# Temperature Dependence of Octanol−Water Partition Coefficient for Selected Chlorobenzenes

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The octanol−water partition coefficients of seven chlorobenzenes (1,2-dichlorobenzene, 1,4-dichlorobenzene, 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene) were measured by a conventional shake-flask, batch-contacting method over the temperature range (5 to 45) °C. The measurements at 25 °C in this study agree well with literature data obtained with comparable methods. The van't Hoff plots of log $K_{OW}$ versus $T^{-1}$ exhibit linearity with values of $K_{OW}$ increasing by 10%−14% over this temperature range. The enthalpy of phase change ranges from (17 to 24) kJ/mol. These temperature relationships can be incorporated into environmental models which predict the fate of chemicals in aquatic and terrestrial systems over a range of environmental temperatures.

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## Introduction

The current emphasis on assessing the environmental impact of both industrial and agricultural chemicals has resulted in an increased reliance on the physical and chemical properties of these compounds to predict their environmental behavior. The key physical−chemical properties are solubility in water, vapor pressure, octanol−water partition coefficient, and the susceptibility of the substance to degradation or transformation reactions. The dimensionless octanol−water partition coefficient ($K_{OW}$) is one of the most important and frequently used descriptors of chemical partitioning in the environment (Mackay et al., 1992). It provides a direct estimate of hydrophobicity, which is widely used to predict the partitioning tendency from water to organic media such as lipids, waxes, and natural organic matter. It is also an indirect indicator of activity coefficient in aqueous phases. It has proved invaluable for predicting soil adsorption (Karickhoff et al., 1979), biological uptake (Thomann, 1989; Oliver and Niimi, 1985; Gobas and Mackay, 1987; Gobas et al., 1988), and biomagnification (Clark and Mackay, 1991; Mackay, 1982). Although numerous studies have been conducted on partitioning of organic substances between water and octanol, the data on temperature dependence of partition coefficients are sparse. Inspection of the literature suggests that little attention is normally given to defining or controlling temperature accurately during determinations (Sangster, 1989). Measuring partition coefficients as a function of temperature may require lengthy and accurate experimentation. Temperature dependence of $K_{OW}$ can be an important factor but is not often taken into account in environmental models. Temperature variation in water bodies can range from (0 to over 30) °C.

Sangster (1989) has compiled data on temperature dependence for a range of compounds. The partition coefficients of resorcinol and some resorcinol monoalkyl ethers (Beezer et al., 1980) and *p*-cresol and phenol (James et al., 1981) have been measured as a function of temperature. Opperhuizen et al. (1988) investigated the partitioning of chlorobenzenes in fish−water and octanol−water systems over the temperature range (13 to 33) °C in an attempt to elucidate the thermodynamics of the partitioning process. Recently, the temperature dependence of octanol−water partitioning of dibenzofuran and aqueous solubility of some chlorobenzenes and dibenzofuran has been reported over the temperature range (5 to 45) °C (Shiu et al., 1997). Data have been reported on temperature dependence of the related octanol−air partition coefficient which is suggested as a valuable descriptor of air−vegetation and air−soil equlibrium (Harner and Mackay, 1995; Harner and Bidleman, 1996).

The present data contribute to the existing data base on temperature dependence and can be important for modeling the fate and behavior of chemicals or for use in situations when data are unavailable or are suspect. Moreover, such studies permit the estimation of the enthalpy or entropy contributions involved in the partitioning of chemicals between *n*-octanol and water.

In this work, the temperature dependence of octanol−water partitioning of selected chlorobenzenes (CBs) was measured by determining the partition coefficients at 10° intervals from (5 to 45) °C. The enthalpies of transfer from octanol to water were also estimated. The technique used was the conventional shake-flask, batch-contacting method with analysis by gas chromatography.

## Experimental Section

***Materials.*** 1,2-dichlorobenzene 98.6%, 1,4-dichlorobenzene 99%, 1,3,5-trichlorobenzene 98%, 1,2,3,4-tetrachlorobenzene 98%, 1,2,3,5-tetrachlorobenzene 99%, pentachlorobenzene 98%, and *n*-octanol 99+% were obtained from Aldrich Chemical Co., Milwaukee, WI; OAS grade hexachlorobenzene was obtained from BDH Chemicals Ltd., Toronto, Ontario. Chemicals were used as purchased without further purification. Milli-Q ultrapure deionized water (Millipore Corp., Milford, MA) was used for all experiments. HPLC grade hexane was obtained from Caledon Laboratories, Georgetown, Ontario.

***Preparation of Solutions.*** Except for hexachlorobenzene, a stock solution of approximately 1 g/L of the compound in 1-octanol was prepared, this concentration being well below the solubility limit. A 2 mL aliquot of stock solution and 20 mL of water were shaken by a wrist-action shaker (Gilson Differential Respirometer) for 24 h in a 125 mL Erlenmeyer flask immersed in a temperature-controlled bath maintained within ±0.1 K of the required

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**Table 1. Logarithm of Octanol−Water Partition Coefficients ($K_{OW}$) of Selected Chlorobenzenes at 25 °C (with Precision Expressed as ±Standard Deviation)**

| chlorobenzene | log $K_{OW}$ | literature values at 25 °C |
|---|---|---|
| 1,2-di- | 3.29 ± 0.05 | 3.38,[a,b] 3.40,[c,d] 3.34,[e] 3.55,[f] 3.43,[g] 3.49[h] |
| 1,4-di- | 3.23 ± 0.03 | 3.37,[a,c,i] 3.38,[b] 3.46,[e] 3.62,[f] 3.52,[d] 3.44[g] |
| 1,3,5-tri- | 4.34 ± 0.04 | 4.15,[f] 4.17,[d,e] 4.02,[b] 4.18,[k] 4.31,[h,l] 4.40[g] |
| 1,2,3,4-tetra- | 4.41 ± 0.06 | 4.46,[f] 4.37,[d] 4.60,[h,l] 4.63,[g] 4.55,[b] 4.41,[e] 4.75[m] |
| 1,2,3,5-tetra- | 4.55 ± 0.02 | 4.50,[f] 4.46,[i] 4.52,[c] 4.56,[d] 4.53,[e] 4.51,[b] 4.61,[k] 4.59,[h,l] 4.66[g] |
| penta- | 4.94 ± 0.03 | 4.88,[f] 4.94,[c,i,k] 5.17,[d,j] 5.06,[e] 5.69,[m] 5.03,[b] 5.20[h,l] 5.18[g] |
| hexa- | 5.46 ± 0.02 | 5.0,[f] 6.22,[n] 5.50,[h,l] 5.66,[e] 5.40,[d] 5.47,[b] 5.60,[o] 5.64,[p] 5.73[g] |

[a] Wasik et al. 1983. [b] Miller et al. 1984. [c] Banerjee et al. 1980. [d] Wateral et al. 1982. [e] Hammers et al. 1982. [f] Könemann et al. 1979. [g] De Bruijn et al. 1989. [h] Pereira et al. 1988. [i] Veith et al. 1980. [j] Banerjee 1984. [k] Garst 1984. [l] Chiou 1985. [m] Bruggeman et al. 1982. [n] McDuffie 1981. [o] Brooke et al. 1986. [p] Mailhot 1987.

**Table 2. Octanol−Water Partition Coefficients of Selected Chlorobenzenes in the Range 5 °C−45 °C**

| | log $K_{OW}$ | | | | | |
|---|---|---|---|---|---|---|
| chlorobenzene | 5 °C | 15 °C | 25 °C | 35 °C | 45 °C | d(log $K_{OW}$)/d$T$ |
| 1,2-di- | 3.51 ± 0.05 | 3.41 ± 0.04 | 3.29 ± 0.05 | 3.20 ± 0.06 | 3.09 ± 0.04 | −0.0105 |
| 1,4-di- | 3.42 ± 0.01 | 3.35 ± 0.04 | 3.23 ± 0.03 | 3.12 ± 0.04 | 3.03 ± 0.05 | −0.0101 |
| 1,3,5-tri | 4.52 ± 0.02 | 4.43 ± 0.04 | 4.34 ± 0.04 | 4.21 ± 0.05 | 4.09 ± 0.04 | −0.0119 |
| 1,2,3,4-tetra- | 4.65 ± 0.02 | 4.53 ± 0.02 | 4.41 ± 0.06 | 4.28 ± 0.05 | 4.15 ± 0.01 | −0.0125 |
| 1,2,3,5-tetra- | 4.80 ± 0.02 | 4.67 ± 0.04 | 4.55 ± 0.02 | 4.42 ± 0.01 | 4.33 ± 0.02 | −0.0119 |
| penta- | 5.20 ± 0.01 | 5.06 ± 0.03 | 4.94 ± 0.03 | 4.79 ± 0.05 | 4.66 ± 0.03 | −0.0135 |
| hexa- | 5.74 ± 0.04 | 5.60 ± 0.07 | 5.46 ± 0.02 | 5.30 ± 0.01 | 5.17 ±0.05 | −0.0144 |

temperature. The contents were then allowed to equilibrate in the temperature bath for about 48 h at the desired temperature. Near-saturated solutions of approximately 0.7 g/L hexachlorobenze in octanol were prepared in the same manner but using a 15 mL aliquot of stock solution and 150 mL of water in a 250 mL Erlenmeyer flask.

***Gas Chromatographic Measurements.*** The aqueous phase and octanol phase were first separated. The aqueous phase was extracted with hexane and then directly injected onto the gas chromatograph column. The octanol phase was diluted 20 to 2000-fold as required to analyze by GC. Analysis was on a Hewlett-Packard 5880A gas chromatograph equipped with a $^{63}$Ni electron capture (EC) detector. A 0.32 mm o.d. by 30 m long J&W DB-17 fused silica capillary column was used for separation. The make-up and carrier gas was a 95:5 by volume argon−methane mixture. Operating conditions were: injection port at 250 °C, oven in isothermal mode between 110 and 210 °C depending on the melting point of the chemical, detector at 300 °C. Peak areas were recorded on a Hewlett-Packard 3392A integrator.

## Results

The logarithm of the octanol−water partition coefficients for selected chlorobenzenes at 25 °C are given in Table 1 with reported literature values for comparison. The mean $K_{OW}$ values as a function of temperature for all the compounds are summarized in Table 2, the data being also depicted in Figures 1 and 2. Each point represents three or four determinations. The precision (standard deviation) of experimentally determined $K_{OW}$ is approximately ±5%. The van't Hoff plots of log $K_{OW}$ versus $T^{-1}$ exhibit linearity with log $K_{OW}$ increasing by 10%−14% over the temperature range of (5 to 45) °C. The variation of log $K_{OW}$ with $T$, i.e., d(log $K_{OW}$)/d$T$, given in Table 2 was between −0.010 and −0.014 K$^{-1}$ with a mean value of −0.01 K$^{-1}$. Sangster (1989) indicated a similar value of approximately −0.01 K$^{-1}$ for variation of log $K_{OW}$ with $T$. The following more thermodynamically rigorous equation is used to model the experimental data:

$$\log K_{OW} = A - \Delta H/2.303RT \qquad (1)$$

All of the chemicals showed a satisfactory correlation of log $K_{OW}$ with $1/T$ (correlation coefficients ranging from 0.985 to 0.998). The regression constants A, and calculated enthalpies of transfer ($\Delta H$) are listed in Table 3, the $\Delta H$ values ranging from 17.1 kJ·mol$^{-1}$ for 1,4-dichlorobenzene to 24.4 kJ·mol$^{-1}$ for hexachlorobenzene.

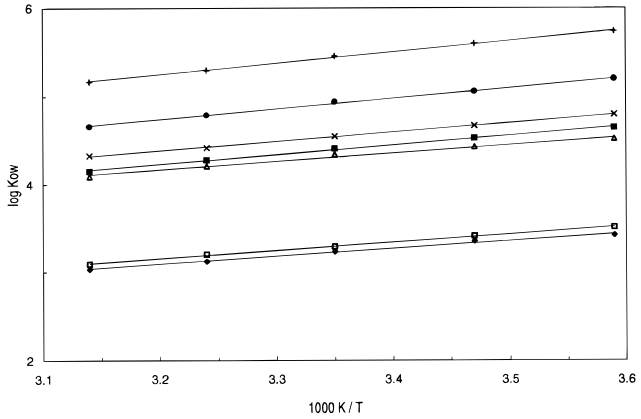

**Figure 1.** Van't Hoff plot of log $K_{OW}$ versus reciprocal absolute temperature for 1,2-dichlorobenzene, □, 1,4-dichlorobenzene ◆, 1,3,5-trichlorobenzene △, 1,2,3,4-tetrachlorobenzene ■, 1,2,3,5-tetrachlorobenzene ×, pentachlorobenzene ●, and hexachlorobenzene +.

## Discussion

The log octanol−water partition coefficients at 25 °C are in good agreement with more recent (post-1983) and accurate determinations reported in the literature (Table 1). For the post-1983 data the average deviation in log $K_{OW}$ between the experimental values reported here and previously reported experimental values is 0.14. For earlier data the deviation is 0.21.

The log linear increase in $K_{OW}$ with $1/T$, though small, clearly indicates the enhanced partitioning to lipid phases at low temperatures. For the chlorobenzene series log $K_{OW}$ increases by an average of 0.56 log units per chlorine added. The difference in log $K_{OW}$ between isomers is less than 0.15 log unit. Only for 1,3,5-tri-, 1,2,3,4-tetra-, penta- and hexachlorobenzene are there previous measurements of temperature dependence (Opperhuizen et al., 1988). As shown in Figure 2, log $K_{OW}$ values are comparable, but

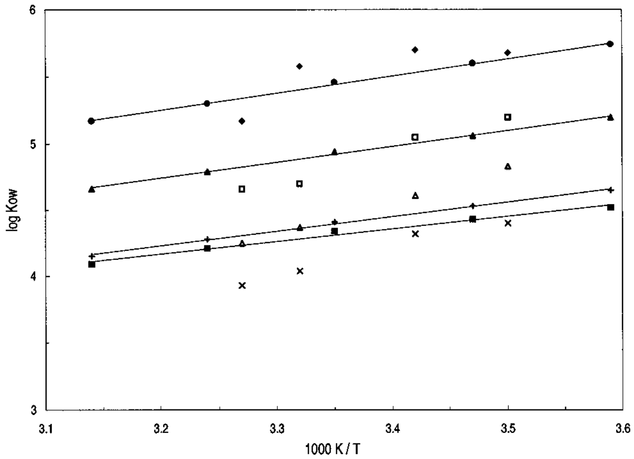

**Figure 2.** Van't Hoff plot of log $K_{OW}$ versus reciprocal absolute temperature for this work, 1,3,5-trichlorobenzene ■, 1,2,3,4-tetrachlorobenzene +, pentachlorobenzene ▲, hexachlorobenzene ●, and previous work (Opperhuizen et al. 1988) 1,3,5-trichlorobenzene ×, 1,2,3,4-tetrachlorobenzene △, pentachlorobenzene □, and hexachlorobenzene ◆.

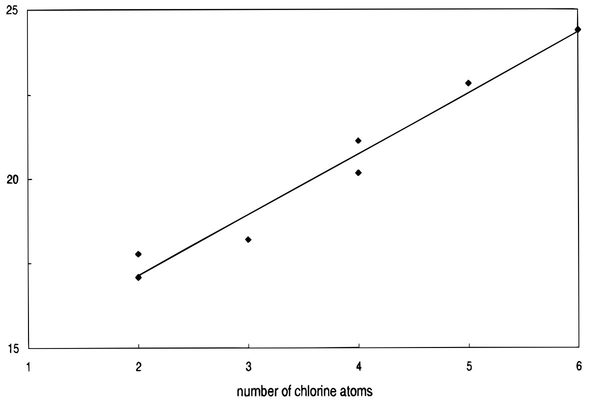

**Figure 3.** Relationship between $\Delta H$ and the number of chlorine atoms.

**Table 3. Regression Constants in Eq 1**

| chlorobenzene | $A$ | $\Delta H$/kJ·mol$^{-1}$ | $r^2$ |
|---|---|---|---|
| 1,2-di- | 0.1831 | −17.8 | 0.998 |
| 1,4-di- | 0.2338 | −17.1 | 0.9923 |
| 1,3,5-tri | 1.1228 | −18.2 | 0.9855 |
| 1,2,3,4-tetra- | 0.6978 | −21.1 | 0.9965 |
| 1,2,3,5-tetra- | 1.0159 | −20.2 | 0.9989 |
| penta- | 0.9255 | −22.8 | 0.997 |
| hexa- | 1.1806 | −24.4 | 0.998 |

slopes differ by up to 55%. It is noteworthy that Opperhuizen et al. determined $K_{OW}$ over a narrower temperature range of (13 to 33) °C. The partitioning of all chlorobenzenes from water to octanol is exothermic with a trend of higher enthalpies for more chlorinated benzenes. Figure 3 shows a plot of $\Delta H$ as a function of chlorine number which yields the relationship

$$\Delta H/\text{kJ·mol}^{-1} = 13.5 + 1.8(\text{Cl No.}) \qquad (2)$$

where Cl No. is number of chlorine atoms in the molecule.

Equation 2 can be used to predict the enthalpies in situations when high accuracy is not required, for example, for environmental assessment purposes. A similar trend in $\Delta H$ was reported by Opperhuizen et al. (1988); however, their enthalpies are generally 16% to 26% higher than the values reported here. The data do not permit any assessment of the effect of temperature on enthalpy. As is apparent from Figure 2, the present data are regarded as more accurate than previous reported data and thus permit more reliable estimation of enthalpies of phase transfer.

## Conclusion

The octanol−water partition coefficients and their temperature dependence for selected chlorobenzenes are reported. It is hoped that these results will be of interest and value for assessing the environmental partitioning behavior of these and related compounds over a range of temperatures. These data are also of interest because there is increasing use of octanol−air partition coefficient $K_{OA}$ for determining partitioning from the atmosphere to vegetation, aerosols, and soils (Harner and Mackay, 1995; Harner and Bidleman, 1996). $K_{OW}$ can be a useful tool for predicting $K_{OA}$ since it is possible to calculate $K_{OA}$ from $K_{OW}$ and the dimensionless air−water partition coefficient, $K_{AW}$; i.e., $K_{OA}$ is $K_{OW}/K_{AW}$. However, there is a possible error inherent in this estimation as $K_{OW}$ necessarily involves partitioning between octanol saturated with water and water saturated with octanol whereas $K_{AW}$ is measured using pure water.

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