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Solubilities of Selected PCDDs and PCDFs in Water and Various Chloride Solutions

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The aqueous solubilities of selected polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), including their non-chlorinated compounds, were measured at 25 °C using the generator column method to prepare their saturated aqueous solutions. Newly measured aqueous solubility data are reported for 1,2,3,4,6,9-hexachlorodibenzo-*p*-dioxin and octachlorodibenzofuran. Additionally, changes in solubilities of dibenzo-*p*-dioxin, 2-monochlorodibenzo-*p*-dioxin, 2,7-dichlorodibenzo-*p*-dioxin, dibenzofuran, and 2,8-dichlorodibenzofuran were studied in sodium, potassium, and calcium chloride solutions at various concentrations of the individual salts. From the measured solubility data, the salinity parameters, known as the Setschenow constants, were derived for the selected PCDDs and PCDFs and are reported here for the first time.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a group of 210 congeners from which those with chlorine substitution in the 2,3,7, and 8 positions (17 congeners) are recognized as persistent, bioacumulative, and toxic.[1,2] These organochlorine compounds formed unintentionally in industrial and thermal processes are released into the atmosphere and then transferred to the other environmental matrices such as soil, water, and sediment[2−4] where they can last for years or decades before degradation.[5] Environmental pollutants may also enter the aqueous system by atmospheric deposition to the land followed by transport of the deposited materials in stormwater runoff, industrial and wastewater treatment discharges, and erosion or runoff from contaminated areas such as industrial or waste disposal sites.[6,7]

The behavior and fate of organic contaminants in the aqueous environment depend largely on their aqueous solubility, which is considered to be a key parameter in determining the mobility and controlling the distribution of the chemicals between different phases (e.g., air−water and sediment−water partitioning). It is well-known that various environmental/operating factors may strongly affect—reduce or enhance—aqueous solubility; therefore, they must be taken into consideration when the water behavior of hydrophobic compounds is studied.[6,8] For example, numerous studies[5,9−14] report an increasing solubility of nonpolar organics (including PCDD/Fs) with rising temperature. Some data give information on enhancement of PCDD/F solubility in the presence of dissolved organic matter such as humic and fulvic acids.[15−17] However, some studies show that the presence of dissolved salts (e.g., Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO^{3-}, $SO_4{}^{2-}$) or minerals reduces the aqueous solubility of nonpolar compounds.[18−22] Unfortunately, there is no reported data on the behavior of PCDDs and PCDFs in aqueous electrolytes.

Although most organic pollutants are diluted in the environment, their aqueous solubility in the laboratory is usually measured under saturated conditions at room temperature. There are two methods (shake flask and generator column)[23,24] used to determine the solubilities of hydrophobic compounds, though for compounds with solubilities well below 1 $mg \cdot L^{-1}$ the generator column technique is the most applicable and was successfully used to determine the solubilities of PCDDs[9−12] and PCDFs[9,13,25] in pure water. A compilation of aqueous solubility data[5,14,26,27] shows that the solubility values of only a few of the 210 PCDD/F congeners have been reported.

To determine the influence of salts, the solubility of an organic solute must be measured in pure water as well as in an electrolyte solution. The shaking flask method is the most common technique used for saturation of the organics (e.g., chlorobenzenes, chlorophenols, aromatic hydrocarbons) in a salt solution.[18−20] However, a few studies provide salinity data for polycyclic aromatic hydrocarbons determined by using the dynamic coupled column liquid chromatographic technique.[22,28] The generator column technique, which is used in this study, has previously been successfully applied[29] for determining the solubility of hexachlorobenzene in various chloride solutions.

In the present study, the solubilities of selected polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), including those of their non-chlorinated congeners, were measured at 25 °C using the generator column method for preparing the saturated solutions. Newly measured aqueous solubility data reported here are those of 1,2,3,4,6,9-hexachlorodibenzo-*p*-dioxin and octachlorodibenzofuran. The changes in the solubilities of dibenzo-*p*-dioxin, 2-monochlorodibenzo-*p*-dioxin, 2,7-dichlorodibenzo-*p*-dioxin, dibenzofuran, and 2,8-dichlorodibenzofuran were studied in sodium, potassium, and calcium chloride solutions at various concentrations of the individual salts. From the measured solubility data, the salinity parameters, known as the Setschenow constants, were derived. To the best of our knowledge, the obtained salinity parameters for PCDD/Fs and their non-chlorinated congeners are reported here for the first time.

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Experimental Method

Chemicals. Dibenzo-*p*-dioxin (DD); 2-monochlorodibenzo-*p*-dioxin (2-MCDD); 2,7-dichlorodibenzo-*p*-dioxin (2,7-DCDD); octachlorodibenzo-*p*-dioxin (OCDD); dibenzofuran (DF); 2,8-dichlorodibenzofuran (2,8-DCDF); octachlorodibenzofuran (OCDF); and the appropriate standard solutions (50 μg·mL^{-1} in isooctane) with purities from 98 % to 100 % were purchased from AccuStandard, Inc. 1,2,3,4,6,9-Hexachlorodibenzo-*p*-dioxin (1,2,3,4,6,9-HxCDD) and 1,2,3,4,7,8-hexachlorodibenzofuran (1,2,3,4,7,8-HxCDF) with purity of 99% were purchased from Cambridge Isotope Laboratories. Hexane (97.8 %), methanol (99.8 %), anhydrous Na_2SO_4, KCl (99.9 %), NaCl (99.5 %), and $CaCl_2$ (99.9 %) were purchased from Wako Pure Chemical Industries, Ltd.

Reagent-grade water was obtained from a NANOpure DIamond 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 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 × 3 mm i.d. made of Pyrex glass) was packed with Chromosorb W (60−80 mesh, Merck) coated with 0.03 % to 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, and the appropriate salt solution, was pumped into the generator column at a constant flow rate by a medium-pressure delivery pump from a thermostatic glass reservoir vessel, and then the outlet solutions were passed through the SPE extractor cartridge. Finally, the extracted solution was directed to a tarred flask. For the initial conditioning of the generator column, 100 mL to 500 mL of water was used.

Conditioning of the SPE Cartridges. Before connection to the generator column, an SPE cartridge was washed sequentially with 3 mL of hexane, 4 mL of methanol, and 5 mL of reagent-grade water. The saturated aqueous solution eluting from the generator column was passed directly through the SPE cartridge, and the quantities of aqueous eluate, collected in the tarred flask, were weighed. After collecting a sufficient volume of eluate, the SPE cartridge was disconnected, washed with reagent-grade water (3 mL), and dried under vacuum for 40 min. The analyte was eluted with an appropriate volume of hexane (determined by trial for individual compounds) under vacuum. Each portion of hexane was left in contact with the sorbent for at least 2 min to reach equilibrium. The collected extract was dried with anhydrous sodium sulfate to remove any remaining water.

Chromatographic Analysis of Extract. A 2 μL aliquot was applied for chromatographic analysis. The quantitative analyses of the selected organic compounds were performed with a Hewlett-Packard 1991Z-413 GC- ECD system and a Hewlett-Packard 5973 GC-MSD system. Each concentration was determined by measuring the peak area and comparing this response to a standard curve. The working standard solutions for the calibration curves were obtained by dilution with hexane from the stock standard solutions. The calibration curves were linear with correlation coefficients ranging from 0.9936 to 0.9999.

Note. The aqueous saturated solutions containing individual hexa- and octachlorinated PCDD/F congeners were collected in a tarred flask (50 mL to 60 mL) and then pretreated (liquid−liquid extraction with dichloromethane, cleanup of sample on a multilayer silica gel column, then on the activated carbon/silica gel column) and analyzed (GC, HP-6890; MS, JMS-700 AutoSpec UltimaNT) at NITTECH RESEARCH Co. Ltd. in Japan, according to the Method 1613.[30]

Results and Discussion

Aqueous Solubility at 25 °C. The generator column method used here was calibrated in accordance with the Office of Prevention, Pesticides and Toxic Substances (OPPTS) guideline.[23,24] The reference compounds (biphenyl, 1,2-dichlorobenzene, and hexachlorobenzene), which are in the solubility range of the non-, mono-, and dichlorinated congeners of the PCDD/Fs studied here, were selected to carry out a preliminary test of the generator column (25 °C at two independent flow rates ranging from 0.5 mL·min^{-1} to 0.7 mL·min^{-1} and from 1.1 mL·min^{-1} to 1.5 mL·min^{-1}). The results were set out in detail in our previous study.[29]

In this study, the aqueous saturated solutions of DD, 2-MCDD, 2,7-DCDD, DF, and 2,8-DCDF were generated at a flow rate of 1.5 mL·min^{-1}. The aqueous solubilities of these compounds were determined twice in two independent runs to verify the analytical (extraction and quantification) procedure. The saturated solutions of hexa- and octa-PCDD/Fs were generated at a flow rate of 0.7 mL·min^{-1}. The aqueous solubility of each compound is an average of 5 to 7 of the mass concentrations determined in consecutive samples eluted from the generator column at constant time intervals. All the values determined at 25 °C are presented in Table 1.

The standard deviations between replicated measurements (t-student test applied to the means of n solubility values determined at a level of significance of 0.99) range from 1.2 % to 19.3 % for the set of compounds, excluding the octachlorinated congeners. The variations in the octachlorinated congeners, calculated by the t-student test at a level of significance of 0.90, were 49.5 % (OCDD) and 17.8 % (OCDF). The obtained percentage variations about the mean values (with the exception only of the OCDD) were consistent with the OPPTS[23] requirements, which specify that the repeatability between the consecutive measurements as a function of time should not exceed ± 30 %.

As can be seen in Table 1, of the aqueous solubilities measured here, those of DF and 2,8-DCDF agree very well with their previously reported literature values.[9,13] However, the aqueous solubilities of DD, 2-MCDD, and 2,7-DCDD are a little higher than in the previous determinations,[9,12] although the same technique was used to generate the saturated solutions. In this study, all the saturated solutions were extracted with hexane, whereas in the previous studies (Table 1), the saturated solutions were extracted with a mixture of methanol/water (if quantified by HPLC) or isooctane (if quantified by GC-ECD or GC-MSD). Hexane was used only for the extraction of dibenzofuran.[13]

In this study, the extraction step was set up for the extraction of saturated solutions of DD and DF, and the appropriate extraction solvent was selected by trials using various volumes of pure hexane and isooctane. The aqueous solubilities of DF were similar when hexane and isooctane were used to extract its saturated solution. However, higher solubility values were obtained for DD when hexane rather than isooctane was used as the extraction solvent (data not presented here). This may explain why the solubilities of the other lower chlorinated

Table 1. Aqueous Solubilities (S_w) at 25 °C of Selected PCDD/Fs (Including Non-Chlorinated Congeners): Comparison with Literature Data

		this study: generator column		literature data		
compound	N	$S_w{}^a$/mg·L^{-1}	quant.	S_w/mg·L^{-1}	method/quant.	ref
DD	7	1.26 ± 0.040	GC-MSD	0.899	gen col /GC-ECD	9
DD	5	1.40 ± 0.190	GC-MSD	0.842	gen col /HPLC	12
2-MCDD	5	0.420 ± 0.018	GC-ECD	0.319	gen col /GC-ECD	9
2-MCDD	7	0.437 ± 0.040	GC-ECD	0.278	gen col /HPLC	12
2,7-DCDD	5	$(4.09 \pm 0.050)\cdot 10^{-3}$	GC-ECD	$3.75\cdot 10^{-3}$	gen col /HPLC	12
1,2,3,4,6,9-HxCDD	5	$(1.23 \pm 0.237)\cdot 10^{-6}$	GC-ECD		N/A	
OCDD	5	$(2.29 \pm 1.130)\cdot 10^{-7}$	GC-MSD^b	$7.40\cdot 10^{-8}$	estimated	9
OCDD (^{14}C-labeled)				$4.0\cdot 10^{-7}$ (20 °C)	gen col /HPLC	10
DF	6	4.73 ± 0.320	GC-MSD	4.22	gen col /GC-ECD	9
DF	6	4.36 ± 0.190	GC-MSD	4.75	gen col /HPLC	13
DF	–	–	–	4.69	shake flask /HPLC	13
2,8-DCDF	5	$(1.57 \pm 0.060)\cdot 10^{-2}$	GC-MSD	$1.45\cdot 10^{-2}$	gen col /GC-ECD	9
2,8-DCDF	6	$(1.24 \pm 0.130)\cdot 10^{-2}$	GC-MSD			
1,2,3,4,7,8-HxCDF	5	$(2.98 \pm 0.464)\cdot 10^{-6}$	GC-MSD^b	$8.25\cdot 10^{-6}$ (22.7 °C)	gen col /GC-MSD	25
OCDF	5	$(4.09 \pm 0.730)\cdot 10^{-7}$	GC-MSD^b	$1.16\cdot 10^{-6}$	estimated	9

[a] Mean value ± SD where SD is the standard deviation. N/A: not available. gen col: generator column. GC: gas chromatography. ECD: electron capture detector. MSD: mass spectrometer detector. HPLC: high-pressure liquid chromatography. [b] Analyzed at NITTECH RESEARCH Co., Ltd.

PCDDs determined here are higher than those already published in the literature, while those of the PCDFs are consistent with the data previously reported.

It is very difficult to verify the accuracies of the hexa- and octa-PCDD/F aqueous solubilities determined in this study by comparison with literature data, as there are only a limited number of experimental determinations for these. It can be seen from Table 1 that the solubility of 1,2,3,4,7,8-HxCDF is a little higher than that determined by Friesen et al.,[25] but the OCDD value ($2.29\cdot 10^{-7}$ mg·L^{-1}) is in good agreement with the solubility ($4.0\cdot 10^{-7}$ mg·L^{-1}) reported by Friesen et al.[10] However, the solubilities obtained here for OCDD and OCDF vary significantly from those reported by Doucette and Andren,[9] which were not in fact experimentally measured at 25 °C but were derived from solubility values determined at higher temperatures (40 °C to 80 °C).

As pointed out in previous studies,[9−11,23,24] accurate determination of aqueous solubility is mainly associated with the preparation of a suitable saturated solution, of which the quality is largely dependent on proper conditioning of a generator column with water and a proper water flow rate. It has been found[10] that, generally, changes in the flow rate ranging from 1 mL·min^{-1} to 2 mL·min^{-1} do not significantly affect the solubility values of lower chlorinated (more soluble) PCDD/Fs. However, the solubilities of the higher chlorinated (less soluble) PCDD/F congeners were found to be slightly lower if a higher flow rate (2 mL·min^{-1}) was used in the system.[10,11] It was concluded that a slower flow rate is better when the solubilities of solutes with high molecular weights are determined. Thus, the flow rate of 0.7 mL·min^{-1} used in this study seems to be reasonable for obtaining valid solubility data for hexa- as well as octa-PCDD/Fs. We suppose that the low standard deviations obtained between replicate measurements of hexachlorinated compounds indicate that the equilibrium in the system was reached. However, the high variation between replicate measurements for OCDD and OCDF may be associated with difficulties with the saturation of their solutions at room temperature. On the other hand, very high percentage deviations (39 % for OCDD and 42 % for OCDF) were reported by Doucette and Andren,[9] who determined the solubilities at a higher (40 °C) temperature. Unfortunately, there is no information on the level of significance for which the percentage variation was calculated.

The problems associated with the determination of reproducible and accurate (low standard deviation) solubility data for PCDD/Fs have been discussed in numerous papers,[19−24] indicating that variables such as the purity of the solid solute and the solvents, the equilibration time, the temperature, and the analysis method (extraction, quantification) are the most important factors affecting the final results. Therefore, these parameters must always be reported when the aqueous solubility is measured to verify the accuracy of the obtained data, particularly if the corresponding literature data is rare or not available.

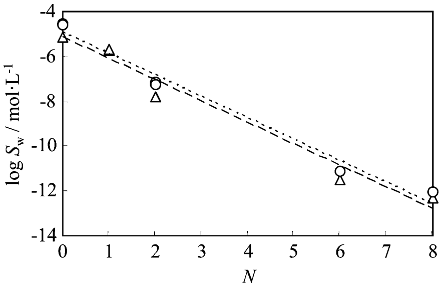

Figure 1. Correlation between aqueous solubilities (S_w) of △, PCDDs and ○, PCDFs measured in this study and the number of chlorine atoms (N).

The obtained solubility data show the expected trend, that the solubilities decrease with an increasing chlorine number in the PCDDs and PCDFs. However, to verify the accuracy of our measurements, these solubilities were correlated with the chlorine number (Figure 1) and the first-order linear regression equations (eqs 1 and 2) were derived

$$\text{PCDDs (6) + DD: } \log S_w = -0.961\text{N} - 5.142\ (R^2 = 0.9869;\ \text{SD} = 0.543) \quad (1)$$

$$\text{PCDFs (5) + DF: } \log S_w = -0.955\text{N} - 4.923\ (R^2 = 0.9791;\ \text{SD} = 0.515) \quad (2)$$

From these equations, the changes in solubilities of PCDDs and PCDFs with the number of chlorine atoms are estimated. It is found that solubilities of PCDDs decrease by a factor of 9.1 for each added chlorine atom, whereas those of PCDFs decrease by a factor of 9.0. The same correlation previously applied by Friesen et al.[25] to all known solubilities of PCDD/Fs measured at room temperature (20 °C to 25 °C) provides factors of 7.8 and 7.6 for PCDDs and PCDFs, respectively. Shiu et al. ,[12] who studied changes in solubilities of subcooled liquids of PCDDs (deduced from the solubilities of previously determined solid solutes), found that their solubilities decrease by a factor of 5 for each additional chlorine atom.

Table 2. Experimental Solubilities Measured in Pure Water (S_w) and Salt Solutions (S_s) at Various Salt Concentrations (C_s) at 25 °C

	C_s	$S_s{}^a$/mg·L^{-1}				C_s	$S_s{}^a$/mg·L^{-1}	
salt	mol·L^{-1}	DD	2-MCDD	2,7-DCDD	salt	mol·L^{-1}	DF	2,8-DCDF
	0.00	1.40 ± 0.190	0.42 ± 0.018	(4.09 ± 0.05) ·10^{-3}		0.00	4.36 ± 0.19	(1.24 ± 0.13)·10^{-2}
KCl					KCl			
	0.16	N/M	0.360 ± 0.043	(3.63 ± 0.27)·10^{-3}		0.16	3.83 ± 0.15	(1.05 ± 0.055)·10^{-2}
	0.32	N/M	0.319 ± 0.017	(3.04 ± 0.54)·10^{-3}		0.32	3.54 ± 0.24	(9.04 ± 0.45)·10^{-3}
	0.49	N/M	0.286 ± 0.020	(2.39 ± 0.39)·10^{-3}		0.48	3.29 ± 0.45	(8.25 ± 0.63)·10^{-3}
	0.66	N/M	0.269 ± 0.018	(1.89 ± 0.22)·10^{-3}		0.65	2.94 ± 0.34	(7.21 ± 1.03)·10^{-3}
	0.75	N/M	0.240 ± 0.005	(1.77 ± 0.30)·10^{-3}		0.76	N/M	(6.21 ± 0.52)·10^{-3}
NaCl					NaCl			
	0.15	1.237 ± 0.067	0.349 ± 0.020	(3.65 ± 0.72)·10^{-3}		0.17	3.63 ± 0.31	(1.06 ± 0.049)·10 $^{-2}$
	0.32	1.046 ± 0.027	0.310 ± 0.046	(2.91 ± 0.98)·10^{-3}		0.32	3.36 ± 0.40	(8.52 ± 1.25)·10^{-3}
	0.48	0.938 ± 0.046	0.251 ± 0.015	(2.35 ± 0.75)·10^{-3}		0.48	3.14 ± 0.33	(7.54 ± 1.31)·10^{-3}
	0.66	0.759 ± 0.013	0.219 ± 0.038	(1.90 ± 0.35)·10^{-3}		0.67	2.75 ± 0.30	(7.05 ± 0.90)·10^{-3}
	0.77	N/M	N/M	(1.67 ± 0.42)·10^{-3}		0.76	N/M	(6.06 ± 0.92)·10^{-3}
$CaCl_2$					$CaCl_2$			
	0.02	N/M	0.392 ± 0.046	N/M		0.02	N/M	N/M
	0.16	N/M	0.326 ± 0.078	(3.20 ± 0.80)·10^{-3}		0.16	3.55 ± 0.70	(1.01 ± 0.13)·10^{-2}
	0.31	N/M	0.260 ± 0.032	(2.59 ± 0.39)·10^{-3}		0.25	3.33 ± 0.34	(9.30 ± 2.10)·10^{-3}
	0.49	N/M	0.196 ± 0.036	(2.02 ± 0.43)·10^{-3}		0.50	2.61 ± 0.21	(7.00 ± 1.76)·10^{-3}
	0.68	N/M	0.165 ± 0.045	(1.29 ± 0.03)·10^{-3}		0.70	2.22 ± 0.32	(5.62 ± 1.82)·10^{-3}
	0.81	N/M	N/M	(1.03 ± 0.28)·10^{-3}		0.81	N/M	N/M

[a] Mean value ± standard deviation. N/M: not measured.

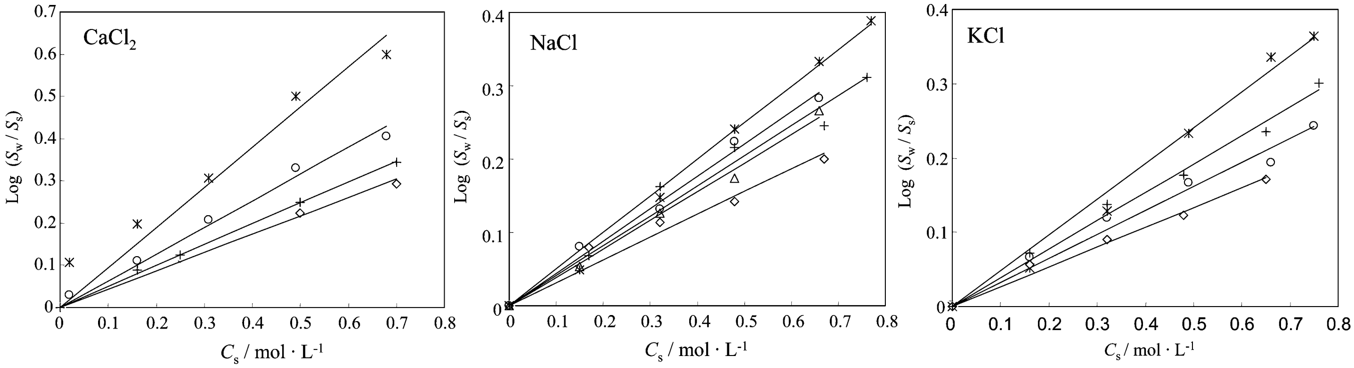

Figure 2. Effect of calcium ($CaCl_2$), sodium (NaCl), and potassium (KCl) chloride solutions on the solubilities of △, DD; ○, 2-MCDD; *, 2,7-DCDD; ◇, DF; +, 2,8-DCDF.

The obtained results indicate that the behaviors of PCDDs and PCDFs in water, as well as the changes in their solubilities as affected by the degree of chlorination, are very similar. The fact that the solubilities of PCDDs are generally lower than those of PCDFs is mainly associated with the differences in their molecular structures.

Salinity Effect. The phenomenon that the solubility of a neutral solute is reduced in the presence of dissolved salt is called the salting-out effect.[6,31] It is related 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). The general relationship between the solubility of a neutral solute in aqueous salt solution, at low salt concentration, is described by the empirical Sestchenow equation

$$\log(S_w/S_s) = K_s \cdot C_s \tag{3}$$

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 empirical salt-effect parameter, the so-called Setschenow constant. This parameter relates to the effectiveness of a particular salt (e.g., KCl, NaCl, etc.), or combination of salts (e.g., seawater), in changing the solubility of a given solute.[6] The positive value of K_s ($S_w > S_s$) indicates the salting-out effect, whereas the negative K_s ($S_w < S_s$) indicates a salting-in effect.

The solubilities of selected PCDD/F congeners determined in pure water and chloride solutions (NaCl, KCl, and $CaCl_2$) at 25 °C are summarized in Table 2. Each value is an average of 5 to 7 replicate measurements, with the percentage deviations (t-student test applied to the means of n solubility values determined to 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 the salt solutions. These values meet the OPPTS guideline[23] 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 at $C_s = 0.32$ mol·L^{-1} and 0.48 mol·L^{-1}, and S_s of 2,8-DCDF in $CaCl_2$ at $C_s = 0.7$ mol·L^{-1}). The Setschenow constants (K_s) derived from the slopes of the plots of log(S_w/S_s) vs salt concentrations (see Figure 2) are shown in Table 3.

In general, the solubilities of the selected compounds decrease gradually with increasing salt concentration in all chloride solutions. For example, the solubility of 2-MCDD (Table 2) decreases by a factor of 0.05, 0.06, and 0.10 for KCl, NaCl, and $CaCl_2$, respectively, for an increase in the salt concentration of 0.16 mol·L^{-1} (in the range of salt concentrations 0.16 mol·L^{-1} to 0.66 mol·L^{-1}). For the same increase in salt concentration, the solubility of 2,7-DCDD decreases by a factor of 0.08 (KCl), 0.09 (NaCl), and 0.11 ($CaCl_2$). When studying the behavior of selected PCDFs, it can be seen that the changes in solubilities of DF and 2,8-DCDF behave the same as those

Table 3. Experimental Setschenow Constants (K_s) at 25 °C[a]

compound	M_v mL·mol^{-1}	K_s/L·mol^{-1} KCl	NaCl	$CaCl_2$
DD	192.0	N/M	0.389 ± 0.009	N/M
2-MCDD	212.9	0.323 ± 0.012	0.440 ± 0.013	0.632 ± 0.020
2,7-DCDD	233.8	0.482 ± 0.015	0.498 ± 0.011	0.712 ± 0.021
DF	184.6	0.266 ± 0.009	0.311 ± 0.018	0.435 ± 0.014
2,8-DCDF	226.4	0.384 ± 0.010	0.409 ± 0.018	0.495 ± 0.006

[a] M_v: molar volume.[5] N/M: not measured.

of DD and 2,7-DCDD; however, the obtained factors range from 0.04 to 0.07 (for DF) and from 0.06 to 0.08 (for 2,8-DCDF) for the different salt solutions.

The observed reduction in solubility is strongly dependent on the type of ion dissolved in water, its concentration, and also the molecular structures of the individual compounds.

The obtained salinity parameters (Table 3) indicate that the salting-out effect is stronger for the calcium chloride solution than for the sodium and potassium chloride solutions. A similar behavior has been noted previously in the solubilities of hexachlorobenzene[29] and other chlorinated benzenes[18,20] in chloride solutions. It was concluded that the differences in the degree of the salting-out effect are caused by differences in the ionic strength, which is larger for bivalent (Ca^{2+}) than for monovalent (Na^+, K^+) ions. Moreover, the ion size (K^+ (300 pm); Na^+ (450 pm); Ca^{2+} (600 pm)) can also be taken into consideration when differences in the salting-out effect, especially in the presence of monovalent ions, are observed.

The Setschenow constants obtained in this study, especially for sodium chloride solution, provide additional information about the possible behavior of the PCDD/Fs in seawater. Generally, seawater is dominated by the presence of NaCl (its molar fraction is about 0.8 of 1 mole of "seawater salt"), whereas the contribution of the other salts ($MgCl_2$, Na_2SO_4, $CaCl_2$, KCl, $NaHCO_3$) is about 0.2 (based on the composition of artificial seawater, given by Gordon and Thorne[32]). Because seawater is dominated by NaCl, it is possible to presume that the salting-out effect of a given solute determined for NaCl solution may approximately reflect its salting-out effect for artificial or real seawater. In ref 6, the authors suggest that the Setschenow constant for NaCl solution "can be used as a surrogate" for seawater. Thus, the K_{NaCl} obtained in this study can be very useful in further studies for prediction of the fate of the other PCDD/Fs in marine environmental or industrial electrolyte solutions.

From the Setschenow constants derived in this study, it can be seen that the salting-out effect is strongly related to the molecular structure of the solid solute. In general, the salinity parameters are higher for individual PCDD congeners than PCDF ones; however, for PCDDs and PCDFs as a group (including non-chlorinated congeners), the Setschenow parameters rise with an increase in the number of chlorine atoms, in the following order: $K_{DD} < K_{2-MCDD} < K_{2,7-DCDD}$ and $K_{DF} < K_{2,8-DCDF}$, respectively.

Long and McDevit[19] developed a theory relating the salting-out effect to the molar volume of 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 effects 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, a larger molecule will show a somewhat increased salting-out effect. The tendency of the salting-out effect to increase with an increasing molar volume of the solute was confirmed by May et al.[22] who studied the solubilities of selected aromatic hydrocarbons (PAHs) in sodium chloride solution and found that the obtained Setschenow constants increased from 0.175 L·mol^{-1} to 0.354 L·mol^{-1} as the molar volumes increased from 89 mL·mol^{-1} to 194 mL·mol^{-1} (e.g., $K_{benzene} < K_{anthracene} < K_{1,2-benzanthracene}$). The same trend was observed between homologues of chlorinated benzenes (CBs) in sodium chloride solutions,[18,20,29] which had molar volumes ranging from 117 mL·mol^{-1} to 221.4 mL·mol^{-1} and a corresponding range of Setschenow constants from 0.198 L·mol^{-1} to 0.343 L·mol^{-1}.

Conclusion

The experimental data presented here indicate that a generator column (including extraction and quantification analysis) allows reasonable data of high accuracy to be obtained. However, the observed discrepancies (which increase for the solutes of the larger molecular structures of the hexa- and octachlorinated congeners) between the values measured in this study and those reported in the literature reflect the experimental difficulties in determining the solubilities of such hydrophobic compounds.

It was shown that the aqueous solubility varies with the molecular structure and the number of chlorines in the PCDD and PCDF molecules. However, the changes that occur in the solubilities with increasing numbers of chlorine atoms are quite similar for PCDDs and PCDFs.

The presence of a strong electrolyte in the water decreases the solubilities of PCDDs and PCDFs. The salting-out effect, expressed by the Setschenow constants, strongly depends on the type of salt solution (ionic strength) and its concentration, as well as on the molar size and molecular structure of the individual solutes.

The fact that PCDD/F compounds are salted out in the presence of very low concentrations of the chloride salts may be valuable information for further studies concerning the removal or separation of these compounds from water solutions. The reported results may also be helpful in estimating the magnitude of the salting-out effect for other hydrophobic, toxic contaminates, as well as in predicting transport of these compounds through hydrologic systems.

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