	ΔT_{corr} / K	T_{corr} / K	K / $\mu V \cdot s \cdot mJ^{-1}$	$\Delta_{fus}H^o$ / $kJ \cdot mol^{-1}$
18.4373	360.00	299.0	1.427	358.57	8.870	16.86
23.4378	359.59	279.6	1.412	358.18	8.868	15.77
27.4697	359.70	284.4	1.416	358.28	8.869	16.04
15.4500	359.68	287.7	1.415	358.26	8.869	16.22
20.2613	360.52	238.6	1.447	359.07	8.873	14.87
	T_{fus} / K	358.5		$\Delta_{fus}H^o$ / $kJ \cdot mol^{-1}$	15.9	

Note:

$\Delta T_{corr} = -0.0000284 \times (T_{onset})^2 + 0.0578 \times T_{onset} + (-15.70)$

$T_{corr} = T_{onset} - \Delta T_{corr}$

$K = -0.0000346 \times (T_{corr})^2 + 0.0303 \times T_{corr} + 2.45$

The temperature and heat flux scales were calibrated by measuring the temperature and the heat of fusion of some reference materials for calorimetry and differential thermal analysis: o-terphenyl, benzoic acid, indium, 4-methoxy-benzoic acid, tin, lead and zinc.

The uncertainties of the experimental results were assigned based on independent experiments as $t \times s/\sqrt{n}$, 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.

Uncertainty in T_{fus} = 0.5 K
Uncertainty in $\Delta_{fus}H^o$ = 0.9 $kJ \cdot mol^{-1}$

TABLE S4: Experimental results obtained for the study of the solid-liquid equilibrium of 10:1 FTOH in a power compensation DSC (SETARAM model 141).

m / mg	T_{onset} / K	φ / μV·s·mg^{-1}	ΔT_{corr} / K	T_{corr} / K	K / μV·s·mJ^{-1}	$\Delta_{fus}H^o$ / kJ·mol^{-1}
7.7988	376.35	368.9	2.030	374.32	8.949	22.68
14.3713	375.84	364.6	2.012	373.83	8.946	22.42
7.9164	376.33	366.7	2.030	374.30	8.948	22.54
8.3245	375.91	361.8	2.014	373.90	8.947	22.25
10.3566	375.65	362.3	2.005	373.65	8.946	22.28
	T_{fus} / K	374.0		$\Delta_{fus}H^o$ / kJ·mol^{-1}	22.4	

Note:

$\Delta T_{corr} = -0.0000284 \times (T_{onset})^2 + 0.0578 \times T_{onset} + (-15.70)$

$T_{corr} = T_{onset} - \Delta T_{corr}$

$K = -0.0000346 \times (T_{corr})^2 + 0.0303 \times T_{corr} + 2.45$

The temperature and heat flux scales were calibrated by measuring the temperature and the heat of fusion of some reference materials for calorimetry and differential thermal analysis: o-terphenyl, benzoic acid, indium, 4-methoxy-benzoic acid, tin, lead and zinc.

The uncertainties of the experimental results were assigned based on independent experiments as $t \times s/\sqrt{n}$, 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.

Uncertainty in T_{fus} = 0.4 K
Uncertainty in $\Delta_{fus}H^o$ = 0.3 kJ·mol^{-1}

TABLE S5: Experimental results of $C_p^\circ(\mathrm{cr}, 298.15\ \mathrm{K})$ for 6:1 FTOH using a drop heat capacity calorimeter.

m / g	ΔT / K	$\langle T \rangle$ / K	A / V·s·K^{-1}	$C_{p,m}^\circ$ / J·K^{-1}·mol^{-1}
0.93751	10.018	298.157	0.192312	476.32
	10.020	298.159	0.192494	476.77
	10.025	298.163	0.192063	475.70
	10.022	298.162	0.192388	476.51
	10.018	298.161	0.192550	476.91
	10.013	298.158	0.192756	477.42
	10.012	298.159	0.192697	477.27
	10.012	298.158	0.192384	476.50
	10.011	298.158	0.192605	477.05
	10.010	298.157	0.192531	476.86
	10.009	298.157	0.192635	477.12
	10.010	298.157	0.192723	477.34

ΔT is calculated as $T_{\mathrm{oven}} - T_{\mathrm{cal}}$. Temperature probes were calibrated with two independents Pt 100.

$\langle T \rangle$ is calculated as $(T_{\mathrm{oven}} + T_{\mathrm{cal}}) / 2$.

A is the compound peak area calculated as $(A_{\mathrm{peak}} / T) - A_{\mathrm{blank}}$ where $A_{\mathrm{blank}} = 0.26064$ V·s.K^{-1}.

$C_{p,m}^\circ$ was calculated as $(\varepsilon/m \times A/M)$ where ε is the calibration constant, m is the mass of compound, A is the compound peak area and M is the molar mass of the studied compound.

	Ampoule
m total / g	4.65996
(Peak area/Δ*T*) / V·s·K^{-1}	0.453153
Electric calibration	
ε / V·W^{-1}	0.151076
MM / g·mol^{-1}	350.078
Final value $C^{\circ}_{p,m}$ / J·K^{-1}·mol^{-1}	**476.8** J·K^{-1}mol^{-1}

The uncertainties of the experimental heat capacity of liquid 6:1 FTOH were assigned as 2xSTDEV of the mean and the electric calibration was performed with water and sapphire experiences which ε is presented in the literature.

Uncertainty in $C^{\circ}_{p,m}$ / J·K^{-1}·mol^{-1} = 0.3

TABLE S6: Experimental results of $C_p^\circ(\mathrm{cr}, 298.15\ \mathrm{K})$ for 7:1 FTOH using a drop heat capacity calorimeter.

m / g	ΔT / K	$\langle T \rangle$ / K	A / V·s·K^{-1}	$C_{p,m}^\circ$ / J·K^{-1}·mol^{-1}
0.46248	10.037	298.155	0.081346	466.767
	10.034	298.155	0.081417	467.172
	10.037	298.157	0.081871	469.780
	10.034	298.157	0.081417	467.173
	10.032	298.157	0.081495	467.620
	10.031	298.157	0.082064	470.889
	10.031	298.157	0.081334	466.699
	10.026	298.155	0.082123	471.225
	10.027	298.155	0.081840	469.604
	10.024	298.155	0.081784	469.280

ΔT is calculated as $T_{\mathrm{oven}} - T_{\mathrm{cal}}$. Temperature probes were calibrated with two independents Pt 100.

$\langle T \rangle$ is calculated as $(T_{\mathrm{oven}} + T_{\mathrm{cal}}) / 2$.

A is the compound peak area calculated as $(A_{\mathrm{peak}} / T) - A_{\mathrm{blank}}$ where $A_{\mathrm{blank}} = 0.20156$ V·s.K^{-1}.

$C_{p,m}^\circ$ was calculated as $(\varepsilon/m \times A/M)$ where ε is the calibration constant, m is the mass of compound, A is the compound peak area and M is the molar mass of the compound studied.

	Ampoule
m total / g	3.22945
(Peak area/Δ*T*) / V·s·K^{-1}	0.28323
Electric calibration	
ε / V·W^{-1}	0.151076
MM / g·mol^{-1}	400.086
Final value $C^{\circ}_{p,m}$/J·K^{-1}·mol^{-1}	**468.6** J·K^{-1}mol^{-1}

The uncertainties of the experimental heat capacity of liquid 6:1 FTOH were assigned as 2xSTDEV of the mean and the electric calibration was performed with water and sapphire experiences which ε is presented in the literature.

Uncertainty in $C^{\circ}_{p,m}$/J·K^{-1}·mol^{-1} = 1.1

Note:

The heat capacity for the solid 7:1 FTOH and liquid 6:1 FTOH was measured using a high precision heat capacity drop calorimeter. The measurement procedure and the description of this apparatus were previously described in detail by Santos et al:

"L.M.N.B.F. Santos, M.A.A. Rocha, A.S.M.C. Rodrigues, V. Štejfa, M. Fulem, M. Bastos, J. Chem. Thermodyn., 43 (2011), 1818-1823".

TABLE S7: Optimized geometries (x, y, z), in Cartesians coordinates, for 6:1 FTOH, 7:1 FTOH, 8:1 FTOH, 9:1 FTOH and 10:1 FTOH, at B3LYP//6-311++G(d,p) level of theory.

6:1 FTOH

1	6	0	3.022768	0.195412	0.128771
2	6	0	1.663260	-0.473471	-0.237254
3	6	0	0.393694	0.424323	-0.027580
4	9	0	-4.580048	0.554175	-0.246930
5	6	0	-3.567188	-0.188852	0.197513
6	6	0	-2.223307	0.490049	-0.231030
7	6	0	-0.949268	-0.391732	0.012734
8	6	0	4.227725	-0.619177	-0.352626
9	9	0	1.536638	-1.596049	0.505262
10	9	0	1.715885	-0.832276	-1.539304
11	9	0	-0.915822	-1.346568	-0.935081
12	9	0	3.090979	0.321234	1.483644
13	9	0	0.330075	1.311512	-1.036945
14	9	0	0.512811	1.092327	1.132249
15	9	0	3.045036	1.442781	-0.396480
16	9	0	-2.313310	0.771472	-1.540741
17	9	0	-2.115145	1.640419	0.459023
18	9	0	-1.054827	-0.982064	1.217232
19	9	0	-3.658726	-0.279804	1.520952
20	9	0	-3.666107	-1.408392	-0.331779
21	8	0	5.430684	-0.050192	0.094140
22	1	0	4.247338	-0.605827	-1.439540
23	1	0	4.102645	-1.652636	-0.015992
24	1	0	5.463825	-0.081591	1.055451

7:1 FTOH

1	6	0	3.677127	-0.240293	-0.120831
2	6	0	2.336654	0.434841	0.300835
3	6	0	1.039282	-0.376731	-0.046538
4	6	0	-4.211866	-0.237826	0.143307
5	6	0	-2.874521	0.425649	-0.328342
6	6	0	-1.583584	-0.362604	0.087395
7	6	0	-0.269728	0.494147	-0.017277
8	6	0	4.900610	0.444116	0.496868
9	9	0	2.273544	1.646352	-0.295201
10	9	0	2.370301	0.624566	1.638714
11	9	0	-4.358503	-0.134238	1.460745
12	9	0	-5.228992	0.389021	-0.446514
13	9	0	-0.221942	1.322571	1.041443
14	9	0	3.779991	-0.182011	-1.478019
15	9	0	0.913463	-1.375176	0.846621
16	9	0	1.166374	-0.904267	-1.275731
17	9	0	3.630982	-1.547701	0.227189
18	9	0	-1.722450	-0.779245	1.358788
19	9	0	-1.474800	-1.437987	-0.712863
20	9	0	-0.319837	1.227789	-1.143381
21	9	0	-2.917226	0.516863	-1.666958
22	9	0	-2.833631	1.665278	0.195071
23	9	0	-4.244352	-1.525359	-0.200055
24	8	0	6.091207	-0.111889	0.003255
25	1	0	4.887731	0.280009	1.571488
26	1	0	4.828685	1.518806	0.304613
27	1	0	6.153796	0.050404	-0.943291

8:1 FTOH

1	6	0	-4.335260	0.170896	-0.219801
2	6	0	-2.997224	-0.399068	0.341490
3	6	0	-1.704273	0.382206	-0.083121
4	6	0	3.528947	0.404658	0.323826
5	6	0	2.232106	-0.356582	-0.122915
6	6	0	0.911988	0.457259	0.135539
7	6	0	-0.379939	-0.440106	0.124288
8	6	0	-5.565693	-0.450025	0.449187
9	9	0	-2.889438	-1.684646	-0.062092
10	9	0	-3.074857	-0.385375	1.690841
11	9	0	3.631624	0.340473	1.660744
12	9	0	-0.449043	-1.094634	1.297123
13	9	0	-4.386164	-0.085785	-1.556814
14	9	0	-1.631406	1.509234	0.648338
15	9	0	-1.796415	0.710271	-1.382766
16	9	0	-4.331027	1.515576	-0.064485
17	9	0	1.001972	1.060379	1.333775
18	9	0	0.803022	1.396397	-0.820041
19	9	0	-0.275832	-1.338271	-0.871707
20	9	0	2.318153	-0.624620	-1.437952
21	9	0	2.174593	-1.517730	0.554018
22	9	0	3.445217	1.695185	-0.049043
23	8	0	-6.748895	-0.003536	-0.159979
24	6	0	4.853038	-0.172952	-0.279604
25	9	0	4.936630	0.080776	-1.582060
26	9	0	5.886380	0.404307	0.331817
27	9	0	4.921121	-1.490097	-0.085792
28	1	0	-5.596580	-0.131922	1.488329
29	1	0	-5.463174	-1.538873	0.417822
30	1	0	-6.772004	-0.301604	-1.074771

9:1 FTOH

1	6	0	-4.996694	0.189667	-0.185276
2	6	0	-3.654733	-0.335305	0.409472
3	6	0	-2.359988	0.365456	-0.134029
4	6	0	2.882407	0.341835	0.157175
5	6	0	1.563285	-0.452311	-0.160508
6	6	0	0.262118	0.414404	0.013258
7	6	0	-1.044608	-0.451892	0.140543
8	6	0	-6.220691	-0.324560	0.579231
9	9	0	-3.577744	-1.661431	0.159190
10	9	0	-3.698962	-0.160710	1.749013
11	9	0	3.008192	0.445428	1.492125
12	9	0	-1.096277	-0.959305	1.385056
13	9	0	-5.084093	-0.221412	-1.481250
14	9	0	-2.251242	1.569580	0.456371
15	9	0	-2.478744	0.539197	-1.461027
16	9	0	-4.967050	1.543031	-0.189555
17	9	0	0.386583	1.163896	1.122690
18	9	0	0.147704	1.224604	-1.053053
19	9	0	-0.980313	-1.464819	-0.742196
20	9	0	1.617674	-0.892363	-1.429613
21	9	0	1.497768	-1.509788	0.667481
22	9	0	2.790479	1.576682	-0.367791
23	8	0	-7.410536	0.072136	-0.051206
24	6	0	4.172083	-0.339531	-0.420542
25	9	0	4.229511	-0.112431	-1.742213
26	9	0	4.114783	-1.667013	-0.205121
27	6	0	5.509158	0.179956	0.206540
28	9	0	5.559303	1.511336	0.167104
29	9	0	5.635689	-0.224062	1.466903
30	9	0	6.527806	-0.308768	-0.499488
31	1	0	-6.220179	0.112573	1.574647
32	1	0	-6.138350	-1.411581	0.672625
33	1	0	-7.460827	-0.329278	-0.924445

10:1 FTOH

1	6	0	-5.649530	0.119116	-0.282735
2	6	0	-4.317945	-0.280458	0.422636
3	6	0	-3.016360	0.334810	-0.201838
4	6	0	2.216247	0.427690	0.221136
5	6	0	0.913079	-0.425396	0.001845
6	6	0	-0.399346	0.442258	-0.001969
7	6	0	-1.701387	-0.406601	0.239409
8	6	0	-6.887631	-0.272638	0.530248
9	9	0	-4.222605	-1.628653	0.401556
10	9	0	-4.396609	0.117110	1.712016
11	9	0	2.308693	0.737497	1.525979
12	9	0	-1.780721	-0.694888	1.550647
13	9	0	-5.701858	-0.507445	-1.491440
14	9	0	-2.933470	1.623381	0.176428
15	9	0	-3.102780	0.277660	-1.541417
16	9	0	-5.631218	1.452177	-0.517087
17	9	0	-0.309249	1.368923	0.968226
18	9	0	-0.493984	1.060559	-1.191572
19	9	0	-1.605432	-1.554428	-0.455474
20	9	0	1.005325	-1.063438	-1.177958
21	9	0	0.832744	-1.336163	0.987563
22	9	0	2.121067	1.562682	-0.493183
23	8	0	-8.064925	-0.002959	-0.185103
24	6	0	3.527217	-0.322044	-0.215689
25	9	0	3.613324	-0.285653	-1.557170
26	9	0	3.454123	-1.605418	0.180528
27	6	0	4.831262	0.303488	0.391870
28	9	0	4.762607	1.645704	0.318363
29	9	0	4.928999	-0.060445	1.680211
30	6	0	6.150564	-0.138377	-0.325958
31	9	0	6.204107	-1.465952	-0.434136
32	9	0	6.239634	0.401635	-1.537559
33	9	0	7.188246	0.275274	0.399833
34	1	0	-6.915372	0.326961	1.436712
35	1	0	-6.798887	-1.326979	0.808723
36	1	0	-8.091860	-0.548475	-0.977523