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Temperature Dependence of Aqueous Solubility of Selected Chlorobenzenes, Polychlorinated Biphenyls, and Dibenzofuran

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The aqueous solubilities of seven chlorobenzenes (1,4-dichlorobenzene, 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzene, 1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene), five polychlorinated biphenyls (4-chlorobiphenyl, 4,4′-dichlorobiphenyl, 2,4,5-trichlorobiphenyl, 2,3,4,5-tetrachlorobiphenyl, and 2,2′,4,4′,6,6′-hexachlorobiphenyl), and dibenzofuran are reported over the range 5 to 45 °C, from which enthalpies of solution are deduced. The octanol−water partition coefficient (K_{OW}) of dibenzofuran deduced from its solubilities in octanol, in octanol saturated with water, and in water saturated with octanol is also reported for the same range in temperature, showing agreement with the previously reported value of K_{OW} and much less sensitivity to temperature.

Introduction

It is important to determine the physical−chemical properties of hydrophobic organic substances such as the chlorobenzenes (CBs), polychlorinated biphenyls (PCBs), dibenzofurans (DBFs), and dioxins in order that their environmental partitioning can be more fully understood, and more reliably predicted. Notable among these properties is aqueous solubility, which provides an estimate of activity coefficient in the aqueous phase, thus affecting processes such as evaporation, absorption, and bioaccumulation. Further, it is apparent that the temperature dependence of these properties be determined to account for differences in environmental behavior, seasonally and even diurnally, and between regions which differ in climate. The octanol−water partition coefficient is also an indirect indicator of activity coefficient in the aqueous phase and of hydrophobicity which is widely used to predict environmental partitioning to lipids and other organic media such as humic matter in soils and sediments.

In this work, the aqueous solubilities of selected hydrophobic chemicals were determined over the range 5 to 45 °C, and the enthalpies of solution were estimated. In addition, the temperature dependence of the octanol−water partitioning of DBF was measured by determining the solubilities in octanol, octanol saturated with water, water, and water saturated with octanol. The techniques used for determination of solubility were both the traditional shake-flask and generator column methods with analysis by gas chromatography and/or high-pressure liquid chromatography.

Experimental Section

Chemicals. 1,4-Dichlorobenzene 99%, 1,2,3-trichlorobenzene 98%, 1,3,5-trichlorobenzene 98%, 1,2,3,5-tetrachlorobenzene 99%, 1,2,4,5-tetrachlorobenzene 99%, pentachlorobenzene 98%, 4-chlorobiphenyl 98%, 4,4′-dichlorobiphenyl 98%, dibenzofuran 99%, and *n*-octanol 99+% were obtained from Aldrich Chemical Co.; OAS grade hexachlorobenzene was obtained from BDH Chemicals Ltd.; and 2,4,5-trichlorobiphenyl, 2,3,4,5-tetrachlorobiphenyl >99%, and 2,2′,4,4′,6,6′-hexachlorobiphenyl >99% were purchased from Ultra Scientific. All chemicals were used without further purification. HPLC grade methanol, hexane, and toluene were obtained from Caledon Laboratories, Georgetown, Ontario. Benzene (99 mol % pure) and ACS acetone were obtained from Fisher Scientific. Chromosorb 750 and Chromosorb W, 30/60 mesh (Johns-Manville), were obtained from Chromatographic Specialties, Bellville, Ontario. Milli-Q ultrapure deionized water (Millpore Corp., Milford, MA) was used for all experiments.

Methods. Determination of Aqueous Solubility. (1) Generator Column Followed by High-Pressure Liquid Chromatography (HPLC). The experimental procedure is similar to that described earlier (Shiu et al., 1988) and employed the generator column, dynamic-coupled-column liquid chromatography method described by May et al. (1978a,b) which has been widely used to measure the solubilities of sparingly soluble solutes in water and in water saturated with octanol. Saturated water solutions were prepared by pumping water through a 0.64 cm o.d. by 30 cm long stainless steel column (generator column), by an Eldex pump Model B-100-S. The generator column was packed with prewashed (acetone, hexane, and toluene) Chromosorb W or Chromsorb 750, 30/60 mesh, and coated with 0.5−2.0% by mass of the chemical of interest. The generator column was thermostated with an Alltech water jacket, to ±0.2 deg with a Neslab refrigerated circulating bath Model Endocal RTE-5. The saturated solution then flowed through an extractor column (0.64 cm × 6 cm long stainless steel tubing) packed with 37−50 μBondapak/Corsil (Waters Associates). By switching an eight-port Valco valve, the absorbed chemical was extracted by the mobile phase and directly injected onto the analytical column.

The HPLC system was operated in an isocratic mode with a mobile phase of methanol/water mixture (85:15, v/v) at a flow rate of 1.2 mL/min. The instrument was a Waters HPLC system consisting of a Model 6000 solvent delivery system, a Model M45 solvent delivery system, a Model 720 system flow controller, and a Model 440 UV absorbance detector with 254 and 280 nm kits. The analytical column was a Waters 3.9 mm o.d. × 300 mm long μBondapak C_{18} column. Integrated peak areas were recorded by a Waters Model 730 data module.

(2) Determination of the Solubilities by Gas Chromatography. Saturated solutions were prepared by either the generator column method or the traditional shake-flask

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Table 1. Aqueous Solubilities and Standard Deviations of Selected Chlorobenzenes (CBs), PCBs, and Dibenzofuran at 25 °C

compound	aqueous solubility, S_W/g·m^{-3}		
	gen column	shake flask	lit. values at 25 °C
1,4-dichlorobenzene	-	81.4 ± 1.5	79.1,[a] 76,[b] 83.1,[c] 85.5,[d] 56.9,[e] 87.2,[f] 90.6[g] 73.7,[h] 73.8,[i] 48.7,[j] 73,[k] 30.9,[l] 65.3[m]
1,2,3-trichlorobenzene	19.3 ± 0.24	23.7 ± 1.3	31.5,[g] 16.6,[ee] 12.0,[j] 12.27,[l] 18.0,[m] 18.0[ff]
1,3,5-trichlorobenzene	8.46 ± 0.26		6.59,[g] 5.87,[k] 4.12,[l] 6.01,[m] 10.6[n]
1,2,3,5-tetrachlorobenzene	3.44 ± 0.15	3.79 ± 0.23 (27 °C)	3.50,[g] 4.02,[i] 2.48,[j] 2.89,[l] 5.10,[m] 3.23,[n] 4.32,[o] 3.58[p]
1,2,4,5-tetrachlorobenzene	0.528 ± 0.018	0.543 ± 0.016 (27 °C)	0.595,[g] 0.29,[j] 2.35,[l] 0.465,[m] 0.54[p]
pentachlorobenzene	0.419 ± 0.018	0.447 ± 0.014 (27 °C)	0.56,[g] 1.33,[i] 1.34,[h] 0.24,[j] 0.831,[l] 0.385,[n] 0.18[q]
hexachlorobenzene	0.00544 ± 0.00018		0.005,[r] 0.006,[s] 0.11,[t] 0.005,[g] 0.0039,[j] 0.0054,[u] 0.047,[bb] 0.0069[n]
4-chlorobiphenyl	1.37 ± 0.042		1.19,[v] 0.90,[r] 0.0151,[w] 1.30,[x] 1.47,[y] 1.207,[z] 1.34,[aa,dd] 1.32[bb]
4,4′-dichlorobiphenyl	0.057 ± 0.0021		0.080,[v] 0.056,[r] 0.062,[e] 0.058,[x] 0.036[z]
2,4,5-trichlorobiphenyl	0.106 ± 0.0045		0.092,[r] 0.14,[x] 0.162[l]
2,3,4,5-tetrachlorobiphenyl	0.0156 ± 0.0004		0.0192,[v] 0.0209,[cc] 0.021,[l] 0.0099,[x] 0.014,[z] 0.0137,[aa,dd] 0.0136[bb]
2,2′,4,4′,6,6′-hexachlorobiphenyl	0.00280 ± 0.00013		0.0009,[r] 0.00041,[l] 0.0023,[z] 0.00109[q] (22 °C), 0.0033[aa,dd] 0.00284[bb]
dibenzofuran	4.75 ± 0.22	4.69 ± 0.18	10.03,[i] 4.22[o]

[a] Klemenc and Löw, 1930. [b] Andrews and Keefer, 1950. [c] Wauchope and Getzen, 1972. [d] Vesala, 1974. [e] Chiou et al., 1977. [f] Aquan-Yuen et al., 1979. [g] Yalkowsky et al., 1979. [h] Veith et al., 1980. [i] Banerjee et al., 1980. [j] Köneman, 1981. [k] Chiou et al., 1982. [l] Miller et al., 1984. [m] Banerjee, 1984. [n] Chiou, 1985. [o] Doucette and Andren, 1988. [p] Kim and Saleh, 1990. [q] Opperhuizen et al., 1985. [r] Weil et al., 1974. [s] Lu and Metcalfe, 1975. [t] Hollifield, 1979. [u] Hashimoto et al., 1982. [v] Wallnöfer et al., 1973. [w] Lee et al., 1979. [x] Billington et al., 1988. [y] Stolzenburg and Andren, 1983. [z] Dunnivant and Elzerman, 1988. [aa] Li et al., 1992. [bb] Li and Andren, 1994. [cc] Haque and Schmedding, 1975. [dd] Li and Doucette, 1993. [ee] Mackay and Shiu, 1981. [ff] Chiou et al., 1986.

(batch contacting equilibration) method. For the generator column method, the saturated aqueous solution was drained into a weighed separatory funnel (instead of being passed through an extractor column as described above) and extracted with hexane, which was then analyzed by GC. For the shake-flask method, an excess amount of the chemical of interest was added into 125 mL or 250 mL Erlenmeyer flasks containing distilled water. The flasks were shaken gently by a wrist-action shaker or stirred by a magnetic stirrer for 24 h and allowed to settle in the temperature bath for at least 48 h at the desired temperature before analysis.

A Hewlett-Packard Model 5890 series II GC equipped with an electron capture and a flame ionization detector was used for analysis of the hexane extracts. A J&W Durabond DB-17 column of 30 m long × 0.32 mm o.d. fused silica capillary column was used. The injection port temperature was at 300 °C, the detector was at 320 °C, and the GC oven was in the isothermal mode between 120 and 200 °C. Peak areas were integrated by a Hewlett-Packard Model 3396A integrator. Calibration standards were prepared by weighing known amounts of the chemical and dissolving in hexane.

Determination of the Octanol−Water Partition Coefficient. ***(1) Generator Column Followed by HPLC.*** The generator column, as described by Tewari et al. (1982) and suitable for K_{OW} determination, was prepared by adding approximately 1 mL of an octantol solution containing 2% by mass of dibenzofuran. The octanol-saturated water was prepared by slowly stirring octanol in a 1 L Erlenmeyer flask containing Milli-Q water subsequently pumped through the generator column with the Eldex pump. The extra steps were necessary to ensure the octanol-saturated solution was free from emulsion and octanol would not be depleted from the generator column. The subsequent procedure was identical to that in the solubility measurement except that the octanol phase was analyzed directly to determine the concentration of solute.

The HPLC system was as described above.

(2) Determination of the Solubilities in Pure Octanol and Water-Saturated Octanol by Gas Chromatography. The procedure outlined here is similar to that described by Miller et al. (1985). Saturated solutions were prepared by the traditional shake-flask method. An excess amount of dibenzofuran was added into a 7 mL sample vial or 25 mL Erlenmeyer flasks containing (a) dry octanol and (b) a water-saturated solution of octanol (with a layer of octanol on the surface to ensure saturation during equilibration), which were capped with a screw top with a Teflon septum or a ground glass stopper. The vials or flasks were shaken gently by a wrist-action shaker or stirred by a magnetic stirrer for 24 h and allowed to settle in the temperature bath for at least 48 h at the desired temperature before analysis.

A Hewlett-Packard Model 5750 GC equipped with a flame ionization detector was used for the analysis of the octanol solutions. A pair of 3 m long × 3.2 mm o.d. stainless steel columns packed with 10% SE30 ultraphase coated on Chromosorb P (DMCS treated, acid washed, 60/80 mesh) was used. The injection port temperature was set at 300 °C, the detector was set at 320 °C, and the GC oven was set at 250 °C. Peak areas corresponding to 0.5 μL of the octanol solution were deterimined on a Hewlett-Packard Model 3390 integrator recorder. Calibration standards were prepared by weighing known amounts of DBF and dissolving in benzene.

Results

The solubility data for CBs and PCBs for 25 °C (or otherwise if indicated) are given in Table 1 with the reported literature values. Table 2 gives the solubilities as a function of temperature, the data being also depicted in Figures 1−4 for 1,4-dichlorobenzene, other chlorobenzenes, PCBs, and dibenzofuran (DBF), respectively. The estimated precision expressed as a standard deviation is ±8%. The van't Hoff plots show linear behavior within experimental error yielding constant enthalpies of solutions in the range 18 to 41 kJ/mol. Solubilities of dibenzofuran in water, in water saturated with octanol, in octanol, and in octanol saturated with water and the octanol−water partition coefficients of dibenzofuran calculated from the concentration ratio and are given in Table 3.

Discussion

The solubilities are generally in good agreement with more recent and accurate determinations reported in the literature, although some reported data are in considerable

Table 2. Aqueous Solubilities and Enthalpies of Solution of Selected Chlorobenzenes and PCBs in the Range 5−45 °C

	aqueous solubility, S_W/g·m^{-3}					
compound	5 °C	15 °C	25 °C	35 °C	45 °C	$\Delta_{sol}H$/kJ·mol^{-1}
1,4-DCB	48.6 ± 1.34	63.0 ± 2.0	81.4 ± 1.5	104.5 ± 1.67	130 ± 3.08	18.2
1,2,3-TCB	7.66 ± 0.07(4 °C)		19.31 ± 0.24		45.61 ± 1.0 (50 °C)	28.8
1,3,5-TCB	4.62 ± 0.20	6.29 ± 0.30	8.46 ± 0.26	11.14 ± 0.49	15.55 ± 0.98	22.04
1,2,3,5-TeCB	1.70 ± 0.013	2.43 ± 0.02	3.44 ± 0.15	5.08 ± 0.18	7.03 ± 0.23	26.3
1,2,4,5-TeCB	0.208 ± 0.01	0.322 ± 0.014	0.528 ± 0.018	0.739 ± 0.036	1.127 ± 0.04	30.8
penta-CB	0.145 ± 0.009	0.254 ± 0.008	0.419 ± 0.018	0.618 ± 0.017	0.856 ± 0.026	32.9
HCB	0.0022 ± 0.00011	0.0035 ± 0.0001	0.00544 ± 0.00018	0.00853 ± 0.0002	0.014 ± 0.00025	33.7
4-PCB	0.822 ± 0.002	1.07 ± 0.004	1.37 ± 0.042	2.17 ± 0.028	3.04 ± 0.12	24.5
4,4′-PCB	0.021 ± 0.001	0.0346 ± 0.0016	0.057 ± 0.0021	0.106 ± 0.0045	0.186 ± 0.002	40.2
2,4,5-PCB	0.0413 ± 0.0026	0.0682 ± 0.0013	0.106 ± 0.0045	0.203 ± 0.0095	0.33 ± 0.012	36.9
2,3,4,5-PCB	0.0056 ± 0.00034	0.0102 ± 0.00043	0.0156 ± 0.0004	0.0285 ± 0.0013	0.056 ± 0.0024	41.3
2,2′4,4′,6,6′-HCB	0.001 ± 0.00005	0.0017 ± 0.0001	0.0028 ± 0.00015	0.0043 ± 0.00035	0.0064 ± 0.0005	34.2
dibenzofuran	1.914 ± 0.052	3.044 ± 0.06	4.75 ± 0.22	7.56 ± 0.24	11.7 ± 0.30	33.3

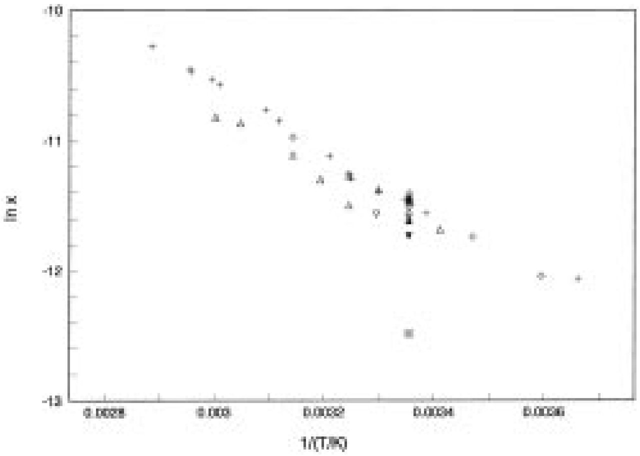

Figure 1. Van 't Hoff plot of the logarithm of the mole fraction solutility x of 1,4-dichlorobenzene versus reciprocal absolute temperature from this and previous studies: (◊) this work; (△) Klemenc and Low, 1930; (▽) Gross and Saylor, 1931; (×) Andrews and Keefer 1950; (+) Wauchope and Getzen, 1972; (■) Vesala, 1974; (⊕) Yalkowsky et al., 1979; (♦) Aquan-Yuen et al., 1979; (▲) Banerjee et al., 1980; (⊗) Miller et al., 1984; (▼) Banerjee, 1984.

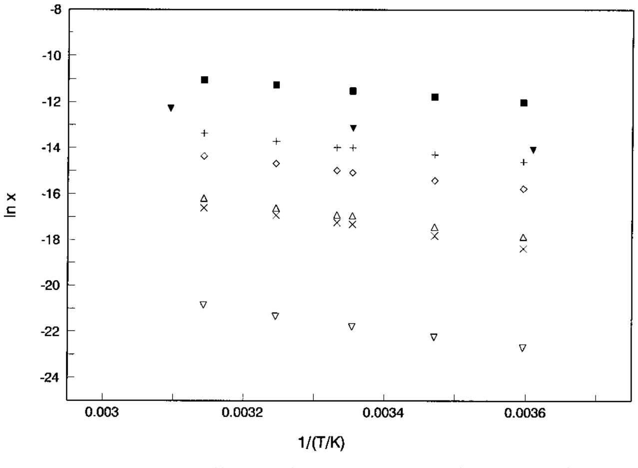

Figure 2. Van 't Hoff plot of the logarithm of the mole fraction solubility x of 1,4-dichlorobenzene (■), 1,2,3-trichlorobenzene (▼), 1,3,5-trichlorobenzene (+), 1,2,3,5-tetrachlorobenzene (◊), 1,2,4,5-tetrachlorobenzene (△), pentachlorobenzene (×), and hexachlorobenzene (▽), versus reciprocal absolute temperature.

error, in some cases by factors of 2 or more for chlorobenzenes. Not surprisingly, the reported values for the sparingly soluble PCBs vary greatly, in some cases by orders of magnitude. This is presumably the result of strong sorption of the solute to glassware which renders experimental handling of these solutions very difficult. The strong effect of melting point on solid solubility is illustrated by the observation that solubility of the 4,4′-dichlorobiphenyl with a melting point of 149 °C is about half that of the more hydrophobic 2,4,6-trichlorobiphenyl with a melting point of 62.5 °C.

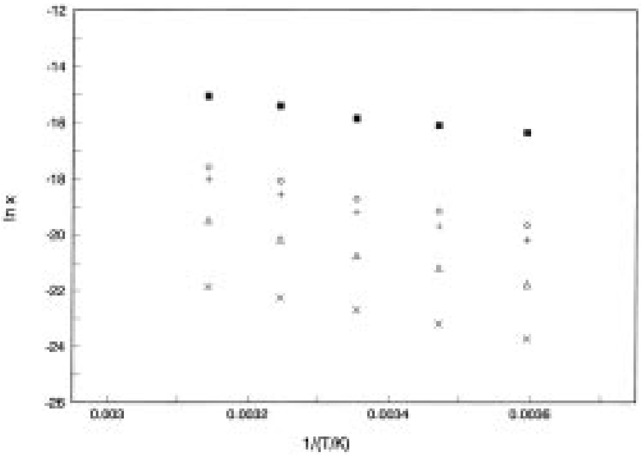

Figure 3. Van 't Hoff plot of the logarithm of the mole fraction solubility x of 4-chlorobiphenyl (■), 4,4′-dichlorobiphenyl (+), 2,4,5-trichlorobiphenyl (◊), 2,3,4,5-tetrachlorobiphenyl (△), and 2,2′4,4′,6,6′-hexachlorobiphenyl (×), versus reciprocal absolute temperature.

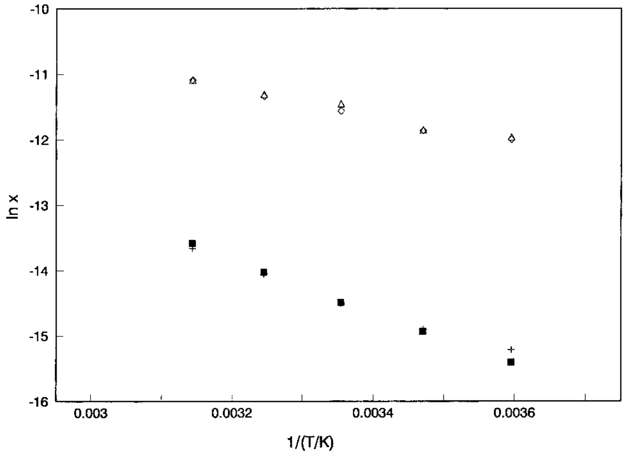

Figure 4. Van 't Hoff plot of the logarithm of the mole fraction solubilities x of dibenzofuran in water (■), water saturated with octanol (+), octanol (◊), and octanol saturated with water (△), versus reciprocal absolute temperature.

The generator column method is generally preferred to the shake-flask method for sparingly soluble compounds because it reduces the probability that microcrystals may be suspended in solution, thus giving an erroneous high solubility. The results in Tables 1 and 3 suggest that both methods can yield equivalent results. The generator column method tends to give low (subsaturation) solubilities for compounds with solubilities exceeding 10 g/m^3,

Table 3. Solubilities of Dibenzofuran in Water (S_W), in Water Saturated with Octanol (S_{WO}), in Octanol (S_O), and in Octanol Saturated with Water (S_{OW}) Determined by HPLC and/or GC between 5 and 45 °C[a]

	S_W/g·m^{-3}	S_{WO}/g·m^{-3}	S_O/kg·m^{-3}		S_{OW}/kg·m^{-3}		log K_{OW}
t/°C	gen col−LC	gen col−LC	SF−LC	SF−GC	gen col−LC	SF−GC	S_{OW}/S_{WO}
5	1.914 ± 0.05	2.31 ± 0.05	57.53 ± 2.04	57.46 ± 4.4	58.7 ± 0.49	59.7 ± 2.4	4.405
15	3.044 ± 0.06	3.16 ± 0.12	66.07 ± 0.7	58.96 ± 3.7	70.2 ± 1.1	66.5 ± 5.5	4.346
25	4.75 ± 0.22	4.70 ± 0.10	89.22 ± 3.80	90.93 ± 4.3	88.2 ± 5.2	99.5 ± 2.4	4.273
35	7.56 ± 0.24	7.39 ± 0.21	111.6 ± 2.7	117.5 ± 5.5	114.8 ± 2.0	114.6 ± 5.5	4.190
45	11.72 ± 0.30	10.89 ± 0.50		145.3 ± 11.3		142.3 ± 10.7	4.116
$\Delta_{sol}H$/kJ·mol^{-1}	33.34	29.0	17.15	17.54	16.58	16.79	-12.4

[a] S_W, S_O, S_{WO}, S_{OW}: solubility in water, octanol, water saturated with octanol, octanol saturated with water. gen col−LC: generator column method followed by HPLC analysis. SF−GC: shake-flask method followed by GC analysis.

possibly because the coated compound is more rapidly depleted by the solution, and if any channeling occurs, the solution may be under-saturated. This could explain the lowest reported value of 30.9 g/m^3 for 1,4-dichlorobenzene at 25 °C by Miller et al. (1984), although there were successful measurments reported for benzene (May et al., 1978a) and alkylbenzenes (DeVoe et al., 1981; Owens et al., 1986). We suggest that for this reason that the shake-flask method is preferable above 1.0 g/m^3, and also because of its experimental simplicity. The generator column method is, we suggest, preferable for solubilities below 1.0 g/m^3, and both methods are suitable in the range of 0.01 to 1.0 g/m^3. These ranges are similar to those suggested by Hashimoto et al. (1982) who compared both methods for measuring solubilities for solid solutes and recommended that a modified shake-flask method could be used to measure solubilities down to approximately 0.01 g/m^3 and the generator column method was suitable for solubilities of up to 10 g/m^3.

The enthalpies of solution range from 18 to 42 kJ/mol with a tendency for higher enthalpies for the more chlorinated compounds, but values for the PCBs show considerable variability, reflecting differences in stability of crystal structure and solute−water interactions. These enthalpies are comparable to those reported by Opperhuizen et al. (1987) for pentachlorobenzene of 31.3 kJ/mol and for hexachlorobenzene of 36.9 kJ/mol and by Dickhut et al. (1986) for PCBs ranging from 28.5 to 67 kJ/mol for 4-chlorobiphenyl to decachlorobiphenyl.

For environmental assessment purposes in which high accuracy is not required, and for the environmental temperature range considered, the enthalpy of solution of solid chlorobenzenes (i.e., excluding benzene and liquid chlorobenzenes, such as 1,2- and 1,3-dichlorobenzenes and 1,2,4-trichlorobenzene) can be estimated as $(13 + 3.5n)$ kJ/mol where n is the number of chlorines. For PCBs, a mean enthalpy of solution of 35 kJ/mol can be used, recognizing that it may be in error by ±10 kJ/mol. The use of a constant enthalpy of solution is only justified over narrow temperature ranges for solid solutes discussed in this work. For liquid solutes, such as benzene and alkylbenzenes, it is well-known that the enthalpy changes, passing through zero around 18 °C (Bohon and Claussen, 1951; Arnold et al., 1958; Owens et al., 1986). Therefore, extreme care must be taken when extrapolating solubilities using reported or estimated enthaplies of solution.

The data for DBF in Table 3 indicate that the presence of octanol in solution affects the solubility of DBF, increasing solubility at low temperatures but decreasing it slightly at high temperatures. The result is a lower enthalpy change of solution by some 13%. The reasons for this are not known, and further, more accurate data are required for this and other substances to substantiate the effect. The effect is maximal at 5 °C where there is a 20% solubility enhancement. The solubilities in octanol measured by the two methods are in good agreement, the enthalpy of solution being significantly lower by nearly a factor of 2 from the water data. The presence of water in the octanol phase does not, apparently, have a significant effect on the solubility of the DBF. The octanol−water partition coefficient deduced from these solubilities agrees well with the logarithmic values at 25 °C of 4.17 determined by Banerjee et al. (1980) and 4.31 by Doucette and Andren (1987, 1988b). There is a negative enthalpy change of phase transfer, i.e., K_{OW} is lower at higher temperatures caused by the larger increase in solubility in water than in octanol with increasing temperature.

These data are also of interest because there is increasing use of the octanol−air partition coefficient K_{OA} for assessing partitioning from the atmosphere to aerosols and other solid organic phases (Harner and Mackay, 1995; Harner and Bidleman, 1996). It is convenient to calculate K_{OA} as K_{OW}/K_{AW}, where K_{AW} is the dimensionless air−water partition coefficient, but this implies that as solvents, pure octanol behaves identically to octanol saturated with water (which appears to be justified from this study) and water behaves identically to water saturated with octanol (which appears not to be justified from this study). For DBF the magnitude of the error appears to be 20% or less, which is probably acceptable for environmental purposes, but the error may be larger for other substances.

Conclusion

Data have been reported for the solubilities in water, and their temperature dependence, of a series of chlorobenzenes and PCBs, which is hoped will be valuable for assessing the environmental partitioning behavior of these and related substances over a range of temperatures. The reported data for dibenzofuran solubility in water, octanol, and mutual solutions show an insignificant effect of the presence of water on the solubility in octanol, but an effect of up to 20% on the solubility in water when octanol is also present in solution. These data contribute to a better fundamental understanding of the partitioning of hydrophobic substances between octanol, water, and ultimately also to air.

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