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Aqueous Solubilities and Octanol−Water Partition Coefficients of Cymenes and Chlorocymenes

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The aqueous solubilities and octanol−water partition coefficients of *o*-cymene, *m*-cymene, *p*-cymene, 2,3-dichloro-*p*-cymene 2,5-dichloro-*p*-cymene, 2,3,6-trichloro-*p*-cymene and tetrachloro-*p*-cymene, were determined at 25 °C using GC and HPLC methods. These properties correlate well with additive LeBas molar volumes.

Introduction

Aqueous discharges to the environment from pulp mill bleach plants of dissolved wood degradation products and products of reactions between bleaching chemicals and the pulp are a continuing source of pollution. Bleaching using chlorine produces a wide variety of chlorinated compounds in the spent bleach liquor. Among these, the neutral or nonpolar compounds are of particular concern, since many of them are persistent and toxic and may accumulate in aquatic food chains because of their hydrophobicity. One group of those nonpolar organochlorines is the chlorinated cymenes and cymenenes (Rantio, 1992; Kuokkanen, 1989), which originate in coniferous softwoods, such as pine and spruce.

The cymenes or isopropyltoluenes, which are structurally related to the monoterpenes, are difficult to remove completely from the pulp before bleaching (Dyrssen, 1978). The halogenated *p*-cymenes result from substitution reactions of the parent molecule during pulp bleaching. Chlorinated cymenes are major components of the neutral fraction of spent bleach liquor of sulfate and sulfite plants (Bjørseth et al., 1979; Kuokkanen, 1981). These compounds have also been found in biota in the receiving waters (Paasivirta, et al., 1983). Rantio (1992) has detected chlorocymene isomers in pulp mill effluents, sludges, and biota at significant levels of μg/L in effluents and μg/g in lipid phases, indicating appreciable bioaccumulation.

Two properties strongly influence the environmental fate of these substances. Aqueous solubility is an indirect measurement of the activity coefficient of the solute in water, and as such it affects the partitioning and transport of the solute in the environment. It can affect adsorption and desorption in soils and sediments and air−water partitioning, i.e., evaporation and absorption. It may also influence processes of transformation by hydrolysis, photolysis, oxidation, reduction, and biodegradation in water (Lyman, 1982). The octanol−water partition coefficient K_{OW} is frequently used as a descriptor of hydrophobicity and characterizes the tendency to partition to lipid phases in aquatic organisms. Rantio and Paasivirta (1996) have discussed how these properties can be used in mass balance models to predict the environmental fate of the chlorocymenes and the resulting exposure experienced by aquatic organisms.

Experimental Section

Chemicals. *o*-Cymene, 99%, *m*-cymene, 99%, *p*-cymene, 99%, and 1-octanol, 99%+, were obtained from Aldrich Chemical Co.; 2,3-dichlorocymene, 2,5-dichlorocymene, 2,3,6-trichlorocymene, and tetrachlorocymene were kindly supplied by Dr. Tiina Rantio of University of Jyväskylä, Finland, and were of unspecified purity. All chemicals were used without further purification. HPLC grade methanol and hexane were obtained from Caledon Laboratories, Ontario. Double-distilled water was used to prepare all saturated solutions, and Milli-Q ultrapure deionized water (Millpore Corp., Milford, MA) was used with methanol as the mobile phase for HPLC analysis.

Methods. (a) Aqueous Solubility. The saturated solutions were prepared by adding excess amounts of cymenes or their chlorinated derivatives to 50 mL Erlenmeyer flasks containing distilled water. The flasks were shaken gently by a wrist-action shaker or stirred by a magnetic stirrer for 24 h and allowed to settle at 25 °C in a temperature chamber for at least 48 h before analysis. Analysis was performed either by a HPLC or a GC system depending on the detector sensitivity.

The HPLC system was a Waters Associates (Millford, MA) liquid chromatograph consisting of a Model 6000 solvent delivery system, a Model M45 solvent delivery system, a Model 721 system flow controller, and a Model 440 UV absorbance detector with 254- and 280-nm kits. The HPLC system was operated in an isocratic mode with a mobile phase of methanol/water mixture (85:15, v/v) at a flow rate of 1.2 mL/min. The analytical column was a Waters 3.9 mm o.d. × 300 mm long μBondapak C_{18} column. Integration of the peak area was recorded by a Waters Model 730 data module. Aqueous samples were directly injected onto the column. Calibration standards were prepared by dissolving known amounts of the chemical in methanol.

(b) Determination of the Solubilities by Gas Chromatography. The saturated aqueous solution was extracted with hexane and directly injected onto the GC analytical column through a capillary injection port. A Hewlett-Packard Model 5890 Series II gas chromatograph equipped with a ^{63}Ni electron capture detector was used for the chlorinated cymenes and a flame ionization detector for the cymenes. A J&W Durabond DB-17 30 m long × 0.32 mm i.d. fused silica capillary column was used. The injection port temperature was set at 300 °C and the detector at 320 °C, and the GC oven was in the isothermal mode at between 120 and 200 °C. Peak areas were

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Table 1. Aqueous Solubilities of Selected Cymenes and Chlorocymenes at 25 °C

compound	molecular mass/g·mol^{-1}	melting point/°C	LeBas molar volume V_M/cm^3·mol^{-1}	measured solubility S/g·m^{-3}	liquid or supercooled liq. solubility C_L^S/mol·m^{-3}	method	lit. value S/g·m^{-3}
o-cymene	134.2	−71.5	184.8	48.2 ± 1.4	0.36	HPLC-UV	
m-cymene	134.2	−63.7	184.4	42.5 ± 2.4	0.32	HPLC-UV	
p-cymene	134.2	−67.9	184.8	50.7 ± 2.3	0.38	HPLC-UV	34.2[a]
2,3-dichloro-*p*-cymene	203.2	<25	226.6	5.9 ± 0.2	0.029	GC-ECD	
2,5-dichloro-*p*-cymene	203.2	<25	226.6	4.9 ± 0.18	0.024	GC-ECD	
2,5,6-trichloro-*p*-cymene	238.6	<25	247.5	1.0 ± 0.01	0.004	GC-ECD	
tetrachloro-*p*-cymene	274.1	60	268.4	0.15 ± 0.004	0.0012	GC-ECD	

[a] Banerjee et al., 1980.

Table 2. Octanol−Water Partition Coefficients (K_{OW}) of Cymenes and Chlorocymenes at 25 °C

compound	concn in aq. phase/(g·m^{-3})	concn in octanol phase/(g·m^{-3})	log K_{OW}	method	lit. value log K_{OW}
p-cymene					4.1[a]
2,3-dichloro-*p*-cymene	0.007 ± 0.002	3220 ± 278	5.5	GC-ECD	
2,5-dichloro-*p*-cymene	0.01 ± 0.0014	4770 ± 150	5.6	GC-ECD	
2,3,6-trichloro-*p*-cymene	(5.0 ± 0.4) × 10^{-4}	797 ± 35	6.2	GC-ECD	
tetrachloro-*p*-cymene	(3.5 ± 0.2) × 10^{-5}	239 ± 9.6	6.8	GC-ECD	

[a] Banerjee et al., 1980.

integrated by a Hewlett-Packard Model 3392A integrator. Calibration standards were prepared by weighing known amounts of the chemical and dissolving in hexane.

(c) Octanol−Water Partition Coefficient. A stock solution of concentration less than 5 g/L of the compound in 1-octanol was prepared for each solute separately. To equilibrate the aqueous and octanol phases, 20 mL of water and a 2 mL aliquot of the stock solution were shaken gently for 48 h in an Erlenmeyer flask and allowed to settle for 24 h before analysis. These conditions had been shown to achieve equilibrium between the phases (Lun et al., 1995). The aqueous and octanol phases were then separated. The aqueous phase was centrifuged, extracted with hexane, and injected directly onto the GC column for analysis. The octanol phase was diluted 10−100 times with octanol and also analyzed by direct injection.

Results and Discussion

The solubility results at 25 °C are given in Table 1 with the reported literature values, molecular mass, melting points, and the additive LeBas molar volumes (Reid et al., 1987). The one supercooled liquid solubility was calculated from the lower solid solubility by dividing by the fugacity ratio, F, using an estimated entropy of fusion of 56.5 J·mol^{-1}·K^{-1} for moderately sized rigid organic molecules, i.e., applying Walden's rule as suggested by Yalkowsky et al. (1979) and Miller et al. (1985)

$$F = C_S^S/C_L^S = \exp\{-6.79[(T_M/T) - 1]\} \qquad (1)$$

where C_S^S and C_L^S (mol·m^{-3}) are the solubilities of the solute in solid and liquid states, respectively. T_M is the melting point of the solute, and T is the system absolute temperature. The solubilities of the liquid solutes are reported and plotted directly.

An equation for LeBas molar volume V_M (cm^3/mol) as a function of the number of chlorine atoms, N, can be derived from the data in Reid et al. (1987) as

$$V_M/(\text{cm}^3\text{·mol}^{-1}) = 184.8 + 20.9N \qquad (2)$$

where 184.8 is the estimated molar volume of the cymenes and 20.9 is the difference between the atomic volumes of chlorine and hydrogen.

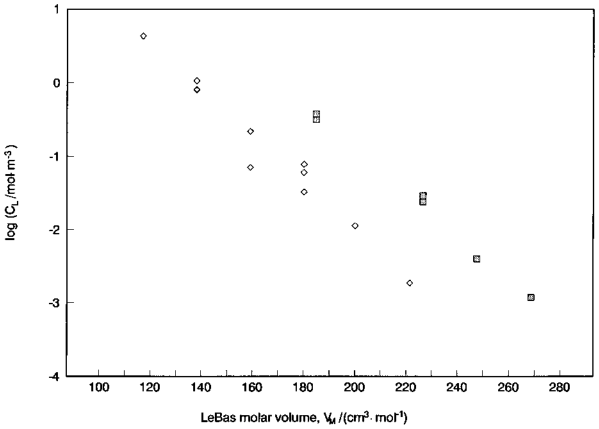

Figure 1. Plot of logarithm of liquid or supercooled liquid solubility C_L^S versus LeBas molar volume V_M for cymenes and chlorocymenes ■ and chlorobenzenes ◇.

The plot of the logarithm of liquid or supercooled liquid solubility C_L^S versus molar volume V_M shown in Figure 1 reveals a consistent logarithmic−linear relationship similar to that of the chlorobenzene series. For interest, the corresponding data for chlorobenzenes are also shown in this and subsequent figures (Mackay et al., 1992). The quantitative-structure-property-relationship can be expressed by eq 3

$$\log (C_L^S/\text{mol·m}^{-3}) = 5.036 - 0.0296(V_M/\text{cm}^3\text{·mol}^{-1}) \qquad (r^2 = 0.995) \quad (3)$$

where r^2 is the correlation coefficient and the standard error of log C_L^S is 0.001.

Table 2 gives the octanol−water partition coefficients, and Figure 2 is a plot of the logarithm of the octanol−water partition coefficient log K_{OW} versus the LeBas molar volume for the chlorocymenes, again indicating a log−linear behavior, correlated as

$$\log K_{OW} = -1.838 + 0.0324(V_M/\text{cm}^3\text{·mol}^{-1}) \qquad (r^2 = 0.996) \quad (4)$$

The standard error of log K_{OW} is 0.0012.

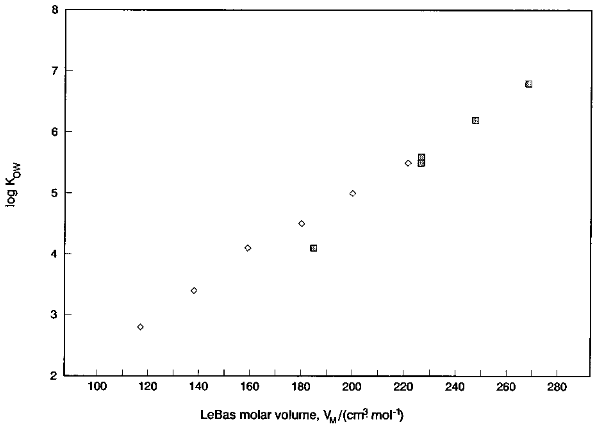

Figure 2. Plot of log K_{OW} versus LeBas molar volume V_M for cymenes and chlorocymenes ■ and chlorobenzenes ◇.

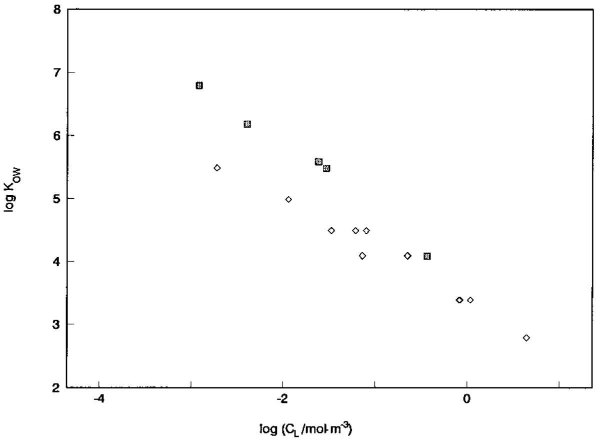

Figure 3. Plot of log K_{OW} versus log C_L^S for cymenes and chlorocymenes ■, chlorobenzenes ◇.

The plot of log K_{OW} versus log supercooled liquid solubility in Figure 3 also reveals a linear relationship with a slope of 1.064

$$\log K_{OW} = 3.749 - 1.064 \log (C_L^S/\text{mol}\cdot\text{m}^{-3}) \quad (r^2 = 0.987) \quad (5)$$

and the standard error of log K_{OW} is 0.07.

It is interesting to note that addition of eqs 3 and 4 yields

$$\log K_{OW} + \log (C_L^S/\text{mol}\cdot\text{m}^{-3}) = 3.198 + 0.0028(V_M/\text{cm}^3\cdot\text{mol}^{-1}) = \log (C_O^S/\text{mol}\cdot\text{m}^{-3}) \quad (6)$$

C_O^S can be regarded as the solubility of the compounds in octanol since K_{OW} can be regarded as the ratio not only of concentrations but also of C_O^S/C_L^S, i.e., the saturation concentration or solubilities in each phase. This solubility is fairly insensitive to chlorine content and ranges from 5160 to 8940 mol·m^{-3}. It is much larger than the corresponding solubility of the higher chlorobenzenes; for example, for hexachlorobenzene C_O^S is only 591 mol·m^{-3}. The chlorocymenes are thus unusually soluble in octanol, forming more ideal solutions. The reasons for this are unknown.

There is growing acceptance in environmental regulations that substances with a log K_{OW} exceeding 5.0 can be classified as highly bioaccumulative and are thus of particular concern. Chlorocymenes containing two or more chlorines fall into this category. Tetrachlorocymene with a log K_{OW} of 6.8 falls into the same category as polychlorinated biphenyls and chlorinated "dioxins" and "furans" as exceptionally bioaccumulative. Since the bioconcentration factor for a typical fish is 5% of K_{OW}, bioconcentration factors of (0.05 × $10^{6.8}$) or 300 000 are expected. Further, food chain biomagnification is expected. The data reported here are at 25 °C, a standard temperature for physical–chemical measurements. It would be valuable to obtain data at generally lower environmental temperatures. The presence of these substances in pulp mill effluents is thus of concern, and there is a compelling incentive to minimize their formation and remove them to the maximum extent possible by process modification and/or effective effluent treatment.

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