Prediction of Water Solubilities for Selected PCDDs/PCCDFs with COSMO-RS model

Sylwia Oleszek-Kudlak[1], Mariusz Grabda[1], Etsuro Shibata[1], Takashi Nakamura[1], Czeslawa Rosik-Dulewska[2]

[1]Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai
[2]Institute of Environmental Engineering of the Polish Academy of Sciences, Zabrze, Poland

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are well identified contaminants ubiquitous in the environment. Of the various parameters that affect the fate and behavior of environmental organic compounds, water solubility is one of the most important. However, when we are studying the aqueous behavior of organic chemicals, we should also take into consideration and evaluate several parameters (temperature, salinity, dissolved organic matter) influencing their solubility[1].

Among the 210 congeners (mono- to octa-chlorinated) of PCDDs and PCDFs, water solubility values are available for a few congeners only. The reported aqueous solubilities of PCDDs and PCDFs are often scattered[2], despite most of them having been measured by the generator column method[3], recognized as the most accurate for the determination of the water solubility of hydrophobic organic chemicals. These discrepancies reflect an important problem associated with difficulties in the preparation of the saturated solution and in the analytical measurements, particularly of compounds with a solubility below 1 ppb. In practice, the high cost of the experimental determinations also limits the field of research.

In recent years, investigators have developed a number of calculational methods to predict the water solubility of organic chemicals. One of them is the Conductor-like Screening Model for Real Solvents (COSMO-RS) introduced by Klamt et al.[4]. This model was successfully used for finding the solubilities of chlorobenzenes (ClBZs) at a wider range of temperatures (from 5 to 60 ^{o}C) and in a salty environment[5].

In this study, we have applied COSMO-RS to determine the aqueous solubilities of 19 PCDDs/ PCDFs at 25 ^{o}C. Additionally, we measured the solubilities of 7 PCDDs/PCDFs using the generator column method at 25 ^{o}C. We used these data and those available from the literature to estimate the accuracy of the COSMO-RS calculations.

Methods and Materials

Chemicals. We obtained dibenzo-*p*-dioxin, 2-chlorodibenzo-*p*-dioxin, 2,7-dichlorodibenzo-*p*-dioxin, octachloro-dibenzo-*p*-dioxin, dibenzofuran, 2,8-dichlorodibenzofuran and octachlorodibenzofuran with purity from 99 to 100 % and as appropriate standard solutions (50 μg/ml in isooctane) with purity from 99.4 to 100 % from AccuStandard, Inc. We purchased hexane, methanol and anhydrous Na_2SO_4 from Wako Pure Chemical Industries, Ltd., and obtained the reagent grade water from a NANOpure® Diamond ™ TOC-UV system. In the solid phase extraction (SPE) process, we used cartridges (200 mg / 3 ml; J.T. Baker) packed with reversed phase octadecylsilane (C_{18}) bonded onto silica gel.

Preparation of the saturated solution using a generator column. The generator column (300 mm x 3 mm i.d.) was made of Pyrex glass, and enclosed in a water jacket connected to an isothermal bath (ThermoHaake K 10 ± 0.01 K). The tubing and connections were made of Teflon. We dissolved each compound in hexane and coated it on Chromosorb W (60-80 mesh, Merck), in an amount of 0.1- 0.4 % (w/w). The pure water was pumped at a flow rate of 1.5 ml/min from a thermostatic glass reservoir vessel through the generator column; finally, it was directed to the extractor cartridge. For the initial conditioning of the generator column, we used 300-500 ml of water.

We weighed the quantities of aqueous eluate collected in the tared flask, and after collecting a sufficient volume of eluate, disconnected the SPE cartridge washed it with reagent-grade water and dried it under vacuum for 40 min. Finally, we eluted the analyte with an appropriate volume of hexane under vacuum.

To perform the analyses, we utilized both GC-MSD (Hewlett Packard 5973) and GC-ECD (Hewlett Packard; Model 1991Z-413) systems[3]. The water samples conteining octa-CDD and octa-CDF congeners were extracted and anaylzed at NITTECH RESEARCH Co. in Japan.

We calibrated the procedure described here, set out in detail in a previous study[6], according to OPPTS guidelines[3].

The COSMO-RS method. The basis of the COSMO-RS[7,8] approaches is the electrostatic theory of locally interacting molecular surface descriptors, computed by quantum chemical methods (QM) combined with a statistical thermodynamics methodology. The theory considers all of the local contact interactions of the molecular surfaces between the solute and the surrounding solvent.

The COSMO-RS is a two-step procedure. In the first step, quantum chemical computations, based on Density Functional Theory (DFT) and utilizing the Gaussian 98 program, are performed for all compounds. In these calculations, the investigator uses the continuum solvation model, COSMO, as implemented in the Gaussian98 program, to simulate a virtual conductor environment for the molecule. The output of the DFT/COSMO calculation is a file providing the total energy of the molecule in its conductor environment, as well as information about the polarization charge density, σ, on the surface of the molecule. The σ is a good local descriptor of the molecular surface polarity.

In the second step of the COSMO-RS, where we consider the statistical thermodynamics of the molecular interactions, this polarization charge density**, σ,** is used to quantify the interaction energy of the pair-wise interacting surface segments (σ, σ`) in the light of the most important molecular interactions model, i.e. electrostatics (E_{misfit}) and hydrogen bonding (E_{hb}). The less specific van der Waals interactions or dispersive interactions are taken into account in a more approximate way by element specific dispersion coefficients. Based on the quantitative expression for the interaction

energy of molecules in a condensed state as local contact energies of molecular surfaces, the thermodynamics of the liquid system is evaluated using a model of pair-wise interacting surface segments of size a_{eff} according to eq. 1:

$$\mu_s(\sigma) = -\frac{RT}{a_{eff}} \ln \left[\int p_s(\sigma') \exp \left(\frac{a_{eff}}{RT} (\mu_s(\sigma') - E_{misfit}(\sigma,\sigma') - E_{hb}(\sigma,\sigma')) \right) d\sigma' \right] \quad (1)$$

where: $\mu_s(\sigma)$ is the chemical potential (σ-potential) of an average molecular contact area of size a_{eff} in the ensemble S at temperature T. The composition of the surface segment ensemble is described by the normalized distribution function $p_s(\sigma')$ called the "σ-profile". If $p_s(\sigma')$ and $p^x(\sigma)$ are the surface composition functions of a solvent S and of a solute X, respectively, the chemical potential of compound X in system S, (μ_s^x) is available from the integration of the σ-potential over the surface of X (eq. 2):

$$\mu_s^x = \int \mu_s(\sigma) p^x(\sigma) d\sigma + \mu_{s,comb}^x \quad (2)$$

The $\mu_{s,comb}^x$ is a combinatorial term accounting for the size and shape differences of the molecules in the system.

From the differences between the chemical potentials of compound (X) in solvent system (S) and in pure (X), we can compute the solubility of a liquid compound. The calculation process of the solubility of the solids in water includes a conversion from the solid to the liquid state, which takes place at a certain free energy cost (ΔG_{fus}). In order to calculate the energy of fusion, we need the enthalpy or entropy of fusion as well as the melting temperature. The appropriate equations have been provided in previous papers[5,7,8].

The average absolute error (AAE) is determined from the following equation:

$$\text{AAE} = \sum \text{ABS}[(\log S_{calc} - \log S_{exp})]/N \quad (3)$$

where, S_{calc} and S_{exp} are the calculated and experimental solubilities (mg/L), respectively, N is the number of compounds used, and ABS is the absolute value.

Results and Discussion

Figures 1 and 2 show the σ-profiles and σ-potentials of the selected PCDDs, PCDFs, ClBZs and water as a solvent. The σ-profiles (Fig.1.) yield information about the molecule polarity properties, and this is reflected in the narrow distribution of the charge densities around zero. The corresponding σ-potential, which is a measure of the affinity of the solvent for a molecular surface of polarity, σ, is a simple parabola centered at $\sigma = 0$ (Fig.2.). Such a shape arises from a misfit contribution only and is equivalent to purely dielectric behaviour. The σ-profile of the water reflects its excellent ability to act as a donor as well as an acceptor for hydrogen bonding. It indicates also a favourable electrostatic interaction of water with itself, a characteristic explaining its high boiling point and surface tension. For the organic compounds, the σ-profiles point to their highly non-polar nature. The corresponding σ-potential of water reflects an unfavourable interaction with a non-polar surface.

To assess the accuracy of the COSMO-RS method, we compared the predicted aqueous solubilities of PCDDs and PCDFs with the literature values and those obtained in this study (Fig.3.).

The experimental aqueous solubility data are summarized in Table 1. Each value constitutes the average of 6 measurements. The calculated percentage standard deviation (SD) between them ranged from 2.1 to 6.8 % for the lower chlorinated PCDDs/PCDFs congeners (including dibenzo-*p*-dioxin and dibenzofuran). For the octa-CDD and octa-CDF, the percentage standard deviations were 49.6 and 24.5 %, respectively.

As can be seen from Figure 3, the COSMO-RS solubilities determined for the 19 PCDDs and PCDFs are in good agreement with most of the experimental values (including the values obtained in this study). However, large discrepancies exist for the aqueous solubilities of the higher chlorinated congeners. These discrepancies reflect the difficulties associated with the analytical determination of such low solubility congeners. In Table 2, there is a summarized statistical relationship between the experimental and calculated results obtained at 25 ^{o}C for both the PCDDs/PCDFs, and the chlorobenzenes. The absolute average errors suggest that the COSMO-RS model proposed in this study is a very accurate method for the prediction of the solubilities of PCDDs and PCDFs at 25 ^{o}C. Our further use of COSMO-RS to study PCDDs/Fs will focus on the prediction of their solubilities at a wider range of temperatures and in three inorganic salty solutions.

References

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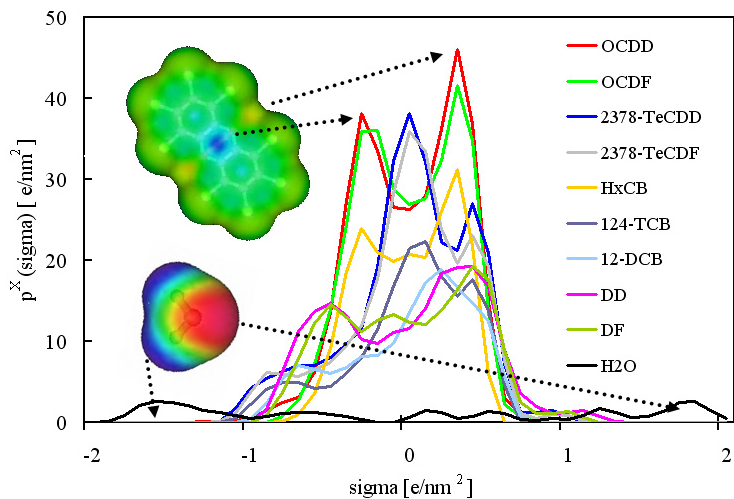
Fig.1. σ-Profiles of water and selected organic pollutants.
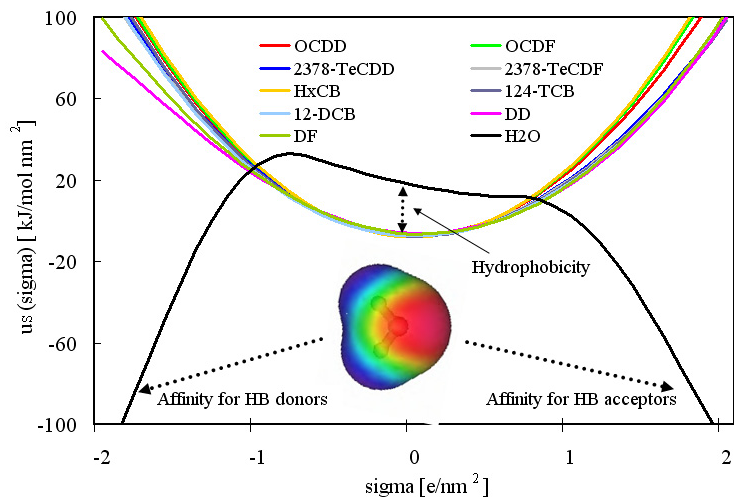
Fig.2. σ-Potentials of water and selected organic pollutants.
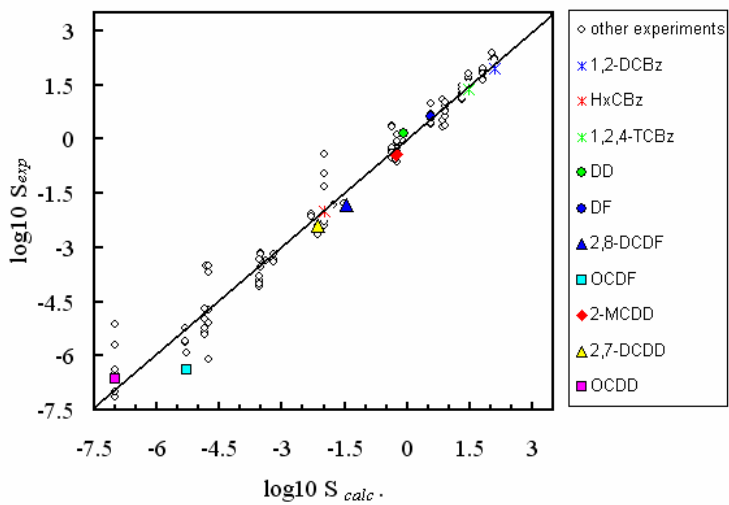
Fig. 3. Comparison of the COSMO-RS calculation and experimental results.

Table 1. Water solubility (S_w) of selected PCDDs and PCDFs measured at 25 $^{\circ}$C.

Aquoeus solubility S_w / mg $\cdot$ L^{-1}		
PCDD/Fs	This study	Literature data [6]
DF	4.73	4.22; 4.75; 4.69; 10.03
2,8-DCDF	0.0157	0.0145
OCDF	4.09*10^{-7}	1.16*10^{-6}
DD	1.24	0.842; 0.900
2-MCDD	0.420	0.319; 0.278
2,7-DCDD	0.00409	0.00375
OCDD	2.29*10^{-7}	4.0*10^{-7}; 1.0*10^{-7}; 7.4*10^{-8}

Table 2. Analysis of COSMO-RS solubilities

Group of compounds	Number of experimental data	Absolute average error (AAE)
ClBZs	105	0.182
PCDDs/PCDFs	64	0.365
Summary	169	0.274