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Spectroscopic measurement of the acid dissociation constant of 2-naphthol and the second dissociation constant of carbonic acid at elevated temperatures

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2-Naphthol can be used to measure the pH of aqueous solutions if the acid dissociation constant for 2-naphthol is known at a given temperature. The temperature dependence of the acid dissociation constant for 2-naphthol was spectroscopically determined in borate buffer solutions under vapor-saturated pressure up to 200 °C. The result was

$$\mathrm{p}K_{\mathrm{i}} = -34.97 + \frac{2947}{T} + 6.086\ \ln(T)$$

where T is in Kelvin. The pH of carbonate buffer solutions was measured by obtaining the UV–visible spectra of 2-naphthol and utilized to determine the second dissociation constant of carbonic acid up to 175 °C under vapor-saturated pressure. The result was

$$\mathrm{p}K_2 = 4201.48 - \frac{229\,200}{T} - 661.21\ \ln(T) + 0.647\,53T + \frac{13\,498\,200}{T^2}$$

where T is in Kelvin. By using the temperature dependence of the dissociation constant, the isocoulombic reaction was studied. The plot of $-\log K_{\mathrm{isoc}}$ against $1/T$ was approximately linear in the temperature range studied. The linearity can be used to predict the dissociation constant by the extrapolation of $-\log K_{\mathrm{isoc}}$ to higher temperatures.

Introduction

Carbonate equilibrium is ubiquitous and plays important roles in oceans, mineral deposits[1–3] and natural hydrothermal solutions.[4,5] Knowledge of the dissociation constant for carbonic acid is of considerable importance in order to predict the solubility of carbonate minerals and understand accurately the chemistry of natural hydrothermal solutions, which are in equilibrium with carbon dioxide and carbonate minerals. As a consequence, a lot of work has been undertaken to estimate the dissociation constant of carbonic acid at various temperatures and pressures. Ryzhenko[6] estimated the ionization constants of carbonic acid to 200 °C from conductivity measurements at the vapor pressure of the system. Read[7] made conductivity measurements and obtained the first dissociation constant of carbonic acid from 25 to 250 °C and to 2000 bar. Patterson *et al.*[8,9] determined the first and the second dissociation constants of carbonic acid in NaCl media using an emf cell up to 300 and 250 °C, respectively.

To understand the equilibrium relating several chemical species in an aqueous solution, it is essential to know the pH of the solution. Especially, the measurement of the pH was a major obstacle in determining and interpreting physicochemical processes in hydrothermal solutions. Techniques such as conductivity,[6,7,10] potentiometric (emf)[8,9,11] and solubility measurements[12] have been utilized to study the equilibrium in hydrothermal solutions. Recently, a spectroscopic method of measuring the pH of high temperature aqueous solutions was developed.[13] The pH of a buffer solution could be determined directly by measuring the acid/base ratios of an optical pH indicator using UV–visible spectroscopy. The optical indicator is a chemical species of which the absorption spectrum is changed over a certain pH range. The change of the absorption spectrum is due to the variation of the relative ratios of the acidic species to the basic species of the optical indicator in the aqueous solution. Several optical indicators have been studied and used to estimate the pH of hydrothermal solutions.[13–16]

2-Naphthol has been used in several experiments elsewhere at low and high temperatures.[17–19] 2-Naphthol is colorless at room temperature because it has an absorption spectrum below 400 nm in aqueous solutions. The absorption spectrum of 2-naphthol is changed in the pH range between 9 and 10 at room temperature. Since 2-naphthol was thermally stable in hydrothermal solutions and had characteristic absorption spectra of the acidic and basic species, it could be used as an optical indicator to measure the pH of hydrothermal solutions. At this laboratory, the first dissociation constants of carbonic acid were determined previously by using the spectroscopic measurement up to 175 °C.[20] In this study, using 2-naphthol as an optical indicator, the second dissociation constants of carbonic acid were determined from 25 to 175 °C and the experimental data were compared with the data which were obtained previously with different experimental methods.

Experimental

Reagent grade 2-naphthol, boric acid and potassium hydroxide (Aldrich) were used as received. Potassium carbonate (Yakuri Pure Chemical Co.) and potassium bicarbonate (Kanto Chemical Co.) were used after drying for at least 48 h in the oven at 90 °C. All solutions were prepared with doubly deionized water. A 2-naphthol stock solution of 1.017×10^{-3} mol kg^{-1} was prepared. Using this stock solution, all the sample solutions were prepared with the same molal concentration (1.017×10^{-4} mol kg^{-1}) of 2-naphthol. To prepare borate buffer solutions, potassium hydroxide was added to boric acid containing 2-naphthol to give a suitable pH between 8.7 and 9.6 at 25 °C. To prepare carbonate buffer in the pH range between 10.0 and 11.0, $KHCO_3$ and K_2CO_3 were used. The pH of the prepared buffer solutions was measured at 25 °C with pH/ion meter DP-880.

All spectra were collected under vapor-saturated pressure at various temperatures at 0.25 nm wavelength intervals from 300 to 450 nm. Baseline correction was made with a spectrum of pure water at 25 °C. Care was taken to ensure sufficient vapor space in the cell for all experiments. In order to check equilibrium was reached, absorption spectra were collected in buffer solutions at 2 min time intervals at given temperatures until spectra remained unchanged. It seemed that equilibrium was reached in less than 6 min at given temperatures. The sample solutions were kept at the desired temperature for at least 10 min to reach equilibrium completely. All solutions were purged with argon gas for at least 30 min to remove excess dissolved oxygen. At the beginning of all experiments, all solutions were filtered with 0.2 μm membrane filters. Other details of the experimental settings were described in the previous paper.[20]

Results and discussion

2-Naphthol as an optical indicator

The equilibrium relating the acidic (HIn) and basic species (In^-) of 2-naphthol in aqueous solutions is

$$\mathrm{HIn(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{In^-(aq)}$$

The acidic species and basic species of 2-naphthol have characteristic absorption spectra in the wavelength range between 300 and 450 nm. The distinctive property of absorption spectra facilitates deconvolution of the absorption spectra. Absorption spectra of the pure acidic and pure basic species of 2-naphthol can be obtained controlling the pH of the solution containing the indicator. Fig. 1 and 2 represent absorption spectra of the pure acidic (pH = 5 at 25 °C) and pure basic species (pH = 12.5 at 25 °C) of 2-naphthol at 25 °C intervals from 25 to 200 °C, respectively. Fig. 3 represents the absorption spectra of 2-naphthol in a borate buffer solution as the temperature increases from 25 to 200 °C. The pH of the borate buffer solution was 8.88 at 25 °C. Compared with Fig. 1 and 2, which are the absorption spectra for the pure acidic and pure basic species, it is clear that the acidic species of the indicator is preferred to the basic species at 25 °C and pH 8.88. Fig. 4 represents the absorption spectra in a carbonate buffer solution as the temperature increases from 25 to 175 °C. The pH of the carbonate buffer solution was 10.11 at 25 °C. The basic species of the indicator predominates the acidic species at 25 °C and pH 10.11. The spectral changes in buffer solutions with temperature result primarily from variation of the ratio of the acidic to basic species.

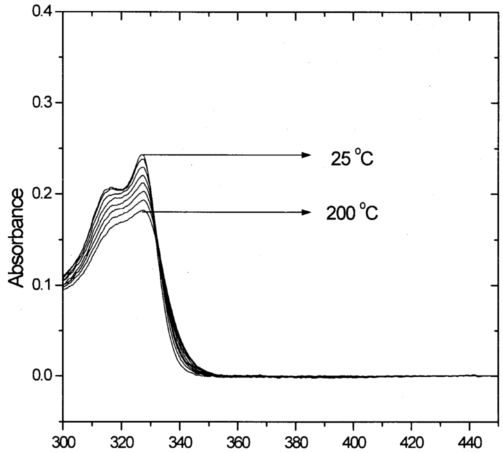

Fig. 1 Absorption spectra of the pure acidic species of 2-naphthol (1.017×10^{-4} mol kg^{-1}) at pH 5 (25 °C).

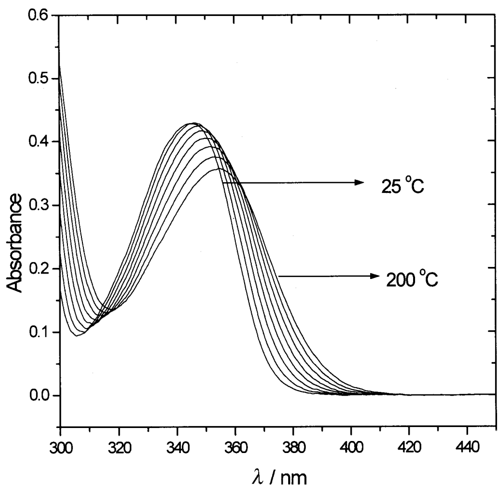

Fig. 2 Absorption spectra of the pure basic species of 2-naphthol (1.017×10^{-4} mol kg^{-1}) at pH 12.5 (at 25 °C).

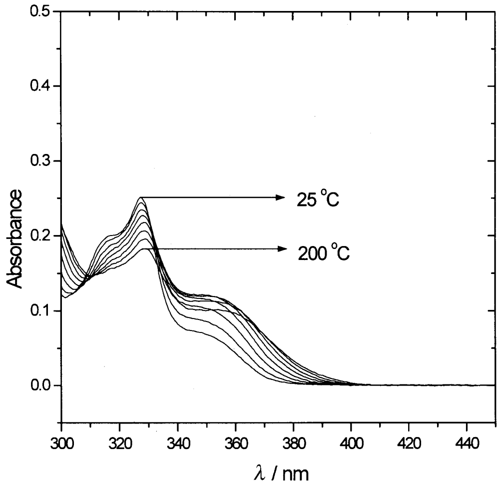

Fig. 3 Absorption spectra of 2-naphthol in a borate buffer solution at the temperature intervals of 25 °C from 25 to 200 °C. The pH was 8.88 (at 25 °C). The acidic and basic species of 2-naphthol coexist in the borate buffer solution.

According to the Beer–Lambert law, the absorbance of the indicator can be written as[21]

$$A(\lambda)/d = a\varepsilon_{\mathrm{HIn}}(\lambda)\{\mathrm{HIn}\} + b\varepsilon_{\mathrm{In}}(\lambda)\{\mathrm{In}^-\}$$

where $A(\lambda)$ is the total absorbance of 2-naphthol, d is the beam path length, $\varepsilon_{\mathrm{HIn}}$ and $\varepsilon_{\mathrm{In}}$ are the extinction coefficients, and $\{\mathrm{HIn}\}$ and $\{\mathrm{In}^-\}$ are the molal concentrations of the pure acidic and pure basic species of 2-naphthol, respectively. The molal concentration ratios of 2-naphthol (a/b) can be obtained by deconvoluting the absorption spectra using the method of least squares. Fig. 5 and 6 show the results for the deconvolu-

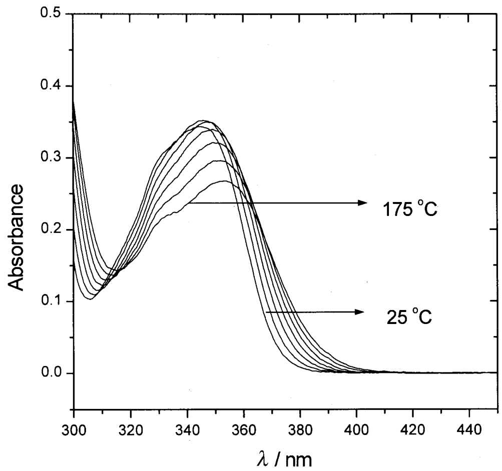

Fig. 4 Absorption spectra of 2-naphthol in a carbonate buffer solution at temperature intervals of 25 °C from 25 to 175 °C. The pH was 10.11 (at 25 °C). The acidic and basic species of 2-naphthol coexist in the carbonate buffer solution.

tion of absorption spectra of 2-naphthol in borate and carbonate buffer solutions, respectively: (a) is the measured spectrum of 2-naphthol in each buffer solution; (b) and (c) are the deconvoluted spectra and represent the pictorial portions of the acidic and basic species for the measured spectrum; (d) is the sum of the deconvoluted spectra (b) and (c). For most of the spectra, the residual (e), which is the difference between the measured and the calculated spectra, is less than 2% of the total absorbance at a given wavelength. For ease of inspection, the residual is artificially shifted by an absorbance of 0.4. Tables 1 and 2 represent the result of deconvolution in the buffer solutions at various temperatures.

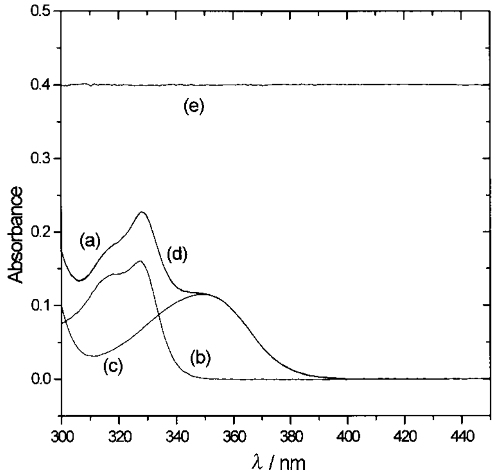

Fig. 5 Deconvoluted spectrum of 2-naphthol in borate buffer (pH = 8.88). The temperature was 100 °C. (a) Measured spectrum, (b) spectrum of acidic species, (c) spectrum of basic species, (d) calculated spectrum [(b) + (c)] and (e) residual [(a) − (d)] + 0.4.

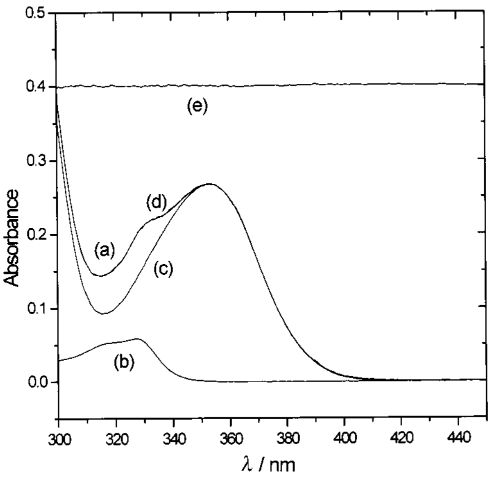

Fig. 6 Deconvoluted spectrum of 2-naphthol in carbonate buffer (pH 10.11). The temperature was 175 °C. (a) measured spectrum, (b) spectrum of acidic species, (c) spectrum of basic species, (d) calculated spectrum [(b) + (c)] and (e) residual [(a) − (d)] + 0.4.

To calculate the equilibrium constant from the measured spectrum, it is assumed that the activity coefficient for neutral chemical species is unit, and for singly charged ionic species, the mean activity coefficient, $\gamma_\pm$, can be approximated by Pitzer's formula,[22,23]

$$\ln \gamma_\pm = -A_\phi\left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2}{1.2}\ln(1 + 1.2\sqrt{I})\right]$$

$$I = \frac{1}{2}\sum_{\mathrm{i}} m_{\mathrm{i}} z_{\mathrm{i}}^2$$

where I is the ionic strength and includes all the ionic species involved, m_{i} and z_{i} are the molal concentration and the ionic charge of the ionic species, i, respectively. The Debye–Huckel parameter, A_ϕ, is taken from Bradley and Pitzer.[24] For multiply charged ionic species, the mean activity coefficient, γ_z, is

$$\ln \gamma_z = z_{\mathrm{i}}^2 \ln \gamma_\pm$$

Acid dissociation constant of 2-naphthol (HIn)

The equilibrium in borate buffer solutions containing the indicator 2-naphthol, is

$$\mathrm{HIn(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{In^-(aq)}$$

$$\mathrm{B(OH)_3(aq)} + \mathrm{H_2O(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{B(OH)_4{}^-(aq)}$$

Therefore, the acid dissociation constants of the indicator and boric acid can be represented by

$$K_{\mathrm{i}} = \frac{\{\mathrm{H^+}\}\{\mathrm{In^-}\}\gamma_\pm^2}{\{\mathrm{HIn}\}}$$

$$K_{\mathrm{a}} = \frac{\{\mathrm{H^+}\}\{\mathrm{B(OH)_4{}^-}\}\gamma_\pm^2}{\{\mathrm{B(OH)_3}\}}$$

where {i} is the molal concentration of chemical species of i and $\gamma_\pm$ is the mean activity coefficient of the ionic species. Using the definition of pK and pH, the equilibrium constants

Table 1 {HIn}/{In$^-$} values of 2-naphthol in borate buffers at various temperatures and pH[a]

pH[b]	25 °C	50 °C	75 °C	100 °C	125 °C	150 °C	175 °C	200 °C
8.80	5.275	4.133	3.218	2.675	2.362	2.191	2.142	2.190
8.88	4.889	3.930	3.103	2.638	2.409	2.314	2.351	2.516
9.03	3.181	2.495	2.009	1.719	1.584	1.538	1.572	1.672
9.26	2.120	1.654	1.345	1.183	1.120	1.131	1.189	1.314
9.37	1.436	1.156	0.9548	0.8565	0.8376	0.8618	0.9370	1.046
9.58	0.9251	0.7417	0.6402	0.6142	0.6334	0.6757	0.7462	0.8363

[a] Values were obtained by the deconvolution of absorption spectra of 1.017 × 10^{-4} mol kg^{-2} 2-naphthol in 0.00997 mol kg^{-1} borate buffer solution. [b] The pH was measured at 25 °C.

Table 2 {HIn}/{In$^-$} values of 2-naphthol in carbonate buffers at various temperatures[a]

pH[b]	25 °C	50 °C	75 °C	100 °C	125 °C	150 °C	175 °C
10.00	0.3331	0.2889	0.2721	0.2823	0.3299	0.3999	0.5046
10.01	0.3111	0.2604	0.2237	0.2170	0.2299	0.2561	0.3039
10.09	0.2526	0.2181	0.1881	0.1810	0.1903	0.2099	0.2478
10.11	0.2419	0.2187	0.1881	0.1791	0.1860	0.2034	0.2335
10.14	0.2387	0.2102	0.1987	0.2067	0.2369	0.2828	0.3461
10.17	0.2102	0.1925	0.1804	0.1741	0.1871	0.1968	0.222

[a] Values were obtained by the deconvolution of absorption spectra of 1.017 × 10^{-4} mol kg^{-1} 2-naphthol in several carbonate buffer solutions. [b] The pH was measured at 25 °C.

can be rearranged to

$$\mathrm{p}K_\mathrm{i} = \mathrm{pH} + \log\frac{\{\mathrm{HIn}\}}{\{\mathrm{In}^-\}} - \log\gamma_\pm \tag{1}$$

$$\mathrm{p}K_\mathrm{a} = \mathrm{pH} + \log\frac{\{\mathrm{B(OH)_3}\}}{\{\mathrm{B(OH)_4}^-\}} - \log\gamma_\pm \tag{2}$$

The mass and charge balances in borate buffer solutions are

$$\{\mathrm{HIn}\}_0 = \{\mathrm{HIn}\} + \{\mathrm{In}^-\} \tag{3}$$

$$\{\mathrm{B(OH)_3}\}_0 = \{\mathrm{B(OH)_3}\} + \{\mathrm{B(OH)_4}^-\} \tag{4}$$

$$\{\mathrm{K}^+\} + \{\mathrm{H}^+\} = \{\mathrm{B(OH)_4}^-\} + \{\mathrm{OH}^-\} + \{\mathrm{In}^-\} \tag{5}$$

where $\{\mathrm{HIn}\}_0$ and $\{\mathrm{B(OH)_3}\}_0$ are the initial molal concentrations of 2-naphthol and boric acid, respectively. The ionization constant of water is

$$K_\mathrm{w} = \{\mathrm{H}^+\}\{\mathrm{OH}^-\}\gamma_\pm^2 \tag{6}$$

As shown in Fig. 5, {HIn}/{In$^-$} was directly obtained from the acid/base ratio by deconvolution of the spectrum. All concentrations of the chemical species involved and the mean activity coefficient of the ionic species were calculated by an iterative method. At first, assuming that $\gamma_\pm$ is unity, all concentrations and ionic strength were calculated from eqns. (1)–(6) using the acid/base ratio of 2-naphthol, the known K_a of boric acid, and K_w. From the ionic strength, $\gamma_\pm$ was calculated. The calculated $\gamma_\pm$ was used repeatedly for the calculation. Iterations were performed until the variation of ionic strength and the concentrations for main chemical species were lower than 10^{-10} mol kg^{-1}. K_a values for boric acid were taken from Sweeton *et al.*[25] and the ionization constant of water, K_w, were from Marshall and Franck.[26] Consequently, pK_i values were obtained at given temperatures. The measured pK_i values can be fitted with the empirical formula[27] by nonlinear regression to give

$$\mathrm{p}K_\mathrm{i} = -34.97 + \frac{2947}{T} + 6.086\ln(T) \tag{7}$$

where T is in Kelvin. Fig. 7 represents the temperature dependence of pK_i for 2-naphthol. It is shown that the dissociation of 2-naphthol in water becomes favorable as the temperature increases from 25 to 200 °C. It appears that the minimum in pK_i exists above 200 °C. In general, the minimum in pK as a function of temperature is shown for the dissociation reaction of most of the weak acids in water. The measured pK_i value was 9.58 at 25 °C. This value is in good agreement with the previously reported values of 9.51 and 9.60 at 25 °C within experimental error.

The second dissociation constant of carbonic acid

The equilibrium in carbonate buffer solutions containing 2-naphthol is given by

$$\mathrm{H_2CO_3{*}(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{HCO_3{}^-(aq)}$$

$$\mathrm{HCO_3{}^-(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{CO_3{}^{2-}(aq)}$$

$$\mathrm{HIn(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{In^-(aq)}$$

where $\mathrm{H_2CO_3}$* is the apparent carbonic acid which is the sum of the true carbonic acid [$\mathrm{H_2CO_3(aq)}$] and aqueous carbon dioxide [$\mathrm{CO_2(aq)}$].[28] The equilibrium constants of carbonic acid are represented by

$$K_1 = \frac{\{\mathrm{H}^+\}\{\mathrm{HCO_3}^-\}\gamma_\pm^2}{\{\mathrm{H_2CO_3}^*\}}$$

$$K_2 = \frac{\{\mathrm{H}^+\}\{\mathrm{CO_3}^{2-}\}\gamma_\pm^4}{\{\mathrm{HCO_3}^-\}}$$

The equilibrium constants can be rearranged to

$$\mathrm{p}K_1 = \mathrm{pH} + \log\frac{\{\mathrm{H_2CO_3}^*\}}{\{\mathrm{HCO_3}^-\}} - \log\gamma_\pm \tag{8}$$

$$\mathrm{p}K_2 = \mathrm{pH} + \log\frac{\{\mathrm{HCO_3}^-\}}{\{\mathrm{CO_3}^{2-}\}} - 3\log\gamma_\pm \tag{9}$$

The ionization constant of water is given by

$$K_\mathrm{w} = \{\mathrm{H}^+\}\{\mathrm{OH}^-\}\gamma_\pm^2 \tag{10}$$

The 2-naphthol, K$^+$ and carbonate mass charge balances in carbonate buffer solutions are

$$\{\mathrm{HIn}\}_0 = \{\mathrm{HIn}\} + \{\mathrm{In}^-\} \tag{11}$$

$$\{\mathrm{K}^+\} = \{\mathrm{KHCO_3}\}_0 + 2\{\mathrm{K_2CO_3}\}_0 \tag{12}$$

$$\{\mathrm{KHCO_3}\}_0 + \{\mathrm{K_2CO_3}\}_0 = \{\mathrm{H_2CO_3}^*\} + \{\mathrm{HCO_3}^-\} + \{\mathrm{CO_3}^{2-}\} \tag{13}$$

$$\{\mathrm{K}^+\} + \{\mathrm{H}^+\} = \{\mathrm{HCO_3}^-\} + 2\{\mathrm{CO_3}^{2-}\} + \{\mathrm{OH}^-\} + \{\mathrm{In}^-\} \tag{14}$$

where $\{\mathrm{KHCO_3}\}_0$ and $\{\mathrm{K_2CO_3}\}_0$ are the initial concentrations of $\mathrm{KHCO_3}$ and $\mathrm{K_2CO_3}$, respectively. Eqn. (1) can be rearranged as

$$\mathrm{pH} = \mathrm{p}K_\mathrm{i} - \log\frac{\{\mathrm{HIn}\}}{\{\mathrm{In}^-\}} + \log\gamma_\pm \tag{15}$$

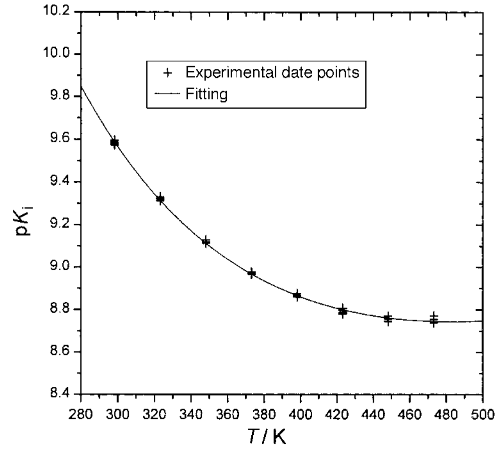

Fig. 7 Temperature dependence of pK_i of 2-naphthol under vapor-saturated pressure. Symbols (+) represent experimental data points. Solid line represents the fitted function, eqn. (7).

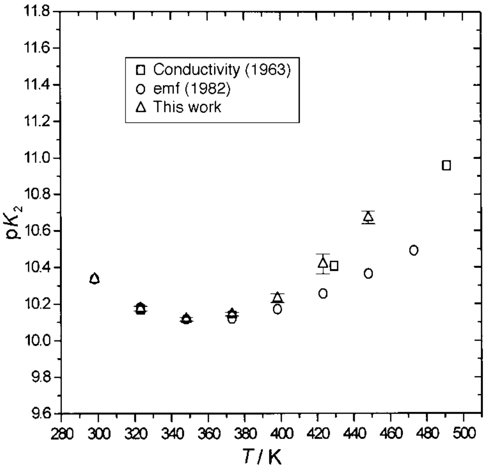

Fig. 8 Comparison of measured pK_2 with reported values. Square: Ryzhenko (ref. 6), circle: Patterson *et al.* (ref. 9).

In fact, because the pH in carbonate buffer solutions at 25 °C was over 10.00, the first dissociation of carbonic acid may be neglected at low temperatures. During the experiment, pH decreased in carbonate buffer solutions as temperature increased. Thus, the first dissociation of carbonic acid was taken into consideration at high temperatures. In carbonate buffer solutions, pH was determined from pK_i and the molal concentration ratios of the acidic to basic species of 2-naphthol using eqn. (15). All calculations were performed by the iterative method as described in the previous section. The pK_1 values of carbonic acid were taken from Park *et al.*[20] The calculated pK_2 values were fitted with the empirical formula[8,9] by nonlinear regression to give

$$\mathrm{p}K_2 = 4201.48 - \frac{229\,200}{T} - 661.21\ \ln(T) + 0.647\,53T + \frac{13\,498\,200}{T^2} \qquad (16)$$

Fig. 8 represents the measured pK_2 values and the previously reported values at various temperatures. It seemed that the minimum pK_2 value was located in between 75 and 100 °C. After the minimum pK_2 value, pK_2 increases with temperature. It appears that dissociation of the bicarbonate ion becomes unfavorable as the dielectric constant of water decreases with temperature. As the measured pK_2 values were compared with the previously reported values, some difference among the experimental methods was shown at high temperatures. Our spectroscopic result was in much closer agreement with conductivity measurements than emf measurements.

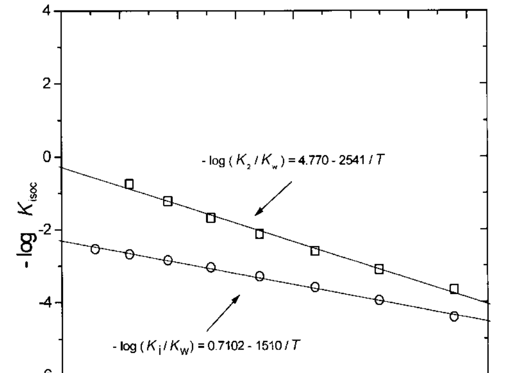

Fig. 9 The plot of $-\log K_{\mathrm{isoc}}$ against $1/T$ for the isocoulombic reactions. Symbols represent measured values for the second dissociation of carbonic acid (square) and for acid dissociation of 2-naphthol (circle), respectively. Solid lines are the linear fit to the measured data.

Isocoulombic reactions for 2-naphthol(HIn) and HCO_3^-

By using the temperature dependence of K_a for weak acids, the equilibrium for isocoulombic reactions can be studied. For 2-naphthol, the isocoulombic reaction[27] is

$$\mathrm{HIn(aq)} + \mathrm{OH^-(aq)} \rightleftharpoons \mathrm{In^-(aq)} + \mathrm{H_2O(aq)}$$

The equilibrium constant, K_{isoc}, for this isocoulombic reaction can be written as

$$K_{\mathrm{isoc}} = \frac{\{\mathrm{In}^-\}}{\{\mathrm{HIn}\}\{\mathrm{OH}^-\}} = \frac{\{\mathrm{In}^-\}}{\{\mathrm{HIn}\}\{\mathrm{OH}^-\}}\,\frac{\{\mathrm{H}^+\}}{\{\mathrm{H}^+\}} = \frac{K_i}{K_w} \qquad (17)$$

Similarly, for the second dissociation reaction of carbonic acid, the isocoulombic reaction can be written as

$$\mathrm{HCO_3^-(aq)} + \mathrm{OH^-(aq)} \rightleftharpoons \mathrm{CO_3^{2-}(aq)} + \mathrm{H_2O(aq)}$$

And the equilibrium constant is

$$K_{\mathrm{isoc}} = \frac{\{\mathrm{CO_3}^{2-}\}\gamma_\pm^2}{\{\mathrm{HCO_3}^-\}\{\mathrm{OH}^-\}} = \frac{\{\mathrm{CO_3}^{2-}\}\gamma_\pm^2}{\{\mathrm{HCO_3}^-\}\{\mathrm{OH}^-\}}\,\frac{\{\mathrm{H}^+\}}{\{\mathrm{H}^+\}} = \frac{K_2}{K_w} \qquad (18)$$

In eqns. (17) and (18), K_{isoc} describes the relative acidity of weak acids, HIn and HCO_3^-, to that of water, respectively. The dissociation reactions for HIn, HCO_3^-, and H_2O are ionogenic reactions in which ions are produced. According to the Born model for ion solvation, the dielectric constant of water has a large effect on ion solvation. While the ionogenic reaction in water becomes favorable when the dielectric constant of water increases, the isocoulombic reaction in water is not largely influenced by the change of the dielectric constant. Therefore, whereas the dielectric constant of water may have a large effect on K_i, K_w and K_2, it may be expected to have a small effect on this relative property K_{isoc}. In Fig. 9, $-\log K_{\mathrm{isoc}}$ values are plotted against $1/T$ in the temperature range from 25 to 200 °C. As shown in Fig. 9, the plot of $-\log K_{\mathrm{isoc}}$ against $1/T$ is approximately linear over the temperature range studied as for other isocoulombic reactions, which means that $\Delta C_p{}^0$ for the isocoulombic reaction is approximately zero. From the linearity, the dissociation constant can be predicted by the extrapolation of $-\log K_{\mathrm{isoc}}$ to higher temperatures.

Conclusions

The optical indicators can be used to measure the pH of aqueous solutions by obtaining the absorption spectra of the indicators over a suitable pH range. This method is applicable to many high temperature aqueous systems if the indicator, which is an organic acid, is thermally stable. Since 2-naphthol was thermally stable at least up to 200 °C, it could be used as an optical indicator to measure the pH of hydrothermal solutions. From the known pK_a of boric acid, the dissociation constant of 2-naphthol was determined using UV–visible spectroscopic measurement up to 200 °C. The absorption spectrum of the optical indicator is changed so sensitively in the pH range of pK_i ± 1 that 2-naphthol can be used effectively in the pH range between 8.5 and 10.5. By obtaining absorption spectra of 2-naphthol in carbonate buffer solutions, the pH of the carbonate buffer solutions was measured and the second dissociation constant of carbonic acid was measured up to 175 °C under vapor-saturated pressure. When the dissociation reactions of 2-naphthol and bicarbonate were written as isocoulombic reactions, the plot of $-\log K_{\text{isoc}}$ against $1/T$ was approximately linear in the temperature range studied. This linearity can be used to predict the dissociation constant by extrapolation of $-\log K_{\text{isoc}}$ to higher temperatures.

Acknowledgement

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