Solubility and Infinite Dilution Activity Coefficient for 5-Chlorovanillin and 4-Chloroguaiacol in Water over the Temperature Range 280 to 363 K

Faïçal Larachi,*,† Marc Leroux,† Safia Hamoudi,† Alain Bernis,‡ and Abdelhamid Sayari†

Department of Chemical Engineering & CERPIC, Laval University, Québec, Canada G1K 7P4, and Laboratoire de Génie des Procédés, Université de Savoie, Domaine Scientifique, 73376 Le Bourget du Lac Cédex, France

New experimental data regarding the solubility of 5-chloro-4-hydroxy-3-methoxybenzaldehyde and 4-chloro-2-methoxyphenol in water were obtained in the temperature range 280 to 363 K. The solubilities were measured by means of two techniques, namely high-performance liquid chromatography (HPLC) and total organic carbon (TOC). Considering the sparingly soluble 5-chloro-4-hydroxy-3-methoxybenzaldehyde, the aqueous infinite dilution activity coefficients were also obtained over the same temperature range by measuring the aqueous solubilities and the organics' enthalpies of fusion. The values of the infinite dilution activity coefficients ranged from 120 to 350 with an average relative deviation of 11%. The solubility−temperature dependence for both organics was well represented by conventional Van't Hoff relationships.

Introduction

Bleaching of the fibers produced by kraft or sulfate pulping of wood usually involves molecular chlorine and chlorine-containing compounds, for example, chlorine dioxide or hypochlorite. When these bleaching agents react with lignin, they generate wastewater effluents containing undesirable biocidal chlorinated compounds such as chlorinated derivatives of phenol.[1−3] For instance, chloroguaiacols and chlorovanillins are typical chlorinated molecules in softwood effluents.[3]

Hazards related to the bioaccumulation of such chlorinated compounds in living organisms and their subsequent impact on public health are forcing the pulp and paper industry to implement a "zero discharge" regulation for their end-of-pipe effluents. This can be achieved, for instance, by abiotic processes which are known to be efficient in the transformation of biorefractory contaminants, such as chlorinated compounds, contained in wastewaters.[4] Catalytic oxidation or reduction and other advanced oxidation processes are particularly efficient for the transformation of these pollutants into innocuous, environmentally benign entities such as carbon dioxide and chloride ions.[5,6]

Abiotic techniques usually require moderate to high temperatures to trigger the process reactivity and to break apart the dissolved pollutants. Therefore, a knowledge of the aqueous solubilities and the infinite dilution activity coefficients of pollutants such as chloroguaiacols and chlorovanillins at these temperature conditions is fundamental to the development of engineered treatment processes to minimize their release into the biosphere.

This work reports new temperature−solubility data for 5-chloro-4-hydroxy-3-methoxybenzaldehyde (or 5-chlorovanillin) and 4-chloro-2-methoxyphenol (or 4-chloroguaiacol) obtained over the temperature range 280 to 363 K. The aqueous infinite dilution activity coefficients versus temperature for 5-chlorovanillin were obtained from measured enthalpies of fusion and very low aqueous solubilities.

Theory

Liquid−Liquid Equilibrium (LLE) of the 4-Chloro-2-methoxyphenol + Water System. It was assumed that mutual solubilities between species are low so that 4-chloroguaiacol remains substantially pure and only the one-sided solubility of the latter in water is determined.[7] The equations[8] which relate the mole fraction solubility of 4-chloroguaiacol to the enthalpy and entropy of dissolution and the activity coefficient at infinite dilution are

$$\ln x = -\frac{\Delta H^{e}}{RT} + \frac{\Delta S^{e}}{R} \tag{1}$$

$$\gamma^{\infty} = x^{-1} \tag{2}$$

where ΔS^{e} is the molar entropy of dissolution, ΔH^{e} is the molar enthalpy of dissolution, R is the universal gas constant, x is the mole fraction aqueous solubility, γ is the activity coefficient of the solute in water, and T is the equilibrium temperature. It was assumed that ΔH^{e} and ΔS^{e} were constant over the temperature range of interest to this study.

Liquid−Solid Equilibrium (LSE) of the 5-Chloro-4-hydroxy-3-methoxybenzaldehyde + Water System. Considering a Hildebrand−Scatchard activity coefficient dependence leads to the following general relationship[7] between the solubility and the infinite dilution activity coefficient:

$$\Delta S^{m} = \frac{\Delta H^{m}}{T^{m}} \tag{3}$$

---

* To whom correspondence should be addressed. Telephone: 001-418-656-3566. Fax: 001-418-656-5993. E-mail: flarachi@gch.ulaval.ca.

† Laval University.

‡ Université de Savoie.

10.1021/je990222g CCC: $19.00

$$\ln(\gamma^{\infty}) = \left(1 + \frac{\bar{V}}{\bar{V}_{\mathrm{w}}}\frac{x}{1-x}\right)^{2}\left[-\ln(x) - \frac{\Delta H^{\mathrm{m}}}{RT}\left(1 - \frac{T}{T_{\mathrm{m}}}\right) - \frac{\Delta C_{\mathrm{p}}}{R}\left\{1 - \frac{T_{\mathrm{m}}}{T} + \ln\left(\frac{T_{\mathrm{m}}}{T}\right)\right\} - \frac{\Delta VP}{RT}\right] \quad (4)$$

where T_m is the melting temperature at atmospheric pressure, ΔH^m and ΔS^m are respectively the molar enthalpy and entropy of fusion at T_m, ΔC_p is the heat capacity difference between the subcooled liquid and the solid, ΔV is the difference in the specific volumes of the liquid and solid states, $\bar{V}_w$ is the specific volume of the solvent phase, that is, water, and $\bar{V}$ is the solute specific volume. Because of the relatively narrow temperature range involved and the scarcity of heat capacity data, the limited effect of the heat-capacity difference, and the usually small contribution of the Poynting factor correction, the last two terms in eq 3 were neglected.[7] Consequently, provided the melting temperature, enthalpy of fusion, and aqueous solubility mole fraction of a component are available, it is possible to calculate its infinite dilution activity coefficient in water.

Materials

Deionized (DI) water obtained from a Culligan Model E1 Plus purification system (electrical conductance < 1 μsiemens) was used in the preparation of the saturated solutions. The chlorinated phenol derivatives of this study were analytical grade 5-chloro-4-hydroxy-3-methoxybenzaldehyde (5-chlorovanillin) with a purity of 97%+ and 4-chloro-2-methoxyphenol (4-chloroguaiacol) with a purity of 99%+, supplied respectively by Helix Biotech Corp. (Richmond, BC) and Sigma-Aldrich Canada Ltd (Oakville, ON). They were used as received without further purification. The other chemicals used were HPLC grade Omnisolv Methanol (E. M. Science, NJ) and water for the mobile phase, technical grade nitrogen, and ultrapure air (Praxair Inc., Québec, PQ).

Procedure for Aqueous Solubility Measurements

The protocol for measuring the aqueous solubilities was based on the saturated flask technique.[2,3,9,10] The Pyrex equilibrium cell consisted of a magnetically or mechanically agitated Erlenmeyer flask. For solubility measurements in the range $280 \leq T \leq 298$ K, the vessel was immersed in a stirred Blue M bath (Blue Island, IL) refrigerated using a Haake EK12 (Berlin, Germany) cooling unit. The temperature was stable to ± 0.1 K. For measurements at higher temperature, that is, in the range $293 \leq T \leq 363$ K, the flask was embedded in an electrical heating coil and placed on a heating/stirring plate. The flask temperature was controlled to ± 0.1 K. A pH probe (Accumet pH meter Model 10, Fischer-Scientific Co.), a bulb thermometer, and a glass tube were inserted into the flask through rubber stoppers. The glass tube was for the sampling of the saturated solution after great care was taken to avoid contamination by the floating crystals or droplets of the organic phase. There was no buffering or pH adjustment of the solutions.

To avoid possible product oxidation during dissolution, the air in the flask headspace was evacuated and the DI water was degassed by nitrogen bubbling. An inert atmosphere within the cell was maintained during all the experiments with a slight overpressure of the nitrogen stream. Large amounts of both chemicals were dissolved in 50 mL of water at a temperature close to its normal boiling point. There was always a sufficient organic phase to distinguish the presence of an aqueous−organic two-phase mixture. The system was then cooled until it reached the temperature at which steady-state equilibrium concentration (or solubility) measurements were planned. It was systematically verified that enough time had elapsed at each temperature so that time-independent concentration values were attained, indicating efficiently mixed and equilibrated solutions. This can be seen in Figure 1, which illustrates the dissolution time course at 359 K for both 4-chloroguaiacol and 5-chlorovanillin along with the temperature profile used.

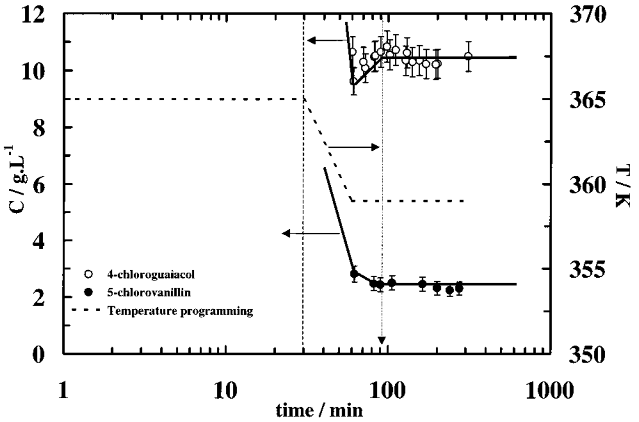

Figure 1. Illustration of the mixing and equilibrium time and temperature profile before sampling 4-chloroguaiacol and 5-chlorovanillin saturated solutions.

Analytical Methods

The equilibrium concentration of the tested chlorinated phenol derivatives was determined using a high-performance liquid chromatograph (HPLC), which consisted of a combination of a model 510 Waters dual-solvent delivery system, a model 490 programmable multiwavelength ultraviolet absorbance detector, an automated gradient controller, and a 30-cm μBondapak C_{18} column (Waters Associates Inc., Milford, MA). The unit was operated isocratically at 0.6 mL·min^{-1} using as a mobile phase 85:15 (volume ratio) v/v methanol/water. UV detection was performed at 270 nm. Peak area recording and integration were achieved using a Hewlett-Packard integrator (HP 3390 A). HPLC calibration was achieved by using a parent concentrated solution from which daughter solutions were obtained by successive dilutions.

To improve the reliability of our data, all solubility measurements were carried out using another independent technique. Saturated solutions were analyzed for their organic carbon content using a total organic/inorganic carbon (TOC/TIC) analyzer (model Shimadzu 5050 TOC analyzer, Mandel Scientific Inc., Montréal, PQ) equipped with a combustion/nondispersive infrared gas detector. The TOC/TIC analyzer was calibrated with analytical grade 99.998+% potassium hydrogen phthalate and sodium carbonate/bicarbonate mixtures.

The concentration of 4-chloroguaiacol and 5-chlorovanillin at saturation was always sufficiently high to allow precise HPLC measurements by direct injection of aliquots of the solutions. Prior to sampling and after equilibration was reached, the agitation was momentarily stopped to allow for turbidity disappearance after the supernatant 4-chloroguaiacol drops (or the 5-chlorovanillin particles) had settled down. After this was done, a pipet was inserted through the glass tube slightly beneath the free surface of the solution. Approximately 1 ± 0.05 mL of saturated aqueous solution was withdrawn from the flask and poured into a sample vial, where it was diluted three times. Before

Table 1. Thermochemical and Thermodynamic Data[a] Relative to 4-Chloroguaiacol (1) and 5-Chlorovanillin (2)

	T_m (K)	M_w (g·mol^{-1})	pK_a[b]	V_{LB}[c] (cm^3·mol^{-1})	ΔH^m (kJ·mol^{-1})	ΔS^m (J·mol^{-1}·K^{-1})
(1)	liq	158.58		153.9[d]		
(2)	442.6 ± 0.2	186.59	6.80	191.1[b]	39.4 ± 1.6[e]	89.1 ± 3.6[f] 56.5[g] 50.0[h]

[a] Uncertainties of measured and fitted values are given as standard deviations. [b] From ref 3. [c] LeBas molar volume. [d] From ref 2. [e] Measured by the DSC technique. [f] Computed from eq 4. [g] Estimation with the Yalkowsky melting entropy correlation.[12] [h] Estimation with the Dannenfelser and Yalkowsky melting entropy correlation.[13]

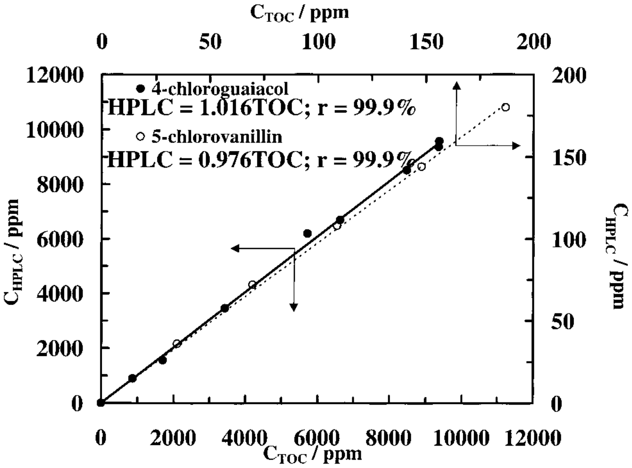

Figure 2. Solubility data: TOC versus HPLC measurements.

Table 2. Temperature Dependence of the 4-Chloroguaiacol Solubility in Water

T/°C	C/ppm (g·m^{-3})	x (σ_x/x in %)	γ^∞
90.0	10255 ± 121	1.20 × 10^{-3} (1)	830 ± 10
85.6	9540 ± 336	1.12 × 10^{-3} (4)	895 ± 31
78.0	9171 ± 428	1.07 × 10^{-3} (5)	936 ± 44
70.5	8639 ± 273	1.00 × 10^{-3} (3)	998 ± 31
66.0	7040 ± 143	8.15 × 10^{-4} (2)	1227 ± 25
54.5	7054 ± 628	8.12 × 10^{-4} (9)	1232 ± 110
50.0	6213 ± 83	7.13 × 10^{-4} (1)	1402 ± 19
41.0	6658 ± 128	7.61 × 10^{-4} (2)	1314 ± 25
36.3	5406 ± 452	6.17 × 10^{-4} (8)	1620 ± 135
25.0[a]	5604 ± 741	6.38 × 10^{-4} (13)	1568 ± 207
19.0	4856 ± 85	5.52 × 10^{-4} (2)	1812 ± 32
15.0	4548 ± 84	5.16 × 10^{-4} (2)	1936 ± 36
11.0	4467 ± 134	5.07 × 10^{-4} (3)	1972 ± 59
10.0	4395 ± 32	5.00 × 10^{-4} (1)	2005 ± 14

[a] From ref 2.

Table 3. Temperature Dependence of the 5-Chlorovanillin Solubility in Water

T/°C	C/ppm (g·m^{-3})	x (σ_x/x in %)	γ^∞
85.9	2314 ± 40	2.30 × 10^{-4} (2)	356 ± 6
80.0	1767 ± 16	1.75 × 10^{-4} (1)	375 ± 3
70.0	1267 ± 26	1.25 × 10^{-4} (2)	356 ± 7
65.0	1139 ± 19	1.12 × 10^{-4} (2)	324 ± 6
59.0	932 ± 61	9.14 × 10^{-5} (7)	308 ± 20
50.0	760 ± 8	7.42 × 10^{-5} (1)	255 ± 3
46.0	629 ± 6	6.13 × 10^{-5} (1)	257 ± 3
36.5	505 ± 172	4.90 × 10^{-5} (34)	204 ± 69
30.0	286 ± 87	2.77 × 10^{-5} (31)	260 ± 79
25.0[a]	932 ± 28		
24.0	249 ± 47	2.41 × 10^{-5} (19)	218 ± 41
19.8	168 ± 19	1.62 × 10^{-5} (11)	256 ± 28
16.8	184 ± 31	1.77 × 10^{-5} (17)	198 ± 33
12.0	171 ± 46	1.65 × 10^{-5} (27)	162 ± 44
7.5	171 ± 3	1.65 × 10^{-5} (2)	124 ± 2

[a] From ref 3.

injection in the HPLC or in the TOC analyzer, it was systematically verified that the solutions were free of organic droplets or crystals that would have been inadvertently drawn into the 1 mL sample.

To ensure highly accurate and precise solubility measurements free from experimental artifacts, and to quantify the experimental random-effect errors due to the experimental protocol, the following procedure was used. For precision, three determinations of solubility were performed on each aliquot. For accuracy and bias-free analysis, the HPLC and TOC calibration curves were used to verify agreement of the solubility measurements by the two analytical techniques. To ensure bias-free solubility determinations where the sole contribution is from random-effect errors, fresh solutions were prepared on two other days and then were analyzed again. This brought the number of repeat tests to 12 to 18 per equilibrium temperature/solubility data. The consistency between HPLC and TOC measurements of 4-chloroguaiacol and 5-chlorovanillin aqueous solubilities is depicted in Figure 2, where almost a unit slope parity plot and a correlation coefficient of 99.9% were obtained for both organic solutes.

The molar enthalpy of fusion for 5-chlorovanillin was measured by means of a differential scanning calorimeter (DSC). A Perkin-Elmer Model DSC 7 computer-monitored with Pyris Series software was used for this purpose. The DSC was first calibrated with high-purity indium, for which an accurate value of the enthalpy of fusion is known. The samples of 5-chlorovanillin sealed in an aluminum pan were placed in one cell of the DSC, while the other cell was blank. Both sample and blank cells with attached thermosensors were heated in the DSC chamber subjected to a temperature ramp from 50 °C to 250 °C with a hold of 0.1 min at 50 °C and a heating rate of 20 °C·min^{-1}. The error on the measured temperature was ± 0.5 K. The integrated difference in heat input to the cells due to the melting of 5-chlorovanillin leads to the enthalpy of fusion per unit mass, which is thereafter converted into the molar enthalpy. The accuracy, in terms of relative error, for the measurements of the molar enthalpy of fusion was estimated to be 2%. The melting point (or T_m) was determined within ±0.1 K.

Results and Discussion

Table 1 lists the thermochemical and some thermodynamic characteristics of 4-chlorguaiacol and 5-chlorovanillin. Tables 2 and 3 give the measured aqueous solubilities for 4-chloroguaiacol and 5-chlorovanillin in terms of mass concentration and mole fraction at their natural pH, as measured between 280 and 363 K by the two aforementioned experimental techniques. The derived infinite dilution activity coefficients are also tabulated. The solubilities of 4-chloroguaiacol and 5-chlorovanillin measured at 298 K by Tam et al.[2] and Varhaničková et al.[3] are shown for comparison, respectively. The standard deviation corresponding to each solubility measurement is also listed in Tables 2 and 3.

The standard deviation of the dependent variables, such as the solubility mole fraction or the infinite dilution

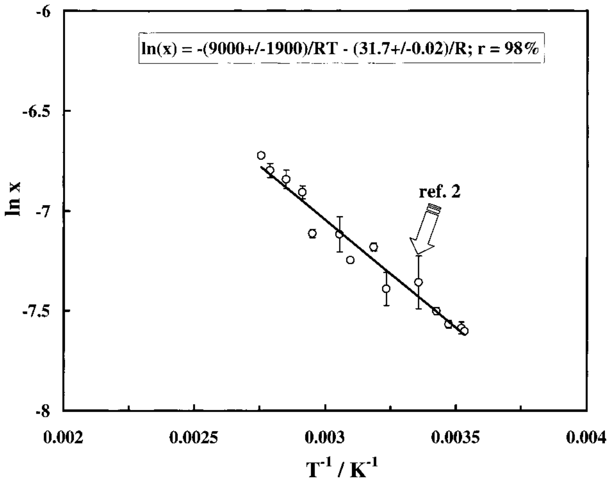

Figure 3. Van't Hoff plot of the solubility mole fraction of 4-chloroguaiacol versus temperature along with the estimated standard deviations.

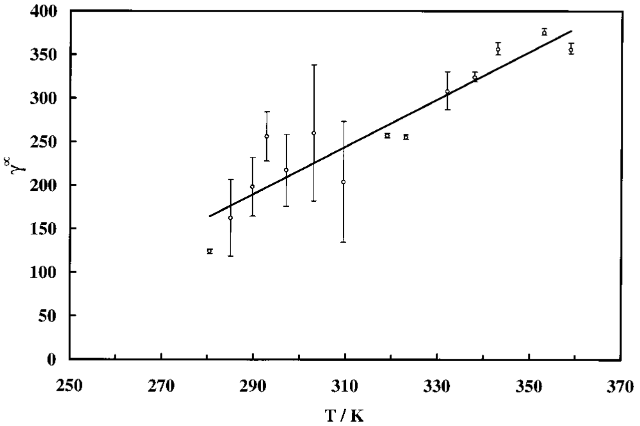

Figure 4. Infinite dilution activity coefficient of 5-chlorovanillin as a function of temperature along with the estimated standard deviations of the activity coefficients. The solid line shows the trend.

activity coefficient, was estimated using the "propagation-of-errors" formula and the individual standard deviations on measured entities

$$\sigma_{y,j}{}^2 = \sum_{i=1}^{l}\left(\frac{\partial y}{\partial x_i}\right)^2 \sigma_{xi,j}{}^2 \tag{5}$$

where the variance $\sigma_y{}^2$ on the dependent variable y is expressed as a function of the variances $\sigma_{xi}{}^2$ of the l x_i independent variables for each j run.

LLE of the 4-Chloro-2-methoxyphenol + Water System. A Van't Hoff plot of the logarithm of mole fraction solubility versus reciprocal absolute temperature is shown in Figure 3 for the 4-chloroguaiacol molecule. The molar enthalpy and entropy of dissolution of 4-chloroguaiacol were estimated from the weighted χ^2 value

$$\chi^2 = \sum_{i=1}^{l}\frac{x^2}{\sigma_x{}^2}\left(\ln x + \frac{\Delta H^{\mathrm{e}}}{RT} - \frac{\Delta S^{\mathrm{e}}}{R}\right)^2 \tag{6}$$

by fitting the regression parameters of eq 1 using a linear least squares parameter estimation procedure wherein the squared ratio of the mole fraction to the mole fraction standard deviation was used as the statistical weight for each solubility data point.[11] The results of this regression analysis led to the enthalpy and entropy of dissolution of 9.0 ± 1.9 kJ·mol^{-1} and −31.7 ± 0.02 J·mol^{-1}·K^{-1}, respectively (uncertainties given as standard deviations). The covariance between the regressed ΔH^{e} and ΔS^{e} was 75%, and the correlation coefficient was 99.6%. Figure 3 also shows the best-fit straight line.

LSE of the 5-Chloro-4-hydroxy-3-methoxybenzaldehyde + Water System. A knowledge of the enthalpy of fusion and the melting temperature is needed to calculate the entropy of fusion of 5-chlorovanillin according to eq 4 above. An estimate for the entropy of fusion can also be made using the Yalkowsky[12,13] correlation, assuming rigid and asymmetrical 5-chlorovanillin molecules. Table 1 shows that the Yalkowsky correlation underestimated the actual value for the entropy of fusion by about 37%. These thermochemical data and other properties of 5-chlorovanillin are listed in Table 1. It is worth mentioning that the enthalpy and entropy of fusion thus determined compare well with typical enthalpies and entropies of fusion reported by Mackay's group[2] for several substituted guaiacol molecules of similar structure.

The solubility data for 5-chlorovanillin are listed in Table 3. Contrary to the close agreement between the 4-chloroguaiacol aqueous solubilities of this work and that of the Mackay group,[2] the discrepancy in the 5-chlorovanillin solubilities at 25 °C reported by the two groups was remarkable.[3] From the solubility information in Table 3, the values of the infinite dilution activity coefficients for 5-chlorovanillin as a function of temperature were calculated using eq 3. The values are plotted in Figure 4 and are also given in Table 3 along with their standard deviations. Confidence intervals were obtained using the "propagation-of-errors formula" (eq 5), which calculates the variance in the quantity γ^∞ from a knowledge of the variances of the saturation mole fraction (x), the enthalpy, and the temperature of fusion of 5-chlorovanillin. The values of the infinite dilution activity coefficients ranged from 120 to 350 and exhibited an almost linear increase with temperature (see Figure 4). These are, to the best of our knowledge, the first reported aqueous infinite dilution activity coefficients for this particular chlorinated phenol derivative.

Acknowledgment

The authors wish to thank Dr. Abdelwahab Ziani for logistic help with the DSC measurements.

Literature Cited

(1) Estridge, R. B.; Holm, R. A.; Day, C. P.; Phenicie, D. K.; Evans, D. E.; Phillips, R. B.; Franklin, E. C.; Stovall, J. H.; Gellman, I. Environmental Concerns In Paper Industry Research Needs. Tappi Workshop, May 26−28, 1992, Syracuse, New York, pp 10−44.

(2) Tam, D.; Varhanıčková, D.; Shiu, W.-Y.; Mackay, D. Aqueous Solubility of Chloroguaiacols. *J. Chem. Eng. Data* **1994**, *39*, 83−86.

(3) Varhanıčková, D.; Lee, S.-C.; Shiu, W.-Y.; Mackay, D. Aqueous Solubilities of Chlorocatechols, Chlorovanillins, Chlorosyringols; and Chlorosyringaldehydes at 25 °C. *J. Chem. Eng. Data* **1995**, *40*, 620−622.

(4) Watts, R. J. *Hazardous Wastes: Sources, Pathways, Receptors*; Wiley: New York, 1997.

(5) Matatov-Meytal, Y. I.; Sheintuch, M. Catalytic Abatement of Water Pollutants. *Ind. Eng. Chem. Res.* **1998**, *37*, 309−326.

(6) Hamoudi, S.; Larachi, F. Catalytic Wet Oxidation of Phenol and Chloroguaïacol. 48th CChE Conf., London, Ontario, October 4−7, 1998.

(7) Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth: Boston, 1985.

(8) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; Wiley: New York, 1993.

(9) Haines, R. I. S.; Sandler, S. I. Aqueous Solubilities and Infinite Dilution Activity Coefficients of Several Polycyclic Aromatic Hydrocarbons. *J. Chem. Eng. Data* **1995**, *40*, 833−836.

(10) Mackay, D.; Shiu, W.-Y. Aqueous Solubility of Polynuclear Aromatic Hydrocarbons. *J. Chem. Eng. Data* **1977**, *22*, 399−408.

(11) Press: W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in Fortran. The Art of Scientific Computing*, 2nd ed.; Cambridge University Press: MA, 1992.

(12) Yalkowsky, S. H. Estimation of Entropies of Fusion of Organic Compounds. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 108−111.

(13) Dannenfelser, R. N.; Yalkowsky, S. H. Estimation of Entropy of Melting from Molecular Structure: A Non-Group Contribution Methodology. *Ind. Eng. Chem. Res.* **1996**, *35*, 1483−1486.

Received for review August 3, 1999. Accepted January 10, 2000. Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC), the Fonds pour la Formation de Chercheurs et d'Aide à la Recherche (Québec), the Program de bourses Rhones-Alpes France, and the Program de Coopération Jacques-Cartier is gratefully acknowledged.

JE990222G