SORPTION OF POPS ON PARTICLES SUSPENDED IN WATER - MEASURING AQUEOUS SOLUBILITY OF SELECTED ORGANIC COMPOUNDS USING A GENERATOR COLUMN

Sylwia Oleszek-Kudlak[1], Etsuro Shibata[1], Takashi Nakamura[1], and Alfons Buekens[2]

1 Institute of Multidisciplinary Research for Advanced Materials, Research Center for Sustainable Materials Engineering, 1,1 Katahira, 2-Chome, Aobaku, Sendai, Japan.
2 Department of Chemical Engineering and Industrial Chemistry, Free University of Brussels, Pleinlaan 2, 1050 Brussels, Belgium

Introduction
Fly ash, collected from incinerator flue gases, is one of the most hazardous by-products from municipal solid waste incineration (MSWI). The presence in fly ash of persistent organic pollutants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are well established[1-3]. Hence, it is classified as a hazardous material and further treatment is required prior to its disposal in landfills in order to reduce a potential leaching to the environment. In the case of heavy metals immobilisation is normally required[4, 5.] One of the treatment methods for removing salts and even POPs from fly ash is washing with water[6]. In order to establish suitable operating conditions for this process, some more data on POPs is required such as: water solubility, octanol/water partition coefficient, vapor pressure, and Henry's Law constant. The relationship between aqueous solubility and some operating conditions affecting solubility (e.g. temperature, pH, salinity etc.) is useful in understanding and modeling the fate of these compounds in aqueous solution. Experimental results, reported in this paper, are initial results in a wider research aiming at testing of the behavior of selected hydrophobic compounds in aqueous system at a laboratory scale. Water solubility of biphenyl, 1,2-dichlorobenzene and hexachlorobenzene is measured using the generator column method. The temperature dependencies on the aqueous solubilities of 1,2-dichlorobenzene and hexachlorobenzene are investigated. Enthalpies of solution, calculated from van't Hoff plots, are derived.

Methods and Materials
Compounds and reagents used are highest purity. The water is distilled and passed through the NANOpure® Diamond ™ TOC-UV system. The column (200 mg/3 ml; J.T. Baker) used for SPE process is packed with reversed phase Octadecylsilane (C_{18}) bonded onto silica gel. The generator column (300 mm x 3 mm i.d.) is made of Pyrex glass, and enclosed in a water jacket connected to an isothermal bath (ThermoHaake K 10 ± 0.01 K). Tubing and connections are of Teflon. Each compound is dissolved in hexane or ethyl acetate and coated on 60-80 mesh Chromosorb W. Solvent is removed using a rotary evaporator for 2-3 h. The coated chromosorb is dry packed into the generator column. The amount of coating applied is ca. 3.0 % (w/w), 0.2 % (w/w), 2.0 % (w/w) for biphenyl (BiPh), hexachlorobenzene (HxCBz), and 1,2-dichlorobenzene (1,2-DCBz) respectively. Water is pumped at a flow rate of 0.5-1.8 ml/min by a Metarol pump, starting from a thermostatic glass reservoir vessel, then through the generator column and finally it is directed either to the tarred flask or through the extractor column. For initial conditioning the generator column 100-300 ml of initial water volumes is used. Aqueous saturated solutions of biphenyl and 1,2-dichlorobenzene collected in the tarred flask are drained into the separator funnel and extracted with appropriate volume of hexane. The hexachlorobenzene-saturated aqueous solution

eluting from a generator column is passed through the SPE cartridge. The quantities of aqueous eluate collected in the tarred flask are weighed. After collection of a sufficient eluate volume, the SPE cartridge is disconnected, washed with reagent-grade water (3 ml) and dried under vacuum. The analyte is eluted from the cartridge with hexane (3 x 0.3 ml) under vacuum. Each portion of hexane is left in contact with sorbent for 2 minutes to reach equilibrium. The collected extract is dried with anhydrous sodium sulfate to remove any remaining water. The concentrations of hexachlorobenzene and 1,2-dichlorobenzene in hexane are determined by GC (a Hewlett Packard Model 1991Z-413) equipped with an electron capture detector (ECD). A methylsiloxane capillary column (HP-1, 30 m x 0.32 μm x 0.25 μm) is used. A GC – MS analysis of biphenyl is performed on a Hewlett Packard 5973 GC-MSD system. A phenylmethyl-siloxane capillary column (HP-5MS 5% 30 m x column. 250 μm x 0.25 μm) is used. Each concentration is determined by measuring peak area and comparing this response to a standard curve.

Results and Discussion
According to The Office of Prevention, Pesticides and Toxic Substances (OPPTS) guidelines[7, 8] the aqueous solubility of reference compounds is determined experimentally to validate the procedure. Preliminary tests for each compound are conducted at 25^oC at two different flow rates. Results are summarized in Table 1. Each of the reported values is determined as the average of at least 5 measurements. Each experiment takes almost 14 -15 hours. The first sample of eluate is taken after 2-3 hours although a saturated concentration is obtained after 1 hour.

OPPTS guidelines[8] accept a percentage variation < 30 % in the measured concentration of a saturated solution when using the elution column method. In this work this percentage deviation amounts to 5.7 % and 5.1 % for hexachlorobenzene, 6.9 % and 5.3 % for biphenyl and 3.8 % and 4.8 % for 1,2-dichlorobenzene in two independent runs.

Table 1: Aqueous solubility of hexachlorobenzene (HxCBz), biphenyl (BiPH) and 1,2-dichlorobenzene (1,2-DCBz): mean value and standard deviations at 25^oC.

Aqueous solubility Sw [mg/L]				
	This study		**Literature data**	
Compd.	**Flow rate, ml/min**	**Generator column GC-ECD**	**Gen. column GC-ECD**	**Other methods[13]**
HxCBz	0.740	0.01010 ± 0.00058	0.005[13]; 0.00544[9]; 0.047[10;]	0.006; 0.110; 0.0039; 0.0054; 0.0052; 0.005; 0.38
	1.510	0.00966 ± 0.00050		
BiPh	0.660	5.366 ± 0.3730	6.71[10]	7.00; 7.45; 7.48; 7.50; 7.08; 5.94; 3.87; 8.08[12];
	1.130	5.323 ± 0.2830		
1,2-DCBz	0.500	93.652 ± 3.6020	92.3[10]	149.4; 137[11]; 169; 152.9; 97.0; 109
	1.100	94.406 ± 4.5700		

[13]Most of these data is collected by Shiu et al. (2000); [9]Shiu et al. (1997); [10]Miller et al. (1984); [11]Banarjee (1984); [12]Bruggeman et al (1982).

This preliminary test shows that the generator column method provides reproducible results. Proper initial conditioning of the generator column with water, clean non-absorbing connection tubes and maintaining stable flow rates are important to get reproducible and accurate results. Table 1 reports on literature results on aqueous solubility and compares them with the results

obtained in this study. For example the experimental average water solubility of hexachlorobenzene measured by generator column in this work is about 0.0100 mg/L. Literature values determined by the same method vary from 0.0054 mg/L[9] to 0.047 mg/L[10], those by other method from 0.005-0.380 mg/L. The range of water solubility values of hexachlorobenzene, as approved by OPPTS 830.7840, is 0.00119 - 0.0231 mg/L at 25° C. A similar variation of aqueous solubility values for biphenyl and 1,2-dichlorobenzene is observed in the references. The wide range of encountered values demonstrates the difficulty of determining the aqueous solubility of hydrophobic persistent compounds.

The dependence of aqueous solubility of hexachlorobenzene and 1,2-dichlorobenzene on temperature is also determined. Their solubility increases with rising temperature (Table 2). Enthalpies of solutions are calculated from van`t Hoff equation: $\ln X = - \Delta H_s / RT + C$, where: X is the molar value of aqueous solubility, T the absolute temperature and R the gas constant.

Table 2: Aqueous solubility and activity coefficient of 1,2-dichlorobenzene (1,2-DCBz) and hexachlorobenzene (HxCBz) at different temperatures, enthalpy of solution.

Compd.	Aqueous solubility S_w [mg/L] Experimental data					$\Delta H_{solution}$ [kJ/mol]	$\Delta H_{solution}$ [kJ/mol]
	15° C (n=10)	**25° C** (n=5)	**35° C** (n=10)	**45° C** (n =10)	**55° C** (n=10)	This study	Ref. value
1,2-DCBz	-	94.406 $\pm$ 4.57	108.012 $\pm$ 3.09	122.665 $\pm$ 7.50	139.107 $\pm$ 5.45	10.49	11.30[13]
γ_w This study	-	$8.65*10^4$	$7.55*10^4$	$6.66*10^4$	$5.87*10^4$		
HxCBz	0.0070 $\pm$ 0.00057	0.0096 $\pm$ 0.00049	0.0175 $\pm$ 0.00073	0.0238 $\pm$ 0.00180	0.0377 $\pm$ 0.00508	33.50	33.70[9] 36.90[13]
γ_w[**)] This study	$8.27*10^7$	$7.78*10^7$	$5.49*10^7$	$5.08*10^7$	$3.97*10^7$		

[9]Shiu et al. (1997); [13]Collected by Shiu et al. (2000); γ_w[**)] the activity coefficient is calculated using reference data[13] (ΔH_{fusion}=18.7 kJ/mol, $T_m=227^o$ C).

The enthalpy of solution for hexachlorobenzene (33.50 kJ/mol) found in this study is comparable to 33.7 kJ/mol reported by Shiu et al. (1997) and to 36.9 kJ/mol reported by Opperhuizen et al. (1987). The enthalpy of solution for 1,2-dichlorobenzene (10.49 kJ/mol) found in this study is also comparable to 11.30 kJ/mol obtained by Klemenc & Low (1930). Shiu et al. (1997) suggested the estimating the enthalpy of solution for solid and liquid chlorobenzenes by form: $13 + 3.5$ n kJ/mol, where n is the number of chlorine atoms. From that correlation the enthalpy of 1,2-dichlorobenzene should be near 20 kJ/mol. In the Figure 1, the experimental results of solubility obtained in this study are compared with literature data (logarithmic scale).

The experimental solubility values are useful for calculation of activity coefficient (Table 2). The thermodynamic equation of the relationship between solubility and activity coefficient for a solid compounds is: $X = 55.56/\gamma_w \exp [-\Delta H_{fusion}/R (1/T – 1/T_m)]$, where: X is the molar aqueous solubility, γ_w is the activity coefficient in pure water, ΔH_{fusion} is the enthalpy of fusion, T_m the melting point, T is an experimental temperature. For a liquid compounds, the aqueous activity coefficient is given by equation: $\gamma_w = 1/ V_w*X$; where V_w is a molar volume of water (0.018 mol/L).
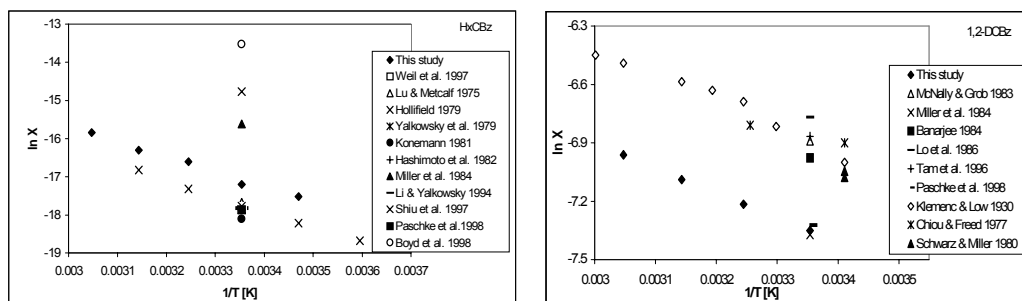
Figure 1: van`t Hoff plot of the logarithm of the mole fraction solubility of hexachlorobenze (HxCBz) and 1,2-dichlorobenzene (1,2-DCBz) versus 1/T (comparison with literature values).

The influence of the temperature on the activity coefficient is significant. In pure water, the activity coefficient of hexachlorobenzene decreases with increasing solubility of this compound. In other words, the activity coefficient decreases when the temperature increases. The same behavior is observed for the activity coefficient of 1,2-dichlorobenzene.

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