Temperature Dependent Vapor Pressures of Chlorinated Catechols, Syringols, and Syringaldehydes

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The vapor pressures of nine chlorinated catechols, syringols, and syringaldehydes were determined as a function of temperature with a gas chromatographic retention time technique. The vapor pressures at 298.15 K were in the range of 0.02−1 Pa, and the enthalpies of vaporization, between 68 and 82 kJ·mol^{-1}. The validity of the technique was established by a calibration involving four chlorinated phenols with well-known vapor pressures. Using these data and previously reported solubility data, Henry's law constants for these substances and some chlorinated guaiacols and veratrols were estimated. The vapor pressure of these substances tends to decrease with increasing polarity and an increasing number of chlorine atoms. Henry's law constants decrease sharply with increasing polarity, suggesting that methylation can result in a significant increase in a chemical's potential for volatilization from water.

Introduction

Pulp and paper effluents contain numerous chlorinated organic substances. Their specific structure and composition are dependent on the raw materials, the bleaching process, and the effluent treatment. Chlorinated catechols, syringols, and syringaldehydes, shown in Figure 1, are among the chemicals identified in effluents from pulp mills which use chlorine bleaching. For many of these substances, even the most basic physical−chemical parameters are often lacking, even though these parameters are required for an evaluation of their environmental fate upon discharge to the aquatic environment.

Varhanícková et al. (1995) recently reported solubilities in water for some of these compounds. In this work we complement these data with vapor pressure measurements. These measurements provide the means for estimating Henry's law constants, which describe air−water partitioning at equilibrium.

The suitability of the gas chromatographic (GC) retention time technique for determining the vapor pressure of chlorinated phenolic compounds has been established previously (Bidleman and Renberg, 1985). It requires only small quantities of chemicals, yields information on the temperature dependence of the vapor pressure, and is relatively fast.

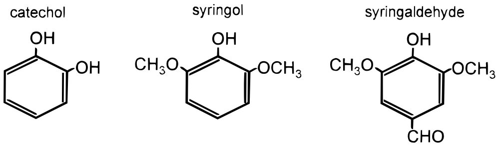

Figure 1. Molecular structure of catechols, syringols, and syringaldehydes.

Table 1. Vapor Pressure Determined by GC, P_{GC}, and Supercooled Liquid−Vapor Pressure, P_L at 298.15 K, of Four Chlorophenols Measured in This Study and Reported in the Literature

compound	P_{GC}/Pa		P_L/Pa	
2,6-dichlorophenol	13.21[a]	12.70[b]	12.70[c]	12.20[d]
2,4,6-trichlorophenol	3.24[a]	3.26[b]	3.44[c]	3.83[d]
2,3,4,6-tetrachlorophenol	0.66[a]	0.564[b]	0.78[c]	0.692[d]
pentachlorophenol	0.12[a]	0.115[b]	0.12[c]	0.0956[d]

[a] This study. [b] Bidleman and Renberg (1985). [c] Selected value in Shiu et al. (1994). [d] Weast (1976−77).

Experimental Section

Chemicals. Chlorocatechols, chlorosyringols, and chlorosyringaldehydes with 99% or greater purity were obtained from Helix Biotech Corp. of Richmond, BC. The chlorinated phenols (CP) used for the calibration of the technique were purchased from Aldrich Chemical Co. (2,6-DiCP, 99%; 2,4,6-TriCP, 98%; PentaCP, 99%) and Ultra Scientific, RI (2,3,4,6-TetraCP, 99%). Chlorocatechols, chlorosyringols, and chlorosyringaldehydes were dissolved in acetone (HPLC grade). The stock solutions were further diluted with hexane (HPLC grade). Between 250 and 800 ng of chemical in hexane was injected.

Instrumentation. A Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and a DB-17 capillary column (0.32 mm i.d. × 1 m length) was used. The experiment was operated isothermally at four to eight temperatures in the range 293.15−323.15 K. The temperature of the GC oven was checked for accuracy using a thermocontroller (Omega Engineering Inc.). The operating conditions were as follows: injection port and detector at 523.15 K, helium carrier gas at a flow rate of approximately 4 mL·min^{-1}, and split ratio 10:1.

Data Processing and Calibration Procedure. Vapor pressures P_{GC} were calculated from the gas chromatographic retention times using procedures described previously (Hamilton, 1980; Bidleman, 1984). The accuracy of this method is dependent on how accurately the vapor

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Table 2. Vapor Pressure Determined by GC, P_{GC} with Standard Deviation, Supercooled Liquid−Vapor Pressure P_L at 298.15 K, and Slopes and Intercepts of the Equation $\log(P_L/\mathrm{Pa}) = m_L/(T/\mathrm{K}) + b_L$ for Chlorocatechols, Chlorosyringols, and Chlorosyringaldehydes, and Enthalpies of Vaporization Estimated from the Slopes m_L

compound	P_{GC}/Pa	P_L/Pa	b_L	m_L	ΔH_{vap}/(kJ·mol^{-1})
4-chlorocatechol	0.936 ± 0.006	0.979	12.28	−3664	−70.2
4,5-dichlorocatechol	0.388 ± 0.001	0.408	11.95	−3680	−70.5
3,4,5-trichlorocatechol	0.099 ± 0.001	0.106	12.89	−4135	−79.3
tetrachlorocatechol	0.064 ± 0.000	0.068	12.48	−4070	−77.9
3-chlorosyringol	0.788 ± 0.001	0.825	11.93	−3580	−68.6
3,5-dichlorosyringol	0.442 ± 0.001	0.465	12.01	−3679	−70.4
trichlorosyringol	0.072 ± 0.000	0.077	12.44	−4041	−77.4
2-chlorosyringaldehyde	0.074 ± 0.001	0.079	12.51	−4058	−77.7
2,6-dichlorosyringaldehyde	0.023 ± 0.000	0.025	12.79	−4293	−82.2

Table 3. Molecular Mass *M*, LeBas Molar Volume V_L, Supercooled Liquid−Vapor Pressure P_L, Aqueous Solubility of the Supercooled Liquid C_L, Henry's Law Constants *H*, and Octanol−Water Partition Coefficient K_{OW} of Selected Chlorinated Organic Compounds at 298.15 K

compound	*M*/(g·mol^{-1})	V_L/(cm^3·mol^{-1})	P_L/Pa	C_L/(mol·m^{-3})	*H*/(Pa·m^3·mol^{-1})	log K_{OW}
4,5-dichlorocatechol	181.0	152.6	0.408[a]	526.7[c]	0.00078[f]	
4,5-dichloroguaiacol	193.0	174.8	1.54[b]	3.46[d]	0.44[f]	3.26[g]
4,5-dichloroveratrol	207.0	200.4		1.35[e]		3.11[e]
3,4,5-trichlorocatechol	216.5	173.5	0.106[a]	25.79[c]	0.0041[f]	3.79[h]
3,4,5-trichloroguaiacol	227.5	195.7	0.640[b]	5.47[d]	0.12[f]	3.77[g]
3,4,5-trichloroveratrol	241.5	221.4	0.415[b]	0.11[e]	3.77[f]	4.01[e]
4,5,6-trichloroguaiacol	227.5	195.7	0.249[b]	1.84[d]	0.14[f]	3.74[h]
tetrachlorocatechol	247.9	194.4	0.068[a]	1.97[c]	0.035[f]	4.27[h]
tetrachloroguaiacol	261.9	216.6	0.138[b]	0.90[d]	0.15[f]	4.45[h]
tetrachloroveratrol	275.9	242.3	0.286[b]	0.026[e]	11.0[f]	4.86[e]
3-chlorosyringol	189.5	183.5	0.825[a]	34.26[c]	0.024[f]	
2-chlorosyringaldehyde	217.5	205.7	0.079[a]	7.45[c]	0.011[f]	
3,5-dichlorosyringol	224.9	204.4	0.465[a]	6.71[c]	0.069[f]	
2,6-dichlorosyringaldehyde	252.9	230.3	0.025[a]	6.84[c]	0.0037[f]	
trichlorosyringol	260.4	225.3	0.077[a]	3.5[c]	0.022[f]	

[a] This study. [b] Bidleman and Renberg (1985). [c] Varhanícková et al. (1995). [d] Tam et al. (1994). [e] Lun et al. (1995). [f] Calculated from P_L/C_L. [g] Saarikoski and Viluksela (1982). [h] Xie et al. (1984).

pressure of a standard reference compound is known (Kim et al., 1984; Bidleman, 1984). *n*-Octadecane was used as a reference compound. Macknick and Prausnitz (1979) have reported vapor pressure data for *n*-octadecane, and their measurements were independently found to be very precise (Chirico et al., 1989). This GC determined vapor pressure P_{GC} is not always identical to the vapor pressure of the (supercooled) liquid P_L but tends to be highly correlated with it. By adopting a method pioneered by Bidleman and Renberg (1985), the measured P_{GC} in pascals (Pa) for four chlorinated phenols, given in Table 1, was regressed against the known liquid-phase vapor pressures of these substances P_L (Shiu et al., 1994). The following relationship was found:

$$\log(P_{GC}/\mathrm{Pa}) = 1.00761 \log(P_L/\mathrm{Pa}) - 0.01916, \quad r^2 = 0.998 \tag{1}$$

and was employed to estimate the P_L of the chlorinated catechols, syringols, and syringaldehydes from the experimentally determined P_{GC}.

Results

Table 2 lists the measured vapor pressures both at 298.15 K and expressed as linear functions of temperature (Antoine equations):

$$\log(P_L/\mathrm{Pa}) = m_L/(T/\mathrm{K}) + b_L \tag{2}$$

The arithmetic mean and the standard deviation of three independent measurements of P_{GC} are given, indicating a very high reproducibility. The vapor pressure P_L of these substances is in the range of 0.02−1 Pa, and enthalpies of vaporization ΔH_{vap} derived from the slopes m_L are in the range of −68 to −82 kJ·mol^{-1}. Among a class of structurally related chemicals, P_L and ΔH_{vap} decrease with the degree of chlorination, which is consistent with findings for chlorinated phenols (Stephenson and Malanowski, 1987) and chlorinated benzenes (Liu and Dickhut, 1994).

Using vapor pressures P_L determined in this study and by Bidleman and Renberg (1985) and supercooled liquid solubilities C_L reported previously (Tam et al., 1994; Varhanícková et al., 1995; Lun et al., 1995), Henry's law constants, that is air−water equilibrium partition coefficients, for these chemicals were estimated at 298.15 K using

$$H/(\mathrm{Pa \cdot m^3 \cdot mol^{-1}}) = (P_L/\mathrm{Pa})/(C_L/(\mathrm{mol \cdot m^{-3}})) \tag{3}$$

The results are listed in Table 3. Most of these chemicals have Henry's law constants *H* which are well below 1 Pa·m^3·mol^{-1}. Only the Henry's law constants of chemicals without hydroxyl groups, such as the chlorinated veratrols, reach higher values.

Discussion

Figure 2 displays the measured vapor pressures of various chlorophenolic compounds as a function of LeBas molar volume (Reid et al., 1987). It can be seen that, within a compound class (such as the catechols, or the guaiacols), the vapor pressure decreases with each additional chlorine atom by a factor of approximately 3. This factor varies from 1.5 to more than 6. Replacement of a hydroxyl group with a methoxy group tends to result in a slight increase in the vapor pressure of a compound despite the increase in molecular volume. This is presumably because the potential for forming hydrogen bonds between the hydroxyl groups reduces the vapor pressure of a compound. Consis-

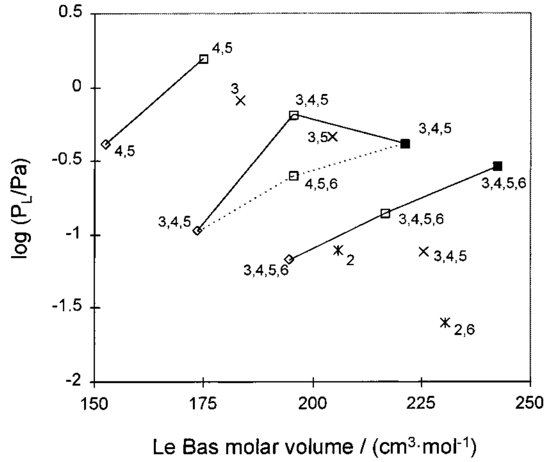

Figure 2. Supercooled liquid−vapor pressure of chlorinated catechols (◇), guaiacols (□), veratrols (■), syringols (×), and syringaldehydes (*) at 298.15 K plotted against the LeBas molar volume.

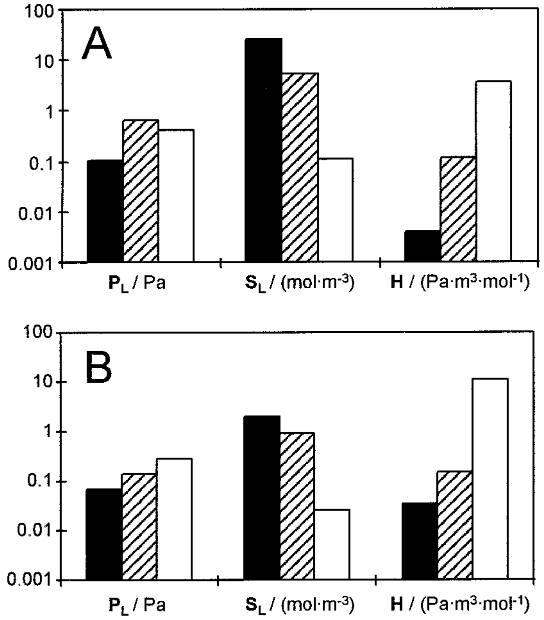

Figure 3. Comparison of the vapor pressures P_L, aqueous solubilities C_L, and Henry's law constants H for two series of structurally related chlorophenolic compounds: (A) 3,4,5-trichloro-substituted compounds; (B) tetrachloro-substituted compounds. Bass: catechols (filled), guaiacols (hatched), and veratrols (open).

tent with that interpretation, the addition of the aldehyde group to the syringols is associated with a large drop in vapor pressure, because it increases chemical volume as well as the potential for hydrogen bonding.

It is particularly illuminating to compare the physical−chemical properties of the 3,4,5-trichlorinated catechol, guaiacol, and veratrol, as well as the tetrachlorinated series of the same compounds, as shown in Figure 3. Methylation reduces the solubility of a compound significantly but, as noted above, slightly increases the vapor pressure. This implies that the Henry's law constant increases sharply with methylation, and indeed the H of 3,4,5-veratrol is estimated to be 3 orders of magnitude higher than the H of 3,4,5-trichlorocatecol.

Chlorophenolic chemicals from bleaching operations are generally discharged into the aqueous phase. Because of the low Henry's law constant, they are likely to stay in the water as they have little incentive to partition into air and volatilize. However, the hydroxyl groups on these compounds can be biologically methylated in effluents and the receiving water (Neilson et al., 1991). This conversion leads to chemicals which tend to be more lipophilic and thus bioaccumulative, and possibly also more persistent and toxic than their precursors (Neilson et al., 1991). They also are more potent odor compounds (Brownlee et al., 1993). As observed above, this methylation is also associated with a strong increase in the Henry's law constant, resulting potentially in a mobilization of chemicals from the effluent and receiving waters into the atmosphere. Chlorinated veratrols with $H > 1$ Pa·m^3·mol^{-1} may be lost significantly from bodies of water by evaporation, whereas chlorinated catechols will be efficiently retained.

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