Measurements of Enthalpies of Fusion and Melting Temperatures for 27 Polychlorinated Dibenzo-p-dioxins and Dibenzofurans

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Introduction

Physical-chemical properties such as aqueous solubility, vapor pressure and partition coefficients (air - water, octanol - water, soil - water) are useful for modeling the fate of organic chemicals in the environment as well as their behavior in industrial processes (e.g. incineration, wastewater treatment plant). In fact, polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are groups comprising 210 chlorinated congeners with different physico-chemical properties that vary according to the degree and position of chlorine substitution. A survey of the literature shows lack of experimentally measured properties for these compounds. In this study, the enthalpies of fusion and melting temperatures were experimentally determined for 21 selected PCDDs and 6 PCDFs (including non-chlorinated congeners) using Modulated Differential Scanning Calorimetry (MDSC). The values obtained, along with the aqueous solubility[1] and vapor pressure[2] data presented previously, were used for the determination of the activity coefficients and Henry's law constants of these compounds. Values of fugacity ratios and entropies of fusion are also presented in this study.

Materials and Methods

Chemicals: Dibenzo-p-dioxin, 1,2,3,4-tetrachlorodibenzo-p-dioxin, 1,2,3,4,6,9-hexachlorodibenzo-p-dioxin, 4-monochlorodibenzofuran, 2,4,6-trichlorodibenzofuran and 1,2,3,4,8-pentachlorodibenzofuran with the purities from 97 to 99 % were obtained from Cambridge Isotope Laboratories. The other PCDDs and PCDFs were obtained from AccuStandard, Inc. with the purities from 98 to 100 %. All the compounds used in this study were in the form of crystalline solids.

Methods: A Modulated Differential Scanning Calorimetry (MDSC) method was used for measuring the enthalpy of fusion (ΔH_{fus}) and melting temperature (T_m) of the selected PCDDs and PCDFs. The measurements were performed at a heating rate of 0.25 ^{o}C/min (from 20 to 360 ^{o}C), with a modulation of 0.5 ^{o}C/80 sec., and at an argon flow rate of 50 mL/min. The samples were hermetically sealed in aluminum pans capable of resisting an internal pressure up to 3 atm, and an empty aluminum hermetic pan served as a reference. The sample and reference pans were of the same weight to ± 0.1 mg. Before the measurements, the apparatus was calibrated using the melting points of pure indium, tin and lead.

Results and Discussion

The measured values of enthalpies of fusion (ΔH_{fus}) and melting temperatures (T_m) are summarized in Table 1. Within this dataset are nine new values of T_m and ΔH_{fus} of compounds that have not been previously reported in the literature. The values of T_m measured in this study agree very well with the experimental determinations reported in the literatures[4,5] and with the predictions of Rordorf[6]. The values of ΔH_{fus} for the higher chlorinated PCDDs/PCDFs (penta-, and octa-) are much lower than those predicted by Rordorf[6]. This discrepancy indicates that Rordorf 's values may be overestimated. However, Rordorf 's enthalpies of fusion f or the lower chlorinated congeners are in good agreement with our experimental values.

We have used these newly determined values of T_m and ΔH_{fus} to calculate the entropy of fusion (ΔS_{fus}) and fugacity ratio (F) values shown in Table 1, according to equation (1):

$$F = f_s/f_l \approx \exp [- \Delta S_{fus} (T_m / T - 1) / R] \quad (1)$$

where f_s/f_l is the ratio of the fugacity of the pure chemical in the solid state to its fugacity in the subcooled liquid state; $\Delta S_{fus} = \Delta H_{fus} / T_m$; T is the experimental temperature and R is the gas constant.

Additionally, we calculated activity coefficients and Henry's law constants shown in Table 2 from the data in Table 1 together with our previously reported values of the aqueous solubilities[1] and vapor pressures[2]. The activity coefficient in pure water (γ_w) was calculated from equation (2):

$$\gamma_w = [1 / (S_w V_w)] \exp [- \Delta H_{fus} / R (1 / T - 1 / T_m)] \quad (2)$$

where S_w is the molar aqueous solubility, and V_w is the molar volume of the aqueous solution, assumed equal to the molar volume of water. The subcooled liquid molar solubilities ($S_{w\ (liquid)}$) and vapor pressures ($P_{(liquid)}$) were obtained from equations (3) and (4):

$$S_{w\ (liquid)} = S_{w\ (solid)} \exp [\Delta H_{fus} / R (1 / T - 1 / T_m)] \quad (3)$$

$$P_{(liquid)} = P_{(solid)} \exp [\Delta H_{fus} / R (1 / T - 1 / T_m)] \quad (4)$$

The partitioning of PCDDs and PCDFs between air and water phases, expressed as the Henry's law constants (H) was calculated from equation (5):

$$H = S_{w\ (liquid)}/P_{(liquid)} = S_{w\ (solid)}/P_{(solid)} \quad (5)$$

The data provided by this study may be useful in the calculation of other unknown physico-chemical properties of PCDDs/PCDFs, and may allow more precise predictions of their environmental fate.

Table 1. The melting temperatures (T_m) and enthalpies of fusion (ΔH_{fus}) measured in this study together with calculated values of the entropy of fusion (ΔS_{fus}) and fugacity ratio (F).

Compound	T_m / °C		ΔH_{fus} / kJ·mol^{-1}		ΔS_{fus} / J·(K·mol^{-1})	F
	This study	Reference	This study	Reference		
DD	119.24	120-122 [4]; 124,2 [4]; 116,75 [5]; **122-123** [6]	25.82	23.9[5]; **22.6** [6]	65.80	0.0819
1-MCDD	100.3	**104.5-105.5** [6]	22.18	**21.4** [6]	59.39	0.1646
2-MCDD	87.04	87-90 [4]; **88-89** [6]	21.34	**18.5** [6]	59.25	0.2270
1,6-DCDD	196.42	**197-199** [6]	35.85	**25.1** [6]	76.35	0.0051
2,7-DCDD	205.91	201-203 [4]; **209-210** [6]	36.61	**26.8** [6]	76.42	0.0038
1,2,3-TCDD	146.77	N/A	28.47	N/A	67.80	0.0358
1,2,4-TCDD	125.68	**128-129** [6]	23.95	**33.9** [6]	60.05	0.0872
1,7,8-TCDD	151.92	N/A	28.84	N/A	67.85	0.0310
2,3,7-TCDD	171.74	**162-163** [6]	33.17	**30.9** [6]	74.56	0.0121
1,2,3,4-TeCDD	186.59	**188-190** [6]	30.47	**31.2** [6]	66.28	0.0133
1,2,6,7-TeCDD	213.14	N/A	28.67	N/A	58.96	0.0114
1,2,7,8-TeCDD	188.76	N/A	32.65	N/A	70.68	0.0094
1,2,8,9-TeCDD	231.21	N/A	30.09	N/A	59.66	0.0070
1,3,6,8-TeCDD	211.80	**219.0-219.5** [6]	37.55	**36.6** [6]	77.43	0.0029
1,3,7,8-TeCDD	192.64	**193.5-195** [6]	31.92	**36.6** [6]	68.53	0.0097
1,3,7,9-TeCDD	200.61	N/A	32.07	N/A	67.69	0.0083

1,2,3,7,8-PeCDD	234.06	**240-241** [6]	31.27	**42.4** [6]	61.65	0.0055
1,2,4,7,8-PeCDD	197.91	**206.0** [6]	30.30	**42.4** [6]	64.32	0.0113
1,2,3,4,6,9-HxCDD	220.29	N/A	27.26	N/A	55.24	0.0129
1,2,3,4,6,7,9-HpCDD	239.61	N/A	23.19	N/A	45.23	0.0199
OCDD	329.17	**330-332** [6];323.5[5]; 325-326 [4]	40.73	40.3[5]; **61.4** [6]	67.62	0.0002
DF	81.91	86.7 [4]; 82 [4]; 84-92 [4]; **86.5** [6]; 78.75 [5]	18.65	19.0[5]; **19.6** [6]	52.53	0.2994
4-MCDF	70.97	N/A	18.83	N/A	54.72	0.3625
2,8-DCDF	191.96	**184-185** [6]; 185 [4]	28.95	**25.1** [6]	63.62	0.0151
2,4,6-TCDF	116.76	**116-117** [6]	19.34	**30.9** [6]	49.60	0.1594
1,2,3,4,8-PeCDF	177.31	**177-178** [6]	26.82	**42.4** [6]	59.54	0.0258
OCDF	256.03	330 [5];253.1[5]; **258-260** [6]	28.25	28.0[5]; **57.5** [6]	53.38	0.0069

Bold letters indicate predicted values (quoted/calculated/extrapolated); N/A- not available

Table 2. Activity coefficients (γ_w) and Henry's law constants (H) for some PCDDs/PCDFs.

Compound	$P_{(solid)}$ [2]/Pa	$P_{(liquid)}$ [a]/Pa	$S_{w\ (solid)}$ [1]/mol·m^{-3}	$S_{w\ (liquid)}$ [b]/mol·m^{-3}	γ_w [c]	H/Pa·m^3·mol^{-1}	
						This study[d]	Reference[4]
DD	5.97x10^{-2}	0.729	7.23x10^{-3}	8.82x10^{-2}	6.3x10^5	8.26	12.39; 12.29; 11.70
1-MCDD	1.17x10^{-2}	7.11x10^{-2}	1.91x10^{-3} [e]	1.16x10^{-2}	4.8x10^6	6.12	8.38; 6.288
2-MCDD	1.82x10^{-2}	8.02x10^{-2}	1.96x10^{-3}	8.63x10^{-3}	6.4x10^5	9.28	14.82; 12.59
2,7-DCDD	6.70x10^{-5}	1.77x10^{-2}	1.62x10^{-5}	4.28x10^{-3}	1.3x10^7	4.14	8.11; 8.096
1,2,4-TCDD	7.50x10^{-5}	8.59x10^{-4}	2.61x10^{-5}[e]	2.99x10^{-4}	1.8x10^8	2.87	3.84; 3.419
1,2,3,4-TeCDD	8.46x10^{-6}	6.36x10^{-4}	1.96x10^{-6} [e]	1.47x10^{-4}	3.8x10^8	4.32	3.77; 3.747
1,3,6,8-TeCDD	6.04x10^{-6}	2.07x10^{-3}	9.94x10^{-7} [e]	3.40x10^{-4}	1.6x10^7	6.08	0.71; 6.90; 0.704
OCDD	2.00x10^{-10}	8.03x10^{-7}	4.98x10^{-10}	2.00x10^{-6}	2.8x10^{10}	0.40	0.683; 0.684
DF	0.390	1.303	2.70x10^{-2}	9.02x10^{-2}	6.2 x10^5	14.44	10.62
2,8-DCDF	2.10x10^{-4}	1.53x10^{-2}	5.93x10^{-5}	3.92x10^{-3}	1.4 x10^7	3.55	6.377
OCDF	1.24x10^{-9}	1.79x10^{-7}	9.22x10^{-10}	1.34x10^{-7}	4.2x10^{11}	1.34	0.191; 0.1

Note: The aqueous solubility values presented here were measured using generator column method[1]. The vapor pressure values were determined by the mass-loss Knudsen effusion technique[2]. The values are calculated from: [a] eq. (4); [b] eq. (3); [c] eq. (2); [d] eq. (5); [e] data from ref. 3.

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