Measurement and Prediction of the Solubility Behaviour of SelectedPersistent Organic Pollutants(POPs) in the Aqueous Environment

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学位論文題目	Measurement and Prediction of the Solubility Behaviour of Selected Persistent Organic Pollutants(POPs) in the Aqueous Environment （残留性有機汚染化合物の水環境中への溶解挙動の測定および計算予測）
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論文内容要旨

Introduction: Aqueous environment (lakes, rivers, sea, ocean) is a very complex system consisting of aqueous phase and suspended particles. Most of persistent organic pollutants (POPs) such as PCDDs, PCDFs and CBs entering the aquatic system (e.g. by direct deposition from the atmosphere to the water, atmospheric deposition to the land followed by transport of the deposited materials in storm-water runoff, from industrial and wastewater treatment plant discharges) are associated with particulate matter. The fate of POPs entered into the water system involves their transport and transfer processes between different phases or compartments (air-water exchange, sediment-water exchange, sorption and accumulation in an organisms). The efficiency of these processes (including microbial, chemical and photochemical transformations of POPs) is determined by their physical and chemical properties that, however, vary, depending on the molecular structure and type of atoms in a molecule. The aqueous solubility is a key parameter in determining mobility and controlling the distribution of the POPs in hydrologic system. Moreover, aqueous solubility values are useful in calculation of Henry's constants (water-air partitioning), soil-water and octanol-water partition coefficients, as well as in estimation of fish bio-concentration factors. The aqueous solubility data find also applications in modeling of POPs fate during some of industrial processes (for example wastewater and sewage sludge treatment). Various environmental or operating (in an industry) factors, such as temperature, dissolved salts (in a marine environment), dissolved organic matter (in soil), or pH (important for organic basis and acids chemicals) may strongly affect the solubility of chemicals as well as their sorption into and desorption from soils and sediments, thus it also is necessary to take these factors into consideration when studying the behavior of organic contaminants.

The literature survey indicates that the behavior of CBs, PCDDs and PCDFs in an aqueous system, in particular in salty solutions, is still poorly recognized and requires very extensive studies in this subject. Since the experimental determination is time consuming and very expensive the accurate predictive methods (with the minimum input data requirements) are considered as an important support when thermodynamics properties of organic pollutants are studied.

Aims and Conclusions: The main aims of the present research involved: (1) determination an aqueous solubility values for CBs, PCDDs and PCDFs at a wider range of temperatures and derivation their enthalpies of solution; (2) measuring their solubility in a salty solutions for various salts concentrations and derivation the salting parameters (Setschenow constants); (3) using these data for study the behavior of CBs, PCDDs and PCDFs in aqueous system. For accomplishment of these purposes the following steps were provided: (a) Experimental determination of the aqueous solubility of selected CBs, PCDDs and PCDFs. This part of work (Part 3) involved: the calibration of generator column (Part 2) with 3 reference compounds at room temperature, the measurement of the aqueous solubility for PCDDs, PCDFs and CBs in a wider range temperatures (including room temperature), the measurement of the ionic strength effect (sodium, potassium and calcium chloride solutions) on solubility of selected PCDDs, PCDFs and CBs. The enthalpies of solution and Setschenow constants were derived from these experimental measurements; (b) Experimental determination of melting temperatures and enthalpies of fusion for selected PCDDs/PCDFs. For this purpose a differential scanning calorimetry method (MDSC) was utilized. This part of study involved calibration (Part 2) of the equipment with 6 reference compounds and then determination of the mentioned quantities for selected PCDDs and PCDFs (Part 4); (c) Determination of the aqueous solubility for selected CBs, PCDDs and PCDFs with Conductor-like Screening Model for Real Solvent (COSMO-RS). In this part of study (Part 4) the determined quantities of enthalpy of fusion and melting temperature were utilized for the determination of free Gibbs energy required in COSMO-RS calculation. The COSMO-RS method (involving those quantities) was validated by comparison of the COSMO-RS prediction with experimental solubility values determined at 25 °C. Then the COSMO-RS solubilities of 52 compounds (involving CBs, PCDDs and PCDFs) were studied for temperatures ranging from 5 to 60 °C. These results were used for estimation the enthalpies of solution. The effect of three chlorine solutions on aqueous solubility of the all 52 compounds was also studied.

In summary the water behavior of three different groups of compounds, namely chlorinated benzenes (CBs) (12 compounds), polychlorinated dibenzo-*p*-dioxins (PCDDs) (28 compounds) and polychlorinated dibenzofurans (PCDFs) (12 compounds) was studied by application of both experimental (generator column) and calculation (COSMO-RS) methods.

The results of preliminary testing showed that the generator column as used in this study (including extraction of the aqueous phase and chromatographic analysis conditions as established here) allows to obtain aqueous solubility values of high accuracy. The observed discrepancies between experimental values measured in this study and those reported in the literature reflect the experimental difficulty of determining the solubilities of hydrophobic compounds. Since such variables as the solute purity, equilibration time, temperature, and analysis method have the potential of strongly affecting the solubility determination it is important to provide full information about the methods used.

The COSMO-RS model applied in this study showed high ability to calculate the solubility of hydrophobic compounds for wider range of temperatures and in salty solutions. The high accuracy of the COSMO-RS predictions was confirmed by statistical analysis and comparing with the experimental results (the criteria handled were absolute average error (AAE) and root means square deviation (RMSD)).

As a main result of this study a large dataset of thermodynamic quantities such as aqueous solubility, Setchenow constant, enthalpy of solution, enthalpy of fusion and melting temperature was constructed. The COSMO-RS predictions together with the experimental data yield comprehensive information about the CBs, PCDDs and PCDFs behavior in aqueous systems allowing to drawn the following conclusion:

(1) The aqueous solubility of chlorinated compounds is strongly affected by (a) the molecular structure of each group of compounds: the larger molecules of PCDDs have lower aqueous solubility values than those determined for PCDFs and CBs; (b) and by number of chlorine atoms in the molecule: the aqueous solubility decreases in the following order: mono > ...> hexa for CBs; and mono > ...> octa for PCDDs/PCDFs.

(2) The aqueous solubility of CBs, PCDDs and PCDFs increases with rising temperature. In a narrow range of temperatures these solubility values show a linear behavior, allowing to determine the enthalpies of solution. Different ranges of the enthalpies of solution for the different groups under scrutiny (CBs, PCDDs and PCDFs) indicate that these quantities are somewhat related to the molecular structure of chlorinated compounds.

(3) The activity coefficients of hydrophobic compounds decrease when the solubility of these chemicals increases. This behavior can be observed for results determined at 25 °C (the highest γ_w characterize the least soluble compounds e.g. OCDD, OCDF) as well as for temperature effect (the increasing temperature increases the solubility of chemicals thus decreasing the γ_w).

(4) In contrast to the temperature effect, the presence of strong electrolyte in water decreases the solubility of CBs, PCDDs and PCDFs. This salting - out effect, expressed as a form of Setschenow constant (K_s), strongly depends on the type of salt solutions (ionic strength) and its concentration as well as on the molar size of the individual solute molecules. However the position of chlorine atoms in the molecules seems not to be important. The range of the Setschenow constants values is highest for the larger molecules of PCDDs and decrease in the following order: $K_{PCDDs} > K_{PCDFs} > K_{CBs}$.

(5) The COSMO-RS predictions together with the experimental data yield comprehensive information about the CBs, PCDDs and PCDFs behavior in aqueous systems. The enthalpies of solution of chlorinated benzenes derived from the COSMO-RS solubility data indicate that the

influence of temperature strongly depends on the substituted chlorine atoms in a molecule and increases from mono- to hexachlorobenzene. This relationship was not observed within homologues of di -, tri -, tetra -, penta -, and hexachlorinated congeners of PCDDs and PCDFs

(6) The COSMO-RS solubilities determined for CBs, PCDDs and PCDFs for various concentrations of sodium, potassium, and calcium chlorine solutions allow to conclude that the salting-out effect is strongly affected by size of molecule and increase with a rising number of chlorine atoms in a molecule. These predicted data reflect also that the effect of the position of the chlorine substitution in a group of isomers of chlorinated benzenes and chlorinated dioxins and furans is not too significant for salting-out.

The experimental and calculated studies showed that there are strong relationships between the thermodynamic quantities and in fact, these relationships differ between individual classes of the compounds studied here. This indicates that the transport and fate of aromatic, chlorinated pollutants through the hydrologic system strongly depend on the molecular structure and number of chlorine substitution in molecules of POPs. These studies also showed that the fate of chlorinated chemicals in watery systems is strongly affected by such factors as temperature and ionic strength. The fact that the CBs, PCDDs and PCDFs tend to be salted out in presence of chlorine salts in water even at small concentrations can be valuable information for further studies concerning the removal of these compounds during some industrial processes (e.g. removing of organic contaminants from fly ash by washing them with water).

In the future, the aqueous solubility values obtained in study can be useful in calculation of water-air, soil-water and octanol-water partition coefficients. In additional the solubility data along with the thermodynamic quantities determined in this study (melting temperature, enthalpy of solution and melting of fusion) can be used for detailed studies of dissolution processes of the solid solutes of PCDDs and PCDFs.

Additional purpose of this thesis was to study the behavior and fate of PCDDs and PCDFs in industrial aqueous system, namely in a selected municipal wastewater treatment plant (MWTP). This research (Part 5) involved determination of the changes in concentrations of selected chlorinated congeners of PCDDs and PCDFs in wastewater samples (incoming to - and outgoing from - the MWTP) and in sewage sludge samples. The changes in concentrations of

PCDDs and PCDFs congeners were also studied in the three different sludge samples (excess, digested, dewatered) collected from the successive stages of sludge treatment in order to check how much the sludge treatment affect the fate of PCDDs and PCDFs. The results presented in this part evidently showed, that the fate of PCDDs and PCDFs in industrial aqueous system is very complex. By large, their behavior, in particular their distribution between aqueous phase and solid particles suspended in the water, can be understand and assessed from their chemical - physical properties. Since the PCDDs/PCDFs have very low solubility it is not surprised that they will cheerful adsorb to the particles of sewage sludge, which, on the other hand, contains organic matter thus can be excellent sorbent (sink) for these hydrophobic compounds. The results presented here and those of the literature survey, indicated that the fate of PCDDs/PCDFs is strongly affected by the biological processes (anaerobic digestion – studied here or aerobic/anaerobic digestion - lit. data) during sludge treatment as well as by presence of the other organic (chlorophenols) pollutants in sludge matrix. Since the effect of these processes/factors differ for individual compounds thus the assessment of the fate of PCDDs and PCDFs in such industrial system becomes more complex and more difficult. In fact, in order to get comprehensive knowledge on the fate of PCDDs/PCDFs and other pollutants during wastewater treatment and in sewage sludge, it requires increase effort and mutual cooperation of many researchers.

論文審査結果の要旨

環境動態予測のみならず排水処理の際の基礎データとなるダイオキシン類の水溶液中における飽和溶解度の報告例は、その必要性にかかわらず、少ない。特にダイオキシン類を含む飛灰を水処理する際に重要となる温度依存性および塩類を含んだ系の実測値は国内外ともにほとんど見当たらず、早急に測定値が求められている。本研究では、種々の塩類を含む水溶液中での有機ハロゲン化合物類の溶解度測定を行った。さらに実験だけでは広範な組成と多くの異性体を持つ有機ハロゲン化合物類の極一部しかカバーできないので、分子軌道法により水溶液中での電子状態の計算による溶解度の推算を行い実測値との対応を行い、種々の条件での有機ハロゲン化合物類の水中の溶解度を求めるための計算科学の手法を確立した。さらには、実機排水処理工程における排水およびスラッジ中のダイオキシン類濃度を測定し、測定・計算した溶解度を用いて挙動の解明を行った。

論文は全6章で構成されている。

第1章は総論であり、本研究の背景および目的を述べている。

第2章は、溶解度の測定法ならびに量子化学計算を行うために必要な基本的物性値の測定方法についてまとめている。

第3章は、クロロベンゼンとダイオキシン類の水中の溶解度を実験で求めている。特にクロロベンゼンは実験手法として採用したジェネレーターカラム法の精度を確認する意味も持たせており、今回の実験手法が十分な精度を持つことを明らかにしている。ダイオキシン類については、塩素数が多いほど溶解度が小さいことを明らかにし、これまでまったく報告がなかった溶解度に及ぼす NaCl, KCl, CaCl2 などの塩類の濃度についても検討し、それぞれ塩類濃度が増加するほど溶解度が小さくなることを見出し、いわゆる塩析効果を確認した。その影響の度合いは、$CaCl_2$>NaCl>KCl で、イオン強度が弱いほど大きいことを示した。

第4章は、溶解度を量子化学手法で推定する方法を確立し、その計算結果を実測値と比較し、誤差範囲で十分一致することを示している。計算手法は、はじめに化合物の立体電子配置を Gaussian98 で求め、化学ポテンシャルを算出し、その後統計熱力学モデル COSMO-RS を用い、具体的に溶解度を算出するものである。既存のプログラムの利用であるが、このような計算手法は初めて採用され、実際に疎水性の有機化合物について適用可能であることを示している。

第5章は、実際の廃水処理場でダイオキシン類含有スラッジを処理した際の処理過程のダイオキシン類のバランスを実測し、基礎的に得られた溶解度の値からスラッジへの吸着ならびに処理過程での分解について考察している。

第6章は総括であり、各章の成果をまとめている。

以上要するに本論文は、環境評価に必要なダイオキシンに代表される有機塩素化合物の溶解度を実測と計算によって求め、特に計算によってかなりの精度で溶解度を求めることに成功しているものであり、環境科学の発展に寄与するところが少なくない。

よって、本論文は博士（学術）の学位論文として合格と認める。