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Aqueous Solubilities of Chlorinated Phenols at 25 °C

Kuo-Ching Ma, Wan-Ying Shiu, and Donald Mackay*

Pulp and Paper Centre, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, M5S 1A4 Canada

The aqueous solubilities at 25 °C of 16 chlorophenols were measured by a conventional shake flask, batch contacting method with analysis by high-pressure liquid chromatography with UV detection. The liquid or subcooled liquid solubilities are satisfactorily correlated with the solute's LeBas molar volume, yielding a structure–property relationship which may be useful for predictive purposes.

Introduction

In addition to their fundamental interest as a widely used, polar, ionizing series of organic chemicals, the chlorophenols are of particular environmental interest because of their formation during wood pulp bleaching by the forest industry, their use as disinfectants, and their relatively high toxicity (*1*). The environmental fate and hence effects of these substances depend on their physical–chemical properties; thus, there is an incentive to establish a sound data base of these properties and develop predictive methods for use in situations when data are unavailable or are suspect. Recently, Suntio et al. (*2*) reviewed the presence of chlorophenols and other organochlorine compounds in pulp mill effluents and emphasized the lack of reported physical–chemical properties of some chlorophenols, rendering an adequate understanding of their fate in the environment difficult and unreliable. Aqueous solubility is a particularly important parameter for assessing environmental partitioning because it influences evaporation and sorption to biotic and abiotic phases. Of the 19 possible chlorophenol isomers only 9 solubilities have been reported, the most notable study being that of Blackman et al. in 1955 (*3*). It is thus important to expand and update these solubility data and establish structure–property relationships with appropriate molecular descriptors.

Experimental Section

Materials. Chlorophenols (of the highest commercial purity available) were purchased from Aldrich Chemical Co., with the exception that the tetrachlorophenols were obtained from K & K Rare and Fine Chemicals. The chemicals were used as purchased and were not purified. Doubly distilled water was used for all saturated solution preparations. Methanol (HPLC grade) was obtained from Caledon Laboratories, Ontario. Milli-Q ultrapure deionized water was used with methanol as the mobile phase for the HPLC system.

Preparation of Saturated Solutions. Excess amounts of chlorophenols were added to 250-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 48 h before analysis. pH values were measured by a Radiometer Model PHM84 research pH meter before aqueous samples were taken for analysis. There was no pH adjustment or buffering. The pH of the doubly distilled water was measured to be 5.60.

Equipment. Analysis was done using a Waters Associates (Millford, 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 720 system flow controller. The system was operated in isocratic mode with a methanol–water mixture (85:15 by volume) as the mobile phase. 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. The peak area was integrated and recorded by a Waters Model 730 data module. Calibration standards were prepared by dissolving known amounts of the chlorophenols in methanol.

Results and Discussion

Table I gives the measured aqueous solubilities of the chlorophenols at 25 °C and previously reported values. The present solubility data have a precision (standard deviation) of approximately 2–7%. The variation in solubility in a homologous series such as this depends primarily on three factors, (i) the molecular size and shape as characterized here by molar volume, (ii) the melting point in the case of solids, and (iii) the extent of dissociation as determined by pH, pK_a, and ionic strength.

Molar Volume. Table I also gives the molar volume V_M as calculated using the simple, additive LeBas method (*12*) which reduces to the equation

$$V_M/(\mathrm{cm^3/mol}) = 103.4 + 20.9N$$

where N is the number of chlorines and 20.9 represents the difference in the atomic volumes of chlorine and hydrogen. The molar volume or possibly the related surface area is clearly the primary determinant of the trend in solubility.

Melting Point. To improve structure–property correlations for solubility, the solid solubilities should be "corrected" to those of the subcooled liquid values. Most chlorophenols are solids with melting points in the range of 40–80 °C, but some, notably pentachlorophenol, have much higher melting points, while 2-chlorophenol melts at 9 °C. The effect of the melting point can be treated by estimating the fugacity ratio (i.e., the ratio of solid and subcooled liquid solubilities) and correlating the calculated (larger) hypothetical subcooled liquid solubility. In the absence of detailed enthalpy of fusion data the fugacity ratio can be estimated by Yalkowsky's method (*13*) as

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

where f_S and f_L are the fugacities of the solid and liquid of the solute, respectively (Pa), T_M is the melting point (K), and T is the system temperature (K).

Figure 1 is a plot of subcooled liquid solubility versus molar volume which shows the consistent log-linear behavior which is expected if addition of each chlorine adds a constant increment to the excess Gibbs free energy or equivalently to

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* To whom correspondence should be addressed.

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Table I. Aqueous Solubilities of Chlorophenols at 25 °C[a]

compound	MP/°C	pK_a (refs 4 and 5)	LeBas mol vol/ (cm^3/mol)	solubility/ (g/m^3)	pH	lit. value/ g/m^3	pH	method	ref
phenol	41	9.92	103.4			88360	5.1	SF, UV spec	3
2-chlorophenol	9	8.52	124.3	23256 ± 400	4.8	24650		SF, UV spec	6
						11350		SF, LSC	7
3-chlorophenol	33	8.79	124.3	22190 ± 487	4.6	22420		SF, UV spec	6
4-chlorophenol	43–44	9.37	124.3	26390 ± 410	4.6	26250		SF, UV spec	6
						27000	5.1	SF, UV spec	3
						9729		gravimetric	8
2,3-dichlorophenol	58–60	7.71	145.2	8215 ± 318	4.9				
2,4-dichlorophenol	42–43	7.90	145.2	5547 ± 205	5.1	6194	5.1	SF, UV spec	3
						4500		not specified	9
2,6-dichlorophenol	65–68	6.78	145.2	2625 ± 125	4.5				
3,4-dichlorophenol	66–68	8.62	145.2	9256 ± 260	5.1				
3,5-dichlorophenol	67–69	8.25	145.2	7394 ± 105	4.7				
2,3,4-trichlorophenol	79–81	6.97	166.1	915 ± 12.0	5.1				
2,3,5-trichlorophenol	62		166.1	771 ± 52	4.7				
2,3,6-trichlorophenol	58	2.80	166.1	591 ± 30	4.5				
2,4,5-trichlorophenol	68–70	6.72	166.1	649 ± 22	4.9	948	5.1	SF, UV spec	3
2,4,6-trichlorophenol	69.5	5.99	166.1	708 ± 43	4.7	434	5.1	SF, UV spec	3
2,3,4,5-tetrachlorophenol	116	5.64	187	166 ± 5.2	4.9				
2,3,4,6-tetrachlorophenol	70	5.22	187			183	5.1	SF, UV spec	3
2,3,5,6-tetrachlorophenol	115	5.03	187	100 ± 3.3	5.0				
pentachlorophenol	174	4.74	207.9	18.4 ± 1.2	4.8	9.60	5.1	SF, UV spec	3
						15.4		gravimetric	10
						10.8	5.0	gravimetric	11
						14.0	5.0	calculated	11

[a] Note: SF = shake flask; UV spec = UV spectrophotometry; LSC = liquid scintillation counting.

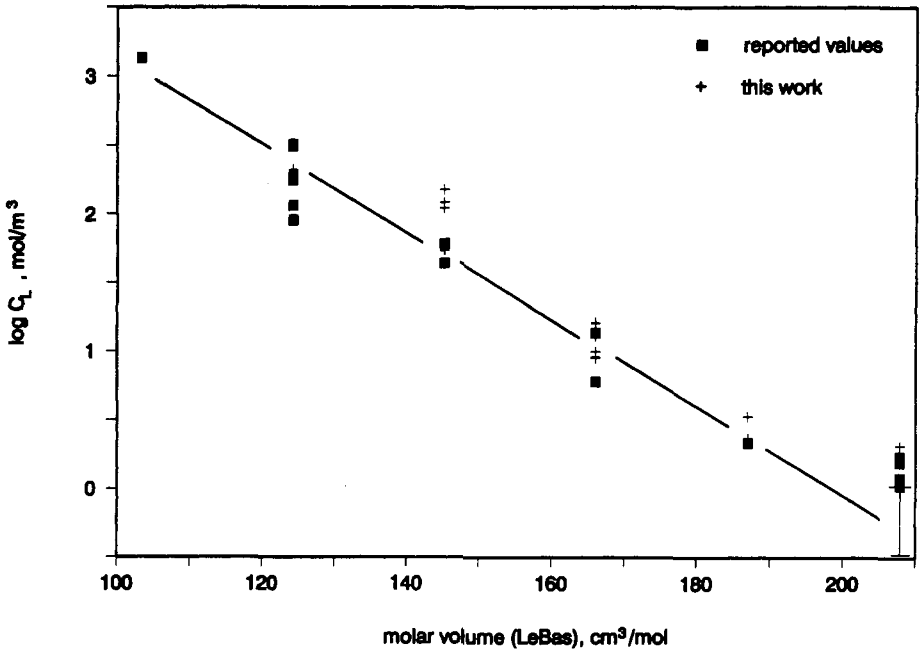

Figure 1. Subcooled liquid solubility of chlorophenols versus LaBas molar volume, with estimated range of solubility shown for undissociated pentachlorophenol.

the logarithm of the activity coefficient. The slope corresponds to a drop in solubility of 0.7 log unit (a factor of $10^{0.7}$ or 5.0) per chlorine added. Pentachlorophenol shows a higher solubility presumably because of its dissociation into phenolate and hydrogen ion.

Dissociation. The higher chlorinated phenols have lower pK_a values and thus tend to dissociate more in aqueous solution. A correction could be applied to calculate the fractions of the dissolved chemical which are in ionic and nonionic forms. All measurements were made at the "natural" pH, i.e., without buffering the aqueous solution; thus, the solubility applies at that pH value. Table I shows these pH values and reported pK_a data (*4*, *5*). To "correct" for this effect, the ratio of dissociated to undissociated forms can be estimated as $10^{-(\mathrm{p}K_a-\mathrm{pH})}$ and the concentration of undissociated solute calculated at the solubility limit. It is likely that the structure–property relationship best expresses the subcooled liquid solubility of the nondissociated species. When the pK_a exceeds the pH by only 1 unit, there is approximately 10% dissociation with less dissociation at greater pK_a–pH separations. No "dissociation correction" is thus needed for mono-, di-, and trichlorophenols for correlating purposes, or when comparing these data with those of Blackman et al. (*3*) which were buffered to a pH of 5.1. No comparable measurements were made of the tetrachlorophenols. Pentachlorophenol is unique because of its low pK_a of 4.74, implying substantial dissociation. The concentrations of the undissociated species of pentachlorophenol as estimated from the experimental pH are (this work) 8.80 g/m^3, (Blackman et al. (*3*)) 4.2 g/m^3 (pH of 5.1), and (Toyota and Kuwahara (*11*)) 3.83 and 4.96

g/m^3 (experimental and calculated values at pH of 5.0). It should also be noted that the melting point correction of pentachlorophenol is substantial and is thus somewhat suspect and that the reported values of pK_a vary from 4.71 (*14*) to 5.25 (*15*). It is believed that the undissociated form has a solubility in the range of 3.0–9.0 g/m^3. This range is shown in Figure 1 and lies fairly close to the correlation line.

This issue has been discussed in the IUPAC compilation of solubility data for phenols by Vesala in ref 16. It is noted that most data are reported at the prevailing pH which varies from chemical to chemical. Yoshida et al. (*17*) have also recently discussed this issue for 2,4,6-trichlorophenol in the context of this chemical's environmental fate. They have pointed out the importance of considering pH as a factor influencing environmental partitioning and hence fate and effects. There is clearly a need to obtain more data on the effect of pH and ionic strength on the solubility for this class of chemicals, particularly the more highly chlorinated substances in which environmental pH may approach the substance's pK_a.

Some differences in solution pH and thus in the reported solubilities of pentachlorophenol are expected from variations in the concentration of acid or base impurities including atmospheric CO_2. For substances such as pentachlorophenol, accurate determination of the solubility and related partitioning quantities such as Henry's law constant and the octanol–water partition coefficient require control of the presence of such impurities. Since the incentive is largely environmental, and natural aquatic systems abound with interacting ionic species, including CO_2, high accuracy may not be justified.

In summary, the data suggest that a simple quantitative structure–property relationship for the chlorophenols (but not including pentachlorophenol) is

$$\log[C_L/(\text{mol/m}^3)] = 6.29 - 0.0315V_M = 3.03 - 0.659N$$

where V_M is the LeBas molar volume, N is the chlorine number, and C_L is the solubility of the undissociated liquid or subcooled liquid chemical at 25 °C at the natural pH. A correction may be applied to calculate the corresponding concentration of dissociated species using reported pK_a data. It is hoped that these data will be of value for assessments of the environmental fate and effects of this class of chemicals.

Literature Cited

(1) Chlorinated Phenols: Criteria for Environmental Quality. National Research Council of Canada, NRC Associate Committee on Scientific Criteria for Environmental Quality, NRCC No. 18578; NRCC Publications: Ottawa, Canada, 1982.
(2) Suntio, L. R.; Shiu, W. Y.; Mackay, D. *Chemosphere* **1988**, *17*, 1259–1290.
(3) Blackman, G. E.; Parke, M. H.; Garton, G. *Arch. Biochem. Biophys.* **1955**, *54*, 55–71.
(4) Dean, J. *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1985.
(5) Ugland, K.; Lundanes, E.; Greibrokk, T.; Bjorseth, A. *J. Chromatogr.* **1981**, *213*, 83–90.
(6) Mulley, B. A.; Metcalf, A. D. *Sci. Pharm.* **1966**, *8*, 481–488.
(7) Banerjee, S.; Yalkowsky, S. H.; Valvani, S. C. *Environ. Sci. Technol.* **1980**, *14*, 1227–1229.
(8) Sigwick, N. V.; Turner, S. L. *J. Chem. Soc.* **1922**, 2256–2263.
(9) Mosso, U. *Jahresber. Fortschr. Chem.* **1887**, 1800.
(10) Carswell, T. S.; Nason, H. K. *Ind. Eng. Chem.* **1938**, *30*, 622–626.
(11) Toyota, H.; Kuwahara, M. *Nippon Dojohiryogaku Zasshi* **1967**, *38*, 93–97.
(12) Reid, R. C.; Prausnitz, J. M.; Polling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.
(13) Yalkowsky, S. H. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 108–111.
(14) Cessna, A. J.; Grover, R. *J. Agric. Food Chem.* **1978**, *16*, 289.
(15) Schellenberg, K.; Leuenberger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1984**, *18*, 652–657.
(16) Horvath, A. L., Getzen, F. W., Eds. *Solubility Data Series: Halogenated Benzenes, Toluenes and Phenols with Water*; Pergamon Press: Oxford, England, 1985; Vol. 20.
(17) Yoshida, K.; Shigeoka, T.; Yamauchi, F. *Chemosphere* **1987**, *16*, 2531–2544.

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