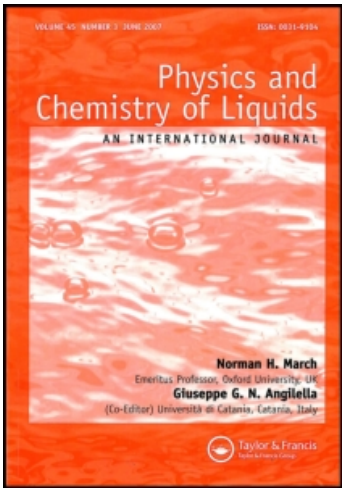

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Quantitative Structure-Property Relationships for Aqueous Solubilities of Halogenated Aromatic Compounds: Melting Point Temperatures of Polychloronaphthalenes and Polychlorophenanthrenes

William E. Acree Jr.[a]; Joyce R. Powell[a]; Diana Voisinet[a]; Andres Salazar[a]
[a] Department of Chemistry, University of North Texas, Denton, Texas, USA

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QUANTITATIVE STRUCTURE-PROPERTY RELATIONSHIPS FOR AQUEOUS SOLUBILITIES OF HALOGENATED AROMATIC COMPOUNDS: MELTING POINT TEMPERATURES OF POLYCHLORONAPHTHALENES AND POLYCHLOROPHENANTHRENES

WILLIAM E. ACREE, Jr., * JOYCE R. POWELL, DIANA VOISINET and ANDRES SALAZAR

Department of Chemistry, University of North Texas, Denton, Texas 76203-5068 (USA)

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Melting point temperatures of select polychloronaphthalenes (PCNs) and polychlorophenanthrenes (PCPs) are compiled from the published chemical literature for use in conjunction with recently derived expressions for predicting the aqueous solubilities of halogenated aromatic compounds. Experimental melting temperatures of PCNs and PCPs are used to assess the applications and limitations of a published functional group contribution melting temperatures estimational method.

KEY WORDS: Aqueous solubilities, melting temperatures.

In an earlier paper,[1] co-authored by one of us, expressions were developed for predicting the aqueous solubilities of halogenated aromatic compounds at 25°C. A generalized correlation took the form of

$$\text{Log } X = a_0 + a_1\,(\text{Molecular size descriptor})^m + a_2\,(\text{MP} - 25) + a_3\,(R \times \text{Molecular size descriptor}) \quad (1)$$

where $1 \leqslant m \leqslant 2$, a_i refers to the ith regression coefficient, MP is the melting point temperature (°C), and R is a molecular redundancy index calculated from the molecular structure. Molecular size descriptors considered included the solute's molecular weight, total molecular surface area, and various zero-order molecular connectivity indices. Discussion focussed primarily on the halogenated benzenes (HBs) and polychlorobiphenyls (PCBs) for which a large data base of experimental solubilities was

*To whom correspondence should be addressed.

available. For each HB and PCB derivative, the "average" aqueous solubility was tabulated, as well as the melting point temperature, redundancy index and all molecular size descriptors used in developing the various correlational expressions.

As part of this earlier study, the limited experimental solubility data of polychloronaphthalenes (PCNs) was discussed, though no effort was made to compile the melting point temperatures for the 75 derivatives in this particular chemical subclass. After the paper appeared in print, several researchers have inquired if melting point temperatures of the PCNs are known. To make this information readily available to all, we have searched the chemical literature and retrieved values for 63 of the 75 derivatives. A paper authored by Brinkman and Reymer[2] serves as an excellent starting reference for half of the PCNs. Readers should note that the paper is *circa* 20 years old, and that more modern instrumentation and purification procedures have yielded compounds of higher purity and melting point temperature. Inclusion of recent studies are reflected by the increased number of compounds and in some instances by the higher melting point temperatures for select PCNs. For roughly one third of the PCNs at least two, and sometimes as many as five, independently determined values were found. Agreement between the various literature sources was generally quite good (± 2°C or less), except for the two heptachloronaphthalenes. Auger *et al.*[3] report a melting point range of 108 – 110°C for a sample of 1,2,3,4,5,6,8-heptachloronaphthalene having a purity of >98% by gas chromatography, whereas Brinkman and Reymer[2] tabulate a much higher temperature of 194°C. This latter value is referenced to a paper by Clark *et al.*[4] and a thesis by Tahir[5]. Both values are given in Table 1. In the case of 1,2,3,4,5,6,7-heptachloronaphthalene Auger *et al.*[3] report a melting point range of 179–182°C, which is in excellent agreement with a value of 175–182°C determined by Sundstrom[6]; however, it is considerably higher than the value of 160–162°C published by Brady *et al.*[7] Because of reasonably good agreement between the first two independently determined melting point temperatures, the much lower value of Brady *et al.* was excluded from our averages. The calculated average melting point temperatures of polychloronaphthalenes, along with those of select polychlorophenanthrenes, are tabulated in Table 1.

A group contribution method, developed by Yalkowsky and coworkers[8–11], provides a means to estimate melting point temperatures for rigid aromatic compounds in the absence of actual experimental data

$$T_{MP}\,(\text{in } K) = \left(\sum_{i=1}^{N} n_i m_i\right) \Big/ [56.5 - 19.1 \log \sigma] \tag{2}$$

where n_i is the number of times the molecular descriptor (i.e., functional group or atom) appears in the molecule, m_i is the contribution of that descriptor to the enthalpy of melting, and σ is defined as the number of orientations of the molecule that are indistinguishable from some reference position. The last column of Table 1 lists calculated values using molecular descriptor parameters of $m_i = 97$ J/mol for an sp^2 carbon, $m_i = 1{,}940$ J/mol for an sp^2 C—H group, $m_i = 97$ J/mol for a bridgehead sp^2 carbon atom, and $m_i = 3{,}400$ J/mol for a chlorine atom attached to an sp^2 carbon atom. A more complete list of group parameters is given elsewhere[8].

Table 1 Melting Point Temperatures of Polychloronaphthalenes and Select Polychlorophenanthrenes.

Chemical Name	$T_{MP}^{exp}(°C)$	$T_{MP}^{cal}(°C)$
Polychloronapthalenes		
1-Chloronaphthalene	2.0	32.5
2-Chloronaphthalene	59.3	32.5
1,2-Dichloronaphthalene	36.0	60.0
1,3-Dichloronaphthalene	61.8	60.0
1,4-Dichloronaphthalene	71.5	97.8
1,5-Dichloronaphthalene	106.7	97.8
1,6-Dichloronaphthalene	49.0	60.0
1,7-Dichloronaphthalene	63.5	60.0
1,8-Dichloronaphthalene	89.5	97.8
2,3-Dichloronaphthalene	120.0	97.8
2,6-Dichloronaphthalene	140.2	97.8
2,7-Dichloronaphthalene	115.0	97.8
1,2,3-Trichloronaphthalene	83.0	87.6
1,2,4-Trichloronaphthalene	92.5	87.6
1,2,5-Trichloronaphthalene	78.0	87.6
1,2,6-Trichloronaphthalene	91.9	87.6
1,2,7-Trichloronaphthalene	87.5	87.6
1,2,8-Trichloronaphthalene	83.3	87.6
1,3,5-Trichloronaphthalene	102.5	87.6
1,3,6-Trichloronaphthalene	81.5	87.6
1,3,7-Trichloronaphthalene	112.8	87.6
1,3,8-Trichloronaphthalene	90.0	87.6
1,4,5-Trichloronaphthalene	131.5	87.6
1,4,6-Trichloronaphthalene	67.3	87.6
1,6,7-Trichloronaphthalene	109.4	87.6
2,3,6-Trichloronaphthalene	91.5	87.6
1,2,3,4-Tetrachloronaphthalene	198.0	159.2
1,2,3,5-Tetrachloronaphthalene	140.5	115.2
1,2,3,6-Tetrachloronaphthalene		115.2
1,2,3,7-Tetrachloronaphthalene	116.0	115.2
1,2,3,8-Tetrachloronaphthalene	128.0	115.2
1,2,4,5-Tetrachloronaphthalene	139.0	115.2
1,2,4,6-Tetrachloronaphthalene	111.0	115.2
1,2,4,7-Tetrachloronaphthalene	143.0	115.2
1,2,4,8-Tetrachloronaphthalene	98.0	115.2
1,2,5,6-Tetrachloronaphthalene	162.0	159.2
1,2,5,7-Tetrachloronaphthalene	115.0	115.2
1,2,5,8-Tetrachloronaphthalene		115.2
1,2,6,7-Tetrachloronaphthalene		115.2
1,2,6,8-Tetrachloronaphthalene	127.0	115.2
1,6,7,8-Tetrachloronaphthalene		115.2
1,3,5,7-Tetrachloronaphthalene	180.5	159.2
1,3,5,8-Tetrachloronaphthalene	131.0	115.2
1,3,6,7-Tetrachloronaphthalene	120.5	115.2
1,3,6,8-Tetrachloronaphthalene		159.2
1,4,5,8-Tetrachloronaphthalene	182.5	215.1
1,4,6,7-Tetrachloronaphthalene	139.3	115.2
2,3,6,7-Tetrachloronaphthalene	135.0[a]	215.1
1,2,3,4,5-Pentachloronaphthalene	168.5	142.7
1,2,3,4,6-Pentachloronaphthalene	147.0	142.7
1,2,3,5,6-Pentachloronaphthalene		142.7
1,2,3,5,7-Pentachloronaphthalene	170.3	142.7
1,2,3,5,8-Pentachloronaphthalene	176.0	142.7

Table 1 (*continued*)

Chemical Name	T_{MP}^{exp}(°C)	T_{MP}^{cal}(°C)
Polychloronapthalenes		
1,2,3,6,7-Pentachloronaphthalene		142.7
1,2,3,6,8-Pentachloronaphthalene	114.0	142.7
1,2,3,7,8-Pentachloronaphthalene	115.0	142.7
1,2,4,5,6-Pentachloronaphthalene	138.0	142.7
1,2,4,5,7-Pentachloronaphthalene		142.7
1,2,4,5,8-Pentachloronaphthalene	150.3	142.7
1,2,4,6,7-Pentachloronaphthalene		142.7
1,2,4,6,8-Pentachloronaphthalene	136.0	142.7
1,2,4,7,8-Pentachloronaphthalene		142.7
1,2,3,4,5,6-Hexachloronaphthalene	132.0	170.3
1,2,3,4,5,7-Hexachloronaphthalene	164.0	170.3
1,2,3,4,5,8-Hexachloronaphthalene	164.3	220.6
1,2,3,4,6,7-Hexachloronaphthalene	202.5	220.6
1,2,3,5,6,7-Hexachloronaphthalene	235.0	220.6
1,2,3,5,6,8-Hexachloronaphthalene	155.0	170.3
1,2,3,5,7,8-Hexachloronaphthalene	147.8	170.3
1,2,3,6,7,8-Hexachloronaphthalene		220.6
1,2,4,5,6,8-Hexachloronaphthalene	176.5	220.6
1,2,4,5,7,8-Hexachloronaphthalene		220.6
1,2,3,4,5,6,7-Heptachloronaphthalene	189.0	198.0
1,2,3,4,5,6,8-Heptachloronaphthalene	194.0[b]; 108–110[b]	198.0
Octachloronaphthalene	201.5	352.8
Polychlorophenanthrenes		
1-Chlorophenanthrene	120.3	104.6
2-Chlorophenanthrene	85.8	104.6
3-Chlorophenanthrene	81.5	104.6
4-Chlorophenanthrene	58.5	104.6
9-Chlorophenanthrene	48.0	104.6
1,4-Dichlorophenanthrene	78.0	132.2
2,4-Dichlorophenanthrene	86.0	132.2
3,6-Dichlorophenanthrene	168.2	178.1
3,9-Dichlorophenanthrene	125.0	132.2
3,10-Dichlorophenanthrene	117.5	132.2
9,10-Dichlorophenanthrene	160.5	178.1
2,4,6-Trichlorophenanthrene	134.5	159.8
3,6,9,10-Tetrachlorophenanthrene	203.0	239.5
Decachlorophenanthrene	230.0	423.6

[a]Reimlinger *et al.*[12], reports that the compound sublimed without previous melting.
[b]Auger *et al.*[3], list the melting point temperature range as 108–110 °C, whereas Brinkman and Reymer[2] list a much higher value of 194 °C.

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