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UV–Vis Spectrophotometric Determination of the Dissociation Constants for Monochlorophenols in Aqueous Solution at Elevated Temperatures

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The dissociation constants of monochlorophenols (2-, 3-, 4-chlorophenols) were examined using direct UV–vis spectroscopy at temperatures from 25 to 175°C and at saturated vapor pressures in a high-temperature, high-pressure cell. The dissociation constant, K_a increased under experimental temperatures in the order: 2-chlorophenol, 3-chlorophenol, and 4-chlorophenol. The dissociation constant of 4-chlorophenol increased with increasing temperature under experimental conditions, while those of 2- and 3-chlorophenol reached maximum values at around 125°C, and then decreased with further increases in temperature. The slope of $\partial(\log K)/\partial\ (1/T)$ was nonconstant and positive, that is, endothermic, below 150°C. The data on dissociation constants were analyzed by simultaneous regression to yield a five-term equation that described the Van't Hoff isobar. The magnitude of enthalpy ΔH increased at 25°C in the order: 3-chlorophenol, 4-chlorophenol, and 2-chlorophenol. The decrease in enthalpy at the absolute temperature was larger for 3-chlorophenol than for either 2- or 4-chlorophenol. Considering the equilibrium constant K_b for the isocoulombic reaction of monochlorophenol with OH^-, the nearly linear relationship of log K_b *vs.* $1/T$ for temperatures between 25 and 175°C indicates that the ΔC_p values for this isocoulombic reaction are low.

KEY WORDS: Monochlorophenol; dissociation constant; UV–vis spectroscopy; high-temperature aqueous solution.

1. INTRODUCTION

Aromatic compounds, particularly chlorinated phenolic compounds, have many applications. Chlorophenols are used as pesticides and herbicides and are the by-products of several industries, being found, for example, in effluents from pulp bleaching processes. Since chlorophenols have been classified as priority water pollutants, properties affecting their removal from water merit special attention.

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The acid dissociation behavior of chlorophenols in aqueous solutions is important in predicting the environmental fate of toxic effluents. Because hydrothermal conditions are increasingly used in industrial processes, such as wastewater treatment,(1) it is important to characterize the reaction equilibria and kinetics of ionic species in sub- and supercritical water. Furthermore, it is useful to determine the effects of temperature and pH on these properties. Although a few studies have determined the dissociation constants of monochlorophenols (2-chlorophenol, 3-chlorophenol, and 4-chlorophenol) at room temperature,(2–14) the effect of temperature on the constant parameters has not been examined except in the study by Chen and Laidler.(14)

Various methods have been used to study hydrothermal reactions. Spectroscopic methods have been utilized widely to study hydrothermal reactions because they can use to measure reactant concentrations directly. Many readily available spectral techniques, including IR,(15,16) Raman,(16–19) and UV-visible,(16,20–42) are being used to characterize reactions, such as equilibria and kinetics, under hydrothermal conditions. Particularly, in spite of the limitation that measurements of equilibria require species containing appropriate chromophores, UV–vis spectroscopy have been used in many studies of ionic equilibria of inorganic compounds,(24–26) complexes,(26–32) and organic compounds,(33–36,42) including phenols(39) in high-temperature aqueous solutions. The hydrothermal equilibria of compounds with insufficient absorbance in the UV–vis region have also been examined using pH indicators that are stable at high temperatures.(37–42)

The purpose of this study was to analyze the acid dissociation of monochlorophenols in high-temperature aqueous solutions and to characterize the behavior of hazardous aromatic organochlorinated compounds under different hydrothermal conditions. The dissociation constants of monochlorophenols at temperatures up to 175°C and at saturated vapor pressures were examined by UV–vis spectroscopy with a high-temperature, high-pressure cell. Since monochlorophenols have absorption peaks in the UV–vis region, they are appropriate substances for *in situ* measurements using UV–vis spectroscopy. The thermodynamic properties at infinite dilution were determined by regression analysis of the dissociation constants of each monochlorophenol and variations in the temperature dependence of acid dissociation equilibria between the different monochlorophenols were examined.

2. EXPERIMENTAL

2.1. Chemicals and Solutions

2–Chlorophenol (99%) and 3-chlorophenol (99%) were purchased from GL Sciences Inc.; 4-chlorophenol (99%) was obtained from Aldrich Chemical Co. Analytical grade sodium hydroxide was obtained from Kanto Chemical Co. Freshly distilled and deionized water from a Millipore QII system, with a specific resistance of 18 MΩ-cm, was used to prepare all of the solutions. For spectra measurements, each monochlorophenol was prepared in aqueous solution to give a sample concentration of $5 \times 10^{-5} M$. The NaOH concentration of the solutions was adjusted using a stock solution of 0.1 M sodium hydroxide.

2.2. Experimental Apparatus and Procedures

The high-pressure, high-temperature cell used for absorption measurements of solutions is illustrated in Fig. 1. It consists of a cylindrical SUS316 cell with quartz window that is sealed with PEEK$^{\lambda}$ gaskets and has a window aperture of 1 cm. The path length of 1 cm was calibrated by comparisons of the absorbances of a series of $K_2Cr_2O_7$/KOH solutions using a 10-mm silica glass cuvette. The overall experimental apparatus is shown in Fig. 2. The optical cell was mounted in a heater box and controlled to $\pm 1^{\circ}$C of the stated temperatures. Pressure was controlled with an HPLC pump (Shimadzu LC-10AT VP) and a spring-loaded back-pressure regulator (TESCOM series 26-1700). During spectrum measurements, the solutions were kept at pressures that were slightly above saturated water vapor pressure for each temperature. A three-way valve was installed in the feed tubing to allow alternate pumping of sample solution and water, each with its own nitrogen sparge. Before taking an absorption spectrum, each solution was deaerated for 30 min by purging with nitrogen gas. The sample solution was then pumped into the cell at a delivery rate of 0.05 to 0.2 ml-min^{-1} for 30 min. All of the spectra were collected at 0.1-nm intervals using a double-beam spectrophotometer (JASCO V-570). The spectra were corrected for background absorbance (windows and solution/solvent) by subtracting the absorbance of a cell filled with pure water at each temperature. The entire process of flushing the apparatus with a new solution or pure water and obtaining the spectra took about 40 min for each temperature setting. During spectral scans, the flow was stopped. The spectra were collected over the range 190 to 350 nm at a scan rate of 100 nm-min^{-1}.

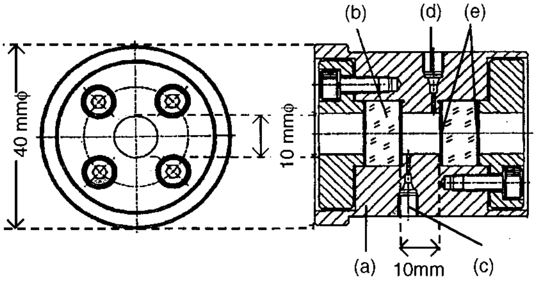

Fig. 1. Side and cross-sectional views of the SUS316 cell with quartz windows: (a) 316SS Body; (b) quartz window; (c) solution inlet; (d) solution outlet; (e) PEEK$^{\lambda}$ gasket.

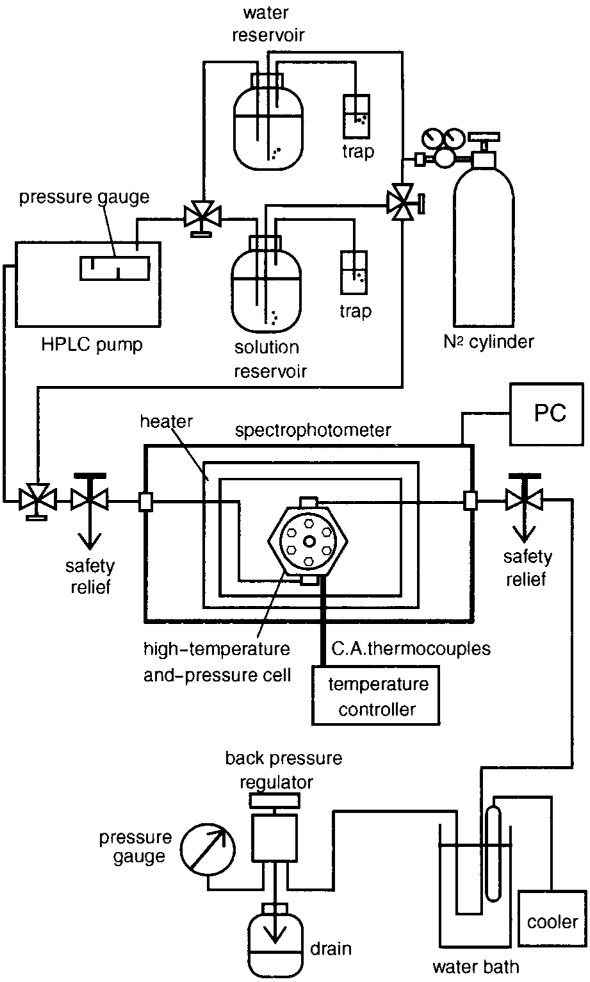

Fig. 2. Experimental set-up.

3. RESULTS AND DISCUSSION

3.1. Spectra of Monochlorophenols

The UV–vis spectra of monochlorophenols (2-, 3-, and 4-chlorophenol) did not change over a 3-h time period under the following conditions:temperature range 25–175°C; NaOH concentration range 0–$2.5 \times 10^{-2} M$; and saturated vapor pressure. This shows that monochlorophenols do not decompose under these conditions.

The acid dissociation equilibrium for monochlorophenol (Ph-OH) solution is

$$\text{Ph–OH} = \text{Ph–O}^- + \text{H}^+ \tag{1}$$

with pK_a at 25°C of 8.3 to 9.4 for 2-chlorophenol, 8.9–9.2 for 3-chlorophenol, and 9.2–9.4 for 4-chlorophenol.(2–14)

Figure 3 shows the spectra of monochlorophenols ($5 \times 10^{-5} M$) under acidic and alkaline conditions. In the range of wavelengths between 200 and 350 nm, each

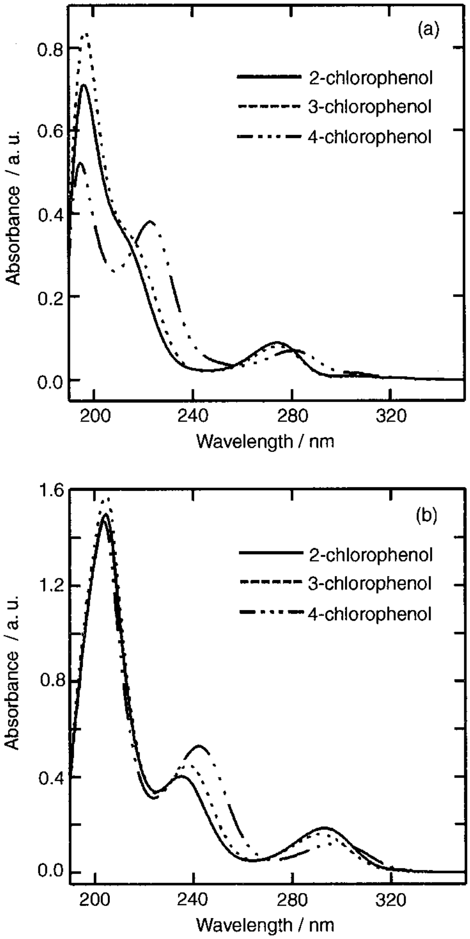

Fig. 3. Typical spectra of $5 \times 10^{-5} M$ monochlorophenols at room temperature and pressure in (a) acidic, and (b) alkaline media: (a) 0 M NaOH; (b) 2.5×10^{-2} M NaOH.

monochlorophenol has two peaks and/or shoulders in both acidic and alkaline aqueous solutions. 2-Chlorophenol and 3-chlorophenol show similar spectra in acidic media (Fig. 3a), *i.e.*, one shoulder at approximately 215 nm and one peak at 275 nm. In contrast, 4-chlorophenol shows two peaks at 225 and 280 nm that are slightly red-shifted compared to those of the 2- and 3-chlorophenols. In alkaline media, each monochlorophenol has two peaks, which are red-shifted compared to those in acidic media, and which are localized around 240 and 295 nm (Fig. 3b). The two absorption bands were shifted to progressively longer wavelengths according to order: 2-, 3-, and 4-chlorophenol.

Figure 4 shows the effect of temperature on the spectrum of a $5 \times 10^{-5} M$ 3-chlorophenol solution containing 2×10^{-4} M NaOH. Increasing temperature leads to gradual decreases in the two absorption bands at 240 and 295 nm. This indicates a shift toward the nonionic protonated form of 3-chlorophenol with increasing temperature at constant NaOH concentration. The spectra of the 2- and 4-chlorophenols show similar changes with temperature. At temperatures above 175°C, additional reactions, such as the decomposition of chlorophenol and interactions between NaOH and chlorophenol, occur and the spectra take on different appearances. Therefore, examination of the acid dissociation equilibria of monochlorophenols was not possible at temperatures above 175°C. The individual spectra of $5 \times 10^{-5} M$ monochlorophenols in aqueous solution without added NaOH remain constant between 25 and 175°C. This is due to the solutions being sufficiently acidic to keep the monochlorophenols fully protonated under experimental conditions. Accordingly, solutions of monochlorophenols without added NaOH were used to calibrate the absorbance of the pure acidic species of

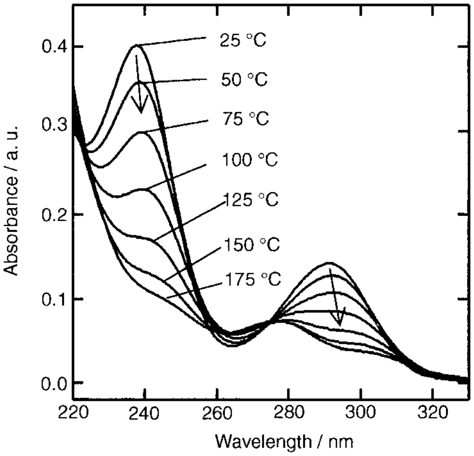

Fig. 4. Effect of temperature on the absorbance spectra of $5 \times 10^{-5} M$ 3-chlorophenol in $2 \times 10^{-4} M$ NaOH.

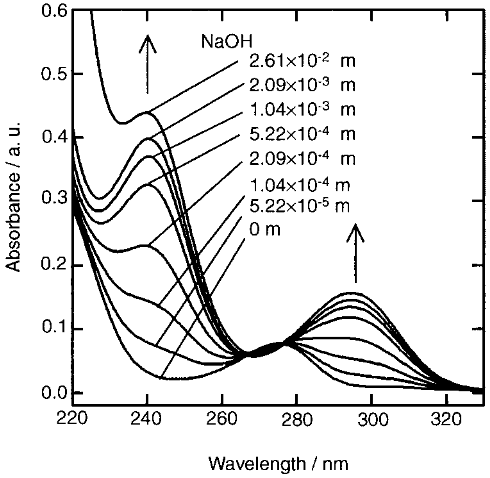

Fig. 5. Effect of NaOH concentration on the absorbance spectra of 5×10^{-5} *M* 3-chlorophenol at 100°C.

monochlorophenols, as described in the next section. The spectra from 240 to 350 nm of monochlorophenols in 2.5×10^{-2} *M* NaOH did not change in appearance with temperature, but a slight red shift was observed.

Figure 5 shows the effect of NaOH concentration on the spectrum of a $5 \times 10^{-}5$ *M* 3-chlorophenol solution at 100°C. There are at least two isosbestic points. Increasing the NaOH concentration leads to gradual increases in the two absorption bands at 240 and 295 nm. This indicates a shift toward the ionic deprotonated form of 3-chlorophenol, the phenolate anion ($Ph{-}O^-$), with increasing NaOH concentration. The spectra of 2- and 4-chlorophenol show similar changes with increasing NaOH concentration. The absorption maxima of PhOH and PhO^-, which appear in the wavelength range from 240 to 330 nm, allow the concentrations of PhOH and PhO^- to be monitored by absorption spectroscopy using deconvolution of the spectra. Therefore, spectral measurement with UV–vis spectroscopy can be used to investigate the equilibrium behavior of monochlorophenols in aqueous solutions.

3.2. Dissociation Constants K_a of Monochlorophenols

The temperature dependence of the monochlorophenol acid–base equilibrium is quantified by the dissociation constant at a constant pressure as a function of temperature. Steady-state absorption spectroscopy is used to determine the concentrations of monochlorophenols and their phenolate anions as described by Ryan *et al.*,(34) and Xing and Johnston.(35)

Monochlorophenols ($Ph{-}OH$) dissociate a proton and form phenolate anions ($Ph{-}O^-$), as described Eq. (1).

The dissociation constant is expressed as

$$K_a = \frac{a_{\mathrm{Ph-O^-}}\, a_{\mathrm{H^+}}}{a_{\mathrm{Ph-OH}}} \tag{2}$$

where a_i denotes the activity of each species. By defining the activity coefficient of each species, rearranging Eq. (2) gives

$$\log \frac{m_{\mathrm{Ph-OH}}}{\gamma_{\pm} m_{\mathrm{Ph-O^-}}} = -\log K_a + \log(\gamma_{\pm}\, m_{\mathrm{H^+}}) \tag{3}$$

where $\gamma_{\pm}$ is the mean activity coefficient of ions and m_i is the molal concentration of each species. Therefore, K_a is determined from (I) $m_{\mathrm{Ph-OH}}/\gamma_{\pm} m_{\mathrm{Ph-O^-}}$ and (II) $a_{\mathrm{H^+}} (= \gamma_{\pm} m_{\mathrm{H^+}})$ at a given temperature.

First, the ratio $m_{\mathrm{Ph-OH}}/m_{\mathrm{Ph-O^-}}$ is obtained by deconvolution of the absorption spectrum. At a given wavelength i the total absorbance of a solution containing both the acidic (Ph−OH) and basic (Ph−O$^-$) species of monochlorophenols, is expressed as the sum of the absorbances of both species:

$$x_A \varepsilon_A(i) + x_B \varepsilon_B(i) = \varepsilon(i) \tag{4}$$

where x_A and x_B are the molar concentration fractions of the acidic and basic species of the monochlorophenols described in Eqs. (5) and (6), and ε (i) is the absorbance of the mixture solution at a given condition. The $\varepsilon_A(i)$ and $\varepsilon_B(i)$ values represent the absorbances of the solutions when all the monochlorophenols are present in the acidic and basic species, respectively.

$$x_A = \frac{[\mathrm{Ph-OH}]}{[\mathrm{Ph-OH}]_0} = \frac{[\mathrm{Ph-OH}]}{[\mathrm{Ph-OH}] + [\mathrm{Ph-O^-}]} \tag{5}$$

$$x_B = \frac{[\mathrm{Ph-O^-}]}{[\mathrm{Ph-OH}]_0} = \frac{[\mathrm{Ph-O^-}]}{[\mathrm{Ph-OH}] + [\mathrm{Ph-O^-}]} \tag{6}$$

$[\mathrm{Ph-OH}]_0$ denotes the initial molar concentration of monochlorophenol, and [Ph−OH] and [Ph−O$^-$] are the molar concentrations of the acidic and basic species, respectively.

The molar concentrations are converted to molal concentrations. For dilute electrolyte solutions, the molality of species S, m_s, may be obtained from the molarity as follows:

$$m_s = [S]/\rho \tag{7}$$

where ρ is the density of pure water.$^{(43)}$ Thus, Eq. (4) becomes

$$\frac{m_{\mathrm{Ph-OH}}}{m_0}\varepsilon_A(i) + \frac{m_{\mathrm{Ph-O^-}}}{m_0}\varepsilon_B(i) = \varepsilon(i) \tag{8}$$

where m_0 is the initial molal concentration of the monochlorophenol.

As mentioned previously, a solution of monochlorophenol without any added NaOH was used to calibrate the absorbance of the pure acidic species and a solution containing 2.5×10^{-2} M NaOH was used to calibrate the absorbance of the pure basic species. Over the wavelength range from 240 to 330 nm, each spectrum was deconvoluted into the acidic and basic contributions by finding the optimum values of x_A and x_B using the nonlinear least squares method to estimate the dissociation constant K_a. The agreement factor U, which is the sum of the least square of the difference between the measured $[\varepsilon(i)_{\text{obs}}]$ and calculated absorbance $[\varepsilon(i)_{\text{calc}}]$ from 240 to 330 nm, was calculated using

$$U = \sum [\varepsilon(i)_{\text{obs}} - \varepsilon(i)_{\text{calc}}]^2 \quad i = 240\text{ - }330\,\text{nm} \tag{9}$$

The optimum values of x_A and x_B, (*i.e.*, those which give the minimum value of U) were calculated. U did not exceed 0.08 in any curve fitting of spectra. Examples of typical deconvoluted spectra of 4-chlorophenol in a 2×10^{-4} MNaOH solution at 125°C are shown in Fig. 6. The calculated spectrum was estimated as the sum of the spectra of acidic and basic fractions. The difference in total absorbance between the observed spectrum and the calculated spectrum was generally less than 4% at any given wavelength. The ratio $m_{\text{Ph-OH}}/m_{\text{Ph-O}^-}$ was estimated from the optimum values of x_A and x_B. The observed ratios of $m_{\text{Ph-OH}}/m_{\text{Ph-O}^-}$ in all experiments are listed in Tables I–III. The sum of the differences between the total absorbance in the observed spectrum and the calculated spectrum was plotted as a function of temperature (Fig. 7a), and initial sodium hydroxide concentration (Fig. 7b). The sums of the differences exhibit no systematic relationship to low

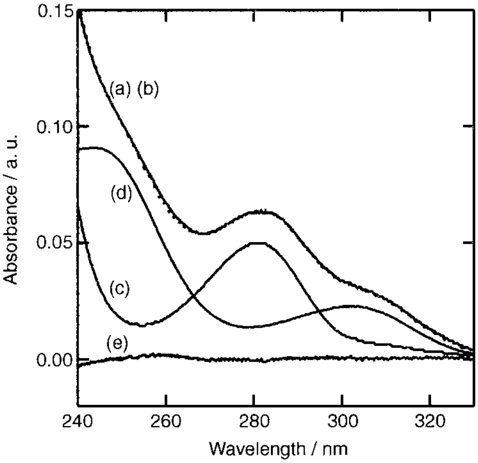

Fig. 6. Deconvoluted spectra of 4-chlorophenol in 2×10^{-4} M NaOH solution at 125°C: (a) observed spectrum; (b) calculated spectrum; (c) spectrum of acidic fraction; (d) spectrum of basic fraction; (e) residual spectrum between (a) and (b).

Table I. Initial Concentration of 2-Chlorophenol and Sodium Hydroxide and Observed and Calculated Values for the $m_{\text{Ph-OH}}/m_{\text{Ph-O}^-}$ Ratio and Molal Concentrations of Protons[a]

°C	$10^5 m^0_{\text{Ph-OH}}$	$10^4 m^0_{\text{NaOH}}$	$m_{\text{Ph-OH}}/m_{\text{Ph-O}^-\text{obs}}$	$m_{\text{Ph-OH}}/m_{\text{Ph-O}^-\text{calc}}$	$\log m_{\text{H}^+}$
25	5.02	0.702	0.493	0.341	−9.51
25	5.02	1.00	0.163	0.163	−9.75
25	5.02	1.50	0.111	0.111	−10.0
25	5.02	19.8	0.163	0.162	−9.74
50	5.06	1.01	0.333	0.334	−9.08
50	5.06	1.52	0.220	0.220	−9.32
50	5.06	2.02	0.111	0.112	−9.47
75	5.13	0.718	1.44	1.44	−8.42
75	5.13	1.03	0.695	0.699	−8.57
75	5.13	1.54	0.389	0.391	−8.78
75	5.13	2.05	0.266	0.264	−8.93
75	5.13	5.13	0.124	0.123	−9.38
100	5.22	1.04	1.27	1.27	−8.18
100	5.22	1.57	0.667	0.669	−8.36
100	5.22	2.09	0.471	0.472	−8.50
100	5.22	5.22	0.191	0.189	−8.94
100	5.22	1.03	1.27	1.28	−8.17
100	5.22	2.06	0.493	0.494	−8.50
100	5.22	10.3	0.099	0.100	−9.26
125	5.32	0.532	5.67	5.66	−7.57
125	5.32	0.745	3.35	3.35	−7.71
125	5.32	1.07	1.94	1.95	−7.86
125	5.32	1.60	1.00	1.01	−8.04
125	5.32	2.13	0.639	0.640	−8.17
125	5.32	5.32	0.163	0.163	−8.60
150	5.45	2.18	1.35	1.35	−7.93
150	5.45	5.45	0.539	0.536	−8.35
150	5.45	10.9	0.282	0.282	−8.66
150	5.45	21.8	0.177	0.177	−8.97
175	5.61	0.785	9.00	9.02	−7.29
175	5.61	1.12	6.14	6.14	−7.45
175	5.61	1.68	3.35	3.35	−7.62
175	5.61	2.24	2.57	2.57	−7.75
175	5.61	5.61	0.961	0.958	−8.16

[a] All concentrations are molalities.

initial NaOH concentration. On the other hand, at high initial NaOH concentration, the sums of the differences were distributed toward positive values. Similarly, the residual values changed from negative to positive with increasing temperature. The absorbance of the observed spectrum was slightly higher than that of the calculated spectrum at the measured wavelength. Due to some ion-pairing reaction at high temperature and high NaOH concentration, the absorbance of the observed spectrum was probably too high. Equilibrium constants were estimated from data that

Table II. Initial Concentration of 3-Chlorophenol and Sodium Hydroxide and Observed and Calculated Values for the $m_{\mathrm{Ph-OH}}/m_{\mathrm{PH-O^-}}$ Ratio and Molal Concentrations of Protons[a]

°C	$10^5 m^0_{\mathrm{Ph-OH}}$	$10^4 m^0_{\mathrm{NaOH}}$	$m_{\mathrm{Ph-OH}}/m_{\mathrm{Ph-O^-obs}}$	$m_{\mathrm{Ph-OH}}/m_{\mathrm{Ph-O^-calc}}$	$\log m_{\mathrm{H^+}}$
25	5.02	0.702	0.852	0.854	−9.63
25	5.02	1.00	0.409	0.410	−9.81
25	5.02	1.50	0.177	0.176	−10.0
25	5.02	2.01	0.136	0.135	−10.2
50	5.06	0.506	2.70	2.70	−8.84
50	5.06	1.01	0.754	0.760	−9.14
50	5.06	1.52	0.429	0.429	−9.34
50	5.06	2.02	0.266	0.265	−9.49
75	5.13	0.513	4.88	4.91	−8.34
75	5.13	1.03	1.44	1.44	−8.62
75	5.13	1.54	0.821	0.821	−8.81
75	5.13	2.05	0.471	0.472	−8.94
75	5.13	5.13	0.136	0.136	−9.38
100	5.22	0.731	3.35	3.33	−8.05
100	5.22	1.04	2.57	2.57	−8.22
100	5.22	1.57	1.56	1.56	−8.40
100	5.22	2.09	1.00	1.00	−8.53
100	5.22	5.22	0.370	0.372	−8.95
100	5.22	10.4	0.191	0.192	−9.26
125	5.32	0.532	11.5	11.5	−7.60
125	5.32	0.745	6.14	6.15	−7.74
125	5.32	1.07	3.76	3.78	−7.89
125	5.32	2.13	1.44	1.43	−8.19
125	5.32	5.32	0.409	0.407	−8.61
125	5.32	10.7	0.136	0.136	−8.92
150	5.45	0.763	10.1	10.1	−7.49
150	5.45	1.09	6.69	6.70	−7.65
150	5.45	1.64	4.56	4.55	−7.82
150	5.45	2.18	3.00	3.01	−7.95
150	5.45	5.45	1.08	1.08	−8.35
150	5.45	10.9	0.539	0.542	−8.66
150	5.45	21.8	0.266	0.268	−8.97
175	5.61	0.785	11.5	11.5	−7.30
175	5.61	1.12	9.00	9.00	−7.46
175	5.61	2.24	4.26	4.24	−7.76
175	5.61	5.61	1.78	1.78	−8.16
175	5.61	11.2	0.887	0.886	−8.47
175	5.61	22.4	0.471	0.471	−8.77

[a] See footnote to Table I.

gave a value of $\log (m_{\mathrm{Ph-OH}}/m_{\mathrm{Ph-O^-}})$ between approximately -1 and 1.2, because values outside this range are sensitive to small errors in the absorbance data.

For singly charged species, the mean ionic activity coefficient of a 1-1 electrolyte was calculated using Pitzer's formulation of the Debye–Hückel

Table III. Initial Concentration of 4-Chlorophenol and Sodium Hydroxide and Observed and Calculated Values for the $m_{\mathrm{Ph-OH}}/m_{\mathrm{PH-O^-}}$ Ratio and Molal Concentrations of Protons[a]

°C	$10^5 m^0_{\mathrm{Ph-OH}}$	$10^4 m^0_{\mathrm{NaOH}}$	$m_{\mathrm{Ph-OH}}/m_{\mathrm{Ph-O^-}\,\mathrm{obs}}$	$m_{\mathrm{Ph-OH}}/m_{\mathrm{Ph-O^-}\,\mathrm{calc}}$	$\log m_{\mathrm{H^+}}$
25	5.02	1.00	0.754	0.752	−9.85
25	5.02	1.50	0.429	0.428	−10.1
25	5.02	2.01	0.299	0.299	−10.2
50	5.06	0.709	2.57	2.59	−9.03
50	5.06	1.01	1.56	1.57	−9.19
50	5.06	1.52	0.754	0.754	−9.36
50	5.06	2.02	0.639	0.639	−9.51
50	5.06	5.06	0.220	0.220	−9.94
75	5.13	0.718	4.88	4.91	−8.51
75	5.13	1.03	3.00	2.99	−8.66
75	5.13	1.54	1.63	1.64	−8.84
75	5.13	2.05	1.22	1.23	−8.97
75	5.13	5.13	0.429	0.430	−9.39
100	5.22	0.731	8.09	8.12	−8.09
100	5.22	1.04	5.67	5.66	−8.25
100	5.22	1.57	3.00	3.00	−8.42
100	5.22	2.09	2.23	2.23	−8.55
100	5.22	5.22	0.754	0.757	−8.96
100	5.22	10.4	0.351	0.350	−9.27
100	5.22	2.06	2.03	2.02	−8.54
100	5.22	10.3	0.370	0.372	−9.26
100	5.22	20.6	0.190	0.189	−9.57
125	5.32	0.745	13.3	13.2	−7.76
125	5.32	1.07	9.00	8.96	−7.92
125	5.32	1.60	4.88	4.90	−8.09
125	5.32	2.13	4.00	4.00	−8.22
125	5.32	5.32	1.27	1.27	−8.62
125	5.32	10.7	0.613	0.612	−8.92
125	5.32	2.10	3.76	3.79	−8.21
125	5.32	10.5	0.695	0.694	−8.92
125	5.32	21.0	0.333	0.333	−9.23
125	5.32	52.6	0.163	0.163	−9.63
150	5.45	1.09	13.3	13.2	−7.66
150	5.45	1.64	7.33	7.31	−7.83
150	5.45	2.18	7.33	7.38	−7.96
150	5.45	5.45	2.03	2.04	−8.36
150	5.45	10.9	1.00	1.00	−8.66
150	5.45	21.8	0.493	0.494	−8.97
150	5.45	2.15	6.69	6.69	−7.96
150	5.45	10.8	1.22	1.22	−8.66
150	5.45	53.8	0.282	0.281	−9.36
175	5.61	1.12	15.7	15.7	−7.47
175	5.61	2.24	7.33	7.31	−7.77
175	5.61	5.61	2.85	2.83	8.17
175	5.61	11.2	1.50	1.50	−8.47
175	5.61	22.4	0.786	0.785	−8.77

[a] See footnote to Table I.

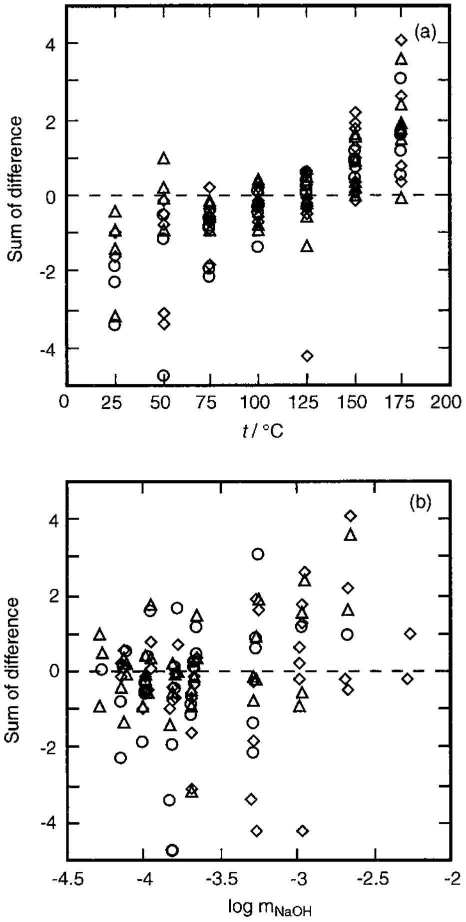

Fig. 7. Deviation plots for the sum of the difference of total absorbance between calculated and observed spectra as a function of (a) temperature and (b) initial NaOH concentration. Symbols designate measurements for solutions of 2-chlorophenol (circles), 3-chlorophenol (triangles), and 4-chloropenol (diamonds).

equation:(44)

$$\ln\gamma_{\pm} = -A_{\phi}\left[\frac{I^{1/2}}{1+bI^{1/2}} + \left(\frac{2}{b}\right)\ln(1+bI^{1/2})\right] \qquad (10)$$

where $b = 1.2$. The ionic strength I is given by

$$I = \frac{1}{2}\sum_{\mathrm{i}} m_{\mathrm{i}} z_i^2 = \frac{1}{2}(m_{\mathrm{H^+}} + m_{\mathrm{Na^+}} + m_{\mathrm{OH^-}} + m_{\mathrm{Ph-O^-}}) \tag{11}$$

where m_{i} and z_{i} are the molalities and charges of all the ionic species in solution, respectively. The Debye–Hückel formulation of the osmotic coefficient A_ϕ is given by

$$A_\phi = \frac{1}{3}\left(\frac{2\pi N_{\mathrm{A}}\rho}{1000}\right)^{1/2}\left(\frac{e^2}{DkT}\right)^{3/2} \tag{12}$$

where N_A is Avogadro's number, e is the charge of the electron, D is the dielectric constant of water calculated by Uematsu and Franck,$^{(45)}$ and ρ is the density of water.$^{(43)}$

The chlorophenol and Na mass balances and the charge balance are given by

$$m^0_{\mathrm{Ph-OH}} = m_{\mathrm{Ph-OH}} + m_{\mathrm{Ph-O^-}} \tag{13}$$

$$m^0_{\mathrm{NaOH}} = m_{\mathrm{NaOH}} + m_{\mathrm{Na^+}} \tag{14}$$

$$m_{\mathrm{H^+}} + m_{\mathrm{Na^+}} = m_{\mathrm{Ph-O^-}} + m_{\mathrm{OH^-}} \tag{15}$$

where $m^0_{\mathrm{Ph-OH}}$ and m^0_{NaOH} are the initial molal concentration of monochlorophenol and sodium hydroxide, respectively.

Using the mean activity coefficient, the acid dissociation constant in Eq. (2) is rewritten as

$$K_{\mathrm{a}} = \frac{m_{\mathrm{H^+}} m_{\mathrm{Ph-O^-}} \gamma_\pm^2}{m_{\mathrm{Ph-OH}}} \tag{16}$$

The equilibrium constant for NaOH association $K_{\mathrm{m}}{}^{(46)}$ and for the ion product of water $K_{\mathrm{w}}^{(47)}$ are given by Eqs. (17) and (18), respectively.

$$K_{\mathrm{m}} = \frac{m_{\mathrm{NaOH}}}{m_{\mathrm{Na^+}} m_{\mathrm{OH^-}} \gamma_\pm^2} \tag{17}$$

$$K_{\mathrm{w}} = m_{\mathrm{H^+}} m_{\mathrm{OH^-}} \gamma_\pm^2 \tag{18}$$

The $m_{\mathrm{H^+}}$ is calculated by Eqs. (13–18) using Newton's iteration method. In order to estimate $m_{\mathrm{H^+}}$, it is necessary to know I to determine $\gamma_\pm$. To determine I, the molalities of the various ions were determined from the relevant equilibrium constants, K_{m} and K_{w}. The molalities of the various ions were then calculated in the following manner. First, preliminary values of K_{a} were estimated. Then, an initial ionic strength was estimated and substituted into Eq. (10) to determine the mean activity coefficient. The concentration of each ionic species was determined using the Newton–Raphson method by the simultaneous solution of Eqs. (13–18) for the hydrogen ions. The ionic strengths of the solutions were calculated from the concentration of each ion and determined by the method of successive approximations. The molalities of Ph—OH ($m_{\text{Ph-OH}}$) and Ph—O$^-$($m_{\text{Ph-O}^-}$) were determined to calculate the value of $m_{\text{Ph-OH}}/m_{\text{Ph-O}^-}$. Then, the experimental data were analyzed with a nonlinear least squares method to determine the best value of K_a (*i.e.*, that which minimized the sum of the squares of the difference between the observed and calculated values of the ratio $m_{\text{Ph-OH}}/m_{\text{Ph-O}^-}$). The resulting values of the mean activity coefficient were close to unity.

Finally, the calculated value of m_{H^+} and the mean activity coefficient and observed value of the ratio $m_{\text{Ph-OH}}/m_{\text{Ph-O}^-}$ were substituted into Eq. (3) to determine the dissociation constants, K_a. The calculated values of m_{H^+} and the ratio $m_{\text{Ph-OH}}/m_{\text{Ph-O}^-}$ are shown in Tables I–III.

Figure 8 displays the data obtained at four temperatures and plotted according to Eq. (3). Similar plots constructed for each temperature studied were all linear. However, contrary to what was expected from Eq. (3), the slope values varied between 0.86 and 1.55. The values of log K_a were determined from the intercepts of these plots.

The measured values of the equilibrium constants (K_{a1}, 2-chlorophenol: K_{a2}, 3-chlorophenol; K_{a3}, 4-chlorophenol) are shown in Table IV. The measured values of log K_{ai} for the dissociation constants of monochlorophenols are plotted in Fig. 9 from 25 to 175°C, at 25°C intervals. The dissociation constants increase in the order 2-chlorophenol, 3-chlorophenol, and 4-chlorophenol, with increasing temperature up to 125°C. The dissociation constant of 4-chlorophenol increases with increasing temperature under experimental conditions, while those of 2- and

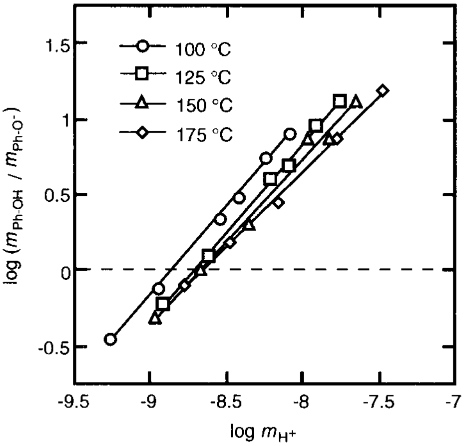

Fig. 8. Dependence of the ratio of neutral 4-chlorophenol and its phenolate anion on molalities of hydrogen ion at 100°C (circles), 125°C (squares), 150°C (triangles), and 175°C (diamonds).

Table IV. Dissociation Constants of 2-Chlorophenol (K_{al}), 3-Chlorophenol (K_{a2}), and 4-Chlorophenol (K_{a3})[a]

°C	log K_{al}	log K_{a2}	log K_{a3}
25	-8.96 ± 0.17	-9.56 ± 0.38	-9.74 ± 0.08
50	-8.69 ± 0.21	-9.10 ± 0.48	-9.34 ± 0.24
75	-8.46 ± 0.27	-8.76 ± 0.59	-9.06 ± 0.22
100	-8.23 ± 0.13	-8.57 ± 0.12	-8.86 ± 0.22
125	-8.06 ± 0.55	-8.31 ± 0.66	-8.72 ± 0.18
150	-8.05 ± 0.21	-8.41 ± 0.14	-8.68 ± 0.20
175	-8.12 ± 0.16	-8.42 ± 0.09	-8.65 ± 0.06

[a] The uncertainties indicate three times the standard deviation.

3-chlorophenol have maximum values around 125°C, which then decrease with further increases in temperature. The slope of $\partial(\log K)/\partial(1/T)$ is not constant over the entire temperature range. Each K_a exhibits a maximum that is similar to the dissociation constants of β-naphthoic acid$^{(28)}$ and 2,5-dinitrophenol$^{(34)}$ below 200°C. Maxima occur at 100 and 110°C for β-naphthoic acid and 2,5-dinitrophenol, respectively. At low temperature, the energy for deprotonation is greater than that for ion solvation. With increasing temperature and decreasing density, the dielectric constant of water decreases. Since the reduction of the dielectric constant makes the solvation of ionic products much less favorable, the effect

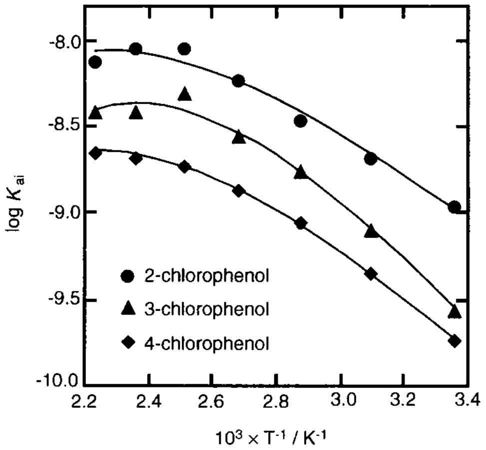

Fig. 9. Correlation of the logarithm of the dissociation constants of 2-chlorophenol (K_{a1}, circles), 3-chlorophenol (K_{a2}, triangles), and 4-chlorophenol (K_{a3}, diamonds) with the inverse of temperature. Solid lines: regression equation (Eqs. 20–22) calculated using the Van't Hoff equation.

of ion solvation becomes much greater. Consequently, the maxima occur under subcritical temperatures. Since monochlorophenols are weaker acids than either β-naphthoic acid or 2,5-dinitrophenol, the energy for deprotonation is greater. The energy for ion solvation becomes less important at a lower temperature than in the case of either β-naphthoic acid or 2,5-dinitrophenol. As a result, the maxima occur at higher temperatures for monochlorophenols than for β-naphthoic acid and 2,5-dinitrophenol.

Assuming that the heat capacity change $\Delta C_{\mathrm{p,ai}}$ for the acid dissociation of monochlorophenols is represented in Eq. (19), the values of $K_{\mathrm{ai}}(i = 1\text{–}3)$ as a function of temperature were fitted to a form of the integrated Van't Hoff isobar $[\partial(\ln K)/\partial(1/T)]_{\mathrm{p}} = -\Delta H^{\mathrm{o}}/R$

$$\Delta C_{\mathrm{p,ai}} = a + bT + cT^{-2} \tag{19}$$

$$\ln K_{\mathrm{al}} = -264 + 44.8 \ln T + 4.84 \times 10^{3}/T - 8.35 \times 10^{-2} T - 2.87 \times 10^{5}/T^{2} \tag{20}$$

$$\ln K_{\mathrm{a2}} = -333 + 58.5 \ln T + 5.19 \times 10^{3}/T - 11.9 \times 10^{-2} T - 4.00 \times 10^{5}/T^{2} \tag{21}$$

$$\ln K_{\mathrm{a3}} = -240 + 40.8 \ln T + 3.65 \times 10^{3}/T - 7.95 \times 10^{-2} T - 3.00 \times 10^{5}/T^{2} \tag{22}$$

The resulting regression curves are shown in Fig. 9. The regression curves for 2- and 4-chlorophenol increase monotonically and the increasing rate for dissociation constants decreases with increased temperature. The regression curve for 3-chlorophenol have a maximum around 150°C, which is similar to the observed values for the dissociation constants.

The thermodynamic quantities ΔH_{ai}, ΔS_{ai}, $\Delta C_{\mathrm{p,ai}}$ $(i = 1\text{–}3)$ in this equilibrium were estimated by differentiation of Eqs. (20–22), and the results are shown in Table V. For the reaction between a weak acid and a weak base (*e.g.*, the dissociation reaction of monochlorophenols in water), the enthalpy is positive. It is an endothermic reaction, since the energy needed to break the O-H bond is greater than that released by solvation of the resulting ions.(28)

The magnitude of the enthalpy ΔH_{ai} was in the order of 3-chlorophenol $>$ 4-chlorophenol $>$ 2-chlorophenol, at 25°C. All values of ΔH_{ai} decreased with increased temperature. Because the energy of ion solvation becomes much effective with increasing temperature, the enthalpy of reaction is controlled by ion solvation rather than the bond energies. The decrease in enthalpy with absolute temperature is larger for 3-chlorophenol than for 2- or 4-chlorophenol.

The Cl substituent on the aromatic ring acts as an electron-withdrawing group, thereby producing an inductive effect that increases the acidity of the phenol. In contrast, halogen substituent groups are *ortho, para* directors because they

Table V. Summary of Thermodynamic Quantities for the Dissociation of Monochlorophenols in Aqueous Solution at the Saturated Vaper Pressure

°C	$\log K_a^a$	ΔH_a^b	ΔS_a^c	$\Delta C_{p,a}^c$
		2-Chlorophenol		
25	−8.98	25.2	−87	12
50	−8.66	22.5	−96	−30
75	−8.41	19.1	−106	−71
100	−8.24	15.0	−118	−111
125	−8.13	10.1	−130	−150
150	−8.08	4.5	−144	−188
175	−8.07	−2.0	−159	−226
		3-Chlorophenol		
25	−9.55	36.1	−62	−30
50	−9.09	31.1	−78	−91
75	−8.76	25.2	−95	−149
100	−8.54	18.2	−115	−206
125	−8.42	10.1	−136	−261
150	−8.37	0.8	−158	−316
175	−8.40	−9.4	−182	−369
		4-Chlorophenol		
25	−9.72	28.8	−90	1
50	−9.35	25.7	−100	−40
75	−9.07	22.0	−111	−80
100	−8.87	17.5	−123	−119
125	−8.74	12.4	−136	−156
150	−8.66	6.6	−150	−193
175	−8.64	0.0	−165	−229

[a] Calculated by fitting to a form of the integrated Van't Hoff isobar.
[b] $kJ\text{-}mol^{-1}$.
[c] $J\text{-}mol^{-1}\text{-}K^{-1}$.

are electron-donating *via* the resonance effect. Since resonance effects oppose inductive effects in the *ortho, para* positions, the electron-withdrawing effect in those position is smaller than in the *meta* position. As a result, the energy needed to break the O-H bond of 3-chlorophenol is greater than that required to break the O-H bond of either 2- or 4-chlorophenol. The maximum of the dissociation constant occurs at lower temperature for 3-chlorophenol than for 2- or 4-chlorophenols. Likewise, the enthalpy of the reaction (endothermic) at lower temperatures is greater for 3-chlorophenol than for 2- or 4-chlorophenol.

3.3. Isocoulombic Reactions of Monochlorophenols with OH^-

The K_b for the isocoulombic reaction of monochlorophenol with OH^- was not measured directly, but was calculated from the measured K_a data, as shown in Fig. 10. For the reaction

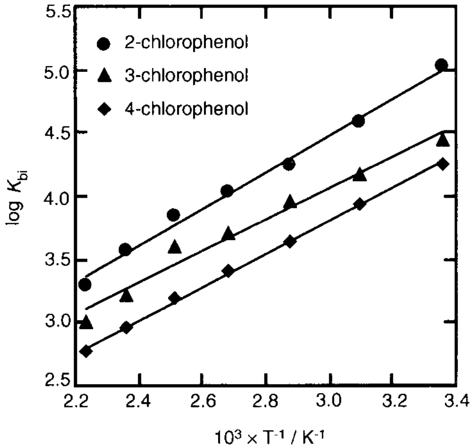

Fig. 10. Effect of temperature on the equilibrium constants, K_b, for the isocoulombic reaction of monochlorophenols with OH^-: 2-chlorophenol (K_{b1}; circles), 3-chlorophenol (K_{b2}; triangles), and 4-chlorophenol (K_{b3}, diamonds). Solid lines: linear regression of the data.

$$\mathrm{Ph-OH + OH^- = Ph-O^- + H_2O} \tag{23}$$

the equilibrium constant is expressed as:

$$K_b = \frac{K_a}{K_w} = \frac{a_{\mathrm{Ph-O^-}}}{a_{\mathrm{Ph-OH}}\, a_{\mathrm{OH^-}}} \tag{24}$$

The most significant difference is that K_a exhibits a maximum, whereas K_b does not. The nearly linear relationship of log K_b vs. $1/T$ for temperatures between 25 and 175°C indicates that the $\Delta C_{p,bi}$ values for this isocoulombic reaction are low. Therefore, assuming that the heat capacity change $\Delta C_{p,bi}$ is zero (*i.e.*, the enthalpy ΔH_{bi} has constant value and is not dependent on temperature), the enthalpies were calculated as the slope of log K_{bi} vs. $1/T$. The resulting values of ΔH_{bi} were -27.8, -23.8, and -25.1 kJ-mol^{-1} for 2-, 3-, and 4-chlorophenol, respectively. For the reaction of β-naphthol with the strong base OH^-, the enthalpy is always negative.(35,36) Similarly, the reaction of monochlorophenols and OH^- is isocoulombic, and so the enthalpy of reaction is controlled primarily by the bond energies and not by ion solvation. Thus, the reaction described in Eq. (23) is exothermic. The enthalpy of Eq. (1) ΔH^*_{ai} was recalculated by adding the enthalpy of dissociation of water, ΔH_w to ΔH_{bi}. The obtained values of ΔH^*_{ai} were 27.7, 31.8, and 30.5 kJ-mol^{-1} for 2-, 3-, and 4-chlorophenol, respectively. The order of the magnitude of ΔH^*_{ai} was in agreement with that at 25°C. However, as mentioned above, since ΔH_{ai} decreases with temperature and the effect is larger for 3-chlorophenol than for 2- or 4-chlorophenol, the order of the magnitude of ΔH_{ai} is reversed with increases in temperature.

4. CONCLUSIONS

Quantitative measurements of the dissociation constants, K_{a} for monochlorophenols (2-, 3-, and 4-chlorophenols) were performed with direct UV–vis spectroscopy between 25 and 175°C. Deprotonation of the monochlorophenols becomes favorable as the solution temperature is raised from 25 to 125°C. K_{a} exhibits endothermic behavior below 150°C for all monochlorophenols, since the energy needed to break the O-H bond for this relatively weak acid is greater than that released by solvation of the resulting ions. The reaction changes from endothermic to exothermic above 150°C for 3-chlorophenol, which is similar to what is observed with 2,5-dinitrophenol and β-naphthoic acid. The decrease in enthalpy with absolute temperature is larger for 3-chlorophenol than for 2- or 4-chlorophenol. The differences in behavior between 3-chlorophenol and 2- or 4-chlorophenol may be described by the halogen substituent group. Since halogen substituent groups are electron-donating by the resonance effect, they act as *ortho*, *para* directors and the electron-withdrawing effect in the *o*-, *p*-position is smaller than in the *m*-position. As a result, the energy needed to break the O-H bond of 3-chlorophenol is greater than that needed to break the O-H bond of 2- or 4-chlorophenol.

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REFERENCES

1. J. W. Tester and J. A. Cline, *Corrosion* **55**, 1088 (1999).
2. T. Kishino and K. Kobayashi, *Water Res.* **28**, 1547 (1994).
3. R. García-Domenech, J. V. De Julián-Ortiz, G. M. Antón-Fos, and J. Galvez Alvarez, *J. Chem. Educ.* **73**, 792 (1996).
4. K. Miyake, F. Kitaura, N. Mizuno, and H. Terada, *Chem. Pharm, Bull.* **35**, 377 (1987).
5. E. P. Serjeant and B. Dempsey, *Ionization Constants of Organic acids in Aqueous Solution*, IUPAC Chemical Data Series No. 23 (Pergamon Press, New York, 1979).
6. M. E. Farquharson, J. C. Gage, and J. Northover, *Brit. J. Pharmacol.* **13**, 20 (1958).
7. K. Ugland, E. Lundanes, T. Greibrokk, and A. Bjørseth, *J. Chromatogr.* **213**, 83 (1981).
8. W. F. O'Hara and L. G. Hepler, *J. Phys. Chem.* **65**, 2107 (1961).
9. C. H. Rochester and D. N. Wilson, *J. Chem. Soc. Faraday* **I73**, 569 (1977).
10. P. D. Bolton, F. M. Hall, and I. H. Reece, *Spectrochim. Acta* **22**, 1825 (1966).

11. P. D. Bolton, F. M. Hall, and I. H. Reece, *Spectrochim. Acta* **22**, 1149 (1966).
12. F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.* **74**, 1058 (1952).
13. L. P. Fernandez and L. G. Hepler, *J. Amer. Chem. Soc.* **81**, 1783 (1959).
14. D. T. Y. Chen and K. J. Laidler, *Trans. Faraday Soc.* **58**, 480 (1962).
15. T. B. Brill, *J. Phys. Chem. A* **104**, 4343 (2000).
16. E. U. Franck, *J. Solution Chem.* **2**, 339 (1973).
17. W. C. Bell and K. S. Booksh, and M. L. Myrick, *Anal. Chem.* **70**, 332 (1998).
18. W. W. Rudolph and M. H. Brooker, *J. Solution Chem.* **28**, 621 (1999).
19. P. J. Murphy, G. Stevens, and M. S. LaGrange, *Geochim. Cosmochim. Acta* **64**, 479 (2000).
20. H.-D. Lüdemann and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **71**, 455 (1967).
21. B. Scholz, H.-D. Lüdemann, and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **76**, 406 (1972).
22. W. F. Giggenbach, *Inorg. Chem.* **13**, 1724 (1974).
23. G. E. Benett and K. P. Johnston, *J. Phys. Chem.* **98**, 441 (1994).
24. J. Chlistunoff, K. J. Ziegler, L. Lasdon, and K. P. Johnston, *J. Phys. Chem. A* **103**, 1678 (1999).
25. J. B. Chlistunoff and K. P. Johnston, *J. Phys. Chem. B* **102**, 3993 (1998).
26. K. J. Ziegler, L. Lasdon, L., J. Chlistunoff, and K. P. Johnston, *Computers Chem.* **23**, 421 (1999).
27. B. Müller and T. M. Seward, *Geochim. Cosmochim. Acta* **65**, 4187 (2001).
28. O. M. Suleimenov and T. M. Seward, *Chem. Geol.* **167**, 177 (2000).
29. J. Bebie, T. M. Seward, and J. K. Hovey, *Geochim. Cosmochim. Acta* **62**, 1643 (1998).
30. O. M. Suleimenov and T. M. Seward, *Geochim. Cosmochim. Acta* **61**, 5187 (1997).
31. C. A. Heinrich and T. M. Seward, *Geochim. Cosmochim. Acta* **54**, 2207 (1990).
32. T. M. Seward, *Geochim. Cosmochim. Acta* **48**, 121 (1984).
33. L. N. Trevani and J. C. Roberts, and P. R. Tremaine, *J. Solution Chem.* **30**, 585 (2001).
34. E. T. Ryan, T. Xiang, T, K. P. Johnston, and M. A. Fox, *J. Phys. Chem. A* **101**, 1827 (1997).
35. T. Xiang and K. P. Johnston, *J. Solution Chem.* **26**, 13–30 (1997).
36. T. Xiang and K. P. Johnston, *J. Phys. Chem.* **98**, 7915 (1994).
37. W. T. Wofford, E. F. Gloyna, and K. P. Johnston, *Ind. Eng. Chem. Res.* **37**, 2045 (1998).
38. K. P. Johnston and J. B. Chlistunoff, *J. Supercritical Fluids* **12**, 155 (1998).
39. T. Xiang, K. P. Johnston, W. T. Wofford, and E. F. Gloyna, *Ind. Eng. Chem. Res.* **35**, 4788 (1996).
40. T.-W. Shin, K. Kim, and I.-J. Lee, *J. Solution. Chem.* **26**, 379 (1997).
41. I.-J. Lee, G.-S. Jung, and K. Kim, *J. Solution Chem.* **23**, 1283 (1994).
42. Y. Huh, J.-G. Lee, D. C. McPhail, and K. Kim, *J. Solution Chem.* **22**, 651 (1993).
43. *1999 JSME Steam Tables* (The Japan Society of Mechanical Engineers, Tokyo, 1999).
44. K. S. Pitzer, J. C. Peiper, and R. H. Busey, *J. Phys. Chem. Ref. Data* **13**, 1 (1984).
45. M. Uematsu and E. U. Franck, *J. Phys. Chem. Ref. Data* **9**, 1291 (1980).
46. P. C. Ho, D. A. Palmer, and R. H. Wood, *J. Phys. Chem. B* **104**, 12084 (2000).
47. W. L. Marshall and E. U. Franck, *J. Phys. Chem. Ref. Data* **10**, 295 (1981).