PHYSICAL-CHEMICAL PROPERTIES OF THREE CONGENERIC SERIES OF CHLORINATED AROMATIC HYDROCARBONS

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ABSTRACT
It is suggested that when assessing the environmental fate or toxicity of organic chemicals, especially those of congenic series such as PCBs, it is useful to together and critically review their basic properties including solubility, vapour pressure, octanol/water partition coefficient and Henry's law constant. This approach is illustrated for three series of chemicals, the chlorobenzenes, the polychlorinated biphenyls and the chlorinated dibenzo-p-dioxins.

KEYWORDS
Chlorinated aromatic hydrocarbons, congenic series, chlorobenzenes (CBs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), solubility, vapour pressure, octanol/water partition coefficient, Henry's law constants, correlations, chlorine number, molar volume.

INTRODUCTION
Accurate values of the physical-chemical properties of chemicals are essential for estimating environmental behaviour and for assembling quantitative structure-activity relationships (QSARs). Each chemical has a set of partitioning, reaction and transport properties controlling partitioning and migration between air, water, soil, sediments and biota, as well as within organisms, and between blood and various tissues, including, it can be presumed, the target tissue in which the toxic effect(s) are manifested. In view of the large number of organic chemicals released into the environment, it is essential to build up a predictive capability in which the behaviour and effects of one chemical can be deduced from those of structurally similar chemicals. These deductions are the subject of the chapters in this text.

R. L. E. Kain (ed.), QSAR in Environmental Toxicology - II: 347-362
One often neglected aspect of this issue is the acquisition and treatment of the basic physical-chemical data. In this chapter we review the relationships between physical-chemical properties and suggest methods of treating data of congeners series using such examples as the chlorobenzenes (CBs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs).

It transpires that chemicals partition between five basic media, and it is the relative extent of partitioning which controls environmental and pharmacokinetic fate. These media are as follows.

Air: Obviously more volatile chemicals such as chloro-methanes will partition primarily into air because of their high vapour pressure. Indeed, vapour pressure is really "solubility in air" in disguise. The common vapour pressure $P^*$ (subscript $S$ designating saturation or maximum value) being convertible into a concentration by dividing $P^*$ by the gas constant temperature product RT.

Water: Water soluble chemicals such as phenols or linear alcohols tend to remain primarily in aqueous solution. In many cases they may dissociate to ionic forms thus further increasing their solubility.

Organic Media: Many hydrophobic, low vapour pressure chemicals (e.g., PCBs) partition primarily into organic media such as natural organic carbon of ligneous origin, lipids or fat. Such chemicals often display large biocentral concentration factors and long retention in fatty tissues. Octanol is the most common surrogate phase for laboratory determinations of partitioning tendency into organic media. Rarely are solubilities in organic media measured, usually concentration ratios such as octanol:water partition coefficients $K_{ow}$ are employed. There may not be a true solubility of, for example, benzene in octanol because the liquids are miscible, but a "pseudo-solubility" can be deduced if it is assumed that $K_{ow}$ is the ratio of the pseudo-solubility in octanol $Q$ to water solubility $Q_W$ Q is thus the product $K_{ow}Q_W$ and shows remarkable constancy at 200 to 3000 mol·m$^{-3}$ (Miller et al. 1985).

Mineral Surfaces: These surfaces tend to be relatively unimportant for organic chemical sorption especially when competing organic media are also present. Indeed it is suspected that in many situations natural mineral surfaces become rapidly coated with organic matter. We ignore this medium.

Pure Phase: Some solid organic chemicals of very high molecular weight including polymers, certain hydrocarbons and some dyes have negligible solubilities in air, water and organic media and thus tend to remain in their pure phases as shown in FIGURE 1. As the amount of chemical is increased, the concentrations in each phase tend to increase linearly maintaining a constant ratio or partition coefficient to each other. At saturation, or the

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FIGURE 1: Generalization

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SHIU ET AL.

The treatment of the new relationships methods of treating data bases (CDBs), polychloro-
p-dioxins (PCDDs), organic media, and it is the venal and pharma-
methanes will partition issue. Indeed, vapour mini vapour pressure study being convertible temperature product linear alcohols tend to they may dissolve to.

1. Chemicals (e.g., natural organic carbon of play large biological-which is the most common partitioning tendency into). Measured, usually coefficients (K_w) are for example, benzene in air-solubility can be dose-solubility in octanol and shows remarkable slightly unimportant for organic media are also natural mineral surfaces in this medium.

High molecular weight dyes have negligible tend to remain in their chemical is increased linearly maintaining a. At saturation, or the

RELATIONSHIPS OF PHYSICAL-CHEMICAL PROPERTIES

Solubility limit, any extra chemical added forms a new pure phase. It is convenient to express these tendencies as solubilities in air, water and organic media, from which the various partition coefficients can be deduced. In principle "solubilities" can also be deduced for tissues such as muscle and liver. A chemical's three key environmental solubilities are those in air, in water and in octanol, i.e., the \( K_{ow} \) C\(^2\) product.

![Figure 1: Generalized partitioning behaviour of chemicals in the environment.](image)

**THERMODYNAMIC BASIS**

Solid and Liquid Solubilities. As has been discussed by several workers, including us in the previous text in this series (Mackay and Shi 1994), it is essential to convert all solubilities and vapor pressures to the values for subcooled liquids, i.e., those solubilities which the solid chemical would have if it could exist at the desired temperature in the liquid state. The ratio of the solid to subcooled liquid solubility can be estimated by the approximate relationship (Prausnitz 1979).
F = \frac{C_s C_L}{C_s^2} = \exp(-6.97(T_m/T - 1)) \tag{1}

where F is the fugacity ratio, T_m is the melting point and T is the system temperature, both in °K. The number 6.97 derives from Walden’s rule and is the entropy of fusion at the melting point divided by the gas constant. Preferably it should be measured calorimetrically and a correction included for solid-liquid heat capacity differences, but for initial assessment purposes this expression is adequate.

Similarly, the ratio of the solid to subcooled liquid vapour pressure is

\[ P_S^0 : P_L^0 \tag{2} \]

The partitioning of organic chemical between air and water can be expressed by the Henry’s law constant, \( H \), \[ [\text{Pa} \cdot \text{m}^2 \cdot \text{mol}^{-1}] \]:

\[ H = \frac{P_S^0 C_s^0}{P_L^0 C_L^0} \tag{3} \]

and the dimensionless air/water partition coefficient is

\[ H' = \frac{H}{RT} \tag{4} \]

The octanol/water partition coefficient is defined as

\[ K_{ow} = \frac{C_{ow}}{C_{wo}} \tag{5} \]

where \( C_{ow} \) is the concentration of solute in octanol saturated with water and \( C_{wo} \) is the concentration of solute in water saturated with octanol.

The relation between aqueous solubility and octanol/water partition coefficient has been studied extensively. Mackay et al. (1980) and Banerjee et al. (1980) found that their product \( Q \) to be relatively constant. However, recently, Miller et al. (1984) have analysed more accurate data for larger molecules (Miller et al. 1984) and shown that \( Q \) varies with molar volume or chlorine number in a homologous series.

\[ \log Q = A - BV = A' - QN \tag{6} \]

where \( A, A', B, V \) are constants, \( V \) and \( N \) are molar volume and chlorine number, respectively. Since \( Q = C_s^0 / K_{ow} \), it can be considered as an approximate “pseudo-solubility” of the chemical in octanol saturated with water.

We suggest that when considering the development of QSARs, some effort should be devoted to ensuring that the physical-chemical properties which are used to describe and correlate biological phenomena are consistent and sufficiently accurate. We illustrate this by considering three series of...
RELATIONSHIPS OF PHYSICAL-CHEMICAL PROPERTIES

chemicals, the well characterized chlorobenzenes, the polychlorinated biphenyls which are less well characterized and much greater in number, and the polychlorinated dibenzo-p-dioxins, which are still poorly characterized.

RESULTS AND DISCUSSION

TABLE 1 gives the reported values or ranges of the physical-chemical properties of chlorobenzenes (CBs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs). Fugacity ratios were obtained from a single estimated entropy of fusion of 56 J·mol⁻¹·K⁻¹ (Yalkowsky 1979), molar volumes were calculated by the Le Bas method, an additive group contribution method (Red et al. 1977). Total surface area (TSA) values were obtained from Yalkowsky et al. (1979 a,b). Solubilities, vapour pressures and octanol/water partition coefficients (Andren et al. 1986; Shi and Mackay 1986; Bobra et al. 1985) are also tabulated. Henry's law constants were calculated as $P_f/C_0$, and the octanol solubility, $Q$ as $C_0/K_{ow}$.

A two-stage process is suggested for the analysis and correlation of the above environmentally relevant properties: $C_0$, $K_{ow}$, $P_f$ and $H$. In the first stage, simple correlation equations can be derived by plotting the experimental data against chlorine number and molar volume. Isomer differences are thus ignored. A more rigorous second stage involves consideration of the difference between isomers using a more refined molecular descriptor, such as TSA.

FIGURE 2: Plot of molar volume (V) versus chlorine number (N) for three congenic series.
TABLE 1: Selected physical-chemical properties of the chlorobenzenes, polychlorobiphenyls, and polychlorodibenzo-p-dioxins, at 25°C. Given are molecular weight (MW), melting point (mp), fugacity ratio (F), total surface area, aqueous solubility of solid (C\text{aq}) and subcooled liquid (C\text{sub}) vapour pressure of solid (P\text{s}) and subcooled liquid (P\text{sub}), Henry’s law constant (H), log octanol/water partition coefficient (log K\text{ow}), and the product Q = C\text{aq} \cdot \log K\text{ow}.

<table>
<thead>
<tr>
<th>Chlorobenzenes</th>
<th>Polychlorobiphenyls</th>
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<tr>
<td>Number of Cl</td>
<td>Molecular Weight</td>
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<tr>
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<td>094.2</td>
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<td>1</td>
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<td>3</td>
<td>289.0</td>
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<td>354.0</td>
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TABLE II (contd.)
### TABLE 1: (cont'd)

<table>
<thead>
<tr>
<th>Species</th>
<th>Composition (Mole %)</th>
<th>Density (g/cm³)</th>
<th>Refractive Index</th>
<th>Specific Conductivity (S/cm)</th>
<th>Surface Tension (mN/m)</th>
<th>Refractive Index (Vacuum)</th>
<th>Refractive Index (Air)</th>
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**Key:***
- **Density (g/cm³)**: Density of the material.
- **Refractive Index**: Refractive index of the material.
- **Specific Conductivity (S/cm)**: Specific conductivity of the material.
- **Surface Tension (mN/m)**: Surface tension of the material.
- **Refractive Index (Vacuum)**, **Refractive Index (Air)**, **Refractive Index (Green)**, **Refractive Index (Blue)**, **Refractive Index (Red)**: Refractive indices in different conditions.
FIGURE 2 shows the linear relationships between chlorine number \( N \) and molar volume \( V \) (cm\(^3\)·mol\(^{-1}\)). The corresponding regressions are given in equations 7 to 9.

\[
\begin{align*}
\text{CBs: } V &= 96 + 20.9 \times N \\
R^2 &= 1 \\
\text{PCBs: } V &= 184.6 + 20.9 \times N \\
R^2 &= 1 \\
\text{PCDDs: } V &= 192 + 20.9 \times N \\
R^2 &= 1
\end{align*}
\]

where \( R^2 \) is the correlation coefficient which is unity for all three congenic series because the Le Bas method (Reid et al. 1977) assumes an incremental molar volume increase of 20.9 cm\(^3\)·mol\(^{-1}\) for each chlorine atom.

FIGURE 3: Plot of aqueous subcooled liquid solubility (\( C_s \)) versus chlorine number (\( N \)).

FIGURE 4: Plot of the relationship between molar volume and chlorine number.

FIGURE 5: Plot of \( P_a \) versus chlorine number.

FIGURE 3 shows the new linear plots of log \( C_s \) versus chlorine number and FIGURE 4 the same data as a function of molar volume. The slopes of the three group regressions are similar but not identical. It is possible to estimate solubility from molar volume from these plots with a probable accuracy of plus or minus a factor of 10 down to \( 10^{-5} \) m\(^3\)·mol\(^{-1}\) and a factor of 100 at \( 10^{-3} \) m\(^3\)·mol\(^{-1}\). Frequently reported data contain considerable error. Plots such as FIGURE 4 help to identify such data.
SHIU ET AL.

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\[ r(C_i) \text{ versus chlorine number and slope of the three \ possible to estimate } \]

\[ \text{accuracy of plus factor of } 100 \text{ at } 10^{-6} \text{ e.e.n.r. Plots such as } \]

\[ \text{FIGURE 4: Plot of the aqueous subcooled liquid solubility } (C_i) \text{ versus molar volume (V).} \]

\[ \text{FIGURE 5: Plot of the subcooled liquid vapour pressure } (P_v) \text{ versus chlorine number (N).} \]
FIGURE 6: Plot of the subcooled liquid vapour pressure (P_v) versus molar volume (V).

FIGURE 7: Plot of the logarithm of the octanol-water partition coefficient (log K_{ow}) versus chlorine number (N).

FIGURE 8: Plot of the logarithm of the molar volume (log V).

FIGURES 7 and 8 give linear behaviour when log K using a consistent molar volume is shown. The quadratic relationship in FIGURES 5 and 10 work in the range 2.5 to 3.5, while at higher molar volume, the relationship is erratic, i.e., less than 100 constants as a function of Henry's law values are established linear relationships.
FIGURE 8: Plot of the logarithm of the octanol/water partition coefficient (log $K_{ow}$) versus molar volume ($V$).

FIGURE 5 and FIGURE 6 give the vapour pressure data in similar form, the linear behaviour being again evident. There is a greater spread in properties at a given molar volume than for solubility.

FIGURES 7 and 8 give the $K_{ow}$ data. There is a distinct trend for nonlinear behaviour when log $K_{ow}$ exceeds 6. Thus extrapolation from low $K_{ow}$ data using a consistent increment per chlorine added is inaccurate. The lines shown are quadratic regressions. This nonlinear progression is also illustrated in FIGURES 9 and 10 which give the plot for log $Q$. Log $Q$ is fairly constant and in the range 2.0 to 3.5 for molar volumes up to 250 cm$^3$mol$^{-1}$ but it tends to fail at higher molar volumes and its behaviour is erratic. It is suspected that much of the variation is attributable to errors in $K_{ow}$. Few log $Q$ values fall below 2, i.e., $Q$ less than 100 mol·m$^{-3}$. FIGURES 11 and 12 give the Henry's law constants as a function of $N$ and $V$. It is remarkable how constant the PCB's Henry's law values are.

Finally, FIGURE 13 gives a plot of log $K_{ow}$ versus log $C$, showing the well established linear relationship with a slope of approximately -0.8 (Miller et al. 1985).
FIGURE 9: Plot of the derived parameter $Q$ (see equation 6) versus chlorine number ($N$).

FIGURE 10: Plot of the derived parameter $Q$ (see equation 6) versus molar volume ($V$).

FIGURE 11: Plot of $\log_{10} P$ versus chlorine number.

FIGURE 12: Plot of $\log_{10} P$ versus molar volume.
**FIGURE 11:** Plot of the Henry's law constant (H) versus chlorine number (N).

**FIGURE 12:** Plot of the Henry's law constant (H) versus molar volume (V).
FIGURE 13: Plot of the logarithm of the octanol/water partition coefficient (log $K_{ow}$) versus the logarithm of the aqueous subcooled liquid solubility (log $C_s$).

We suggest that it is useful to prepare plots such as those presented here for a series of congeners. It appears that there are broad similarities in dependence of properties on N and V. Estimates can then be made of physical-chemical properties and "reasonableness" can be assessed. Erroneous data can be identified and discarded before they become too widely accepted.

These data enable assessments to be made of how chemicals in a series will differ in their environmental behavior as they partition between air, water and organic phases. As is discussed by Gobas et al. (1987) elsewhere in this text, extreme caution must be used when calculating partitioning coefficients into organic media when log $K_{ow}$ exceeds 5. It is suspected that octanol then ceases to be a satisfactory surrogate for lipids and probably also for organic matter sorption.

From these plots an impression can also be obtained of the relative partitioning behavior expressed as solubilities. For example, if we consider three hydrophobic organic chemicals typical of these series, we can estimate solubilities to be in the order of values given in TABLE 2, as follows (air solubility being PRT as discussed earlier).

TABLE 2: Environment

<table>
<thead>
<tr>
<th>Molar volume, cm$^3$/mol</th>
<th>Solubility in air</th>
<th>Solubility in water</th>
<th>Solubility in octanol</th>
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<td></td>
<td>Typical $log K_{ow}$</td>
<td>Typical $log C_s$</td>
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The picture which emerges is a strong trend: air/water partition coefficients of air are larger values of $10^{-3}$ to $10^{-5}$ ml $10^{-3}$ are very large. The trend to enter or remain in low vapor pressure will be subject to wet.

CONCLUSION

In conclusion, we suggest such as the chlorinated assessments it is important to consider the chemical property data before experimental data becomes available. The development stage is to establish reliable useful environmental data. It is difficult to conclude obtained or interpreted.

REFERENCES

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The picture which emerges is of a fairly constant organic medium solubility. The result is a strong tendency to partition into biota and sediments. The low air/water partition coefficients are potentially misleading. Environmental volumes of air are larger than those of water by a factor of 10³ to 10⁵, thus K_{aw} values of 10⁻² to 10⁻¹ must be regarded as appreciable and values exceeding 10⁰ are very large. Therefore a substantial fraction of chemicals A and B will tend to enter or remain in the atmosphere. But those of high molar volume and low vapour pressure will tend to partition onto atmospheric particulates and become subject to wet and dry deposition.

CONCLUSION
In conclusion, we suggest that when a new chemical or series of chemicals, such as the chlorinated dibenzo-prepare for the subject of environmental assessment, it is important to obtain, correlate and interpret their physical-chemical property data using the approach suggested here. As more reliable experimental data become available, more refined property-structure relationships can be developed including isomer differences, but a necessary first stage is to establish reliable initial estimates of three key "solubilities." Much useful environmental fate information can be deduced from these data; indeed it is difficult to conceive how reliable environmental fate information can be obtained or interpreted without such data.

REFERENCES


**THE RELATIONSHIP BETWEEN LIPID CONTENT OF FISH**

**ABSTRACT**

Bioaccumulation of the lipophilicity of chemicals. Hence, lipid contents of fish measured in common fish species of different lipid contents of fish, correlations between BCFs (bioconcentration factors) and lipid contents of fish. The octanol-water partition coefficient and lipid contents is used to predict bioaccumulation and lipid contents of fish.

**KEYWORDS**

Bioaccumulation, lipid content, environmental partitioning.

**INTRODUCTION**

Bioaccumulation of chemicals depend on the lipid content (Veith et al.) in lipid of fish accord factors (BCFs) for a 1% Aroclor 1254 for rainbow trout than those for fathead (Lepomis cyanellus) (V not accompanied by data contents may vary five within a single test species). Organisms influence these BCFs, connection we tried to using a test fish species.