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DETERMINATION OF AQUEOUS SOLUBILITIES OF TETRACHLOROBENZYLTOLUENES INDIVIDUALLY AND IN A MIXTURE BY A MODIFIED GENERATOR COLUMN TECHNIQUE

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Abstract

Aqueous solubilities of nine tetrachlorobenzyltoluenes (TCBTs) were determined at 25 °C using a generator column technique. The aqueous solubility of 2,2',4,4',6,6'-hexachlorobiphenyl was determined and appeared to be relatively high, but still comparable with literature values of this PCB. Solubility values of TCBTs ranged from 0.00139 to 0.01829 g.m⁻³. Additional aqueous solubilities of the same TCBTs added as a mixture were determined, ranging from 0.00076 to 0.00489 g.m⁻³. No correlations were found between the aqueous solubilities of TCBT isomers, determined individually and in a mixture and between the aqueous solubilities and 1-octanol/water partition coefficients, respectively. Copyright © 1996 Elsevier Science Ltd

Introduction

Commercial mixtures of polychlorinated biphenyls (e.g. Aroclors) have been widely used in a variety of industrial applications, because of their unique physical and chemical properties, such as low volatility, high thermal stability, low dielectric constant, resistance to oxidation and reduction, and non-flammability. However, the same chemical properties that make these commercial mixtures of PCBs desirable for industrial use, render them environmentally persistent, since they are resistant to degradation by most ecosystems. Knowing the environmental impact of PCBs, an effort was going on to replace almost every industrial application of PCBs. One group of PCB replacements in underground mining are the tetrachlorobenzyltoluenes (TCBTs). TCBTs are the main components in products marketed as Ugilec 141. Theoretically 96 TCBT isomers are possible (Fig. 1).

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Figure 1. Molecular structure of TCBT isomers

This current study reports the determination of aqueous solubilities of TCBTs. Knowledge of the aqueous solubility is fundamental for describing processes that control the environmental fate and distribution of contaminants. Many reports have been published on measurements of aqueous solubility of polychlorinated biphenyls (PCBs) (Miller *et al.*, 1984; Dickhut *et al.*, 1986; Opperhuizen *et al.*, 1988; Billington *et al.* 1988), however, no data on the aqueous solubility of TCBTs have been published before. A conventional method for preparing aqueous solubilities is referred to as the shake flask method (Weil *et al.*, 1974). An excess amount of chemical is added to a flask containing distilled water and stirred or shaken until equilibrium is reached. This method works well for fairly soluble compounds. For compounds such as PCBs, few accurate measurements are available because of the experimental difficulty to determine very low solubilities. A more useful technique for low solubility measurements is the generator column method (May *et al.*, 1978; DeVoe *et al.*, 1981; Sokol *et al.*, 1992; Wasik *et al.*, 1983). Briefly, with this technique water can be saturated very quickly by passing it through a temperature-controlled generator column packed with inert material on which the test chemical is coated. In several other studies (Miller *et al.*, 1984; May *et al.*, 1978; DeVoe *et al.*, 1981; Wasik *et al.*, 1983) flow-through systems for saturation with loaded generator columns were applied. In this study a method comparable to those reported by Veith and Comstock (1975), Bruggeman *et al.* (1983) and Opperhuizen *et al.* (1988) has been used. These authors used a recirculation system instead of a flow-through systems.

In order to compare the solubility values from this study with literature values, the aqueous solubility of a low soluble compound, 2,2',4,4',6,6'-hexachlorobiphenyl, was determined. Besides aqueous solubilities of individual TCBTs, aqueous solubilities of TCBTs added as a mixture were determined. Measuring isomers together might be less time consuming, therefore, less expensive and result in more systematic differences between isomers. Both relationships between individual and mixture values and relationships between aqueous solubilities and 1-octanol/water partition coefficients (Van Haelst *et al.*, 1994) were discussed.

Experimental section

Reagents

Nine TCBTs (nomenclature and numbering according to Ehmann and Ballschmiter (1989), were purchased from Promochem; 2,2',4,6'-5Me (no 28); 2,2',4,5'-5Me (no 25); 2,2',5,5'-4Me (no 36); 2,2',4,4'-5Me (no 22); 2,2',4,6'-3Me (no 27); 2',3,4,6'-6Me (no 80); 2,2',4,4'-3Me (no 21); 2,3',4,4'-5Me (no 52); 2',3,4,4'-6Me (no 74). 2,2',4,4',6,6'-hexachlorobiphenyl, IUPAC numbering PCB 155, was obtained from Promochem, chromosorb G AW (60-80 mesh) from Chrompack and silica (60, 70-230 mesh) from Merck. n-Hexane was obtained from Janssen Chimica and 2,2,4-trimethylpentane from Rathburn. Both solvents were redistilled before use. The water was distilled in an all-glass apparatus.

Generator Column

The generator column was placed in series with a small recycling pump, all connections were either Teflon or glass. Around 2 litres of water were recirculated by the pump through the saturation system. The recycle rate was controlled by varying the voltage of the pump. Aqueous concentrations of PCB 155 and TCBTs were found to be independent of flow rate within the region used here. The column was packed with Chromosorb G AW, coated with the respective chemical(s). Packings were held in place by glass wool plugs at the ends of the column. A filter was placed directly after the generator column. Two specimen of the apparatus were used in this study. Both were temperature controlled to ± 0.1 °C in water baths by using a constant temperature water circulator.

To prepare the coated Chromosorb G AW, the chemical was dissolved in 15 cm³ hexane, which was slurried with 20 g Chromosorb G AW. While the mixture was continuously shaken, the solvent was slowly evaporated from the slurry leaving the Chromosorb G AW coated with the chemical. For the determination of aqueous solubilities of PCB 155 or the individual TCBTs, 0.5 mg chemical was used. For the determination as a mixture, 0.4 mg of each of the eight TCBT isomers was dissolved in hexane.

Procedure

To examine the time needed to reach equilibrium duplicate 50 cm³ samples of water saturated with PCB 155 were taken after 2, 3 and 4 days. 50 cm³ samples saturated with TCBTs, added individually or as a mixture, were collected after 5 days, having verified for one TCBT that equilibrium was reached within 5 days. Only for TCBT samples the water was filtered after sampling to exclude possible colloidal emulsions. The extraction method was liquid/liquid extraction using hexane (9 cm³) as the extractant. As clean-up a 0.7 g silica column was used. The extract was eluted with 15 cm³ n-hexane and the eluates were concentrated to approximately 1 cm³ by a gentle stream of nitrogen.

Two internal standards were used for all samples for the total analytical procedure: the first internal standard (TCBT 22) was added in the beginning of the procedure, directly after sampling to determine the recovery of the analytical procedure of the sample, the second internal standard, the injection standard, was added just prior to GC-analysis to correct for injection volume and fluctuations in detector response. To obtain an indication of losses during separate steps of the analytical procedure recoveries of a hexane solution spiked with a mixture of TCBTs were determined. A mean recovery value of 71% was found for liquid-liquid extraction and 86% for silica column clean-up. This implied an overall mean recovery of not greater than 61%, which needs to be improved in future research. All samples here were recovered in an amount in between 55 and 61%. Considering the low obtainable overall mean recovery of maximum 61%, this seemed to be acceptable.

GC analysis

For analysis, 1 μ l of the extract of the water sample was injected automatically three times into a Hewlett-Packard 5890A gas chromatograph, equipped with a ^{63}Ni electron capture detector and an on-column injector with autosampler A200S (Carlo Erba). The GC was connected to a HP 3396A integrator. A 30-m J&W DB-5 0.32 mm i.d. fused silica capillary column (film thickness: 0.25 μm) was used with a 2 m 0.53 mm retention gap. The carrier gas was helium and the make-up gas was Ar/CH_4 0.5-5%. The temperature program was: 120°C for 0.4 min; 70°C/min; 200°C for 1 min; 1°C/min; 211°C for 0 min; 40°C/min; 320°C for 6 min.

Results and discussion

Aqueous solubility determinations

The experimental values of aqueous solubilities for PCB 155 and TCBTs individually and TCBTs determined as a mixture are given in Table I and II. All the results in Table I and II showed no outliers after performing the Dixon's outlier test (Miller and Miller, 1993).

Table I Determination of the aqueous solubilities (S) of PCB 155 after 2, 3 and 4 days

t/day	S/g.m ⁻³
2	0.00125
	0.00505
3	0.00330
	0.00430
4	0.00065
	0.00605
mean	0.0034* $\pm$ 0.0021

mean of six samples with standard deviation

Table I reports the aqueous solubilities for PCB 155 determined in two test systems after 2, 3, and 4 days of saturation. No significant difference in solubility values of PCB 155 was shown after 2, 3 and 4 days, therefore, equilibrium seems to be established within 4 days. The mean of these six aqueous solubility determinations of PCB 155 was $0.0034 \pm 0.0021 \text{ g.m}^{-3}$ (Table I).

In Table II, experimental values are listed of the aqueous solubility of 9 individual TCBTs and of 8 TCBTs added as a mixture. The mean of *n* samples collected from both saturation systems is given along with standard deviation. All samples were taken after 5 days of saturation at 25°C. Aqueous solubility values of individual TCBT isomers ranged from (0.00139 ± 0.00066) to $(0.01829 \pm 0.00648) \text{ g.m}^{-3}$, whereas aqueous solubility values of TCBTs determined as a mixture ranged from 0.00076 ± 0.00046 to $0.00489 \pm 0.0016 \text{ g.m}^{-3}$. The melting points of the TCBTs are given in Table II to facilitate the interpretation of the aqueous solubility data.

Table II Aqueous solubilities (S) of TCBT-isomers

TCBT (No.) [*]	m.p./°C ^{**}	S/g.m ⁻³	
		individual (n)	mixture (n)
2,2',4,6'-5Me (28)	114	$0.00139 (3) \pm 0.00066$	0.00145 ± 0.00050
2,2',4,5'-5Me (25)	78.7-80.5	$0.00281 (4) \pm 0.00033$	0.00191 ± 0.00030
2,2',5,5'-4Me (36)	74.3-75.6	$0.00302 (2) \pm 0.00016$	0.00076 ± 0.00046
2,2',4,4'-5Me (22)	61.9-63.7	$0.01041 (12) \pm 0.00150$	...
2,2',4,6'-3Me (27)	87	$0.00326 (2) \pm 0.00032$	0.00382 ± 0.00021
2',3,4,6'-6Me (80)	107	$0.01829 (4) \pm 0.00648$	0.00489 ± 0.0016
2,2',4,4'-3Me (21)	76	$0.01283 (9) \pm 0.00305$	0.00097 ± 0.00029
2,3',4,4'-5Me (52)	75	$0.00211 (4) \pm 0.00080$	0.00328 ± 0.0011
2',3,4,4'-6Me (74)	83	$0.0116 (6) \pm 0.00282$	0.00452 ± 0.0018

^{*} in order of elution, nomenclature and numbering according to Ehmann and Ballschmïter (1989)

^{**} kindly provided by Promochem, Germany

^{***} TCBT 22 was used as an internal standard

Method evaluation

With regard to the reproducibility of the method, the results should be compared with literature values derived with exactly the same method. As no determinations of aqueous solubilities of TCBTs are available in the literature, the aqueous solubility value of PCB 155 was used to evaluate the reproducibility of the method.

Reported aqueous solubility values of PCB 155 determined by the generator column technique vary from 0.00041 g.m⁻³ (Miller *et al.*, 1984), 0.00055 g.m⁻³ (Dickhut *et al.*, 1986), 0.0009 g.m⁻³ (Weil *et al.*, 1974), 0.00109 g.m⁻³ (Oppenhuizen *et al.*, 1988) to 0.0023 g.m⁻³ (Dunnivant and Elzerman, 1988). The variation in these values, determined with the same method, displays the difficulty of measuring the aqueous solubility of hydrophobic compounds. A consequence of using a generator column technique with a recirculation system might be the formation of stable micro-crystals. These stable micro-crystals usually give higher aqueous solubility values, which might explain the relatively high aqueous solubility value of PCB 155 (0.0034 ± 0.0021 g.m⁻³) determined in this study. However, high values are still found after four days of recirculation and a lower value of PCB 155 is found by Oppenhuizen *et al.* (1988) (0.00109 ± 0.0001 g.m⁻³), who used a fairly similar method. As our PCB 155 value was not completely out of order and considering the fact that in contrary to the PCB 155 samples, the TCBT samples were filtered, we found the method reproducible enough to determine the TCBT values. Furthermore, in contrary to the relatively large deviations between the aqueous solubilities of PCB 155, variation in the TCBT determinations were quite small, considering the amount of determinations of some isomers (Table II).

Individual-mixture differences

No correlation is found between the aqueous solubility data of individual and mixture TCBTs ($r=0.22$) (Table II). Some isomers have similar solubilities (TCBT 28), added individual or in a mixture, whereas others decrease (TCBT 25, 36, 80, 21) or increase (TCBT 27, 52, 74) added in a mixture. The variability of these data might partly be due to the narrow range of the experimental values and the large experimental errors compared with these ranges.

Banerjee (1984) determined aqueous solubilities of mixtures of liquid components, of solid components, and of both liquid and solid components in various 'mixture' compositions. The results varied with the phase of the solute mixture, the hydrophobicity of the components and the composition of the mixture. A calculation of the deviation from ideality as a possible adjustment by the UNIFAC equation might correct the 'mixture' results for activity coefficients (Banerjee, 1984). Unfortunately, this theory could not be applied to our results as the exact phase of TCBT isomers in the mixtures on the generator column was not known. In addition, only one composition i.e. equal amounts of TCBT isomers (0.4 mg) were added in the mixture.

Relation with 1-octanol/water partition coefficients

There has been considerable interest in the relationship between the aqueous solubility of subcooled liquids and 1-octanol/water partition coefficient. The approximately inverse correlation between aqueous solubility and 1-octanol/water partition coefficients has been demonstrated years ago by Hansch *et al.* (1968) and Chiou *et al.* (1977). Compounds, which are solid at 25°C require a correction leading to the solubility of subcooled liquids (Banerjee *et al.*, 1980). Subcooled liquid aqueous solubilities, calculated by introducing the melting point temperature effect, only slightly improved the correlation between the experimental values of aqueous solubilities and the 1-octanol/water partition coefficients of the nine respective TCBT-isomers ($r = 0.11$ instead of $r = 0.07$ before correction).

Conclusions

New solubility data of TCBTs were measured with a generator column method in duplicate systems. The determined aqueous solubility of PCB 155 was relatively high compared with literature data, but still within the range of these data. The aqueous solubilities of TCBTs, determined as a mixture showed no correlation with the values determined individually and, therefore, cannot be recommended in order to save time and money or in order to obtain more systematic differences between isomers.

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