EFFECT OF INORGANIC SALTS ON THE SOLUBILITY OF SELECTED POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS

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Introduction

It is well known that the aqueous solubility of organic compounds is modified (increased or decreased) by the presence of inorganic salts. For example, the presence of ions, such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, and SO_4^{2-} in natural waters will decrease the aqueous solubility of non-polar or weakly polar organic compounds. This salting-out effect relates to the different types of molecular interactions (ion-solvent, ion-solute and solute-solvent), between the ions and water, leading to the formation of hydration shells and a reduction in the volume of the aqueous solution (the electrostriction effect)[1].

The salting-out phenomenon has a significant influence on the transport and fate of neutral solutes in an aqueous environment (e.g. it may increase their sorption to suspended particles) and is commonly used to separate non-polar compounds from aqueous solutions.

A compilation of salting-out data in the form of salinity parameters (Setschenow constants) for aromatic and alkane hydrocarbons and their chlorinated derivatives were carried out by Xie et al.[2]. Previously[3], we reported Setschenow constants of hexachlorobenzene determined for various aqueous salt solutions. As far as we know, no other experimental data on the salting-out effect of organic pollutants of environmental importance have been reported up to know.

In the present work, the solubilities of selected polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) (including non-chlorinated congeners) in pure water, and in sodium and calcium chloride solutions, at various concentrations are reported and the Setschenow constants obtained are presented. The reported results may be helpful in estimating the magnitude of the salting-out effect for the hydrophobic, toxic contamination~~,~~ commonly present in environmental waters (e.g. lakes, rivers, sea) and industrial aqueous solutions (e.g. wastewater treatment plants, wet scrubbing systems) and be useful in predicting their transport through the hydrologic system.

Materials and Methods

Chemicals: Dibenzo-*p*-dioxin (DD), 2-monochlorodibenzo-*p*-dioxin (2-MCDD), 2,7-dichlorodibenzo-*p*-dioxin (2,7-DCDD), dibenzofuran (DF), 2,8-dichlorodibenzofuran (2,8-DCDF) and appropriate standard solutions with purity from 98 to 100 % were obtained from AccuStandard, Inc. Hexane (97.8 %), methanol (99.8 %), anhydrous Na_2SO_4, NaCl (99.5 %) and $CaCl_2$ (99.9 %) were purchased from Wako Pure Chemical Industries, Ltd.

The reagent grade water was obtained from a NANOpure® DIamond TM ultrapure water system equipped with an ultraviolet lamp and a total organic carbon monitoring (UV-TOC) system. The salt solutions were prepared by accurately weighing the individual salt and dissolving it in the reagent-grade water. Each salt solution was filtered through a membrane filter (0.22 µm, Duvapore) and the concentration was analyzed before and after passing through the generator column by inductively coupled plasma spectrometry (PERKIN ELMER Optima 3300 SYS). In the solid phase extraction (SPE) process, cartridges (200 mg / 3 ml; J.T. Baker) packed with reversed phase octadecylsilane (C18) bonded onto silica gel were used.

Preparation of the saturated solution using a generator column: The generator column (300 mm x 3 mm i.d. made of Pyrex glass) was packed with Chromosorb W (60-80 mesh, Merck) coated with 0.1-0.6 % (w/w) of the compound of interest and enclosed in a water jacket connected to an isothermal bath (ThermoHaake K 10 ± 0.01 K). The water, or the appropriate salt solution, was pumped through the generator column at a flow rate of 1.5 mL/min from a thermostatic glass reservoir vessel, and directed to the SPE cartridge. After collecting a sufficient volume of eluate in the tared flask, the SPE cartridge was disconnected, washed with reagent-grade water and dried under vacuum for 40 min. The analyte was eluted with the proper volume of hexane under vacuum and then analyzed by both a gas chromatograph (GC), a Hewlett Packard Model 1991Z-413 equipped with an electron capture detector (ECD) fitted with DB5 capillary column (30 m x 323 µm x 0.25 µm) or by gas chromatograph (GC), a Hewlett Packard 5937 equipped with mass spectrometer detector (MSD) fitted with HP-5MS capillary column (30 m x 250 µm x 0.25 µm). The analyte concentration was determined by measuring the peak area and comparing this response to a standard curve. The calibration curves were linear with correlation coefficients ranging from 0.9936 to 0.9999. The working standard solutions for the calibration curves were obtained by dilution with hexane from the stock solutions.

The generator column method used here was calibrated in accordance with the Office of Prevention, Pesticides and Toxic Substances (OPPTS) guideline[4] and has been set out in detail in our previous study[3].

Results and Discussion

The general relationship between salinity and solubility is described by the following equation:

$$\log (S_w/S_s) = K_s \cdot C_s \qquad (1)$$

where S_w and S_s are the solubilities of the solute in pure water and a salt solution, respectively, C_s is the molar concentration of the salt solution, and K_s is the salt-effect parameter**,** the so-called Setschenow constant. This parameter relates the effectiveness of a particular salt, or combination of salts, to change the solubility of a given solute.

The solubility values of selected PCDD/F compounds determined in pure water and chloride solutions (NaCl and $CaCl_2$) at 25 ^oC are summarized in Table 1. Each value is an average of 5 to 7 replicate measurements with the percentage deviation (t-Student test applied to the means of *n* solubility values determined for a level of significance of 0.99) ranging from 1.2 to 10.5 % for the pure water and from 2.3 to 27.3 % for salty solutions. These values meet the OPPTS guideline[4] stating that the repeatability of the concentration of the eluted saturated solution as a function of time should not exceed 30 %. However, for three measured values of solubility the percentage deviation marginally exceeded 30 % (S_s of 2,7-DCDD in NaCl: C_s = 0.32 and 0.48 mol·L^{-1}, and S_s of 2,8-DCDF in $CaCl_2$: C_s= 0.7 mol·L^{-1}).

The Setschenow constants (K_s) derived from the slope of the plots of log (S_w/S_s) versus salt concentrations (see Figures 1 and 2) are given in Table 2 with the corresponding correlation coefficients (R^2).

Generally, the solubilities of the selected compounds decrease gradually with increasing salt concentration in both sodium and calcium chloride solutions. The observed salting-out effect is stronger for the calcium than for the sodium chloride solution: $K_{Ca2+} > K_{Na+}$. Similar behavior has been noted previously[3] in the solubilities of hexachlorobenzene in such solutions. The observed differences in degrees of the salting-out effect can be explained as an aspect of the ionic strength, which is larger for bivalent (Ca^{2+}) than for monovalent (Na^+) ions.

As can be seen from Table 2, the reported Setschenow constants are higher for individual congeners of PCDD than for PCDF, however in group of PCDD and PCDF (including non-chlorinated congeners) the Setschenow parameters rise with increasing chlorine numbers in the following order: $K_{DD} < K_{2\text{-}MCDD} < K_{2,7\text{-}DCDD}$ and $K_{DF} < K_{2,8\text{-}DCDF}$, respectively. These results indicate that the salting out effect is strongly related with the molar volumes (M_v) (see Table 2) of the solutes.

Long and McDevit[5,6] developed a theory relating the salting-out effect to molar volume for liquid hydrocarbons. They correlated the salt effect with the changes in solution volume that take place when a salt is dissolved in water, and suggested that a large part of the variation in the effect of different salts could arise from the displacement of water molecules by the added ions. The solvation of an organic molecule can be affected by its size; thus, the larger molecule will show a somewhat increasing salting out effect. The tendency of the salting-out effect to rise with the molar volume of the solute was confirmed by May et al.[7] who studied solubility of selected aromatic hydrocarbons

(PAHs) in sodium chloride solution and found that the obtained Setschenow constants increased from 0.175 to 0.354 L·mol^{-1} along with molar volumes that increased from 89 to 194 ml·mol^{-1} (e.g. $K_{Benzene}$ <$K_{Anthracene}$<$K_{1,2\text{-}Benzanthracene}$). The same trend was observed between homologues of chlorinated benzenes (CBs) in NaCl solutions[3,8,9] , which had molar volumes ranging from 117 to 221.4 ml·mol^{-1} and a corresponding range of the Setschenow constants from 0.198 to 0.343 L·mol^{-1}.

The experimental data shown here indicate that the transport and fate of chlorinated aromatic compounds through the hydrologic systems is strongly affected by the type of electrolytes present and their concentrations and also depends on the size of the non-polar solutes. The fact that PCDD/F compounds are salted out in the presence of chloride salts in water even at very low concentrations of the salts may be valuable information for further studies concerning the removal of these compounds from aqueous solutions.

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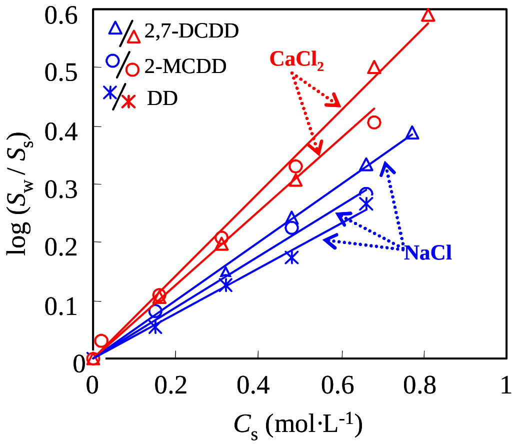

Fig. 1 Effect of sodium and calcium chloride solutions on the solubility of selected PCDD.

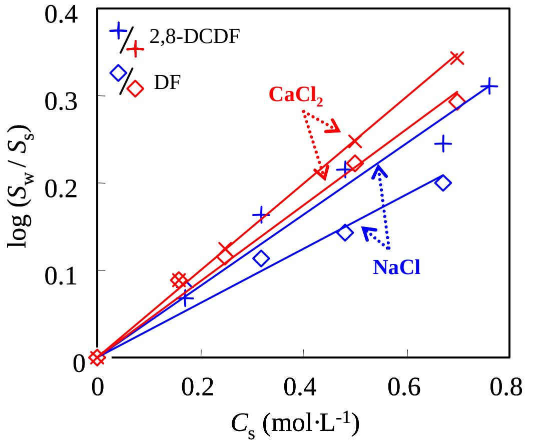

Fig. 2 Effect of sodium and calcium chloride solutions on the solubility of selected PCDF.

Table 1 experimental value of the solubilities (S_s) of the selected compounds in various aqueous salt solutions (C_s) at 25 °C.

Salt	C_s / mol·L^{-1}	S_s */ mg·L^{-1}	S_s */ mg·L^{-1}	S_s */ mg·L^{-1}	Salt	C_s / mol·L^{-1}	S_s */ mg·L^{-1}	S_s^* / mg·L^{-1}
PCDD		DD	2-MCDD	2,7-DCDD	PCDF		DF	2,8-DCDF
S_w /mg·L^{-1}		1.40 ± 0.190	0.42 ± 0.018	(4.09 ± 0.05) x 10^{-3}	S_w /mg·L^{-1}		4.36 ± 0.19	(1.24 ± 0.13) x 10^{-2}
NaCl	0.15	1.237 ± 0.067	0.349 ± 0.020	(3.65 ± 0.72) x 10^{-3}	NaCl	0.17	3.63 ± 0.31	(1.06 ± 0.049) x 10 $^{-2}$
	0.32	1.046± 0.027	0.310 ± 0.046	(2.91 ± 0.98) x 10^{-3}		0.32	3.36 ± 0.40	(8.52 ± 1.25)x 10 $^{-3}$
	0.48	0.938 ± 0.046	0.251 ± 0.015	(2.35 ± 0.75) x 10^{-3}		0.48	3.14 ± 0.33	(7.54 ± 1.31) x 10 $^{-3}$
	0.66	0.759 ± 0.013	0.219 ± 0.038	(1.90 ± 0.35) x 10^{-3}		0.67	2.75 ± 0.30	(7.05 ± 0.90) x 10^{-3}
	0.77	N/M	N/M	(1.67 ± 0.42) x 10^{-3}		0.76	N/M	(6.06 ± 0.92) x 10^{-3}
$CaCl_2$	0.02	N/M	0.392 ± 0.046	N/M	$CaCl_2$	0.02	N/M	N/M
	0.16	N/M	0.326 ± 0.078	(3.20± 0.80) x 10^{-3}		0.16	3.55 ± 0.70	(1.01 ± 0.13) x 10^{-2}
	0.31	N/M	0.260 ± 0.032	(2.59 ± 0.39) x 10^{-3}		0.25	3.33 ± 0.34	(9.30 ±2.10) x 10^{-3}
	0.49	N/M	0.196 ± 0.036	(2.02 ± 0.43) x 10^{-3}		0.50	2.61 ± 0.21	(7.00 ± 1.76) x 10^{-3}
	0.68	N/M	0.165 ± 0.045	(1.29 ± 0.03) x 10^{-3}		0.70	2.22± 0.32	(5.62 ± 1.82) x 10^{-3}
	0.81	N/M	N/M	(1.03 ± 0.28) x 10^{-}		0.81	N/M	N/M

*Mean value ± standard deviation; N/M – Not measured.

Table 2 Experimental Setschenow constants (K_s) at 25 °C.

Compound	M_v^{10} / ml ·mol^{-1}	K_s / L·mol^{-1}	
		NaCl	$CaCl_2$
DD	192.0	0.3889 (R^2 = 0.9936)	N/M
2-MCDD	212.9	0.4403 (R^2 = 0.9901)	0.6317 (R^2=0.9884)
2,7-DCDD	233.8	0.4980 (R^2 = 0.9932)	0.7124 (R^2=0.9882)
DF	184.6	0.3112 (R^2 = 0.9544)	0.4349 (R^2=0.9884)
2,8-DCDF	226.4	0.4090 (R^2 = 0.9664)	0.4954 (R^2=0.9985)

N/M-not measured.