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Effects of pH on the Aqueous Solubility of Selected Chlorinated Phenols

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The aqueous solubilities are reported and correlated for 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, and pentachlorophenol over the pH range 2 to 14 as measured by high-pressure liquid chromatography with UV detection at 25 °C. Correlation equations are proposed to estimate the aqueous solubility of these chlorophenols as a function of pH.

Introduction

Chlorinated phenolic compounds are weak acids, produced in pulp bleaching processes and found in pulp mill effluents. They are also widely used as insecticides, fungicides, and disinfectants and are regarded as having relatively high toxicities. Aqueous solubility influences the fate and toxicity of chemicals; thus, it is useful to determine the effects of environmental factors, such as temperature and pH, on their properties.

Kaiser and Valdmanis (1982), Westall et al. (1985), Schwarzenbach et al. (1988), Jafvert et al. (1990), Johnson and Westall (1990), and Schwarzenbach et al. (1993) have reviewed the effect of pH and ionic strength on the distribution of these chemicals in the environment. Physicochemical properties are often reported at one temperature, mostly at room temperature (20−25 °C), without specifying the pH of the solution; thus, considerable discrepancies often exist among reported data. Their pK_a values range from 10.0 for phenol to 4.74 for pentachlorophenol (PCP); thus, they dissociated in water, and pH affected their apparent solubility and other properties such as air−water partitioning and sorption.

Aqueous solubilities of chlorophenols have been critically reviewed by IUPAC (1985), Shiu et al. (1994), and the Handbook by Mackay et al. (1995). Blackman et al. (1955) reported solubilities buffered at pH 5.1. Toyota and Kuwahara (1964) measured the dependence of the solubility of PCP on the pH and proposed an empirical equation for the effect of pH. Ma et al. (1994) reported the solubility of some chlorophenols and their pH values at saturation concentrations. Recently, Achard et al. (1996) reported the aqueous solubilities of five chlorophenols at temperatures from 15 °C to 48 °C. Yoshida et al. (1987) and Achard et al. (1996) reported the effect of pH on the solubilities of 2,4,6-trichlorophenol (TCP) and pentachlorophenol.

The degree of dissociation of a weak organic acid in aqueous solution is characterized by the acid dissociation constant K_a, expressed as the negative logarithm pK_a. The dissolved concentration is the sum of the undissociated parent or protonated compound and the dissociated phenolate ionic form. The ratio *r* of the concentrations and solubilities of the ionic and nonionic or dissociated to undissociated species is given by

$$r = \text{ionic/nonionic} = 10^{(\mathrm{pH}-\mathrm{p}K_a)} = S_I/S_N \qquad (1)$$

where S_N and S_I are the solubilities of the nonionic species and the ionic species, respectively, and the total solubility S_T is ($S_N + S_I$). The total solubility is thus

$$S_T = S_N(1 + 10^{(\mathrm{pH}-\mathrm{p}K_a)}) \qquad (2)$$

This equation is frequently used for correlation purposes. When pK_a exceeds pH by 2 or more units, dissociation is 1% or less and for most purposes is negligible. When pK_a is less than or equal to the solution pH, the extent of the dissociation is substantial, as illustrated for PCP by Shiu et al. (1994) and Mackay et al. (1995).

Yoshida et al. (1987) studied the effect of pH (range from 4 to 7.2) on the solubility of 2,4,6-TCP and proposed the equation for solubility (mg/L or g/m^3)

$$S_T/(\mathrm{g/m^3}) = 312 \times (1 + 10^{(\mathrm{pH}\,-\,6.06)}) \qquad (3)$$

Arcand et al. (1995) studied the effect of pH (range from 4 to 7.2) on the solubility of PCP and suggested a corresponding equation

$$S/(\mu\mathrm{M}) = 10(1 + 10^{(\mathrm{pH}-4.35)}) \qquad (4)$$

The solubility of the neutral PCP of 10 μM was shown to be unaffected by pH.

Here we revisit the solubility/pH relationship for these two substances, extending the pH range, and add two additional compounds.

Experimental Section

Chemicals. 2,4-Dichlorophenol (DCP) 99%, 2,4,6-trichlorophenol 98%, 2,3,4,6-tetrachlorophenol (TeCP) 98%, and pentachlorophenol 99% were obtained from Aldrich Chemical Co. Sodium hydroxide and hydrochloric acid were of analytical grade and were obtained from Tianjin First

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Table 1. Aqueous Solubilities of 2,4-Dichlorophenol, 2,4,6-Trichlorophenol, 2,3,4,6-Tetrachlorophenol, and Pentachlorophenol at Different pHs at 25 °C[a]

2,4-DCP			2,4,6-TCP			2,3,4,6-TeCP			PCP		
pH	S_T/(10^3·g·m^{-3})	RSD (%)	pH	S_T/(10^3·g·m^{-3})	RSD (%)	pH	S_T/(10^3·g·m^{-3})	RSD (%)	pH	S_T/(10^3·g·m^{-3})	RSD (%)
4.80	4.66	0.73	3.18	3.81×10^{-1}	1.34	2.22	1.26×10^{-1}	0.61	1.74	7.64×10^{-3}	2.62
4.98	4.96	0.11	3.29	4.10×10^{-1}	0.76	4.45	1.52×10^{-1}	1.13	3.05	8.00×10^{-3}	0.5
7.40	7.35	1.91	3.40	4.07×10^{-1}	1.74	4.62	1.66×10^{-1}	1.60	4.17	1.08×10^{-2}	2.88
7.72	8.18	1.17	3.45	3.87×10^{-1}	1.56	6.84	3.93	1.62	4.55	1.30×10^{-2}	0.77
8.20	1.62×10	0.39	3.74	4.59×10^{-1}	0.47	7.25	1.04×10	0.21	6.73	1.39	0.67
8.93	5.58×10	0.24	5.32	5.03×10^{-1}	2.7	7.35	1.09×10	0.47	6.88	2.00	0.85
9.00	5.74×10	0.39	6.69	1.78	0.92	7.49	1.49×10	0.30	7.13	3.67	0.76
9.09	6.77×10	0.7	7.04	4.02	0.78	8.04	3.78×10	0.58	7.68	1.09×10	0.44
9.30	1.10×10^2	1.13	7.15	5.17	0.88	8.17	5.21×10	1.46	7.92	1.92×10	0.90
			7.37	8.75	0.17	8.27	6.13×10	0.38	8.11	2.77×10	0.74
			7.55	1.25×10	0.3	9.20	1.65×10^2	0.4	8.44	5.27×10	0.21
			7.60	1.50×10	0.45	10.25	1.67×10^2	0.86	9.05	2.38×10	0.98
			7.76	1.82×10	0.7	11.80	1.67×10^2	1.15	10.2	2.34×10^2	0.37
			8.53	1.12×10^2	0.15	13.35	1.67×10^2	1.3	11.8	2.33×10^2	0.5
			8.62	1.26×10^2	0.39				13.2	2.43×10^2	0.78
			8.99	1.71×10^2	0.42						
			10.23	1.76×10^2	0.63						
			11.52	1.83×10^2	0.52						

[a] Data were obtained from 6 replicates.

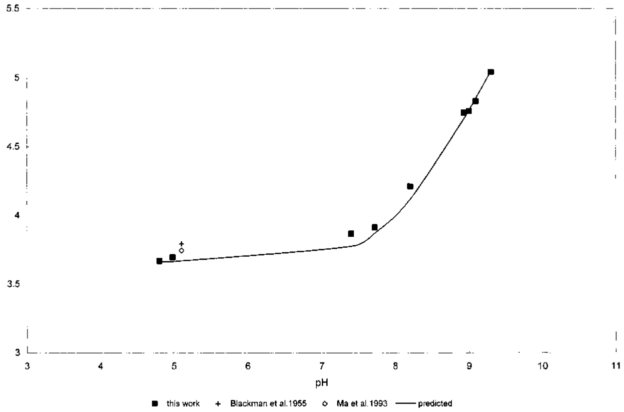

Figure 1. Effect of pH on the solubility of 2,4-dichlorophenol at 25 °C.

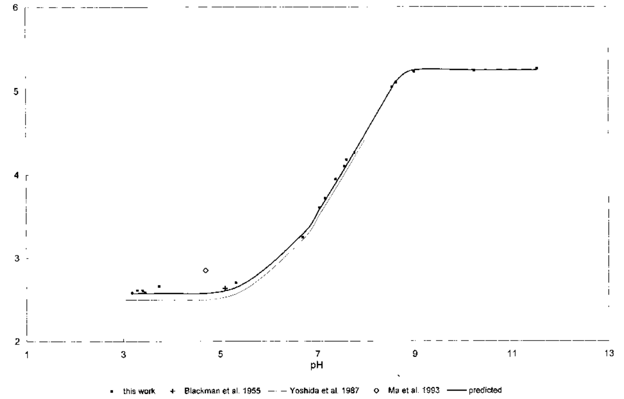

Figure 2. Effect of pH on the solubility of 2,4,6-trichlorophenol at 25 °C.

Reagent Manufactory. Double-distilled water was used to prepare saturated solutions.

Procedure. Saturated aqueous solutions were prepared by adding an excess of the solid chlorophenol of interest to a 50 mL Erlenmeyer flask containing approximately 20−30 mL of doubly-distilled water (pH = 5.54). The pH was adjusted with HCl and NaOH solutions. The flasks were placed in a thermostatic shaker (Model TH288-1) controlled at the desired temperature within ±0.5 °C, were shaken gently for 24 h, and then were allowed to settle for 48 h.

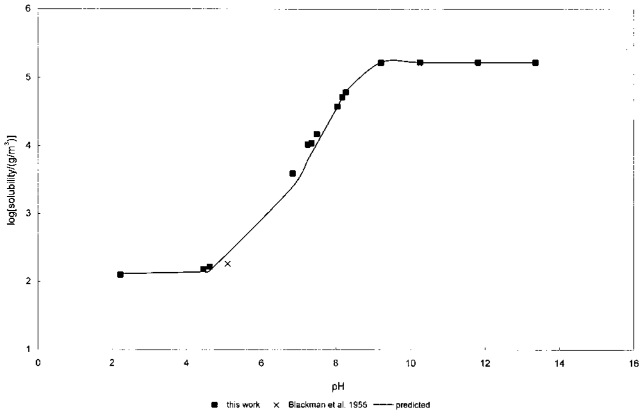

Figure 3. Effect of pH on the solubility of 2,3,4,6-tetrachlorophenol at 25 °C

Table 2. Correlation Parameters for the Solubility of the Chlorophenols for Eq 2, $S_T = S_N(1 + 10^{(pH-pK_a)})$

chlorophenol	pK_a	S_N/(g·m^{-3})	max. S_T/(g·m^{-3})	and pH
2,4-dichlorophenol	7.934	4600	110 000	9.30
2,4,6-trichlorophenol	6.078	375	177 000	7.74
2,3,4,6-tetrachlorophenol	5.579	130	167 000	8.67
pentachlorophenol	4.588	7.70	243 000	9.07

Aqueous samples were taken through a 0.45 μm Millipore filter, and the pH of the solution was determined. The aqueous samples were diluted with redistilled water to suitable concentrations before analysis by HPLC.

Equipment. A Waters Associates high-pressure liquid chromotograph system (HPLC Model 244), a Model 481 variable-wavelength UV detector (measurement set at 280 nm), a Model 680 system flow controller, and a Model 730 data station were used for analysis. The HPLC system was operated in isocratic mode with a methanol−acetic acid buffer solution (pH 4.0) mixture at 85:15 by volume as the mobile phase and a flow rate of 1.0 mL/min. The analytical column was a 4.6 mm × 250 mm, 10 μm Irregular-H C_{18} column (Tianjin Second Reagent Manufactory) and was maintained at (25 ± 0.5) °C. A PHS-3C precision pH meter supplied by the Shanghai Electromagnetic Instrumentation Manufactory was used to measure the pH of the aqueous solutions.

Table 3. Aqueous Solubilities of Chlorophenols and Literature at 25 °C

compound	mp/°C	pK_a	solubility/ (g/m^3)	measd at pH	lit. value/ (g/m^3)	measd at pH	method	ref
2,4-dichlorophenol	42−43	7.10−8.09	4980	4.98			shake flask-HPLC/UV	this work
					4500		gravimetric	Messo, 1887
					6194	5.1	shake flake − UV	Blackman et al., 1955
					5000		shake flake − AS	Roberts et al., 1977
					5547	5.1	shake flask-HPLC/UV	Ma et al., 1993
					5517		conductivity measurement	Achard et al., 1996
2,4,6-trichlorophenol	69.5	5.99	503	5.32			shake flask-HPLC/UV	this work
					858		gravimetric	Daccomo, 1885
					434	5.1	shake flake—UV	Blackman et al., 1955
					900		shake flake—AS	Roberts et al., 1977
					339	5	shake flask-HPLC/UV	Yoshida et al., 1987
					708	4.7	shake flask-HPLC/UV	Ma et al., 1993
					692		conductivity measurement	Achard et al., 1996
2,3,4,6-tetrachlorophenol	70	5.22	166	4.62			shake flask-HPLC/UV	this work
					183	5.1	shake flake—UV	Blackman et al., 1955
pentachlorophenol	174	4.74	13.0	4.55			shake flask-HPLC/UV	this work
					15.4		gravimetric	Carswell and Nason, 1938
					9.59	5.1	shake flake—UV	Blackman et al., 1955
					14		shake flake—UV	Bevenue and Beckman, 1967
					10.8	5	shake flake—gravimetric	Toyota and Kuwahara, 1967
					32	5	shake flake—UV	Vajsarak et al., 1991
					18.4	4.8	shake flask-HPLC/UV	Ma et al., 1993
					21.5	5.066	shake flask-HPLC/UV	Arcand et al., 1995[a]
					21.4		conductivity measurement	Achard et al., 1996

[a] The data reported in this reference was measured at 22.7 °C.

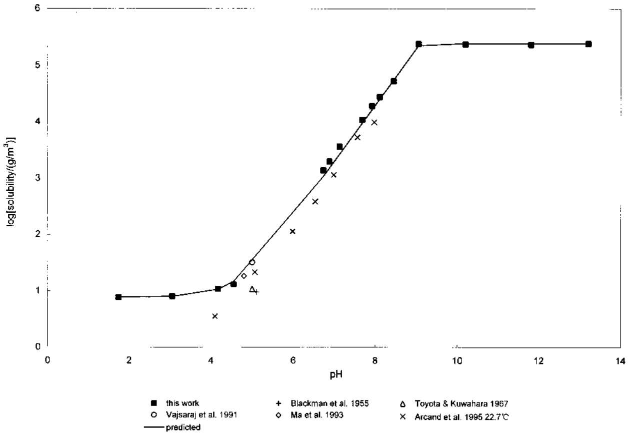

Figure 4. Effect of pH on the solubility of pentachlorophenol at 25 °C

Results and Discussion

Table 1 gives the experimental solubilities of the four chlorophenols 2,4-DCP, 2,4,6-TCP, 2,3,4,6-TeCP, and PCP at (25 ± 0.5) °C for pH ranging from 1.74 to 13.35. Figures 1−4 show the solubility as a function of pH.

The results were fitted to the regression, but it was found necessary to impose a maximum solubility at high pH; that is, the solubility does not increase indefinitely as pH is increased to values beyond about 8.7 to 9.1. Coefficients deduced from the results are given in Table 2 which include the maximum value and the corresponding pH. The corresponding lines are plotted in Figures 1−4.

The experimental solubilities of these four chlorophenols at 25 °C within the pH range between 4.7 and 6.06 or at the natural unbuffered pH compare favorably with literature values as compiled in Table 3.

The pH dependences of the solubilities of the four substances are similar in nature, as illustrated in Figures 1−4. At low pH, below the pK_a, the solubility is fairly constant, but it rises near the pK_a as a result of the additional contribution of the ionic species. In theory, the total solubility should double when pH equals pK_a and ionic and nonionic forms are present at equal concentrations. At a pH of about 9, the solubilities level off at approximately (100 to 250) g/L and the 2,4-DCP solution becomes a viscous, brownish mixture in which a maximum solubility of the ionic species is apparently approached. These highly concentrated solutions are of little environmental relevance, but they may occur in chemical processing.

Conclusions

It is suggested that the coefficients in Table 2 be used to estimate the pH dependence of the aqueous solubilities of these substances and the ionic and nonionic concentrations up to the stated maximum pH when there is an apparent maximum concentration of the ionic species.

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