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Aqueous Solubilities, Octanol/Water Partition Coefficients, and Entropies of Melting of Chlorinated Benzenes and Biphenyls

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The aqueous solubilities and octanol/water partition coefficients at 25 °C are determined for 12 chlorobenzenes and 16 polychlorinated biphenyls (PCBs) and for biphenyl by using the modified generator column method. These values are correlated with chlorine number and with either boiling point for the chlorobenzenes or the relative retention time of a polychlorinated biphenyl eluting from a gas-chromatographic (GC) column. Using differential scanning calorimetry (DSC), we have determined the melting points and enthalpies of melting for those compounds which are solid at room temperature. A correlation between the octanol/water partition coefficient and corrected aqueous solubility is also presented, and the universality of the derived equation is demonstrated.

Introduction

Many of the chlorobenzenes and polychlorinated biphenyls (PCBs) are classified by the Environmental Protection Agency as hazardous waste, priority toxic pollutants, and carcinogens (*1*). The chlorobenzenes are often used as intermediates in the manufacture of certain dyestuffs and many pesticides and are formed from the degradation of other organochlorine compounds (*1*). The PCBs possess physical and chemical properties which have satisfied numerous industrial demands during the last several decades (*2*). These same properties, however, have rendered the PCBs inert to many degradation pathways (*2*).

The environmental fate of both the chlorobenzenes and the PCBs is governed primarily by their partitioning processes. Partitioning processes which are of particular interest to environmentalists include the octanol/water partition coefficient ($K_{o/w}$) and the aqueous solubility (C_s^w). $K_{o/w}$ is a measure of the hydrophobicity of a substance. In this respect, it has been used to predict the extent of bioconcentration of organic pollutants in trout muscle (*3*) as well as to make other chemical and biological correlations (*4*). C_s^w is a measure of the partitioning of a substance between itself and water and is important for predicting the distribution of pollutants in aquatic environments including their tendency to sorb or bioaccumulate (*5*).

$K_{o/w}$ and C_s^w data have been reported for the chlorobenzenes (*6*) and for several of the 209 possible PCBs (*2*, *5*, *7–16*). The literature $K_{o/w}$ values, however, often are not experimental but rather are calculated by addition of either substituent π-constants (*4*) or hydrophobic fragmental constants (*f*) (*17*). In both cases, the same constant is used for each chlorine added to the phenyl or biphenyl molecule, regardless of its position. It has been shown that the planarity of the biphenyl molecule is strongly influenced by the degree of ortho substitution (*18*, *19*), and evidence is accumulating that the degree of ortho substitution is an important feature in various biological properties of specific PCBs (*20*). Also, the *o*-, *m*-, and *p*-dichlorobenzenes exhibit different toxicological effects (*1*). Therefore, it is reasonable to expect different π or *f* values depending on the chlorine position or the number of chlorine atoms already on the ring.

In order to evaluate $K_{o/w}$ and C_s^w data and to predict these values for compounds not measured, investigators have used expressions of the form

$$\log (1/C_s^w) = a + b(\mathrm{mp}) + cX$$

where mp is the melting point of solutes which are solid at the experimental temperature, *a*, *b*, and *c* are series constants, and *X* is a parameter which is sensitive to the molecular structure of the solute. For compounds which are liquid at the experimental temperature, the mp term is zero. Either experimental or calculated properties may be used for *X*. Examples of experimental properties are $K_{o/w}$ (*2*, *6*, *11*, *21*), the solute boiling point, and GC retention data. Examples of calculated values are the solute parachor, molar volume, carbon or chlorine number, and surface area (*5*, *6*). In each case, however, it is assumed that the entropy of melting (ΔS_m), which is the ratio of the enthalpy of melting (ΔH_m) to the melting point (T_m), is equal to 13.5 cal/(mol deg) for those compounds which are solids at room temperature. Yalkowsky (*22*), however, has stated that the value of ΔS_m may be between 10 and 17 cal/(mol deg) for rigid molecules.

In this paper, the $K_{o/w}$ and C_s^w values for the chlorinated benzenes and biphenyls are determined by using the modified generator column method (*23*). These values are correlated with the solute chlorine number and with either the solute boiling point in the case of chlorobenzenes or the chromatographically determined relative retention time of the PCB solute eluting from a GC column containing C-87 as the stationary phase. Also, ΔH_m and T_m determined by using differential scanning calorimetry are reported for those compounds which are solid at room temperature. $K_{o/w}$ is then correlated with corrected C_s^w.

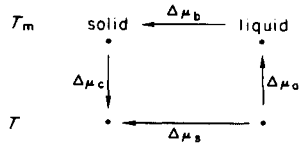
Thermodynamic Background

Equilibrium partitioning of a solute between two phases is achieved when the solute chemical potential is equal in each phase. When the pure solid solute is in equilibrium with the solute in an aqueous solution, the following equation applies:

$$\mu_s^s = \mu_s = \mu_s^l + RT \ln (\gamma_\phi^w \phi_s^w) \quad (1)$$

where μ_s^s and μ_s^l are the pure solute chemical potential in the solid and liquid states, respectively, μ_s is the solute chemical potential in aqueous solution, γ_ϕ^w is the solute volume fraction activity coefficient in the aqueous phase, and ϕ_s^w is the solute volume fraction in the aqueous solution.

Our goal is to link the solid–liquid equilibrium at an experimental temperature (T) to a well-defined solid–liquid equilibrium at the melting temperature T_m ($T_m > T$). This link is depicted in the following diagram:



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Since $\Delta\mu_b = 0$, the change in chemical potential in the solution process at temperature $T(\Delta\mu_s)$ may be expressed as

$$\Delta\mu_s = \Delta\mu_a + \Delta\mu_c \qquad (2)$$

At constant pressure

$$d\mu = -S\,dT \qquad (3)$$

where

$$dS = C_p(dT/T) \qquad (4)$$

S and C_p are respectively the entropy and heat capacity of the solute in a given phase. Integrating eq 3 and 4 between the limits of T_m (melting temperature) and T (experimental temperature, 25 °C), one obtains

$$\Delta\mu_a = -(T_m - T)S_{liq}(T_m) + C_{p,liq}T\ln(T/T_m) + C_{p,liq}(T_m - T) \qquad (5)$$

$$\Delta\mu_c = (T_m - T)S_{sol}(T_m) + C_{p,sol}T\ln(T_m/T) + C_{p,sol}(T - T_m) \qquad (6)$$

Substituting eq 5 and 6 into eq 2 and combining eq 1 and 2 yields

$$\ln \gamma_\phi^{w}\phi_s^{w} = \frac{-\Delta S_m}{RT}(T_m - T) - \frac{\Delta C_{p,m}}{R}\ln\left(\frac{T_m}{T}\right) + \frac{\Delta C_{p,m}}{R}\left(\frac{T_m}{T} - 1\right) \qquad (7)$$

where

$$\Delta S_m = S_{liq}(T_m) - S_{sol}(T_m) = \Delta H_m/T_m \qquad (8)$$

$$\Delta C_{p,m} = C_{p,liq} - C_{p,sol} \qquad (9)$$

An expression similar to eq 7 has been derived by Prausnitz and co-workers (*24*, *25*) for the activity coefficients of solid solutes in aqueous solution.

Previously (*23*), we derived the expression

$$\log K_{o/w} = \log \gamma_\phi^{w} - \log \gamma_\phi^{o} \qquad (10)$$

where γ_ϕ^{w} and γ_ϕ^{o} are the solute volume fraction activity cofficients in the aqueous and octanol phases, respectively. Combining eq 7 and 10, one obtains

$$\log K_{o/w} = -\log \phi_s^{w} - \log \gamma_\phi^{o} - \frac{\Delta H_m}{2.3R}\left[\frac{1}{T} - \frac{1}{T_m}\right] + \frac{\Delta C_{p,m}}{2.3R}\left[\left(\frac{T_m}{T} - 1\right) - \ln\left(\frac{T_m}{T}\right)\right] \qquad (11)$$

It was shown earlier (*23*) that for sparingly soluble solutes

$$\phi_s^{w} = C_s^{w}V_s \qquad (12)$$

where V_s is the molar volume of the solute. Also

$$\gamma_\phi^{o}V_s = \gamma_x^{o}V_0^{o} \qquad (13)$$

where γ_x^{o} is the solute mole fraction activity coefficient in octanol and V_0^{o} is the molar volume of octanol. After substitution, eq 11 becomes

$$\log K_{o/w} = \log\left(\frac{1}{C_s^{w}}\right) - \frac{\Delta H_m}{2.3R}\left(\frac{1}{T} - \frac{1}{T_m}\right) + \frac{\Delta C_{p,m}}{2.3R}\left[\left(\frac{T_m}{T} - 1\right) - \ln\left(\frac{T_m}{T}\right)\right] - \log \gamma_x^{o}V_0^{o} \qquad (14)$$

A similar expression has been derived by Mackay et al. (*26*); however, they ignored the correction term arising from the change in heat capacity at the melting temperature. Also, in their treatment of the data, they have assumed that $\Delta H_m/T_m$ = 13.5 cal/(mol deg). We have measured $K_{o/w}$, C_s^{w}, ΔH_m, $\Delta C_{p,m}$, and T_m for the chlorobenzenes and for several PCBs, as well as for biphenyl, and analyzed the data using eq 14.

Experimental Section

The chlorobenzenes were obtained from Aldrich Chemicals, and the PCBs were obtained from Ultra Scientific, Inc. (Certain trade names and company products are identified in order to adquately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, or does it imply that the products are necessarily the best available for the purpose.) The purities of the 1-octanol and *n*-hexane were checked by gas chromatography (GC) and found to be at least 99%. Distilled water was used for generating aqueous solutions.

The $K_{o/w}$ and C_s^{w} of the chlorobenzenes were measured by using the modified generator column coupled with a high-pressure liquid chromatography (HPLC). The details of this method are described elsewhere (*23*).

For the PCBs, the $K_{o/w}$ and C_s^{w} measurements were also made by using the generator column; however, analyses were done by using GC (*27*). An extractor column (*23*) was connected to the outlet of a generator column, and the aqueous solution was eluted from the generator column through an extractor column to the collecting vessel. After a period of time, the extractor column was disconnected, and the volume of aqueous solution collected was determined by weighing. Nitrogen was then passed through the extractor column to remove any excess water. The dried extractor column and a second eollecting vessel were weighed, and a minimal volume of *n*-hexane was used to extract the PCB from the extractor column and collected in the vessel. After the extractor column and vessel plus *n*-hexane were reweighed, the amount of PCB in the hexane extract was determined by GC using an electron capture detector. As a separate experiment, the GC retention times for the PCBs were measured by using columns containing 3% C-87 hydrocarbon by weight on 100/120 Chromosorb W HP at 150 °C. The column lengths varied from 1.5 to 6 ft.

The ΔH_m, T_m, and $\Delta C_{p,m}$ were determined by using differential scanning calorimetry (DSC). Samples of each chlorobenzene and PCB which were solid at room temperature as well as samples of 10 standards (99.99% purity) were prepared by accurately weighing from 3 to 10 mg of sample (to the nearest 0.002 mg).

The temperature axis of the DSC was calibrated (*28*) in the range −36 to 325 °C by using the known melting points of the 10 standards. Each calibrant was run at four different scanning rates (10, 5, 2.5, and 1.25 K/min), and the "true" or "static" transition temperature was determined by extrapolation to zero scanning rate. The correct T_m for each compound was determined from its static melting temperature and a calibration curve constructed from the standards.

The enthalpies of melting (ΔH_m) were determined by comparing the chart peak area per milligram of sample with that of a known weight of ultrapure indium. At a constant heating rate, the DSC ordinate displacement due to sample heat capacity is (*29*)

$$\frac{dH}{dt} = \frac{dH}{dT}\frac{dT}{dt} \qquad (15)$$

where dH/dt is the rate of heat absorption, dT/dt is the scanning rate, and $(dH/dT)(C_p)$ is the sample heat capacity for 1 g of sample. Therefore, under linear scanning conditions, the DSC ordinate readout provides the basis of a direct and simple measurement of C_p. This investigation showed that ordinate deflection was approximately the same for the liquid and solid phases of a given chlorobenzene or PCB, i.e., $\Delta C_{p,m} \doteq 0$.

Table I. Boiling Points, Solubilities, and Octanol/Water Partition Coefficients of Chlorobenzenes

		C_s^w, M		log $K_{o/w}$	
	bp, °C	this study[a]	lit.[b]	this study[a]	lit.[c]
chlorobenzene	132	$(2.62 \pm 0.05) \times 10^{-3}$	4.47×10^{-3}	2.98 ± 0.02	2.83
o-dichlorobenzene	180.5	$(6.28 \pm 0.08) \times 10^{-4}$	6.31×10^{-4}	3.38 ± 0.01	3.59
m-dichlorobenzene	173	$(8.47 \pm 0.07) \times 10^{-4}$	8.13×10^{-4}	3.48 ± 0.02	3.59
p-dichlorobenzene	174	$(2.10 \pm 0.05) \times 10^{-4}$	6.17×10^{-4}	3.38 ± 0.03	3.59
1,2,3-trichlorobenzene	218	$(6.76 \pm 0.36) \times 10^{-5}$	1.74×10^{-4}	4.04 ± 0.03	4.27
1,2,4-trichlorobenzene	213.5	$(2.54 \pm 0.20) \times 10^{-4}$	1.91×10^{-4}	3.98 ± 0.02	4.27
1,3,5-trichlorobenzene	208	$(2.27 \pm 0.06) \times 10^{-5}$	3.63×10^{-5}	4.02 ± 0.03	4.27
1,2,3,4-tetrachlorobenzene	254	$(5.65 \pm 0.00) \times 10^{-5}$	2.00×10^{-5}	4.55 ± 0.01	5.05
1,2,3,5-tetrachlorobenzene	246	$(1.34 \pm 0.11) \times 10^{-5}$	1.62×10^{-5}	4.65 ± 0.01	5.05
1,2,4,5-tetrachlorobenzene	243	$(1.09 \pm 0.04) \times 10^{-5}$	2.76×10^{-6}	4.51 ± 0.03	5.05
pentachlorobenzene	277	$(3.32 \pm 0.10) \times 10^{-6}$	2.24×10^{-6}	5.03 ± 0.01	5.79
hexachlorobenzene	322	$(1.65 \pm 0.02) \times 10^{-7}$	1.74×10^{-8}	5.47 ± 0.02	6.53

[a] The uncertainty is the standard deviation for at least three replicate measurements. [b] Yalkowsky et al. (*6*). [c] Calculated by the method of Nys and Rekker, as reported by Yalkowsky et al. (*6*).

Table II. Aqueous Solubilities and Octanol/Water Partition Coefficients of Polychlorinated Biphenyls

compd no.	compd	log α[a]	C_s^w, M		log $K_{o/w}$	
			this study[b]	lit.	this study[b]	lit.
1	biphenyl	−1.03	$(4.35 \pm 0.14) \times 10^{-5}$	3.91×10^{-5} [c] 4.80×10^{-5} [d] 5.51×10^{-5} [e] 4.83×10^{-5} [f] 4.58×10^{-5} [g] 4.52×10^{-5} [h]	3.76 ± 0.01	3.89[i] 4.04[c] 3.75[m] 4.03[h]
2	2-chlorobiphenyl	−0.82	$(2.68 \pm 0.03) \times 10^{-5}$	3.05×10^{-5} [f] 2.19×10^{-5} [n]	4.50 ± 0.01	
3	2,5-dichlorobiphenyl (liquid)	−0.42	$(8.70 \pm 0.21) \times 10^{-6}$	1.49×10^{-6} [j] 9.37×10^{-6} [f] 2.60×10^{-6} [n]	5.16 ± 0.01	
4	2,6-dichlorobiphenyl	−0.59	$(6.23 \pm 0.13) \times 10^{-6}$	1.49×10^{-6} [j]	4.93 ± 0.02	
5	2,4,5-trichlorobiphenyl	0	$(6.32 \pm 0.31) \times 10^{-7}$	4.62×10^{-7} [j] 7.49×10^{-7} [f] 3.57×10^{-7} [n]	5.51 ± 0.11	5.81[i]
6	2,4,6-trichlorobiphenyl	−0.22	$(8.76 \pm 0.47) \times 10^{-7}$	4.62×10^{-7} [j]	5.47 ± 0.03	
7	2,3,4,5-tetrachlorobiphenyl	0.43	$(7.17 \pm 0.34) \times 10^{-8}$	1.83×10^{-7} [j] 1.80×10^{-7} [f] 6.58×10^{-8} [n]	5.72 ± 0.07	
8	2,2′,4′,5-tetrachlorobiphenyl	0.19	$(5.63 \pm 0.33) \times 10^{-8}$	1.83×10^{-7} [j]	5.73 ± 0.09	
9	2,3,4,5,6-pentachlorobiphenyl	0.63	$(1.68 \pm 0.08) \times 10^{-8}$	6.34×10^{-8} [j] 2.77×10^{-8} [f] 2.08×10^{-8} [n]	6.30 ± 0.05	
10	2,2′,4,5,5′-pentachlorobiphenyl	0.58	$(5.92 \pm 0.27) \times 10^{-8}$	3.05×10^{-8} [k] 6.34×10^{-8} [j] 3.15×10^{-8} [l] 4.99×10^{-8} [f] 1.29×10^{-8} [n]	5.92 ± 0.01	6.11[k] 6.44[m]
11	2,2′,3,3′,6,6′-hexachlorobiphenyl	0.54	$(1.67 \pm 0.08) \times 10^{-8}$	2.75×10^{-8} [j]	6.63 ± 0.06	
12	2,2′,3,3′,4,4′-hexachlorobiphenyl	1.12	$(7.84 \pm 0.36) \times 10^{-10}$	2.75×10^{-8} [j] 3.66×10^{-9} [f] 1.22×10^{-9} [n]	6.98 ± 0.04	
13	2,2′,4,4′,6,6′-hexachlorobiphenyl	1.53	$(1.13 \pm 0.05) \times 10^{-9}$	2.75×10^{-8} [j] 5.65×10^{-9} [f] 2.49×10^{-9} [n]	7.55 ± 0.21	
14	2,2′,3,3′,4,4′6-heptachlorobiphenyl	0.64	$(5.49 \pm 0.24) \times 10^{-9}$	1.58×10^{-8} [j]	6.68 ± 0.20	
15	2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl	1.17	$(9.15 \pm 0.50) \times 10^{-10}$	2.05×10^{-10} [f] 4.19×10^{-10} [n]	7.11 ± 0.30	
16	2,2′,3,3′,4,5,5′,6,6′-nonachlorobiphenyl	1.70	$(3.88 \pm 0.17) \times 10^{-11}$		8.16 ± 0.22	
17	2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl	1.88	$(1.49 \pm 0.19) \times 10^{-11}$	3.21×10^{-11} [n] 8.02×10^{-13} [g]	8.26 ± 0.10	

[a] α = (retention time of compound)/(retention time of 2,4,5-trichlorobiphenyl) measured by using a C-87 chromatographic column. [b] The uncertainty is the standard deviation for three replicate measurements. [c] Banerjee et al. (*7*). [d] Eganhouse and Calder (*8*). [e] Hollifield (*9*). [f] Mackay et al. (*5*). [g] Wauchope and Getzen (*10*). [h] Yalkowsky and Valvani (*11*). [i] Woodburn (*2*). [j] Dexter and Pavlou (*12*). [k] Chiou et al. (*13*). [l] Hague and Schmedding (*14*). [m] Veith et al. (*15*). [n] Weil et al. (*16*).

Results and Discussion

The boiling points and the experimental values of C_s^w and $K_{o/w}$ for the chlorobenzenes are given in Table I along with the literature values reported by Yalkowsky et al. (*6*). The literature $K_{o/w}$ values were calculated by using hydrophobic fragmental constants (*17*), whereas the literature C_s^w values were measured by using a spectrophotometric method. Our solubility results are generally in good agreement with the literature values.

For the PCBs, the experimental values of C_s^w, $K_{o/w}$, and α, which is the ratio of the corrected retention time of a solute eluting from a GC column containing a nonselective stationary phase (at constant temperature and flow) to the corrected re-

Table III. Temperatures, Enthalpies, and Entropies of Melting for the Chlorobenzenes and Polychlorinated Biphenyls

compd	T_m, K	ΔH_m, kJ[a]/mol	ΔS_m, cal[a]/(mol deg)
p-dichlorobenzene	326.7	19.0	13.9
1,2,3-trichlorobenzene	325.8	18.5	13.6
1,3,5-trichlorobenzene	336.3	18.8	13.4
1,2,3,4-tetrachlorobenzene	320.0	17.0	12.7
1,2,3,5-tetrachlorobenzene	323.9	19.0	14.0
1,2,4,5-tetrachlorobenzene	412.2	24.1	14.0
pentachlorobenzene	357.7	20.6	13.8
hexachlorobenzene	501.1	22.4	10.7
biphenyl	342.6	17.5	12.2
2-chlorobiphenyl	305.3	15.3	12.0
2,6-dichlorobiphenyl	307.9	12.6	9.8
2,4,5-trichlorobiphenyl	349.5	22.8	15.6
2,4,6-trichlorobiphenyl	334.3	16.5	11.8
2,3,4,5-tetrachlorobiphenyl	363.9	25.2	16.6
2,2',4',5-tetrachlorobiphenyl	339.1	23.4	16.5
2,3,4,5,6-pentachlorobiphenyl	397.6	21.8	13.1
2,2',4,5,5'-pentachlorobiphenyl	350.1	18.8	12.8
2,2',3,3',6,6'-hexachlorobiphenyl	385.2	21.1	13.1
2,2',3,3',4,4'-hexachlorobiphenyl	424.9	29.2	16.4
2,2',4,4',6,6'-hexachlorobiphenyl	386.7	17.5	10.8
2,2',3,3',4,4',6-heptachlorobiphenyl	395.4	20.3	12.2
2,2',3,3',5,5',6,6'-octachlorobiphenyl	433.8	22.8	12.6
2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	455.8	22.6	11.9
2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	578.9	28.7	11.8

[a] 1 cal = 4.184 J.

tention time of a reference solute (2,4,6-trichlorobiphenyl), are given in Table II along with literature C_s^w and $K_{o/w}$ values. The C_s^w values range from 10^{-5} to 10^{-11} M while the $K_{o/w}$ values range from 10^3 to 10^8.

Experimental values of ΔH_m, T_m, and ΔS_m are given in Table III for the chlorobenzenes and PCBs which are solid at room temperature. The average ΔS_m is 13.1 cal/(mol deg) with values ranging from 9.8 to 16.6 cal/(mol deg).

In order to evaluate our values of C_s^w and $K_{o/w}$ and to predict such parameters for other halobenzenes and other PCB isomers, we present correlations of $K_{o/w}$ and C_s^w against certain molecular properties, one of which is chlorine number. According to Hansch and Leo's estimation scheme (*4*), the $K_{o/w}$ for a chlorobenzene, $K_{o/w}$(CB), or $K_{o/w}$ for a PCB, $K_{o/w}$(PCB), can be estimated by

$$\log K_{o/w}(\mathrm{CB}) = \log K_{o/w}(\mathrm{benzene}) + n_{\mathrm{Cl}}\pi_{\mathrm{Cl}} \qquad (16)$$

$$\log K_{o/w}(\mathrm{PCB}) = \log K_{o/w}(\mathrm{biphenyl}) + n_{\mathrm{Cl}}\pi_{\mathrm{Cl}} \qquad (17)$$

where n_{Cl} is the number of chlorines on the phenyl or biphenyl molecule, $K_{o/w}$(benzene) and $K_{o/w}$(biphenyl) are the $K_{o/w}$'s for benzene and biphenyl, respectively, and π_{Cl} is the substituent constant for chlorine. This equation is based on the assumption that each chlorine has the same π_{Cl} value regardless of its position on the phenyl or biphenyl structure.

In Figure 1, log $K_{o/w}$ values are correlated against n_{Cl} for both the chlorobenzenes and PCBs. The solid line for the chlorobenzenes is from the equation

$$\log K_{o/w} = 0.522 n_{\mathrm{Cl}} + 2.43 \qquad (18)$$

The correlation coefficient is 0.996. The dashed line for the PCBs is from the equation

$$\log K_{o/w} = 0.432 n_{\mathrm{Cl}} + 4.08 \qquad (19)$$

The correlation coefficient is 0.967. Table IV lists the percent derivations (100[exptl − calcd]/calcd) for each point in Figure 1. The average of the absolute values of the percent deviations is 1.21 for the chlorobenzenes and 3.54 for the PCBs.

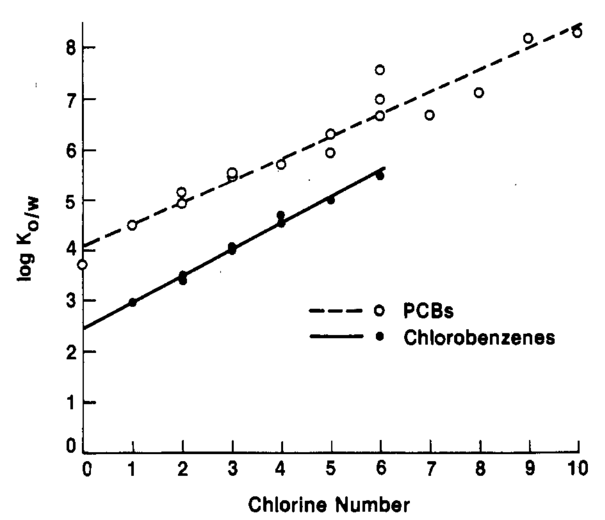

Figure 1. log $K_{o/w}$ as a function of chlorine number for the chlorobenzenes (●) and PCBs (○) from the data given in Tables I and II, respectively.

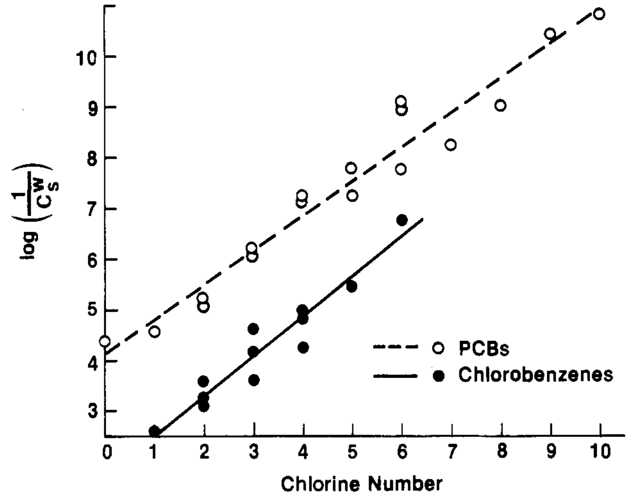

Figure 2. log $1/C_s^w$ as a function of chlorine number for the chlorobenzenes (●) and PCBs (○) from the data given in Tables I and II, respectively.

Hansch and Leo's value for π_{Cl} is 0.71 (*4*). When this value of π_{Cl} is substituted into eq 16, none of the chlorobenzenes can be estimated with any degree of accuracy. Using $\pi_{\mathrm{Cl}} = 0.71$ in eq 17, only two PCBs, 2-chlorobiphenyl and 2,5-dichlorobiphenyl, can be estimated with any degree of accuracy.

Figure 2 shows the correlations of log ($1/C_s^w$) against chlorine number for the chlorobenzenes (solid line) and PCBs (dashed line). The solid line is from the equation

$$\log (1/C_s^w) = 0.785 n_{\mathrm{Cl}} + 1.72 \qquad (20)$$

The correlation coefficient is 0.956, and the average of the absolute values of the percent deviations between the experimental values and those calculated via eq 20 is 6.27 (Table IV). The dashed line is from the equation

$$\log (1/C_s^w) = 0.678 n_{\mathrm{Cl}} + 4.13 \qquad (21)$$

The correlation coefficient is 0.975, and the average of the absolute values of the percent deviations between the experimental values and those calculated via eq 2 is 4.91 (Table IV).

Wasik et al. (*30*) have shown that for series compounds log $K_{o/w}$ and log ($1/C_s^w$) are related to the solute boiling point T_b such that

$$\log K_{o/w} = a + bT_b \qquad (22)$$

$$\log (1/C_s^w) = a' + b'T_b \qquad (23)$$

Table IV. Percent Deviation[a] in Various Plots

	$\log K_{o/w}$ vs.				$\log 1/C_s^w$ vs.		
compd	n_{Cl}	bp	$\log \alpha$	$\log (1/C_s^w) - (\Delta H_m/2.3R)\cdot(1/T - 1/T_m)$	n_{Cl}	bp	$\log \alpha$
chlorobenzene	1.02	3.83		−1.00	2.79	7.05	
o-dichlorobenzene	−2.59	−5.06		−3.43	−2.74	−6.98	
m-dichlorobenzene	0.29	0.58		2.35	−6.69	−6.40	
p-dichlorobenzene	−2.59	−2.59		−3.29	11.85	11.52	
1,2,3-trichlorobenzene	1.25	−1.22		0.25	2.21	−1.42	
1,2,4-trichlorobenzene	−0.25	−1.24		4.19	−11.76	−12.83	
1,3,5-trichlorobenzene	0.75	1.77		−7.59	13.73	15.42	
1,2,3,4-tetrachlorobenzene	0.89	−1.09		8.85	−12.55	−14.83	
1,2,3,5-tetrachlorobenzene	3.10	3.56		0.65	0.21	1.04	
1,2,4,5-tetrachlorobenzene	0.00	1.35		13.60	2.26	2.94	
pentachlorobenzene	−0.20	2.03		3.93	−3.01	0.00	
hexachlorobenzene	−1.62	−1.80		7.68	5.44	5.44	
biphenyl	−8.33		−8.60	−9.00	5.59		4.96
2-chlorobiphenyl	−0.22		2.60	−0.88	−4.96		−1.00
2,5-dichlorobiphenyl	4.33		4.31	3.61	−7.80		−7.91
2,6-dichlorobiphenyl	−0.32		4.72	−2.18	−5.17		1.62
2,4,5-trichlorobiphenyl	2.45		−0.45	1.66	0.52		−3.41
2,4,6-trichlorobiphenyl	1.71		4.65	−1.08	−1.80		2.06
2,3,4,5-tetrachlorobiphenyl	−1.53		−6.81	−4.67	4.34		−2.97
2,2′,4′,5-tetrachlorobiphenyl	−1.36		−1.22	−9.34	5.87		6.04
2,3,4,5,6-pentachlorobiphenyl	0.95		−1.84	−1.10	3.30		−0.37
2,2′,4,5,5′-pentachlorobiphenyl	−5.14		−6.74	−6.33	−3.97		−6.06
2,2′,3,3′,6,6′-hexachlorobiphenyl	−0.34		5.69	2.78	−5.19		2.29
2,2′,3,3′,4,4′-hexachlorobiphenyl	4.60		−1.76	0.00	10.97		2.55
2,2′,4,4′,6,6′-hexachlorobiphenyl	13.14		−1.68	0.40	9.07		−8.50
2,2′,3,3′,4,4′,6-heptachlorobiphenyl	−5.97		3.86	−2.20	−7.01		5.57
2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl	−5.65		−0.91	−0.56	−5.48		0.56
2,2′,3,3′,4,5,5′,6,6′-nonachlorobiphenyl	2.41		3.03	0.25	1.66		2.58
2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl	−1.65		1.10	8.26	−0.87		2.62
av of absolute value of % dev	2.57	2.18	3.53	3.96	5.58	7.16	3.59

[a] Percent deviation = 100(exptl − calcd)/calcd.

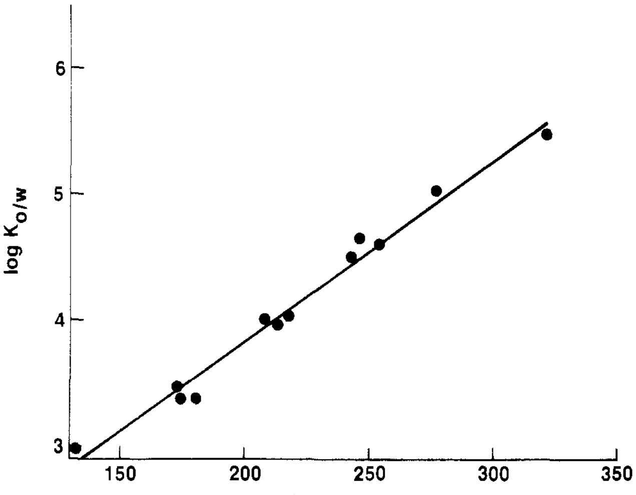

Figure 3. log $K_{o/w}$ as a function of boiling point for the chlorobenzenes from the data given in Table I.

where a, a', b, and b' are series constants. Using the T_b, C_s^w, and $K_{o/w}$ data listed in Table I for the chlorobenzenes, we show plots of log $K_{o/w}$ and log ($1/C_s^w$) against T_b in Figures 3 and 4, respectively. The solid line in Figure 3 is from the equation

$$\log K_{o/w} = (1.42 \times 10^{-2})T_b + 1.00 \qquad (24)$$

The correlation coefficient is 0.991, and the average of the absolute values of the percent deviations is 2.18 (Table IV). The solid line in Figure 4 is from the equation

$$\log (1/C_s^w) = (2.11 \times 10^{-2})T_b - 0.378 \qquad (25)$$

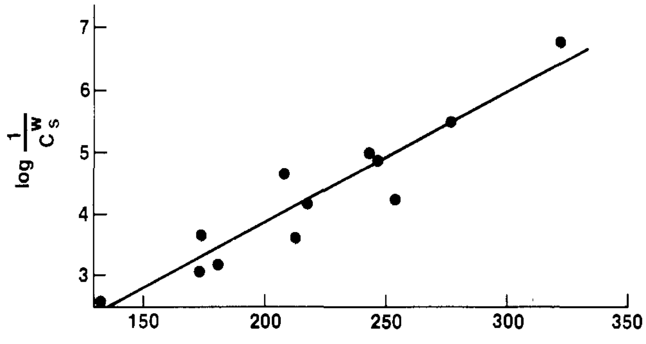

Figure 4. log $1/C_s^w$ as a function of boiling point for the chlorobenzenes from the data given in Table I.

The correlation coefficient is 0.943, and the average of the absolute values of the percent deviations is 7.16 (Table IV).

For the PCBs where T_b data are not available, one can use GC theory to relate T_b with α (*31*) such that

$$\log \alpha = k + k_1 T_b \qquad (26)$$

where α is the ratio of the corrected retention time of a solute eluting from a GC column containing a nonselective stationary phase (at constant temperature and flow) to the corrected retention time of a reference solute and k and k_1 are series constants. The α values are sensitive to molecular structure of the solute molecule and can be measured quickly. Combining eq 22 and 26 as well as eq 23 and 26, one obtains

$$\log K_{o/w} = k' + k_1' \log \alpha \qquad (27)$$

$$\log (1/C_s^w) = k'' + k_1'' \log \alpha \qquad (28)$$

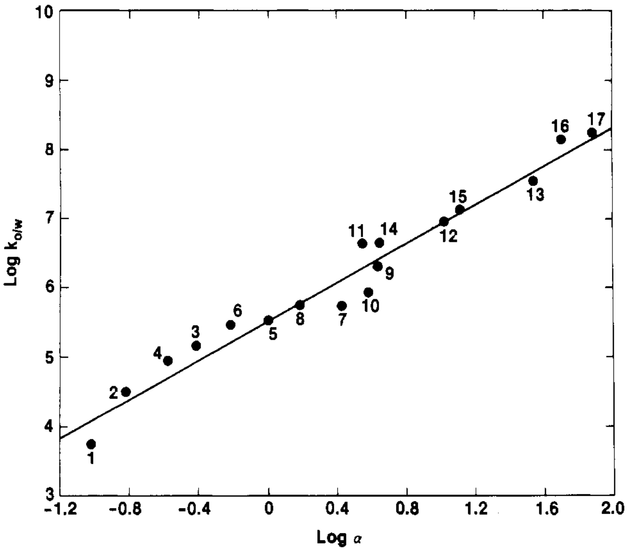

Figure 5. log $K_{o/w}$ as a function of log α for the PCBs from the data given in Table II.

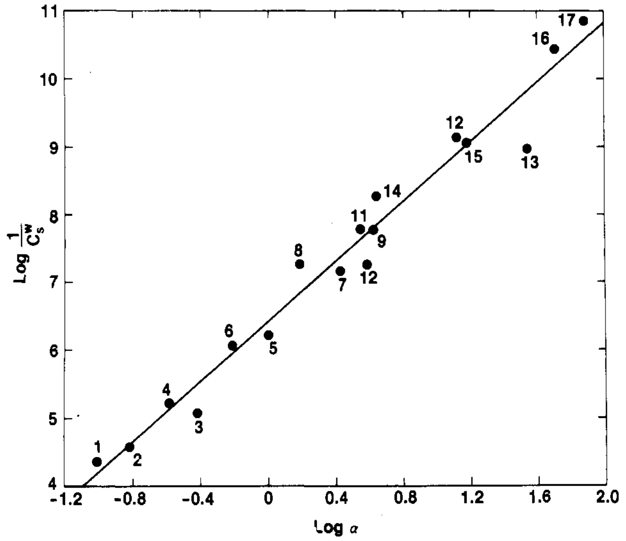

Figure 6. log $1/C_s^w$ as a function of log α for the PCBs from the data given in Table II.

where k', k_1', k'', and k_1'' are new constants.

The α values given in Table II for the PCBs are measured on a GC column containing C-87 as a stationary phase. C-87 is chosen because it is thermally stable and nonselective; i.e., the elution order of a series of compounds depends only on their boiling points.

Figure 5 and 6 show plots of log $K_{o/w}$ and log $(1/C_s^w)$, respectively, against log α using the PCB data in Table II. The solid line in Figure 5 is from the equation

$$\log K_{o/w} = 1.40 \log \alpha + 5.54 \qquad (29)$$

The correlation coefficient is 0.980, and the average of the absolute values of percent deviations between the experimental values and those calculated via eq 29 is 3.53 (Table IV).

The solid line in Figure 6 is from the equation

$$\log (1/C_s^w) = 2.20 \log \alpha + 6.42 \qquad (30)$$

The correlation coefficient is 0.984, and from Table IV the average of the absolute values of the percent deviations between the experimental values and those calculated via eq 30 is 3.59.

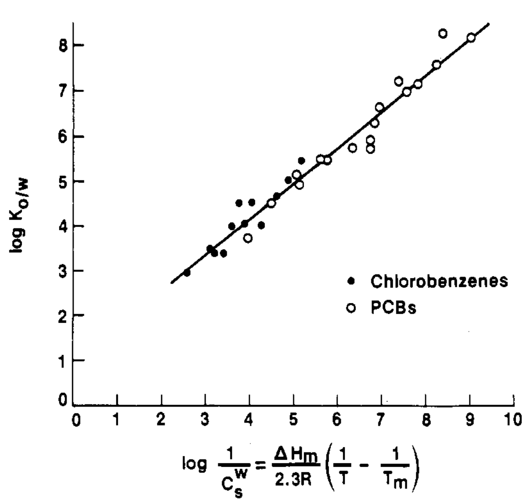

Figure 7. log $K_{o/w}$ as a function of log $(1/C_s^w)$ minus a melting point correction for the chlorobenzenes (●) and PCBs (○) from the data given in Tables I and II, respectively, as well as Table III.

Table V. Experimental[a] and Calculated[b] log $K_{o/w}$ for Miscellaneous Organics

compd	T_m, K	log $K_{o/w}$ exptl[a]	log $K_{o/w}$ calcd[b]	% dev[c]
n-heptane		4.66	4.50	3.56
1-bromopentane		3.49	3.41	2.35
bromobenzene		2.98	3.01	−1.00
iodobenzene		3.28	3.35	−2.09
naphthalene	354.2	3.35	3.40	−1.47
hexamethylbenzene	436.2	4.61	4.51	2.22

[a] Tewari et al. (*23*). [b] Calculated via eq 31. Note that, where melting point corrections are needed, $\Delta H_m/T_m$ is set equal to 13.5 cal/(mol deg). [c] % dev = 100(exptl − calcd)/calcd.

Finally, eq 14 with $\Delta C_{p,m} = 0$ is used to correlate log $K_{o/w}$ against log $(1/C_s^w) - (\Delta H_m/2.3R)(1/T - 1/T_m)$ as shown in Figure 7. The solid points represent chlorobenzene data from Tables I and III while the open circles represent PCB data from Tables II and III. For the four chlorobenzenes and one PCB which are liquid at room temperature, T_m is set equal to 298.2 K. The solid line in Figure 7 is from the equation

$$\log K_{o/w} = 0.795[\log (1/C_s^w) - (\Delta H_m/2.3R)(1/T - 1/T_m)] + 0.960 \qquad (31)$$

The correlation coefficient is 0.982, and the average of the absolute values of percent deviations between the experimental values and those calculated via eq 31 is 3.96 (Table IV).

The thermodynamically derived equation (eq 14) predicts a slope equal to 1 and an intercept equal to log $\gamma_x{}^\circ V_0{}^\circ$ for eq 31. The slope in eq 31, however, is 0.795. This difference may be attributed to variations in the intercept (activity coefficient term) for the various solutes. If one assumes a slope of 1 and calculates the log $\gamma_0{}^\circ V_0{}^\circ$ term, this term varies from −0.72 to 1.02 for the solutes studied.

Of the correlations presented in this paper, the correlation based on eq 14 is the most universal. In Table V are compared experimental log $K_{o/w}$ values determined previously by the modified generator column method (*23*) to log $K_{o/w}$ values calculated via eq 31 for a *n*-alkane, a halogenated alkane, and five aromatics. For naphthalene and hexamethylbenzene, which are solid at room temperature, $\Delta H_m/T_m$ is set equal to 13.5 cal/(mol deg) (*22*). The agreement between the experimental and calculated log $K_{o/w}$ values in Table V is fairly good, indicating the universality of eq 31.

Registry No. Octanol, 111-87-5; chlorobenzene, 108-90-7; *o*-dichlorobenzene, 95-50-1; *m*-dichlorobenzene, 541-73-1; *p*-dichlorobenzene, 106-46-7; 1,2,3-trichlorobenzene, 87-61-6; 1,2,4-trichlorobenzene, 120-

82-1; 1,3,5-trichlorobenzene, 108-70-3; 1,2,3,4-tetrachlorobenzene, 634-66-2; 1,2,3,5-tetrachlorobenzene, 634-90-2; 1,2,4,5-tetrachlorobenzene, 95-94-3; pentachlorobenzene, 608-93-5; hexachlorobenzene, 118-74-1; 2-chlorobiphenyl, 2051-60-7; 2,5-dichlorobiphenyl, 34883-39-1; 2,6-dichlorobiphenyl, 33146-45-1; 2,4,5-trichlorobiphenyl, 15862-07-4; 2,4,6-trichlorobiphenyl, 35693-92-6; 2,3,4,5-tetrachlorobiphenyl, 33284-53-6; 2,2′,4′,5-tetrachlorobiphenyl, 41464-40-8; 2,3,4,5,6-pentachlorobiphenyl, 18259-05-7; 2,2′,4,5,5′-pentachlorobiphenyl, 37680-73-2; 2,2′,3,3′,6,6′-hexachlorobiphenyl, 38411-22-2; 2,2′,3,3′,4,4′-hexachlorobiphenyl, 38380-07-3; 2,2′,4,4′,6,6′-hexachlorobiphenyl, 33979-03-2; 2,2′,3,3′,4,4′,6-heptachlorobiphenyl, 52663-71-5; 2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl, 2136-99-4; 2,2′,3,3′,4,5,5′,6,6′-nonachlorobiphenyl, 52663-77-1; 2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl, 2051-24-3.

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Solubility of Uranium Hexafluoride in Some Low-Temperature Solvents

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The solubility of UF_6 has been measured in several liquefied gases. Phosgene, nitrous oxide, and sulfur dioxide are found to be good solvents for UF_6 at temperatures below 0 °C. The results are compared with ideal and regular solution theory. Regular solution theory provides a reasonably good description of the $UF_6/COCl_2$ system but is less good for the UF_6/SO_2 system.

Introduction

The solubility of uranium hexafluoride (UF_6) in liquids has been studied many times, particularly in halocarbons (*1-3*) and fluorinated halogens (*4-8*). A few of these studies have included temperatures below 0 °C (*2*, *5*, *7*) but there has been more interest in the solubilities at temperatures above 0 °C.

It is the purpose of this paper to report the solubilities of UF_6 in liquefied gases of small, inorganic molecules. Solubilities have been measured for temperatures between about 160 and 270 K, and the experimental observations are compared with regular solution theory.

Experimental Methods

The apparatus is a calibrated, 80-mL, graduated, cylindrical, borosilicate glass flask measuring about 4 cm in diameter by 8 cm high and attached to a vacuum system through a glass tube. The flask is surrounded by a clear glass Dewar, and the top of the Dewar is closed with a Styrofoam plug that fits around the vacuum line. A glass-encapsulated magnetic stirring rod is inside the flask. An iron-constantan thermocouple is inserted into a thin-walled glass well that protrudes into the interior of the flask; this thermocouple well is fused to the top of the flask and reaches nearly to the bottom.

The experimental procedure is as follows. The flask is evacuated to about 10^{-4} torr and is heated to drive off any residual water. The bottom of the flask is then cooled with dry ice or liquid nitrogen, and the solute, UF_6, is condensed out from its gas phase. The Dewar is raised into position and closed with the Styrofoam plug. Further cooling of the flask is accomplished by blowing cold N_2 gas into the Dewar through a hole in the Styrofoam plug. The solvent is condensed into the flask, and the mixture of UF_6 and solvent is stirred vigorously. The temperature of the liquid is held constant, and solvent is *slowly* condensed into the flask in small increments. After each addition of solvent, the mixture is stirred for a period that depends on the solvent, the temperature, and the amount of undissolved UF_6. After most of the UF_6 has been dissolved, solvent is added in very small increments and the stirring times between additions are lengthened, to ensure that the solution is saturated with UF_6. Some of the data points reported here have been obtained with a small fraction (<2%) of the total UF_6 still undissolved. When the UF_6 crystals just disappear under bright illumination, the stirring motion is stopped, and the level of the

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