Aqueous Solubilities of Chlorocatechols, Chlorovanillins, Chlorosyringols, and Chlorosyringaldeydes at 25 °C

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The aqueous solubilities of 13 chlorinated derivatives of phenol (3,5-dichlorocatechol, 4,5-dichlorocatechol, 3,4,5-trichlorocatechol, tetrachlorocatechol, vanillin, 5-chlorovanillin, 6-chlorovanillin, 5,6-dichlorovanillin, 3-chlorosyringol, 3,5-dichlorosyringol, trichlorosyringol, 2-chlorosyringaldehyde, and 2,6-dichlorosyringaldehyde) were determined at 25 °C, by using a conventional shake-flask, batch contacting method with analysis by high-pressure liquid chromatography with UV detection. The liquid or supercooled liquid solubilities are satisfactorily correlated with the solute's LeBas molar volume, yielding structure–property relationships that may be useful for predictive purposes.

Introduction

The use of molecular chlorine and chlorine-containing compounds as bleaching agents in the pulp and paper industry results in the formation of a variety of chlorinated organic compounds which may be discharged to the aquatic environment. The chemical composition of bleached pulp mill effluents is variable and depends on factors such as the type of wood used, the nature of the in-plant processes, and the effluent treatment employed. In general, softwood produces greater quantities of phenolic byproducts than hardwood. Chlorinated softwood effluent contains chlorophenols, chloroguaiacols, chlorocatechols, and chlorovanillins. Hardwood effluents also contain chlorinated syringols and chlorinated syringaldehydes (*1*).

The National Council of the Paper Industry for Air and Stream Improvement (NCASI) (*2*) has compiled the available information on certain chemical and biological properties of 28 chlorinated phenolic compounds including chlorinated phenols, guaiacols, catechols, vanillins, syringols, and syringaldehydes, the structures of which are shown in Figure 1. No data have been reported of the aqueous solubility of chlorinated catechols (1,2-dihydroxybenzene), vanillin (4-hydroxy-3-methoxybenzaldehyde) and chlorovanillins, syringols (2,6-dimethoxyphenol), and syringaldehydes (4-hydroxy-3,5-dimethoxybenzaldehyde).

Aqueous solubility is an important parameter for assessing environmental partitioning because it influences air–water partitioning, evaporation, and partitioning or sorption to biotic and abiotic phases. There is thus a need to obtain experimental solubility data for these substances and establish structure–property relationships. Of thermodynamic interest is the activity coefficient in the aqueous phase, which can be estimated from the solubility.

Experimental Section

Materials. The chemicals which were >99% pure were obtained from Helix Biotech Corp. of Richmond, BC. Vanillin (99% purity) was obtained from Aldrich Chemical Co., Milwaukee, WI. The chemicals were used as purchased and were not purified. Doubly distilled water was used for all saturated solutions preparation. Methanol (HPLC grade) was obtained from Caledon Laboratories, Georgetown, ON. Milli-Q ultrapure deionized water was used with methanol as the mobile phase for the HPLC system.

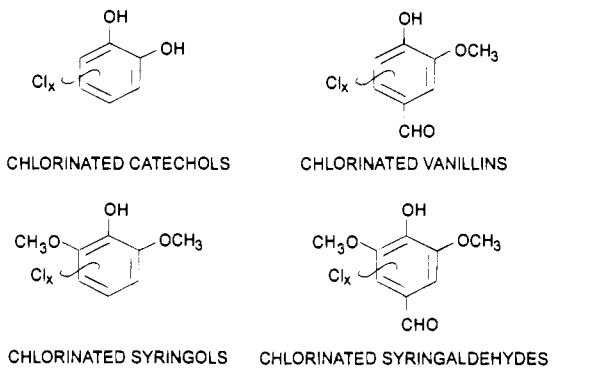

Figure 1. Structures of chlorocatechols, chlorovanillins, chlorosyringols, and chlorosyringaldehydes.

Preparation of Saturated Solutions. Excess amounts of chemicals were added to 25 or 50 mL Erlenmeyer flasks containing doubly distilled water. They were stirred or shaken gently for 24 h and allowed to settle at 25 °C for at least 24 h before analysis. pH values were measured by a Canlab Model 607 pH meter. There was no pH adjustment or buffering. The pH of the doubly distilled water was measured to be 7.05. It should be noted that certain of these methoxy and aldehyde compounds are susceptible to oxidation, thus confounding the solubility determination. No oxidation products were detected, and attempts were made to minimize the possibility of oxidation by analyzing solutions rapidly, but some reaction cannot be precluded.

Equipment. A Waters Associates (Milford, MA) liquid chromatograph (HPLC system) consisting of a Model 6000 solvent delivery system, a Model M45 solvent delivery system, a Model 440 UV absorbance detector with 254 and 280 nm kits, and a Model 721 system flow controller was used for analysis. It was operated in isocratic mode with methanol–water mixture as the mobile phase. The methanol–water ratio used varied between analytes from 85:15 to 95:5 by volume. The analytical column was a Waters 3.9 mm o.d. × 300 mm long μBondapak C_{18} column. Aqueous samples were directly injected onto the column. Peak areas were integrated and recorded by a Waters Model 730 data module. Calibration standards were prepared by dissolving measured masses of the phenolic substances in methanol.

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Table 1. Aqueous Solubility of Chlorocatechols, Chlorovanillins, Chlorosyringols and Chlorosyringaldehydes at 25 °C[a]

compound	mp/°C	MW/g·mol^{-1}	pK_a	LeBas molar vol V_L/(cm^3·mol^{-1})	solubility S/(g·m^{-3})	C_L/(mol·m^{-3})	at pH
catechol	105	110.1	9.356 (*7*)	110.8	450000 (*8*)	24330	
3,5-dichlorocatechol	83–4	181.0	7.78	152.6	7910 ± 186	163.7	4.70
4,5-dichlorocatechol	116–7	181.0	8.17	152.6	12000 ± 380	526.7	3.20
3,4,5-trichlorocatechol	130	216.5	6.95	173.5	511 ± 12.5	25.79	4.05
tetrachlorocatechol	110	247.9	5.83	194.4	70.5 ± 3.1	1.97	5.13
vanillin	80–81	152.2	7.62	155.2	2480 ± 49	57.13	4.50
5-chlorovanillin	169	187.6	6.80	191.1	932 ± 28	132.0	4.55
6-chlorovanillin	171–2	187.6	6.11	191.1	132 ± 3.4	19.56	5.35
5,6-dichlorovanillin	198–9	223.1	5.28	212	23 ± 0.6	5.30	4.00
3-chlorosyringol	35–36	189.5	9.09	183.5	5170 ± 123	34.26	4.30
3,5-dichlorosyringol	105–6	224.9	7.27	204.4	244 ± 6	6.71	5.80
trichlorosyringol	122–3	260.4	7.73	225.3	100 ± 1.3	3.50	3.90
2-chlorosyringaldehyde	196–7	217.5	6.80	205.7	33 ± 0.72	7.45	5.30
2,6-dichlorosyringaldehyde	195.6	252.9	5.97	230.3	36 ± 1.2	6.84	4.60

[a] With the exception of catechol, all pK_a values were estimated (*6*).

Results and Discussion

Table 1 gives the measured aqueous solubilities of the compounds at 25 °C. The present solubility data have a precision (relative standard deviation) of less than 3.5%. Also given is the molar volume V_M (cm^3·mol^{-1}) as calculated using the simple, additive LeBas method (*3*), which for chlorinated catechols can be summarized by

$$V_M = 110.8 + 20.9N \qquad \text{(catechols)} \qquad (1)$$

where N is the number of chlorines and 20.9 represents the difference in atomic volume between chlorine and hydrogen. Similar equations can be established for vanillins and syringols:

$$V_M = 155.2 + 20.9N \qquad \text{(vanillins)} \qquad (2)$$

$$V_M = 183.5 + 20.9N \qquad \text{(syringols)} \qquad (3)$$

For correlating solubilities as a function of molar volume, the solubilities of solid solutes should be "corrected" to those of the supercooled liquid values. The melting points of the chemicals range from 35 to 199 °C. The effect of melting point can be treated by estimating the fugacity ratio f_S/f_L, where f_S is the fugacity of the solid substance and f_L that of the supercooled liquid. The supercooled liquid solubility C_L^S can then be estimated from the measured solid solubility C_S^S as $C_S^S/(f_S/f_L)$. Essentially by using C_L^S, which is larger than C_S^S, the effect of solid crystal structure on solubility is eliminated. Values of the enthalpy change $\Delta_{fus}H$ or entropy change $\Delta_{fus}S$ of fusion (if reported) can be used to estimate the fugacity ratios from the system temperature T (298 K) and the melting point T_M (K) using the expression

$$f_S/f_L = \exp[-\Delta_{fus}H(1/T - 1/T_M)/R] = \exp[-\Delta_{fus}S(T_M/T - 1)/R] \qquad (4)$$

No values of $\Delta_{fus}S$ were found for the chemicals considered here. Accordingly, Walden's rule (*4*) was applied, i.e., $\Delta_{fus}S$ was assumed to be 13.5 cal·mol^{-1}·K^{-1} or 56 J·mol^{-1}·K^{-1} in the form suggested by Yalkowsky (*5*), namely

$$f_S/f_L = \exp[-6.79(T_M/T - 1)] \qquad (5)$$

where 6.79 is $\Delta_{fus}S/R$. It must be emphasized that in the absence of actual measurements of $\Delta_{fus}S$ this is only an approximate correction.

When dissociation affects the measured solubility, a correction may be applied to account for the presence of ionized phenols in solution. A structure–property relationship, for example relating solubility to molar volume, is likely to apply to the nonionized form. The concentration of the nonionized form of monoprotic acids can be estimated from the measured total (ionized plus nonionized) solubility from

$$\text{(nonionized concentration)} = \text{(total concentration)}/(1 + 10^{(\text{pH}-\text{p}K_a)}) \qquad (6)$$

For compounds for which no measured pK_a is reported, this quantity can be estimated from the Hammett equation, as discussed by Perrin at al. (*6*)

$$\text{p}K_a = \text{p}K_a^0 - \varrho(\Sigma\sigma) \qquad (7)$$

where σ is a constant assigned to a particular substituent, ϱ is a constant for a specific series, and pK_a^0 refers to the parent compound. For each substituent a different σ value applies for each position (*ortho*, *meta*, and *para*). The pK_a values of all compounds reported in this paper can be calculated from the equation for phenolic compounds

$$\text{p}K_a = 9.92 - 2.23\Sigma\sigma \qquad (8)$$

The estimated values of pK_a are shown. For chlorine the values of σ are 0.37 for σ_{meta} and 0.24 for σ_{para}, indicating that increased chlorination strongly reduces pK_a and increases the tendency to ionize at environmental pH. The presence of a CHO group also has a strong influence (0.36 for σ_{meta} and 1.03 for σ_{para}). Addition of an OH in the *ortho* position changes the pK_a value of $\sigma_{ortho} = 0.04$ for phenols and CH_3O group values are 0.11 for σ_{meta} and −0.11 for σ_{para}.

Some of the pH values measured at saturation were surprisingly low and were remeasured. Variation of up to 2 pH units was obtained, suggesting the presence of a small and variable quantity of acidic contaminant. The reported pH values should thus be viewed as tentative. Fortunately, all pH values are well below pK_a and correction was needed only in the case of tetrachlorocatechol, where the difference between the experimental pH and estimated value of pK_a is 0.70 and the ratio of ionized and nonionized forms is about 0.20.

Figure 2 is a plot of supercooled liquid solubility of catechol, chlorocatechols, vanillin, chlorovanillins, and chlorosyringols versus LeBas molar volume. The chlorocatechols show a slope of 4.8 log units/100 cm^3·mol^{-1}. Chlorovanillins display a slope of 3.6 log units/100 cm^3·mol^{-1} and chlorosyringols a slope of 2.8 log units/100 cm^3·mol^{-1}.

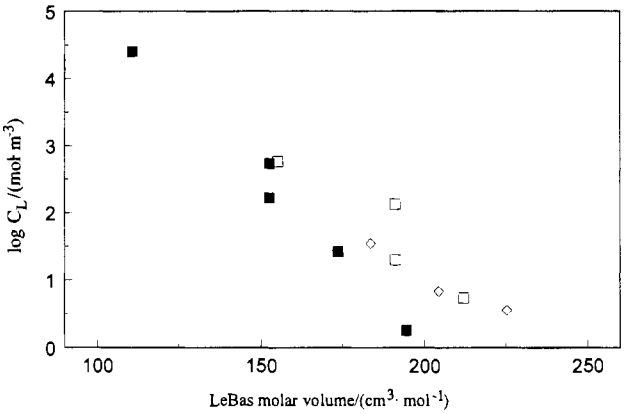

Figure 2. Plot of log supercooled liquid aqueous solubility of catechol, chlorocatechols, vanillin, chlorovanillins, and chlorosyringols versus LeBas molar volume: ■, chlorocatechols; □, chlorovanillins; ◇, chlorosyringols.

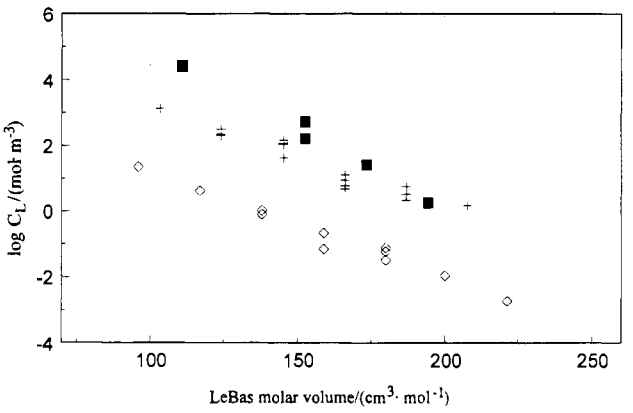

Figure 3. Plot of log supercooled liquid aqueous solubility of chlorophenols, chlorobenzenes, catechol, and chlorocatechols versus LeBas molar volume: ■, chlorocatechols; +, chlorophenols; ◇, chlorobenzenes.

We prefer not to present regressions for these plots since we view them as providing only guidance about trends in solubility within the series.

Figure 3 shows solubility data for the chlorobenzenes (*9*), chlorophenols (*10*), catechol, and chlorocatechols. Addition of one OH group to an aromatic ring increases solubility by about 1.8 log units (factor of 62). Addition of a second OH group has less effect, especially for more highly chlorinated substances. The use of simple group contribution correlations is thus unlikely to be successful. Presumably the second OH group is shielded by adjacent chlorines.

Figure 4 shows solubility data for chlorophenols, chloroguaiacols (methoxyphenols) (*11*), and chlorosyringols (dimethoxyphenols). The chlorophenol and chloroguaiacol data appear to fall on a common regression line, with the

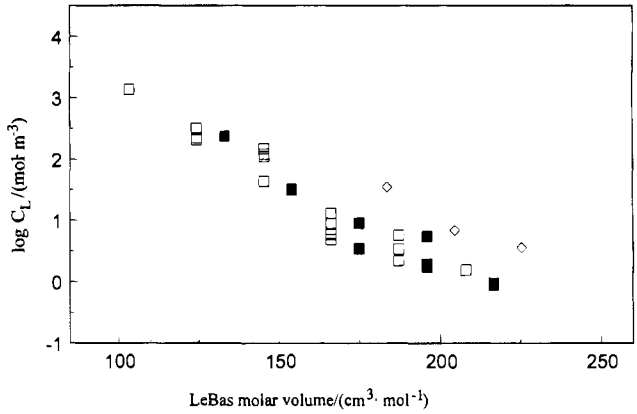

Figure 4. Plot of log supercooled liquid aqueous solubility of chlorophenols, chloroguaiacols, and chlorosyringols versus LeBas molar volume: ◇, chlorosyringols; ■, chloroguaiacols; □, chlorophenols.

chlorosyringols about 0.5−1.0 log unit higher. The reason is not known.

It is hoped that these data will be of thermodynamic interest and of value for assessing the environmental fate and effects of these compounds.

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