Available online at www.sciencedirect.com

SCIENCE DIRECT

Thermochimica Acta 447 (2006) 5–12

thermochimica acta

www.elsevier.com/locate/tca

Evaluation of entropies of fusion of polychlorinated naphthalenes by model congeners: A DSC study

M. Lahtinen [a,*], J. Paasivirta [a], V.A. Nikiforov [b]

[a] *Department of Chemistry, University of Jyväskylä P.O. Box 35, FI-40014, Finland*
[b] *Department of Chemistry, St. Petersburg University, 198504, Universitetskii pr., 26, St. Petersburg, Petrodvorets, Russia*

Received 2 February 2006; received in revised form 5 April 2006; accepted 5 April 2006
Available online 29 April 2006

Abstract

Thirteen congeners of polychlorinated naphthalenes (PCN) were synthesized and studied by differential scanning calorimetry (DSC). Melting points (T_m) were obtained for all thirteen, and enthalpies of fusion (ΔH_f) were obtained for nine congeners. Melting points of other PCNs, except for five, were found in literature. In addition, experimental ΔH_f values determined by DSC were found only for 1- and 2-mono-chloronaphthalenes in the literature. The missing or uncertain values of the eight melting points and 64 enthalpies of fusion were estimated by multiple linear regressions using a set of thirteen molecular descriptors as candidates for independent variables. The stepwise model of regression (SMLR) appeared to be most effective. The perfect linearity for melting points was reached with three variables: solubility parameter (DB), ionization potential (IP) and dipole moment (μ). Similarly, SMLR produced linear result for ΔH_f values with descriptors μ, S (polarizability), and L (the logarithm of the gas–hexadecane partition coefficient). The individual entropy of fusion values (ΔS_f) were calculated for all 75 PCNs as ratio of ΔH_f and melting point (in Kelvin).
© 2006 Elsevier B.V. All rights reserved.

Keywords: Chlorinated naphthalenes; DSC; Enthalpy of fusion; Entropy of fusion; Melting point; Molecular descriptors; Multiple linear regression; Thermal analysis

1. Introduction

Polychlorinated naphthalenes (PCN) are commercial products used in electrical devices, as impregnating agents to produce waterproof materials, flame retardants and pesticides [1]. Also they are formed in metallurgy and in waste disposal, especially by incineration. They are leaked as persistent contaminants to the environment. Some tetra- to hexa-CN congeners show high biomagnification rates and dioxin-type of toxicity and thus can be considered as significant ecotoxic hazard especially to the aquatic wildlife [1,2]. Therefore, the determination of property data of PCN congeners for modeling their environmental fate is an important and necessary task, as it has been with polychlorinated biphenyls (PCB), polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzo-furans (PCDF). This data is necessary for determining the temperature dependence coefficients of physical properties to predict the fate of a chemical compound at different environmental conditions. The first temperature coefficients published for PCNs were those for the liquid state vapor pressure (Pl) derived from gas chromatographic data [3]. To obtain coefficients for water solubility (S), octanol-water partition coefficient (K_{ow}) and volatility (H), reliable values of melting point (T_m K) and enthalpy of fusion (ΔH_f) corresponding the entropy of fusion ($\Delta S_f = \Delta H_f/T_m$) are necessary parameters [4,5]. Most data for T_m are available [1,6–11] but ΔH_f (or ΔS_f) have been previously measured only for the two monochloro naphthalene congeners [12,13].

The aim of the present work was to measure accurate melting point and ΔH_f values from available pure PCN compounds with differential scanning calorimetry (DSC). These values and measured melting points from literature were used to estimate the missing T_m and ΔH_f values of all the other PCN congeners. Finally, ΔS_f values were calculated for all 75 congeners (see appendix for molecular structures with Cl substitution, PCN codes and CAS registry numbers for all 75 PCNs; Fig. A.1 and Table A.1) for use in the QSAR estimation of S_w, K_{ow} and H temperature coefficients.

---

* Corresponding author. Tel.: +358 14 2602624; fax: +358 14 2602501.
E-mail address: manu.lahtinen@jyu.fi (M. Lahtinen).

0040-6031/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2006.04.011

2. Materials and methods

2.1. Reference compounds

Experimental DSC data from literature was only found for 1-chloronaphthalene (PCN1) [12] and 2-chloronaphthalene (PCN2) [12,13]. The other substances for the study were synthesized in the St. Petersburg University via a sequence of selective substitutions in the naphthalene ring system (Fig. 1) [9,14–20].

Starting materials for the syntheses were naphthalene, 1, 2,3,4-tetrachloronaphthalene-bis(hexachlorocyclo-pentadiene) adduct (Aldrich), 1,2,-dichloro-3-nitronaphthalene-bis(hexachlorocyclopentadiene) adduct (Aldrich) and Naphthol Yellow S (Aldrich). Purities determined by NMR and GC-ECD were 97–99%.

2.2. DSC measurements

Samples of 13 *tri*- to *hepta*-CN model compounds could be studied by DSC. Melting transitions and enthalpy changes of the PCN model compounds were determined on power compensation type Perkin-Elmer PYRIS 1 DSC device. The measurements were carried out under nitrogen atmosphere (flow rate 50 ml min^{-1}) using 50 μl sealed aluminum sample pans with pin holes. The sealing was made by using a 30 μl aluminum pan with pinholes as sealer pan to ascertain good thermal contact between the sample and pan, and to minimize the free volume inside the pan, because the sample volume is gently squeezed by the cover-pan. The temperature calibration was carried out using three standard materials (*n*-decane, In, Zn) and energy calibration by using an indium standard (ΔH = 28.45 J g^{-1}). The samples were first heated at a rate of 10 °C min^{-1} from the room temperature to ca. 40 °C below the expected (literature) melting point of each compound. Then samples were held for 5 min at the selected temperature before heating ca. 15 °C above the observed melting transitions with heating rate of 2 °C min^{-1}. To set the final experimental conditions, the preliminary measurements were carried out with a heating rate of 10 °C min^{-1} to find out the approximate melting point for the compounds. Two or three samples of each congener were measured using sample weights from 2 to 4 mg. The absolute average error for temperature was 0.5 °C and for melting enthalpies 0.7 kJ mol^{-1}. Measured samples were weighed afterwards to verify that sample weights remained unchanged during the measurement.

The measurement setup of compounds PCN41 and PCN61 deviated slightly from the others as the available sample amounts

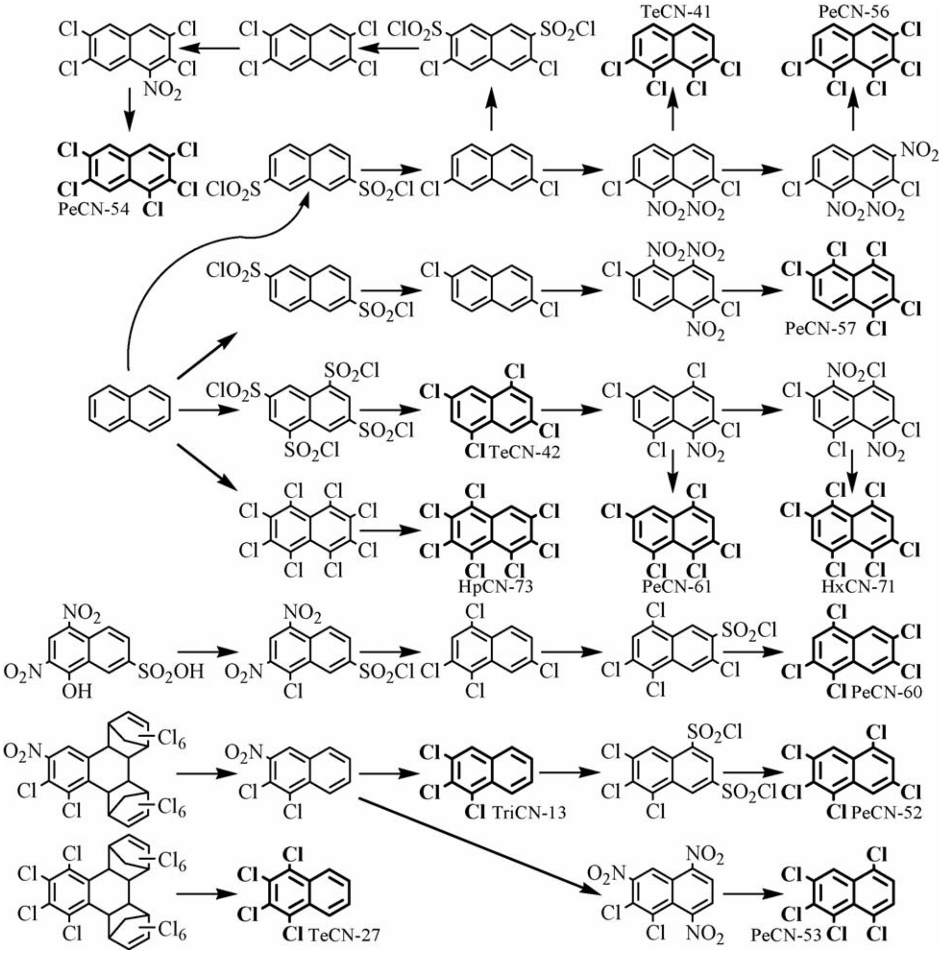

Fig. 1. Scheme of syntheses. H → Cl:$SO_2Cl_2/SbCl_3$; H → SO_2Cl: (1) H_2SO_4 or H_2SO_4/SO_3; (2) $SOCl_2$; H → NO_2:NO_2BF_4/Sulfolane; NO_2 → Cl:C_5Cl_6, reflux; SO_2Cl → Cl:C_5Cl_6, reflux; Cl → H:Zn/AcOH, reflux; decomposition of substituted naphthalene/hexachlorocyclopenta-diene adducts: heat in vacuo at 150–200 °C.

of these compounds were very small compared to the others. Therefore, the final enthalpy measurements were carried out with a heating rate of 10 °C $\min^{-1}$ to increase the sensitivity of the measurements as about 1/10 of the above given sample weights (0.15–0.6 mg) were used on the final measurements. For these measurements the calibration of the equipment was made with given heating rate.

The compounds that showed several endothermic transitions (PCN27, PCN53, PCN57 and PCN73), the melting point was confirmed by comparing all the found endothermic peak values to the reported literature values and consequently the minor endothermic transitions were designated to be caused either by the solid-solid phase transitions and/or the melting of a potential polymorph, as based on the GC-MS analyses the samples were highly pure. For these compounds, the phase transition temperatures and enthalpies can also be seen in Table 1. This way, melting points of these compounds were usable for the evaluation. But the melting enthalpies of above-mentioned compounds were rejected from the regression analysis, as it could not be ascertained that the observed enthalpy would represent melting of a whole sample weight. In addition, closer inspection of these four compounds suggested that they may be somewhat less crystalline as their physical appearance resembled cotton.

All the tabulated melting points were obtained as a peak maximum value instead of an extrapolated onset, since the maximum value describes better the completeness of the melting transition and in that regard it is more comparable to the literature values which are in most cases measured only by a melting point apparatus. Secondly, the peak maximum value is somewhat less affected by the lack of crystallinity and purity of the sample than the extrapolated onset value of a melting transition.

2.3. *Utilization of the measured values to estimate T_m, ΔH_f and ΔS_f for all PCNs*

Extrapolation of the experimental DSC results of melting points (T_m; 15 compounds) and enthalpies of fusion (ΔH_f; 11 compounds) by the multiple linear regressions (MLR) [21] proved to be the most suitable method to estimate T_m, ΔH_f and ΔS_f values for all the other PCNs. In this work statistic software package SPSS was used. T_m and ΔH_f estimates (dependent variables) were regressed by a set of molecular descriptors (MD) as independent (explanatory) variables. The analysis was carried out so that the variables were selected from the total MD set using set criteria of F values and using “enter” and “remove” by trial regression. In basic mode (MLR) the trial was made once for all MDs.

With only few training values of ΔH_f (experimental DSC), use of a stepwise multiple linear regression mode (SMLR) appeared to be the best method to carry out the regression analysis. Same regression mode was utilized successfully also for the regression analysis of the previously unknown melting points of the five PCNs. In SMLR analysis, the MDs was added one at the time in step-by-step manner and the regression trial was repeated until the overall correlation (R) and significance (p) of F in ANOVA could not be improved any further by the enter/remove procedures of MDs. The independent variables applied to the analysis were as follows:

(1) Molecular descriptors (MDs; for RRT estimation) of Rayne and Ikonomou [22]: MW: molecular weight, SQRN: square root of the number of chlorine atoms, μ: dipole moment, IP: ionization potential, NORT: number of chlorines in

Table 1
Melting points, enthalpies and entropy changes of the reference compounds

Code	CAS No.	Cl substitution	T_m °C	ΔH_f J mol^{-1}	ΔS_f J K^{-1} mol^{-1}	ΔS_f Cal K^{-1} mol^{-1}	Reference
PCN1	90-13-1	1	−2.3	12900	47.63	11.38	[12]
PCN2	91-58-7	2	58.0	14004	42.29	10.10	[12,13]
PCN13	50402-52-3	1,2,3	81.5	18440	51.99	12.42	This work
PCN27	20020-02-4	1,2,3,4	167.3[a]	10530[b]			This work
			181.1[a]	1330[b]			
			197.6	11540[c]	24.50		
PCN41	149864-82-4	1,2,7,8	128.1	14620	36.43	8.70	This work
PCN42	53555-64-9	1,3,5,7	179.8	27140	59.92	14.31	This work
PCN52	53555-65-0	1,2,3,5,7	171.7	25740	57.86	13.82	This work
PCN53	150224-24-1	1,2,3,5,8	114.6[a]	14390[b]			This work
			170.2[a]	920[b]			
			180.1	8440[c]	18.63		
PCN54	150224-16-1	1,2,3,6,7	143.4	22940	55.07	13.15	This work
PCN56	150205-21-3	1,2,3,7,8	108.4	17550	45.99	10.98	This work
PCN57	150224-20-7	1,2,4,5,6	131.0[a]	15640[b]			This work
			139.5	8410[c]	20.39		
PCN60	150224-17-2	1,2,4,6,7	131.1	22580	55.86	13.34	This work
PCN61	150224-22-9	1,2,4,6,8	155.8	19750	46.05	11.00	This work
PCN71	90948-28-0	1,2,4,5,6,8	176.2	28890	64.29	15.36	This work
PCN73	58863-14-2	1,2,3,4,5,6,7	181.3[a]	8540[b]			This work
			182.8	8750[c]	19.20		

ΔH_f values of (a and b) were not used in regression analysis.

[a] Transition temperature.

[b] Enthalpy of the suggested solid-solid phase transition or melting of a polymorph.

[c] Melting enthalpy.

positions 1,4,5,8, and NMET: number of chlorines in positions 2,3,6,7.

(2) The solvation descriptors of Abraham and Al-Hussaini [23]: *E*: excess molar refraction, *S*: the dipolarity/polarizability, *L*: the logarithm of the gas–hexadecane partition coefficient, B: the hydrogen bond basicity, and *V*: the McGovan volume.

(3) Finally, three new MDs were added: NC: number of carbon atoms fully substituted to C and Cl atoms, VB: liquid state molar volume calculated from increments [24,25], and DB: solubility parameter from dividing the dispersion component ΣF_{di} of the molar attraction constant [26] with VB [25].

With given variable set, the previously unknown values of PCN congeners were able to predict by the SMLR. In addition, it was noted that, the values for variables μ and IP for five of the *di*-CN congeners were absent from the reported set of Rayne and Ikonomou [22]. In our case, variable μ was first estimated as dependent and the other MDs as independent variables by SMLR, and then contrary, IP as dependent and the other MDs (including μ data) as independent, and consequently the MD table was completed also by μ and IP for all 75 PCNs. Estimations of the five unknown and three uncertain melting points (study set) together with 67 known and most reliable values (training set) were achieved by SMLR as the training set. Similarly, ΔH_{f} values were produced by SMLR using nine experimental and two literature [12,13] values as the training set. The entropies of fusion, ΔS_{f} ($\mathrm{J\,K^{-1}\,mol^{-1}}$), were calculated for all the 75 PCN congeners by dividing the observed or predicted enthalpies of fusion, ΔH_{f} ($\mathrm{J\,mol^{-1}}$), by the melting temperatures, T_{m}, in Kelvin scale.

3. Results and discussion

3.1. Differential scanning calorimetry

Examples of the DSC scans are illustrated in Fig. 2.The DSC results for two mono-CNs [12,13] and 13 PCNs (model substances) are presented in Table 1.

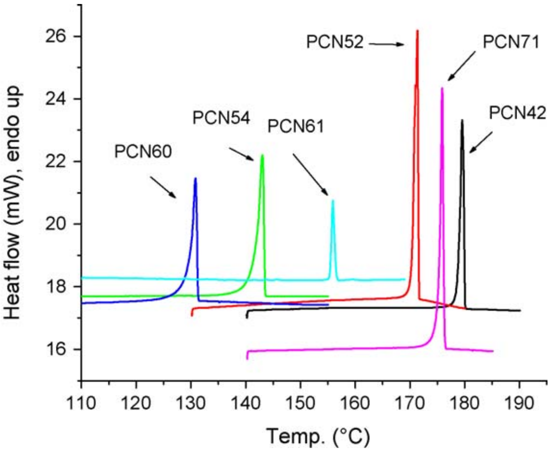

Fig. 2. DSC scans of some of the PCNs. Measurements are made with a heating rate of 2 °C $\mathrm{min^{-1}}$ (except for PCN61; 10 °C $\mathrm{min^{-1}}$) and are slightly shifted on *y*-axis for clarity.

3.2. Molecular descriptors

The five missing μ and IP values were obtained by SMLR as dependent variables and all other molecular descriptors (MDs) as the candidate explanatory variables. Summary of the regression results is shown in Table 2.

Values of μ found in literature [7,27] deviated from those of Rayne and Ikonomou [22], which were used in our MD table. As can be seen on Table 2, the SE of the dipole moment (μ) values was rather high. This indicates that Rayne and Ikonomou values [22] used as training set ($N = 70$) might be inaccurate. Furthermore, values of μ found in literature [7,27] for some PNS seemed to be inaccurate also. The adding of five regressed values of the low-chlorinated naphthalenes could be justified by practical reasons as the set of μ appeared to be generally applicable explanatory variable both for T_{m} and ΔH_{f} values in regressions (see below). Accordingly, total set of dipole moment values was necessary to include in the MD table. Instead, for IP values low SE values indicated a high accuracy of training set values.

Table 2
Summary of the SMLR results for μ and IP of five PCN congeners

Dependent variable: μ		S.E. of mean predicted value = 11.7%				Regressed values		
ANOVA model 4	Sum of square	d*f*	Mean square	*F*	Significance	Compound	μ registry	S.E.
Regression	10.82	4	2.705	13.857	3.16E-08	PCN4	0.865	0.1254
Residual	12.69	65	0.195			PCN7	0.9421	0.1213
Total	23.51	69				PCN8	0.9976	0.1203
Predictors:	(Constant)	NC	S	L	DB	PCN11	1.4801	0.1343
Coefficients:	27.501	−2.177	9.354	0.829	−1.525	PCN12	0.9561	0.1209

Dependent variable: IP		S.E. of mean predicted value = 0.18%				Regressed values		
ANOVA model 3	Sum of square	d*f*	Mean square	*F*	Significance	Compound	IP registry	S.E.
Regression	0.3771	3	0.12571	27.459	1.21E-11	PCN4	8.9539	0.0166
Residual	0.3022	66	0.00458			PCN7	8.9518	0.0163
Total	0.6793	69				PCN8	8.9502	0.0162
Predictors:	(Constant)	NMET	S	μ		PCN11	9.0016	0.0169
Coefficients:	9.276	0.087	−0.363	−0.028		PCN12	9.0368	0.0215

Table 3
SMLR results of estimation of T_m (in °C) for five unknown and three uncertain PCNs

Model summary			Dependent variable: T_m	
Model	R	R^2	Adj. R^2	S.E. of the estimate
1	0.772	0.597	0.590	28.386
2	0.790	0.625	0.613	27.601
3	0.801	0.642	0.625	27.177

1 Predictors: (Constant), DB
2 Predictors: (Constant), DB, IP
3 Predictors: (Constant), DB, IP, μ

ANOVA		Sum of square	df	Mean square	F	Significance
Model 3	Regression	83323	3	27774	37.605	4.72E-14
	Residual	46530	63	739		
Total	129853	66				

Coefficients		S.E. of mean predicted value = 4.9%		
Model 3	(Constant)	DB	IP	μ
	760.42	−59.61	71.09	−10.52

Table 4
SMLR regression of ΔH_f values as KJ mol^{-1}

Model summary			Dependent variable: ΔH_F (KJ mol^{-1})	
Model	R	R^2	Adj. R^2	S.E. of the estimate
1	0.714	0.510	0.456	4.425
2	0.887	0.787	0.734	3.092
3	0.932	0.869	0.813	2.592

1 Predictors: (Constant), μ
2 Predictors: (Constant), μ, S
3 Predictors: (Constant), μ, S, L

ANOVA		Sum of square	df	Mean square	F	Significance
3	Regression	312.763	3	104.254	15.522	0.002
	Residual	47.015	7	6.716		
	Total	359.778	10			

Coefficients			S.E. of mean predicted value = 7.28%	
Model 3	(Constant)	μ	S	L
	−22.782	−6.690	77.347	−5.542

3.3. *Melting points*

Experimental melting points of five PCNs are still unknown. The reported melting temperatures of 70 PCNs are mostly measured using a melting point apparatus [1,6–11] and only few by DSC ([12,13], this work). Due to deviations found in some of the reported data, the melting points of three other PCNs were considered as "uncertain" and were excluded from the training set and because of this the SMLR was performed using 67 "best known" T_m values. As a result of SMLR of melting points, only three predictors remained as a significant variable once the optimal R value was reached with satisfactory significance of ANOVA F (37.6, $p = 4.7\text{E}^{-14}$). Part of the summary of SMLR is shown in Table 3.

Model summary and ANOVA statistics were identical whether the SMLR was made by using melting points in Celsius or in Kelvin scale due to their constant difference of 273.15 degrees. However, this interrelation influenced the standard error of the mean prediction, which was in Celsius values, 4.9% (Table 3) and in Kelvin values only 1.6%. The latter error is significantly smaller than the error observed for the enthalpies (only 11 DSC measured values available, see Table 4). Therefore, the eight predicted T_m values are most probably good estimates for entropy determination ($\Delta S_f = \Delta H_f/T_m$). The melting points of the other 67 PCNs used for the entropy of fusion calculation were taken from the literature or from our model substance syntheses [9,14–20]. The T_m values selected for the entropy of melting calculation are listed in the Table 5. Based on the regression analysis, our estimated T_m values deviated significantly from the theoretical results of quantitative structure activity relationship (QSAR) procedures [10,28]. Both QSAR estimation methods produce only mean T_m values within each isomer group, while our observed and regressed T_m values (Table 5) are specific for each PCN congener, are in good agreement with each other, and in that respect, appear to be the most accurate to be used in ΔS_f calculation.

3.4. *Values of the enthalpy of fusion*

The SMLR result for the ΔH_f values is described in Table 4 and Fig. 3. The significance of the linearity in the ANOVA results with four predictors was excellent: $F = 15.47$; $p = 0.002$. Plot of the predicted ΔH_f (X) against the eleven experimental DSC values (Y) is illustrated in Fig. 3.

Despite the limited number of experimental values, the statistical SE of the mean predicted value was 7.3%. As can be seen in Fig. 3, the trend line shows exact slope of 1 and is intercepting

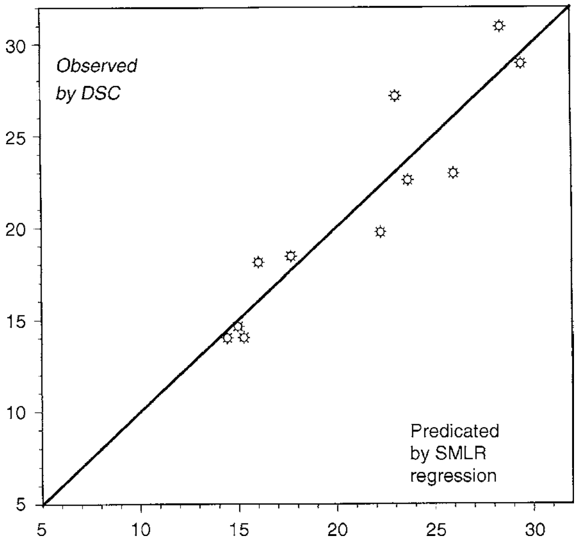

Fig. 3. ΔH_f values K J mol^{-1} of PCNs.

Table 5
Final estimation results of T_m, ΔH_f, and ΔS_f

Code	T_m (°C)	Reference	ΔH_f (J mol^{-1})	ΔS_f (J K^{-1} mol^{-1})
PCN1	−2.30	[12]	**12900**	**51.72**
PCN2	58.00	[13]	**14004**	**42.29**
PCN3	37.00	[1,6]	14942	48.30
PCN4	62.00	[1,6]	16425	49.98
PCN5	72.00	[1,6]	19290	56.00
PCN6	107.00	[6,7,10]	21484	56.61
PCN7	49.00	[1,6,7]	15394	48.61
PCN8	64.00	[1]	14651	44.13
PCN9	89.50	[1,6,7]	11906	32.92
PCN10	121.50	[1]	16728	55.52
PCN11	141.00	[1]	16590	41.14
PCN12	116.00	[1,6]	14928	38.66
PCN13	81.50	DSC	**18440**	**51.99**
PCN14	92.00	[1,6]	18225	49.98
PCN15	79.00	[1,6]	20271	57.62
PCN16	92.50	[1,6]	20898	57.21
PCN17	88.00	[1,6]	14263	39.57
PCN18	83.00	[1,6]	8225	23.16
PCN19	103.00	[1,6]	14768	39.35
PCN20	81.00	[1,6]	20399	57.69
PCN21	113.00	[1,6]	15444	40.06
PCN22	89.50	[1,6]	8859	24.51
PCN23	133.00	[1,6]	13308	32.85
PCN24	68.00	[1,6]	16728	49.13
PCN25	109.50	[1,7,10]	13719	35.91
PCN26	90.50	[1,7]	19162	52.74
PCN27	197.60	DSC	13400	28.49
PCN28	141.00	[1,6,7,10]	15615	37.74
PCN29	*146.50*	*reg*	20039	48.62
PCN30	115.00	[1,6]	15997	41.25
PCN31	128.00	[1,7,9]	8617	21.51
PCN32	139.00	[1,7]	17825	43.29
PCN33	111.00	[1,6,7]	25302	65.91
PCN34	144.00	[1,6]	21983	52.74
PCN35	98.00	[1,7]	14928	40.25
PCN36	164.00	[1,6]	24571	56.23
PCN37	114.00	[1,7]	22177	57.32
PCN38	181.00	[1]	16043	35.34
PCN39	156.90	[9]	16190	35.67
PCN40	127.00	[1,6,7]	14173	31.22
PCN41	128.10	DSC	**14620**	**33.22**
PCN42	179.80	DSC	**27140**	**67.82**
PCN43	131.00	[1,6,7,10]	15366	38.36
PCN44	179.80	[1,6]	16687	36.89
PCN45	*136.90*	*reg*	15709	38.49
PCN46	183.00	[6]	17834	45.40
PCN47	139.00	[1,6,10]	12932	29.95
PCN48	205.00	[1]	24360	53.43
PCN49	*142.10*	*reg*	23780	57.67
PCN50	*156.00*	*reg*	25301	52.91
PCN51	*158.00*	*reg*	25776	59.73
PCN52	171.70	DSC	**30930**	**72.92**
PCN53	180.10	DSC	20707	49.78
PCN54	143.40	DSC	**22940**	**51.57**
PCN55	114.00	[1,7,9]	22124	48.80
PCN56	108.40	DSC	**18110**	**43.48**
PCN57	139.50	DSC	25120	64.88
PCN58	*156.20*	*reg*	26166	64.90
PCN59	151.00	[1,9]	24124	58.45
PCN60	131.10	DSC	**22580**	**52.83**
PCN61	155.80	DSC	**19750**	**46.56**
PCN62	*146.90*	*reg*	21096	49.63
PCN63	134.00	[1,7,9]	20570	47.94
PCN64	166.00	[1,9]	26196	62.96
PCN65	164.50	[1,9]	19975	49.02
PCN66	206.00	[1,9]	24735	56.29
PCN67	235.00	[1,7,9]	31363	71.63
PCN68	154.00	[1,9]	26870	56.06
PCN69	149.00	[1,9]	26744	52.60
PCN70	160.00	[1,9]	19581	45.79
PCN71	176.20	DSC	**28890**	**68.44**
PCN72	139.50	[1,9]	26450	61.02
PCN73	182.80	DSC	24996	54.76
PCN74	194.00	[1,6,7]	24706	52.83
PCN75	*197.60*	*reg*	24930	52.27

Entropies of fusion (ΔS_f) calculated from observed (DSC) and regressed enthalpies of fusion (ΔH_f) values obtained by dividing by T_m [K] (= T_m [°C] + 273.15). Regressed T_m's are printed in italics and underlined; others are experimental (DSC) or literature values.

at zero. At the moment, produced results seem to be the most accurate available, until more DSC measurements are performed for other PCN congeners in further studies.

3.5. Entropies of fusion

The estimated ΔS_f values were calculated as ratios of ΔH_f and T_m values. Results are presented together with the final observed and predicted estimated T_m and ΔH_f values in Table 5. The results were quite different (individual values) compared with those have been obtained by incremental calculation [29] and of QSAR estimates from MDs [30], because these two latter sets consist of overall value ("mean") of PCNs in each isomer group. However, Ruelle and Kesselring succeeded to estimate solubilities of several PCN congeners at 25 °C using only one default entropy of fusion value ($56.48\,\mathrm{J\,K^{-1}\,mol^{-1}} \approx 13.5\,\mathrm{cal\,K^{-1}\,mol^{-1}}$) and the value of T_m [31]. Our entropy results include more differences between isomers, which will facilitate surveys of different environmental fate and risk. Therefore, individual ΔS_f values can be more practical for determination at least interim water solubility and $\log K_{ow}$ temperature coefficients [5] of all PCN congeners.

4. Conclusions

The using accurate experimental DSC data of enthalpies of fusion together with precise melting points proved to be successful to obtain thermodynamic properties of polychlorinated naphthalenes for temperature dependent environmental fate estimation. More accurate temperature adjustments by these methods enable obtaining of more realistic risk estimations of PCN pollution in environment, as already have been demonstrated on modeling the fate of synthetic musks [5]. It can be concluded that, from a limited number of experimental results of pure model substances, several thermodynamic values of other congeners of the PCN family can be extrapolated with high probability by multivariate statistics using molecular descriptors. Also, it must be pointed out that confirming the predicted results with additional pure model compounds is necessary task to make in the long run. However, producing of pure congeners in the PCN family is both time consuming and difficult task to carry out for some of the congeners, and in that regard the extrapolated values can substantially speed up determination of the environmental fates of these ecotoxic compounds. Finally, computational chemistry [32] could also offer another way to compare experimental and predicted thermodynamic data.

Acknowledgement

We thank Spec. Lab. Tech. Mirja Lahtiperä for recording the GC-MS data.

Appendix A

See Table A.1 and Fig. A.1.

Table A.1
Codes, structures by Cl numbering [33] and CAS registry numbers of chlorinated naphthalene congeners

Code	Cl substitution	CAS registry number
Napht.	(Nonsubst.)	91-20-3
PCN1	1	90-13-1
PCN2	2	91-58-7
PCN3	1,2	2050-69-3
PCN4	1,3	2198-75-6
PCN5	1,4	1825-31-6
PCN6	1,5	1825-30-5
PCN7	1,6	2050-72-8
PCN8	1,7	2050-73-9
PCN9	1,8	2050-74-0
PCN10	2,3	2050-75-1
PCN11	2,6	2065-70-5
PCN12	2,7	2198-77-8
PCN13	1,2,3	50402-52-3
PCN14	1,2,4	50402-51-2
PCN15	1,2,5	55720-33-7
PCN16	1,2,6	51570-44-6
PCN17	1,2,7	55720-34-8
PCN18	1,2,8	55720-35-9
PCN19	1,3,5	51570-43-5
PCN20	1,3,6	55720-36-0
PCN21	1,3,7	55720-37-1
PCN22	1,3,8	55720-38-2
PCN23	1,4,5	2437-55-0
PCN24	1,4,6	2437-54-9
PCN25	1,6,7	55720-39-3
PCN26	2,3,6	55720-40-6
PCN27	1,2,3,4	20020-02-4
PCN28	1,2,3,5	53555-63-8
PCN29	1,2,3,6	149864-78-8
PCN30	1,2,3,7	55720-41-7
PCN31	1,2,3,8	149864-81-3
PCN32	1,2,4,5	6733-54-6
PCN33	1,2,4,6	51570-45-7
PCN34	1,2,4,7	67922-21-8
PCN35	1,2,4,8	6529-87-9
PCN36	1,2,5,6	67922-22-9
PCN37	1,2,5,7	67922-23-0
PCN38	1,2,5,8	149864-80-2
PCN39	1,2,6,7	149864-79-9
PCN40	1,2,6,8	67922-24-1
PCN41	1,2,7,8	149864-82-4
PCN42	1,3,5,7	53555-64-9
PCN43	1,3,5,8	31604-28-1
PCN44	1,3,6,7	55720-42-8
PCN45	1,3,6,8	150224-15-0
PCN46	1,4,5,8	3432-57-3
PCN47	1,4,6,7	55720-43-9
PCN48	2,3,6,7	34588-40-4
PCN49	1,2,3,4,5	67922-25-2
PCN50	1,2,3,4.,6	67922-26-3
PCN51	1,2,3,5,6	150224-18-3
PCN52	1,2,3,5,7	53555-65-0
PCN53	1,2,3,5,8	150224-24-1
PCN54	1,2,3,6,7	150224-16-1
PCN55	1,2,3,6,8	150224-23-0
PCN56	1,2,3,7,8	150205-21-3
PCN57	1,2,4,5,6	150224-20-7
PCN58	1,2,4,5,7	150224-19-4
PCN59	1,2,4,5,8	150224-25-2
PCN60	1,2,4,6,7	150224-17-2
PCN61	1,2,4,6,8	150224-22-9
PCN62	1,2,4,7,8	150224-21-8
PCN63	1,2,3,4,5,6	58877-88-6
PCN64	1,2,3,4,5,7	67922-27-4
PCN65	1,2,3,4,5,8	103426-93-3
PCN66	1,2,3,4,6,7	103426-96-6
PCN67	1,2,3,5,6,7	103426-97-7
PCN68	1,2,3,5,6,8	103426-95-5
PCN69	1,2,3,5,7,8	103426-94-4
PCN70	1,2,3,6,7,8	17062-87-2
PCN71	1,2,4,5,6,8	90948-28-0
PCN72	1,2,4,5,7,8	103426-92-2
PCN73	1,2,3,4,5,6,7	58863-14-2
PCN74	1,2,3,4,5,6,8	58863-15-3
PCN75	1,2,3,4,5,6,7,8	60983-69-9

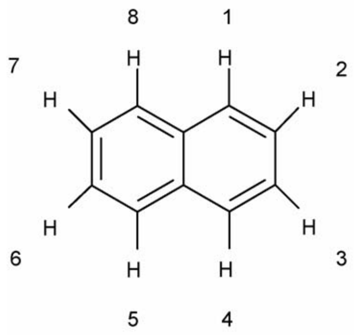

Fig. A.1. Molecular structure of naphthalene and numbering of substitution sites for Cl.

References

[1] E. Jakobsson, L. Asplund, Chapter 5 in: J. Paasivirta, (Ed.), The Handbook of Environmental Chemistry, Vol. 3, Part K. New Types of Persistent Halogenated Compounds, Springer Berlin, 2000. pp. 97–126.

[2] D.L. Villeneuve, K. Kannan, J.S. Khim, J. Falandysz, V.A. Nikiforov, A.L. Blankenship, J.P. Giesy, Arch. Environ. Contam. Toxicol. 39 (2000) 273–281.

[3] Y.D. Lei, F. Wania, W.Y. Shiu, J. Chem. Eng. Data 44 (1999) 577–582.

[4] J. Paasivirta, S. Sinkkonen, P. Mikkelson, T. Rantio, F. Wania, Chemosphere 39 (1999) 811–832.

[5] J. Paasivirta, S. Sinkkonen, A.-L. Rantalainen, D. Broman, Y. Zebühr, Environ. Sci. Pollut. Res. 9 (2002) 345–355.

[6] H. Dressler, in: Kirk Othmer (Ed.), Encyclopedeia of Chemical Technology, vol. 5, 3rd ed., Wiley, New York, 1959, pp. 838–843.

[7] J. Falandysz, M. Raciniewska, J. Blazejowski, I. Golaszewska, P. Skurski, Organo-halogen Compounds 36 (1998) 471–476.

[8] E.G. Turner, W.P. Wynne, J. Chem. Soc. (1941) 243–257.

[9] V.A. Nikiforov, Organohalogen Compds. 67 (2005) 681–684.

[10] W.E. Acree Jr., J.R. Powell Jr., D. Voisinet, A. Salazar, Phys. Chem. Liq. 29 (1995) 145–149.

[11] E. Jakobsson, C. Lönnberg, L. Eriksson, Acta Chem. Scand. 48 (1994) 891–898.

[12] M.S. Khanna, S.C. Khetarpal, L. Krishnan, H.L. Bhatnagar, Indian J. Chem. A 20 (1981) 544–546.

[13] J.C. Van Miltenburg, Ml.L. Verdonk, J. Chem. Thermodyn. 213 (1991) 273–279.

[14] V.A. Nikiforov, P. Auger, R.H. Wightman, M. Malaiyandi, D.T. Williams, Organohalogen Compds. 8 (1992) 123–124.

[15] V.A. Nikiforov, V.S. Karavan, S.A. Miltsov, V.G. Tribulovich, Organohalogen Compounds 14 (1993) 229–230.

[16] V.A. Nikiforov, S.A. Miltsov, V.S. Karavan, V.G. Tribulovich, Organohalogen Compds. 19 (1994) 137–138.

[17] V.A. Nikiforov, V.S. Karavan, S.A. Miltsov, V.G. Tribulovich, Organohalogen Compds. 35 (1998) 159–162.

[18] V.A. Nikiforov, S.A. Miltsov, V.S. Karavan, V.V. Varentsov, Organohalogen Compds. 47 (2000) 171–173.

[19] S.A. Miltsov, V.S. Karavan, V.A. Nikiforov, V.G. Tribulovich, V.V. Varentsov, Zh. Org. Khim. (rus) (1999) 724–727.

[20] V.A. Nikioforov, R. Wichtman, Chimia 51 (1997) 472.

[21] C.W. Snedecor, W.G. Cochran, Statistical Methods, 7th ed., University Press, The Iowa State, 1980, pp. 334–364.

[22] S. Rayne, M.G. Ikonomou, Anal. Chem. 75 (2003) 1049–1057.

[23] M.H. Abraham, A.J.M. Al-Hussaini, J. Environ. Monit. 3 (2001) 377–381.

[24] P. Ruelle, A. Farina-Cuendet, U.W. Kesselring, Int. J. Pharm. 157 (1997) 219–232.

[25] P. Ruelle, Chemosphere 40 (2000) 457–512.

[26] D.W. Van Krevelen, Properties of Polymers: Their Correlation with Chemical Structure; Their Numeral Estimation and Prediction from Additive Group Contributions, 3rd Ed, Elsevier, Amsterdam, 1990, pp. 212–213.

[27] A. Weissberger, R. Sangewald, G.C. Hampson, Trans. Faraday Soc. 30 (1934) 884–891.

[28] P. Simamora, S.H. Yalkowsky, Ind. Eng. Chem. Res. 33 (1994) 1405–1409.

[29] J.S. Chickos, C.M. Braton, D.G. Hesse, J.F. Liebman, J Org. Chem. 56 (1990) 927–938.

[30] R.-M. Dannenfelser, S.H. Yalkowsky, Ind. Eng. Chem. Res. 35 (1996) 1483–1486.

[31] P. Ruelle, U.W. Kesselring, Chemosphere 34 (1997) 275–298.

[32] Z. Zhai, Z. Wang, Theochem 724 (2005) 221–227.

[33] T. Wiedmann, K. Ballschmiter, Fresenius J. Anal. Chem. 346 (1993) 800–804.