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D_2O Isotope Effects on the Ionization of β-Naphthol and Boric Acid at Temperatures from 225 to 300 °C using UV-Visible Spectroscopy

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Abstract The deuterium-isotope effects on the ionization constants of β-naphthol (2-naphthol) and boric acid, $\Delta\log_{10}K = [\log_{10}K_{\mathrm{D2O}} - \log_{10}K_{\mathrm{H2O}}]$, have been determined from measurements in light and heavy water at temperatures from $225\ ^{\circ}\mathrm{C} \le t \le 300\ ^{\circ}\mathrm{C}$ and pressures near steam saturation. β-Naphthol is a thermally-stable colorimetric pH indicator, whose ionization constant lies close to that of $H_2PO_4^-$ (aq), the only acid for which $\Delta\log_{10}K$ is accurately known at elevated temperatures. A newly designed platinum flow cell was used to measure UV-visible spectra of β-naphthol in acid, base, and buffer solutions of $H_2PO_4^-/HPO_4^{2-}$ and $D_2PO_4^-/DPO_4^{2-}$, from which the degree of ionization at known values of pH and pD was determined. Values of the ionization constants of β-naphthol in light and heavy water were calculated from these results, and used to derive a model for $\log_{10}K_{H_2O}$ and $\log_{10}K_{D_2O}$ over the experimental temperature range with an estimated precision of ± 0.02 in $\log_{10}K$. The new values of K_{H2O} and K_{D2O} allowed us to use β-naphthol as a colorimetric indicator, to measure the equilibrium pH and pD of the buffer solutions $B(OH)_3/B(OH)_4^-$ and $B(OD)_3/B(OD)_4^-$ up to 300 °C, from which the ionization constants of boric acid were calculated. The magnitude of the deuterium isotope effect for $H_2PO_4^-$ (aq) is known to fall from $\Delta\log_{10}K = -0.62$ to $\Delta\log_{10}K = -0.47$, on the "aquamolal" concentration scale, as the temperature rises above 125 °C, but then remains almost constant. Although the temperature range is more limited, the new results for β-naphthol and boric acid appear to show a similar trend.

Keywords Deuterium isotope effects · D_2O · Heavy water · Ionization constants · 2-Naphthol · Boric acid · Phosphate buffers · Colorimetric pH indicators · Hydrothermal solutions

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1 Introduction

Deuterium isotope effects on ionization constants in hydrothermal systems are of scientific interest, because they provide a means of probing solvation effects under extreme conditions. They are also important in nuclear technology, because CANDU pressurized heavy water reactors use D_2O as a neutron moderator and as the heat-transport fluid in the primary coolant system. Operating strategies to minimize activated corrosion product transport require detailed models for the chemical behavior of metal oxides, dissolved hydrogen, and LiOH at temperatures as high as 310 °C. The effects of isotopic substitution on ionization constants and related thermodynamic functions at room temperature have been reviewed by Bates [1], Laughton and Robertson [2], Arnett and McKelvey [3], and Jancso and Van Hook [4]. Typical deuterium isotope effects at 25 °C range from about -0.2 to -0.7 units of $\log_{10} K$. Only a few studies of ionization and metal ion hydrolysis have been carried out at elevated temperatures and pressures. The ionization of heavy water has been studied at elevated temperatures by Shoesmith and Lee [5] and by Mesmer and Herting [6]. Mesmer and Herting also reported the ionization constant of $D_2PO_4^-$ (aq) up to 300 °C. To our knowledge, the $D_2PO_4^-/DPO_4^{2-}$ system is the only pD buffer for which accurate ionization constants in heavy water are known at high temperature and pressure.

Recent work in our laboratory, and others, has made use of thermally stable, colorimetric pH indicators that can be used in aqueous systems at temperatures as high as 400 °C [7–10]. One of these, β-naphthol (2-naphthol) [7], overlaps the range of the $D_2PO_4^-/DPO_4^{2-}$ buffer, which thus provides an opportunity for determining its acid ionization constant. Ionization constants of β-naphthol have been studied in light water up to 400 °C by Xiang and Johnston [7] using UV-visible techniques. The deuterium isotope effect on β-naphthol ionization at low temperatures has been determined by Wehry and Rogers [11].

This paper reports values for the D_2O isotope effects, $\Delta \log_{10} K = [\log_{10} K_{D_2O} - \log_{10} K_{H_2O}]$ for the ionization of β-naphthol at temperatures $225\,^\circ\mathrm{C} \le t \le 300\,^\circ\mathrm{C}$ and pressures near steam saturation, using UV-visible spectroscopy with a newly constructed high-pressure platinum flow cell. The new values for K_{D_2O} of β-naphthol were then used to determine the ionization constant of boric acid in heavy water, which are also reported in this paper.

2 Experimental Methods

2.1 Platinum UV-Visible Flow Cell

Equilibrium constants and time-dependent thermal decomposition spectra were measured in a UV-visible spectrometer, high-pressure cell and flow injection system similar to that described by Trevani et al. [12]. Preliminary experiments demonstrated that our existing titanium and stainless steel cells were not suitable for this study because they form intensely colored soluble complexes with phosphate that interfere with the UV-visible measurements. A new cell and pre-heater, designed and constructed from a platinum/iridium alloy, successfully avoided the problem [13].

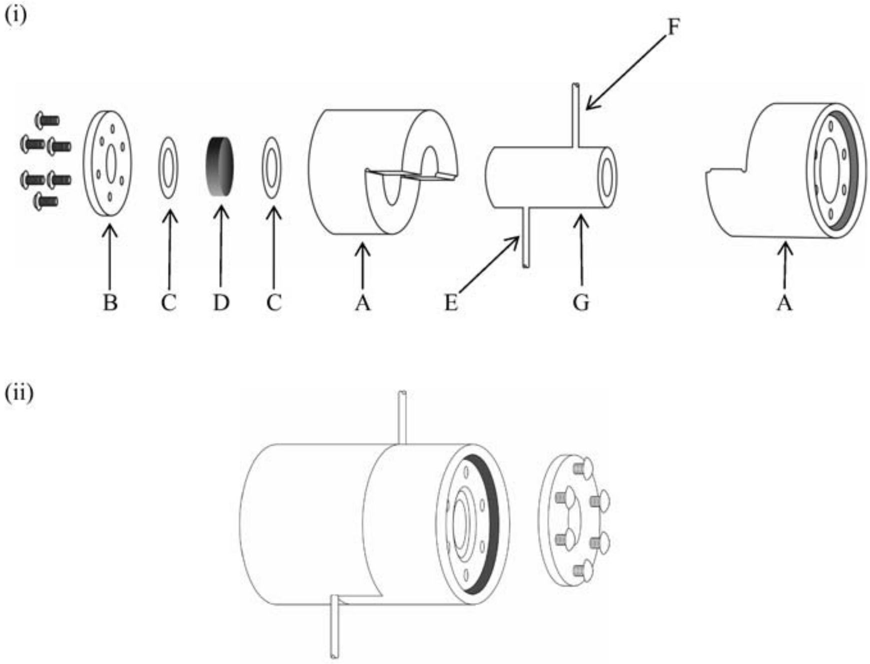


Fig. 1 Schematic diagram of the UV-visible platinum flow cell: (**i**) an exploded view showing the platinum liner and other parts (above); and (**ii**) fully assembled (below). A, cylindrical titanium casing; B, titanium retaining ring; C, gold gasket; D, sapphire window; E, sample solution inlet; F, sample solution outlet; G, platinum/iridium inner cell

Figure 1 shows two views of the new flow cell, which is constructed so that sample solutions contact only with platinum, gold and sapphire surfaces at elevated temperatures and pressures. The inner body of the cell consists of a short cylindrical platinum-iridium cylinder (Technic Inc.; 90% Pt + 10% Ir alloy; 12 mm o.d. × 5 mm i.d. × 10 mm long). The ends of the cylinder were cut and polished to provide a flat perpendicular seat for the sapphire windows. The alloy material and thickness of the walls were chosen to provide enough support for the sapphire windows without deforming. Inlet and outlet platinum tubes (Technic Inc.; 99.9% Pt; 1.59 mm o.d. × 0.79 mm i.d.) were gold soldered into the entrance and exit ports, which were displaced by 8 mm along the length of the cell and mounted at a 180 ° angle to one other.

The inner platinum cell fitted into a supporting titanium container (32 mm o.d. × 12 mm i.d. × 40 mm length), similar to the single-bodied cell used in our earlier work [9], but with a split design so that the inner cell could be accommodated. The titanium jacket serves to provide thermal contact with the thermostatted brass block that surrounds the cell, and provides support for mounting the windows. Hemlux-grade sapphire windows (Crystal Systems Inc.; 10.00 mm diameter × 5.00 mm thick) were mounted at each of the two ends of the tube. The windows were held in place by flat titanium rings, secured by six bolts screwed into the outer titanium cell body. To compensate for imperfections on the 90%Pt-10%Ir cylinder surfaces, a gold foil gasket (Premion®, 99.99%) ~0.127 mm thick was placed between each sapphire window and the two seating surfaces of the inner platinum cell. On the low-pressure side of the window, Kapton® polymide film was used to reduce friction between the highly polished surface of the windows and the titanium discs that are used as seals. Although Pt and Ti have similar thermal expansivity coefficient, $8.9 \times 10^{-6}\ \mathrm{K}^{-1}$, leaks can arise at high temperatures due to the differential expansion of the metals (Pt, Ti, Au) and sapphire. As in our earlier cell design [12], the sealing pressure was maintained through the use of belleville washers. The internal volume of the cell is 0.20 cm^3.

The inlet tubing was wound tightly over the three-piece brass oven to serve as a pre-heater. This was done carefully to minimize unnecessary stress on the gold-soldered joints. The brass oven was constructed so the pre-heater could be removed without unwinding it, and thus the cell could be easily disassembled for repair. The temperature was maintained to within ±0.2 °C with an Omega CN76000 temperature controller and monitored with a Chromega-Alomega thermocouple inserted directly into the small-diameter well drilled into the Ti cell body. The pressure of the flow system was maintained by a nitrogen-filled cylinder and a back-pressure regulator (Tescom model 26-1700). The design and construction of the flow injection system and temperature controller are identical to that of Trevani et al. [12]. This cell has been used at temperatures up to 350 °C and pressures of 200 bars.

2.2 Chemicals

Solutions were prepared by mass from dried solids or carefully standardized stock solutions, to an estimated accuracy of ±0.2%. Stock solutions of NaOH(aq) and NaOD(aq) were prepared from carbonate-free solutions of NaOH (Fisher Certified ACS, 50%) and NaOD (Aldrich, 40 wt.% in D_2O, 99 + atom %D), and standardized by titration against potassium hydrogen phthalate (Fisher Scientific, 100.05%). The potassium hydrogen phthalate salt was dried at 110 °C for 2 h prior to use. Stock solutions of HCl(aq) (35 wt.%, Fisher Certified ACS) and DCl(aq) (Aldrich, 35 wt.% solution in D_2O, 99 atom %D) were prepared by mass and standardized by titration with standard NaOH(aq). Trifluoromethanesulfonic "triflic" acid (Alfa Aesar, 99%) was used as received, diluted in H_2O or D_2O, and standardized by titration against NaOH(aq) and NaOD(aq), respectively.

The light-water phosphate stock solutions were prepared from NaH_2PO_4(s) (Aldrich "Reagent Plus") and Na_2HPO_4(s) (Sigma Aldrich, ACS "99% Plus"), then standardized by titration with NaOH(aq) and HCl(aq), respectively. The stock solutions of NaD_2PO_4(aq) and Na_2DPO_4(aq) were made by dissolving the light hydrogen salts in D_2O, where they undergo complete exchange of the ionizable hydrogen with deuterium from the solvent, and were then titrated with NaOH(aq) and HCl(aq). Phosphate buffer solutions were prepared from the standardized stock solutions by adding a known mass of NaH_2PO_4(aq) or NaD_2PO_4(aq) to an appropriate mass of Na_2HPO_4(aq) or Na_2DPO_4(aq).

Table 1 Concentrations of standard solutions used to prepare acid, base and buffer solutions

Solute	m_{aq}/ (mol·(1.1117 kg-D_2O)$^{-1}$)	m/ (mol·(kg-D_2O)$^{-1}$)
NaD_2PO_4	0.0494	0.0445
Na_2DPO_4	0.0484	0.0434
NaOD	0.1932	0.1738
Triflic (in D_2O)	0.1348	0.1212
Triflic (in H_2O)	0.1729	0.1729
$B(OD)_3$	0.2012	0.1810
$B(OH)_3$	0.2120	0.2120
NaOH	0.1180	0.1180
NaH_2PO_4	0.0522	0.0522
Na_2HPO_4	0.0525	0.0525

Reagent-grade boric acid, $B(OH)_3$, (99.99% reagent grade) and deuterated boric acid-d$_3$, $B(OD)_3$, ("98 atom %D") were purchased from Aldrich Chem. Co. and were used without further purification. D-Mannitol (ACS reagent, Aldrich Chem. Co.) was found not to contain acidic or basic impurities, and was used without further purification. Boric acid stock solutions were prepared by dissolving the solid in fresh nanopure water, and the solutions were standardized by potentiometric titration with NaOH(aq) at room temperature. The titrations of boric acid were carried on in the presence of D-mannitol, which improves the end point [14]. Subsequent solutions were prepared by mass and stored in dark glass bottles. Similar methods were used for the boric acid-d$_3$ stock solution in D_2O.

The concentrations of the standard solutions, used to prepare the acid, base and buffer solutions described above, are listed in Table 1.

β-Naphthol (Aldrich Chem. Co., 98%) was used as received and was stored as the solid in a dark brown bottle to minimize photo decomposition. The solubility of β-naphthol in acid solutions is limited. To avoid precipitation, standard solutions of β-naphthol were prepared by dissolving the solid at concentrations $< 10^{-3}$ mol·kg^{-1} in dilute carbonate-free NaOH and NaOD (0.0110 and 0.0167 mol·kg^{-1}, respectively). The same stock solution was then used to prepare solutions of known *relative* concentrations of β-naphthol, by mass, in the standard acid, base and buffer solutions required for these measurements.

Nanopure water (resistivity 18.2 MΩ·cm) and deuterium oxide (99.8 mol %-D) were used to prepare all of the solutions. The isotopic purity of the D_2O was confirmed by NMR using methods described in our previous work [15].

All solutions were prepared and stored under an argon atmosphere. Transfers were made by syringe and all other sample manipulations during measurements were done under an argon blanket, to avoid interference from ambient carbon dioxide and isotopic dilution with H_2O vapor.

2.3 Experimental Design and Methods

The procedure for determining the acid ionization constants of β-naphthol required preparing quantitative solutions in acid, base and several phosphate buffers, which were then pumped through the spectroscopic cell in sequence, all at elevated temperatures and pressures above steam saturation. The equilibrium constant was determined from the spectrum and the known relative concentration of β-naphthol in each of the buffer solutions. Measurements in strong acid and strong base yielded spectra for the acidic and basic forms of the indicator under the exact conditions of the study on that day. The spectra of the β-naphthol in the phosphate buffer solutions is a linear combination of the spectra of the two forms of the indicator, at the known buffer pH or pD, from which the ionization constant can be calculated. This colorimetric indicator method requires measurable concentrations of the ionized and neutral forms of the indicator be present in order to make meaningful pH measurements. As a result, it is desirable to use buffer solutions whose pH or pD is of the same order of magnitude as $-\log_{10} K$ of the β-naphthol. Our choice of conditions was based on light water calculations, described below in Sect. 4. Measurements were performed at 25 °C intervals using pressures near steam saturation, over the temperature range $225\,^{\circ}\mathrm{C} \leq t \leq 300\,^{\circ}\mathrm{C}$, at a flow rate of $0.2\ \mathrm{cm^3 \cdot min^{-1}}$. Comparisons of the spectra from runs at higher and lower flow rates, and stopped-flow experiments, confirmed that thermal equilibrium had been achieved under these conditions. The overall ionic strength of the phosphate buffer solutions was held constant at approximately 0.1 aquamolal.

A Varian Cary 50 spectrophotometer (190–1100 nm), interfaced to a computer equipped with Cary Win UV Scan Application software, was used to record the absorption spectra. All spectra were obtained at wavelength intervals of 1 nm, over the range $200\ \mathrm{nm} < \lambda < 1100\ \mathrm{nm}$, at a scan rate of $600\ \mathrm{nm \cdot min^{-1}}$. Six consecutive spectra, taken at two-minute intervals, were obtained for each sample solution and then averaged to minimize noise. At this flow rate, the residence time of solution in the cell was ~ 1 min, and the total exposure to hydrothermal conditions in the pre-heater and cell was less than 5 min. To ensure that no thermal decomposition took place at the highest temperatures, the system was operated as a stopped-flow reactor so that time-dependant changes in the spectrum could be observed.

3 Spectroscopic Analysis

The acid dissociation equilibrium for β-naphthol is described by Eq. 1

$$\mathrm{NapOH(aq)} \leftrightarrows \mathrm{NapO^-(aq)} + \mathrm{H^+(aq)} \tag{1}$$

where NapOH(aq) and $\mathrm{NapO^-(aq)}$ are the acidic and basic forms of β-naphthol, respectively. The equilibrium constant for this reaction is expressed in terms of the “aquamolality”,

m_{aq}, and activity coefficient, γ_i, of each species:

$$K_{\mathrm{NapOH}} = \left(\frac{m_{\mathrm{aq,H^+}} m_{\mathrm{aq,NapO^-}}}{m_{\mathrm{aq,NapOH}}}\right)\left(\frac{\gamma_{\mathrm{aq,H^+}} \gamma_{\mathrm{aq,NapO^-}}}{\gamma_{\mathrm{aq,NapOH}}}\right) \tag{2}$$

The activity coefficient of the neutral species, "NapOH", is assumed to be unity. Aquamolality, m_{aq}, is defined as mol-solute per 55.509 mol-solvent {i.e. $m_{\mathrm{aq}}, =$ (mol-solute)/(kg-H_2O) = (mol-solute)/(1.1117 kg-D_2O)}. The "aquamolal" concentration scale has been adopted by a number of workers, as a means of comparing thermochemical properties of solutes in light and heavy water, using a standard state that does not depend on temperature and has the same mole fraction of solute in both D_2O and H_2O. (See Arnett and McKelvey [3], Jacso and Van Hook [4], Trevani et al. [15], and references cited therein.) The other commonly used scale for expressing transfer properties, molarity {(mol-solute)/(dm^3-solvent)}, is not suitable for temperature-dependent studies because it is affected by thermal expansion.

In a similar fashion, the second dissociation reaction of the phosphoric acid is expressed as

$$\mathrm{H_2PO_4^-(aq)} \leftrightarrows \mathrm{HPO_4^{2-}(aq)} + \mathrm{H^+(aq)} \tag{3}$$

The equilibrium constant, $K_{\mathrm{H_2PO_4^-}}$ is given by Eq. 4,

$$K_{\mathrm{H_2PO_4^-}} = \left(\frac{m_{\mathrm{aq,H^+}} m_{\mathrm{aq,HPO_4^{2-}}}}{m_{\mathrm{aq,H_2PO_4^-}}}\right)\left(\frac{\gamma_{\mathrm{aq,H^+}} \gamma_{\mathrm{aq,HPO_4^{2-}}}}{\gamma_{\mathrm{aq,H_2PO_4^-}}}\right) \tag{4}$$

which can be rearranged to give hydrogen ion aquamolality as shown below:

$$m_{\mathrm{aq,H^+}} = \left(\frac{m_{\mathrm{aq,H_2PO_4^-}} K_{\mathrm{H_2PO_4^-}}}{m_{\mathrm{aq,HPO_4^{2-}}}}\right)\left(\frac{\gamma_{\mathrm{aq,H_2PO_4^-}}}{\gamma_{\mathrm{aq,H^+}} \gamma_{\mathrm{aq,HPO_4^{2-}}}}\right) \tag{5}$$

The values of $K_{\mathrm{D_2PO_4^-}}$ from Mesmer and Herting [6], which use the hypothetical one molal standard state, were converted to the aquamolal scale using the relationships $m_{\mathrm{aq}} = m$ in H_2O, and $m_{\mathrm{aq}} = m/1.1117$ in D_2O. For dilute solutions at elevated temperatures, the activity coefficient, γ_i, may be considered independent of the relative compositions of the mixture and dependent only on the total ionic strength. The ionization constant for β-naphthol can be obtained by substituting Eq. 5 into Eq. 2 to yield the expression:

$$K_{\mathrm{NapOH}} = \left(\frac{K_{\mathrm{H_2PO_4^-}} m_{\mathrm{aq,H_2PO_4^-}}}{m_{\mathrm{aq,HPO_4^{2-}}}}\right)\left(\frac{\gamma_{\mathrm{aq,H_2PO_4^-}}}{\gamma_{\mathrm{aq,HPO_4^{2-}}}}\right)\left(\frac{m_{\mathrm{aq,NapO^-}} \gamma_{\mathrm{aq,NapO^-}}}{m_{\mathrm{aq,NapOH}}}\right) \tag{6}$$

The experimental indicator ratios, $(m_{\mathrm{NapOH}}/m_{\mathrm{NapO-}}) = (m_{\mathrm{aq,NapOH}}/m_{\mathrm{aq,NapO-}})$, were determined by a least-squares fit to the experimental spectra, in which the total absorbance at each experimental wavelength over the entire digitized spectrum was treated as a linear combination of the spectra of both forms of the indicator. This yields the expression,

$$A(\lambda) = \{\varepsilon_{\mathrm{NapOH}}(\lambda) b m^*_{\mathrm{NapOH}} + \varepsilon_{\mathrm{NapO^-}}(\lambda) b m^*_{\mathrm{NapO^-}}\}\rho_{\mathrm{solution}} \tag{7}$$

where $A(\lambda)$ is the absorbance at each wavelength, λ. For convenience in working with densities to convert Beer's law to mass units, an "effective" concentration was defined as $m^* = (\text{mol-solute})/(\text{kg-solution})$ and ρ_{solution} is the solution density. The terms $\varepsilon_{\mathrm{NapOH}}(\lambda)$ and $\varepsilon_{\mathrm{NapO^-}}(\lambda)$ are the absorptivities of the indicator in the acid form and its conjugate base, which were determined independently using indicator solutions in excess of triflic acid and sodium hydroxide, respectively.

$$\varepsilon_{\mathrm{NapOH}}(\lambda) = \frac{A_{\mathrm{acid}}(\lambda)}{b m^*_{\mathrm{acid}} \rho_{\mathrm{acid}}} \tag{8}$$

$$\varepsilon_{\mathrm{NapO^-}}(\lambda) = \frac{A_{\mathrm{base}}(\lambda)}{b m^*_{\mathrm{base}} \rho_{\mathrm{base}}} \tag{9}$$

where m^*_{acid} and m^*_{base} represent the concentrations of NapOH(aq) and $\mathrm{NapO^-}$(aq) in acidic and basic solutions, respectively. The terms, ρ_{acid} and ρ_{base} are the density of the acidic and basic solutions, respectively. Substituting Eqs. 8 and 9 into Eq. 7 yields the result

$$\frac{A(\lambda)}{b\rho_{\mathrm{solution}}} = \frac{A_{\mathrm{acid}}(\lambda)}{b m^*_{\mathrm{acid}} \rho_{\mathrm{acid}}} \left(b m^*_{\mathrm{NapOH}} + \frac{D m^*_{\mathrm{NapO^-}} \rho_{\mathrm{acid}} A_{\mathrm{base}}(\lambda)}{\rho_{\mathrm{base}} A_{\mathrm{acid}}} \right) \tag{10}$$

where $D = m^*_{\mathrm{acid}}/m^*_{\mathrm{base}}$ is simply the ratio of concentrations of β-naphthol in the acidic and basic solutions. A less cumbersome version of Eq. 10 was obtained by assuming the densities to be approximately equal. Errors due to this assumption are considered to be negligibly small as the solutions were so dilute.

$$A(\lambda) = A_{\mathrm{acid}}(\lambda) \frac{m^*_{\mathrm{NapOH}}}{m^*_{\mathrm{acid}}} + A_{\mathrm{base}}(\lambda) D \frac{m^*_{\mathrm{NapO^-}}}{m^*_{\mathrm{base}}} \tag{11}$$

This equation was then further simplified by writing it in terms of constants 'k' and 'l' to give Eq. 12. The indicator ratio can be easily found from the expression of Eq. 13 once the ratio of 'k' to 'l' is known.

$$A(\lambda) = A_{\mathrm{acid}}(\lambda) k + A_{\mathrm{base}}(\lambda) D l \tag{12}$$

$$\frac{k}{l} = \frac{m^*_{\mathrm{NapOH}}}{m^*_{\mathrm{NapO^-}}} = \frac{m_{\mathrm{aq,NapOH}}}{m_{\mathrm{aq,NapO^-}}} \tag{13}$$

Table 2 Debye-Hückel parameters, A^a

t/°C	$p(H_2O)$/MPa	$p(D_2O)$/MPa	A_{H2O}	A_{D2O}
Experimental pressure, p_{expt}				
225	4.000	4.000	0.8771	0.9434
250	5.000	5.000	0.9697	1.0416
275	7.000	7.000	1.0855	1.1649
300	10.000	10.000	1.2370	1.3283
Steam saturation pressure, p_{sat}				
25	0.003	0.003	0.5100	0.5444
50	0.012	0.011	0.5345	0.5708
100	0.101	0.096	0.5991	0.6422
150	0.476	0.465	0.6863	0.7380
200	1.555	1.546	0.8039	0.8652
250	3.976	3.995	0.9723	1.0444
300	8.588	8.690	1.2470	1.3387

[a] Calculated according to the equation $A = A\gamma/\ln 10$ [16]

Values for the constants k and l were obtained at each experimental temperature from linear regression of Eq. 12 to the spectrum of each buffer solution, using the data between 280 and 400 nm. These were used to calculate values for the equilibrium quotient at each buffer ratio,

$$Q_{\mathrm{NapOH}} = \frac{m_{\mathrm{aq,H^+}} m_{\mathrm{aq,NapO^-}}}{m_{\mathrm{aq,NapOH}}} \tag{14}$$

The activity coefficients, γ_i, required to calculate the corresponding equilibrium constants and buffer pH were approximated by a form of the Davies' equation given by

$$\log_{10}\gamma_i = \frac{-z_i^2 A\sqrt{I_{\mathrm{aq}}}}{1+\sqrt{I_{\mathrm{aq}}}} + 0.2Az_i^2 I_{\mathrm{aq}} \tag{15}$$

where z_i is the ionic charge, A is the Debye-Hückel limiting slope and I_{aq} is the aquamolal ionic strength. The Debye-Hückel parameters for H_2O and D_2O, $A = (A_\gamma/\ln 10) = 3(A_\phi/\ln 10)$ [16], were obtained from the expressions reported by Uematsu and Franck [17] and Trevani et al. [15], respectively. The values are listed in Table 2. The coefficient $2Az_i^2$ was chosen to fit the phosphoric acid equilibrium constant data for light water [18].

4 Ionization Constants for β-Napthol

Ionization constants for β-naphthol [7], $H_2PO_4^-$ [18], and boric acid [19, 20] in light water are plotted as a function of temperature in Fig. 2. The plot shows the range in which both the

Fig. 2 The calculated indicator range of β-naphthol, defined as $-\log_{10} K_{\mathrm{NapOH}} \pm 1$ log unit, and the temperature dependence of $-\log_{10} K_{2,\mathrm{H_2PO_4^-}}$ of phosphoric acid and $-\log_{10} K_{\mathrm{B(OH)_3}}$ of boric acid

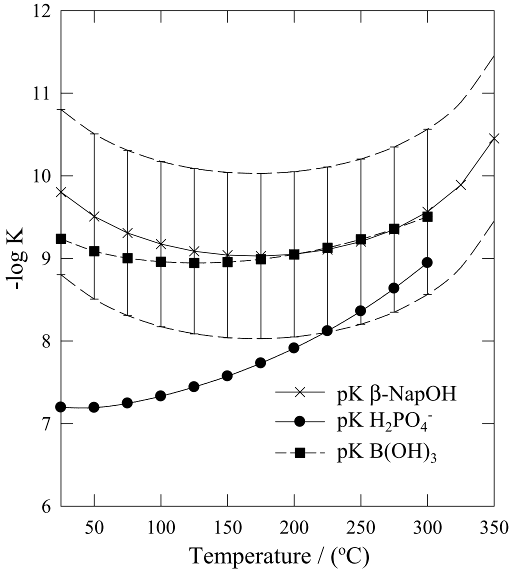
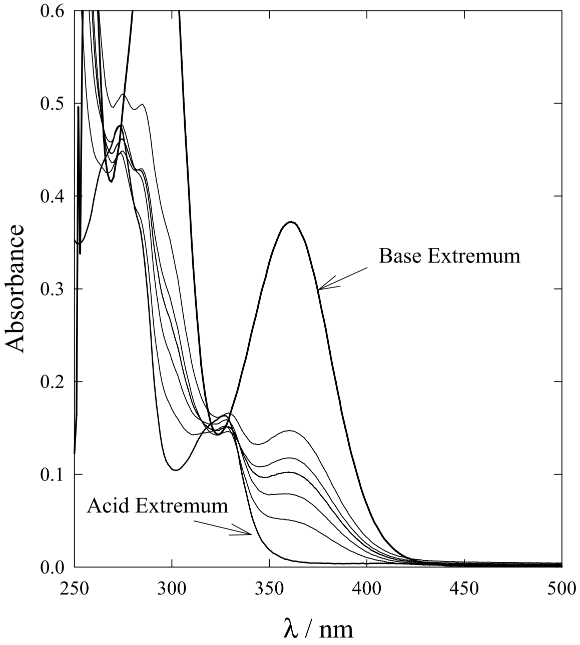


Fig. 3 The spectra of β-naphthol in 0.1348 aquamolal triflic acid solution ("acid extremum"); 0.1932 aquamolal sodium hydroxide solution ("base extremum"); and phosphate buffer solutions at 250 °C and $p = 5$ MPa, without correction for small differences in the relative concentrations



ionized and neutral forms of β-naphthol co-exist in sufficient quantities to determine their concentration ratio by UV-visible spectroscopy. Typical experimental results are shown in Fig. 3, which compares the spectra of β-naphthol in triflic acid solution, sodium hydrox-

Table 3 The fitting parameters '*k*' and '*l*' obtained from regression of Eq. 12,[a] NapOH(aq) $\leftrightarrows$ NapO$^-$(aq) + H$^+$(aq)

t/°C	Concentration ratio, *D*	Buffer ratio	Indicator ratio	Parameter, *k*	Parameter, *l*
225	0.9969	0.846	14.04	0.8271 ± 0.04	0.0589 ± 0.02
		0.404	6.12	0.7205 ± 0.02	0.1177 ± 0.01
		0.286	4.41	0.7367 ± 0.03	0.1671 ± 0.01
		0.174	2.66	0.6513 ± 0.02	0.2449 ± 0.01
		0.152	2.32	0.6151 ± 0.02	0.2653 ± 0.01
250	1.0373	0.863	11.53	0.8933 ± 0.02	0.0775 ± 0.01
		0.415	4.94	0.7782 ± 0.02	0.1576 ± 0.01
		0.305	3.53	0.7567 ± 0.02	0.2142 ± 0.01
		0.224	2.58	0.6958 ± 0.02	0.2699 ± 0.01
		0.163	1.87	0.6454 ± 0.02	0.3456 ± 0.01
275	0.9969	0.897	8.38	0.8091 ± 0.04	0.0965 ± 0.02
		0.455	4.11	0.7572 ± 0.03	0.1843 ± 0.01
		0.340	3.04	0.7059 ± 0.02	0.2322 ± 0.01
		0.232	2.08	0.6280 ± 0.02	0.3012 ± 0.01
		0.210	1.88	0.5944 ± 0.01	0.3157 ± 0.01
300	1.0373	0.930	7.32	0.7997 ± 0.03	0.1093 ± 0.01
		0.480	3.64	0.6822 ± 0.03	0.1876 ± 0.01
		0.372	2.77	0.6631 ± 0.03	0.2394 ± 0.01
		0.295	2.15	0.5622 ± 0.02	0.2609 ± 0.01
		0.230	1.70	0.5793 ± 0.03	0.3399 ± 0.01

[a] Error limits are standard deviations of the parameters obtained from the regression

ide solution, and phosphate buffer solutions at a fixed temperature of 250 °C and pressure 5 MPa. The solutions of β-naphthol in triflic acid and sodium hydroxide were assumed to contain only the neutral β-naphthol, NapOH(aq), and the naphthoate ion, NapO$^-$(aq), respectively. The spectrum of β-naphthol in each buffer solution was found to be a linear combination of the spectra in triflic acid and sodium hydroxide, confirming that NapOH(aq) and NapO$^-$(aq) coexist in the buffer solutions. The relative amounts of naphthoate ion and neutral β-naphthol in solution depend on the phosphate buffer ratio used, in a manner consistent with Eqs. 4 and 13. The experimental conditions, solution compositions, and the fitted values of parameters *k* and *l* are listed Tables 3 and 4, along with the corresponding values of $m_{\mathrm{aq,H^+}}$ and $m_{\mathrm{aq,D^+}}$ calculated from Eqs. 5 and 15, using ionization constants from Refs. [6, 18].

Experimental values for $\log_{10} K_{\mathrm{NapOH}}$ and $\log_{10} K_{\mathrm{NapOD}}$ were calculated from Eqs. 2–15. These are listed in Tables 5 and 6, and plotted as a function of temperature in Fig. 4, along with the light-water values [7, 21] and the heavy-water value of Wehry and Rogers [11]. The statistical uncertainty for each experimental value of the equilibrium constant in

Table 4 The fitting parameters 'k' and 'l' obtained from regression of Eq. 12,[a] NapOD(aq) $\leftrightarrows$ $NapO^{-}(aq) + D^{+}(aq)$

t/°C	Concentration ratio, D	Buffer ratio	Indicator ratio	Parameter, k	Parameter, l
225	0.9363	0.724	8.98	0.9689 ± 0.05	0.1078 ± 0.01
		0.395	5.46	0.9345 ± 0.04	0.1712 ± 0.01
		0.215	3.03	0.7827 ± 0.04	0.2580 ± 0.01
		0.134	1.95	0.6446 ± 0.04	0.3302 ± 0.01
		0.097	1.45	0.6610 ± 0.04	0.4571 ± 0.01
250	1.0311	0.756	7.88	0.9492 ± 0.04	0.1205 ± 0.01
		0.411	4.22	0.9634 ± 0.08	0.2285 ± 0.03
		0.226	2.44	0.8664 ± 0.11	0.3546 ± 0.04
		0.161	1.80	0.6664 ± 0.13	0.3702 ± 0.04
		0.126	1.45	0.6797 ± 0.15	0.4678 ± 0.05
275	1.0311	0.776	7.37	0.8992 ± 0.02	0.1220 ± 0.01
		0.434	3.82	0.8789 ± 0.05	0.2301 ± 0.01
		0.252	2.24	0.7538 ± 0.05	0.3365 ± 0.02
		0.187	1.67	0.5800 ± 0.05	0.3471 ± 0.02
		0.153	1.37	0.5800 ± 0.06	0.4240 ± 0.02
300	0.9363	0.786	6.45	0.9071 ± 0.01	0.1405 ± 0.01
		0.461	3.78	0.8824 ± 0.01	0.2337 ± 0.01
		0.288	2.45	0.7638 ± 0.02	0.3115 ± 0.01
		0.211	1.87	0.6798 ± 0.02	0.3631 ± 0.01
		0.177	1.60	0.7281 ± 0.03	0.4560 ± 0.01

[a] Error limits are standard deviations of the parameters obtained from the regression

Tables 5 and 6 were calculated from the standard deviations of k and l in Tables 1 and 3. The uncertainties in the average value of $\log_{10} K$ at each temperature were taken to be the 95% confidence interval of the mean of the values from individual measurements, which corresponds to an average uncertainty of ±0.04. This is a higher level of precision than those reported by that Xiang and Johnston [7], who considered the uncertainty in the hydrothermal colorimetric indicator technique to be in the range ±0.2 units in $\log_{10} K$. Experimental values for the D_2O isotope effects, $\Delta \log_{10} K = [\log_{10} K_{D2O} - \log_{10} K_{H2O}]$ calculated from our results are plotted in Fig. 5, along with the combined 95% confidence limit at each temperature.

Our light-water ionization constants of β-naphthol are compared with those reported by Xiang and Johnston [7] in Fig. 4. Although their values were measured at higher pressures, the difference between the two sets of results lies just outside the combined experimental uncertainties ($\pm 0.2 \log_{10}$ units). All other studies in the literature were limited to tempera-

Table 5 Experimental values for equilibrium constants for β-naphthol ionization in H_2O, NapOH(aq) $\leftrightarrows$ $NapO^-(aq) + H^+aq$

t/°C	$-\log_{10} K_{H_2PO_4^-}$ [a]	I/ mol·kg^{-1}	Buffer ratio	Indicator ratio	$-\log_{10} Q$	$-\log_{10} K$	avg. ($-\log_{10} K$)
225	8.119	0.0883	0.846	14.04[b]	(8.60)	(8.97 ± 0.12)	8.90 ± 0.01
		0.1034	0.404	6.12	8.52	8.91 ± 0.04	
		0.1094	0.286	4.41	8.51	8.91 ± 0.04	
		0.1171	0.174	2.66	8.49	8.90 ± 0.02	
		0.1195	0.152	2.32	8.49	8.90 ± 0.02	
250	8.360	0.0868	0.863	11.53[b]	(8.67)	(9.08 ± 0.05)	8.98 ± 0.01
		0.1027	0.415	4.94	8.57	9.00 ± 0.03	
		0.1075	0.305	3.53	8.55	8.99 ± 0.02	
		0.1127	0.224	2.58	8.53	8.98 ± 0.02	
		0.1166	0.163	1.87	8.52	8.97 ± 0.02	
275	8.634	0.0877	0.897	8.38[b]	(8.69)	(9.15 ± 0.07)	9.09 ± 0.01
		0.1023	0.455	4.11	8.63	9.11 ± 0.03	
		0.1081	0.340	3.04	8.60	9.10 ± 0.02	
		0.1153	0.232	2.08	8.59	9.09 ± 0.02	
		0.1177	0.210	1.88	8.58	9.08 ± 0.01	
300	8.945	0.0860	0.930	7.32[b]	(8.80)	(9.32 ± 0.05)	9.26 ± 0.02
		0.1014	0.480	3.64	8.73	9.28 ± 0.03	
		0.1059	0.372	2.77	8.71	9.26 ± 0.03	
		0.1115	0.295	2.15	8.68	9.24 ± 0.02	
		0.1146	0.230	1.70	8.68	9.25 ± 0.03	

[a] Calculated from the equation and data of Mesmer and Baes [18]

[b] Not included in the average due to the very high indicator ratio. Units: aquamolal, m_{aq} = mol-solute/(55.509 mol-solvent) = mol · (kg-H_2O)$^{-1}$

tures below 50 °C. The only reported study in heavy water is that of Wehry and Rogers [11], measured at 25 °C.

We chose to use a simplified form of the “density” model adopted by Xiang and Johnston [7], to model our experimental data:

$$\log_{10} K = a + (e + f/T)\log_{10}\rho \tag{16a}$$

Here, ρ is the density of light or heavy water in g·cm^{-3} and a, e and f are adjustable parameters obtained from fitting Eq. 16 to the experimental results for light water, $\log_{10} K_{\mathrm{NapOH}}$, from this work. The fitted expression is plotted in Fig. 4. The parameters and their standard errors are listed in Table 7.

Table 6 Experimental values for equilibrium constants for β-naphthol ionization in D_2O, NapOD(aq) $\leftrightarrows$ $NapO^-(aq) + D^+(aq)$

t/°C	$-\log_{10} K_{D_2PO_4^-}$[a]	I_{aq}[b]	Buffer ratio	Indicator ratio	$-\log_{10} Q$	$-\log_{10} K$	avg. ($-\log_{10} K$)
225	8.554	0.0866	0.724	8.98	8.88	9.27 ± 0.06	9.29 ± 0.02
		0.0966	0.395	5.46	8.90	9.30 ± 0.03	
		0.1064	0.215	3.03	8.88	9.29 ± 0.03	
		0.1125	0.134	1.95	8.88	9.30 ± 0.03	
		0.1124	0.097	1.45	8.90	9.31 ± 0.03	
250	8.797	0.0870	0.756	7.88	8.97	9.39 ± 0.06	9.38 ± 0.01
		0.0963	0.411	4.22	8.93	9.37 ± 0.07	
		0.1047	0.226	2.44	8.93	9.38 ± 0.07	
		0.1128	0.161	1.80	8.92	9.38 ± 0.10	
		0.1133	0.126	1.45	8.94	9.40 ± 0.11	
275	9.067	0.0868	0.776	7.37	9.10	9.57 ± 0.03	9.52 ± 0.03
		0.0959	0.434	3.82	9.03	9.52 ± 0.04	
		0.1041	0.252	2.24	9.01	9.51 ± 0.04	
		0.1121	0.187	1.67	8.99	9.50 ± 0.04	
		0.1124	0.153	1.37	8.99	9.50 ± 0.05	
300	9.367	0.0858	0.786	6.45	9.21	9.74 ± 0.01	9.73 ± 0.01
		0.0954	0.461	3.78	9.17	9.72 ± 0.01	
		0.1046	0.288	2.45	9.15	9.72 ± 0.01	
		0.1102	0.211	1.87	9.15	9.73 ± 0.02	
		0.1100	0.177	1.60	9.16	9.74 ± 0.02	

[a] Calculated from the equation and data by Mesmer and Herting [6], corrected to the aquamolality scale

[b] Units: aquamolal, $m_{aq} = \text{mol} \cdot (1.1117\ \text{kg-}D_2O)^{-1}$

The corresponding equation for heavy water yields an expression for the deuterium isotope effect, $\Delta \log_{10} K = (\log_{10} K_{\mathrm{D2O}} - \log_{10} K_{\mathrm{H2O}})$, as given below,

$$\begin{aligned}\Delta \log_{10} K = {} & \Delta a + (\Delta e + \Delta f/T)\{\log_{10} \rho_{\mathrm{D2O}}\} \\ & + (e + f/T)\{\log_{10}(M_{\mathrm{D2O}}/M_{\mathrm{H2O}})\},\end{aligned} \tag{16b}$$

where T is temperature in kelvin; ρ_{D_2O} is the density of heavy water in g·cm^{-3}; M is the molar mass of H_2O or D_2O; and Δa, Δe, and Δf are the differences in adjustable fitting parameters. This model is based on the premise that the isotope effect is primarily a function of temperature and solvent molar volume.

Our procedure for developing the equation of state was to fit Eq. 16a to our light-water data, then to fit Eq. 16b to the $\Delta \log_{10} K$ data, from which the parameters for $\log_{10} K_{\mathrm{NapOH}}$ were derived. The fitted parameters and their standard errors are tabulated in Table 7. The

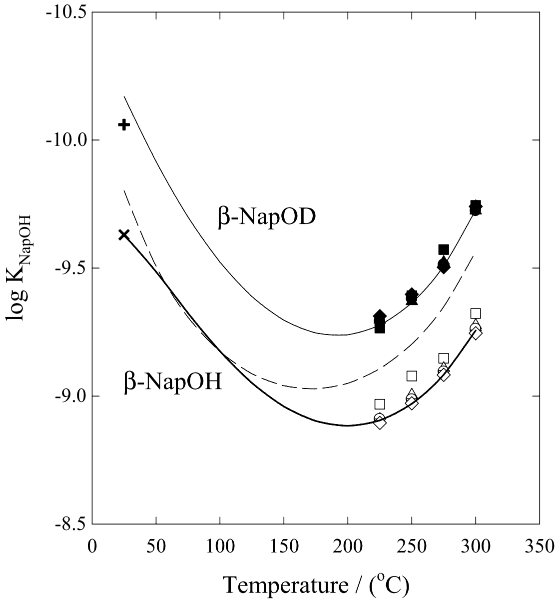


Fig. 4 Ionization constants of β-naphthol in light and heavy water plotted as a function of temperature. For H_2O: this work at different buffer ratios; □, Δ, ∘, ◊; Xiang and Johnston [7], —; Albert and Sargeant [21], H; Eq. 16a, —. For D_2O: this work at different buffer ratios, ■, ▲, ●, ♦; Wehry and Rogers [11], +; Eqs. 16a, 16b, —

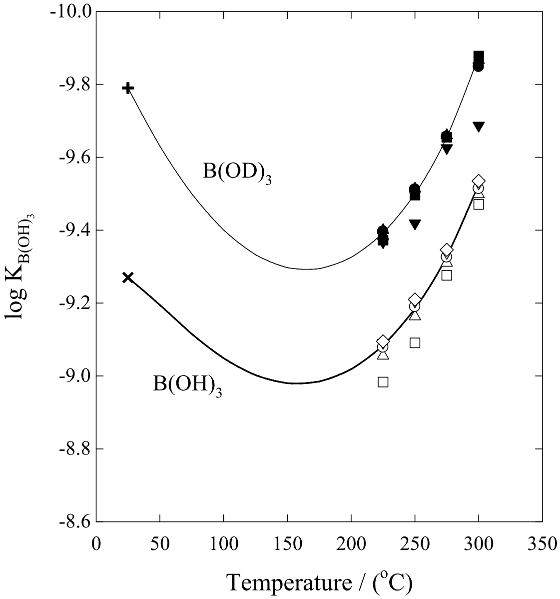


Fig. 5 Ionization constants of boric acid in light and heavy water plotted as a function of temperature. For H_2O: this work at different buffer ratios, □, Δ, ∘, ◊; Edwards et al. [22]; **x**, Eq. 16a, —. For D_2O: this work at different buffer ratios, ■, ▲, ●, ♦; Edwards et al. [22]; +, Eqs. 16a, 16b, —

fitted values for $\Delta \log_{10} K$ are tabulated in Table 8, along with the experimental values from which they were derived. They are plotted in Fig. 4.

Table 7 Fitted parameters obtained for the ionization constants of β-naphthol and boric acid as a function of temperature and solvent density, Eqs. 16a and 16b[a]

Parameter	β-Naphthol	Boric acid
a	-9.6893 ± 0.0113	-9.3019 ± 0.0070
e	43.51 ± 1.06	29.897 ± 0.653
$f/(\mathrm{K}^{-1})$	-26624 ± 601	-16269 ± 372
a	0.4472 ± 0.0111	0.0177 ± 0.0055
e	-12.569 ± 0.646	-6.313 ± 0.324
$f/(\mathrm{K}^{-1})$	11469 ± 283	6004 ± 142

[a] Error limits are standard errors

Table 8 Comparison of experimental $\log_{10} K$ values for β-naphthol, in the aquamolal standard state, $\mathrm{NapOH(aq)} \leftrightarrows \mathrm{NapO^-(aq)} + \mathrm{H(aq)}$

t/°C	p/MPa	$-\log_{10} K$ (expt.)	$-\log_{10} K$ (fit at p_{sat})[a]	$-\log_{10} K$ (lit.)
$-\log_{10} K$ (in H_2O)				
25	0.10	–	9.63	9.63[b]
225	4.00	8.90	8.91	
250	5.00	8.98	8.97	
275	7.00	9.09	9.08	
300	10.00	9.25	9.26	
$-\log_{10} K$ (in D_2O)				
25	0.10	–	10.17	10.06[c]
225	4.00	9.29	9.28	
250	5.00	9.38	9.36	
275	7.00	9.52	9.51	
300	10.00	9.73	9.73	
$-\Delta \log_{10} K$				
25	0.10	–	0.54	0.54[c]
225	4.00	0.37	0.37	
250	5.00	0.38	0.39	
275	7.00	0.42	0.42	
300	10.00	0.46	0.47	

[a] Calculated values from Eq. 16

[b] Literature data from Albert and Serjeant [21]

[c] Literature data from Wehry and Rogers [11]

5 Ionization Constants for Boric Acid

Boric acid ionizes according to the reaction:

$$\mathrm{B(OH)_3(aq) + H_2O(l) \leftrightarrows B(OH)_4^-(aq) + H^+(aq)} \tag{17}$$

Table 9 The fitting parameters 'k' and 'l' obtained from regression of Eq. 12,[a] $B(OH)_3(aq) + H_2O(l) \leftrightarrows B(OH)_4^-(aq) + H^+(aq)$

t/°C	Concentration ratio, D	Buffer ratio	Indicator ratio	Parameter, k	Parameter, l
225	1.0388	0.622	1.03	0.4563 ± 0.01	0.4412 ± 0.01
		0.504	1.29	0.4990 ± 0.01	0.3880 ± 0.01
		0.362	1.84	0.6086 ± 0.01	0.3301 ± 0.01
		0.246	2.86	0.6806 ± 0.01	0.2379 ± 0.01
		0.108	(7.70)[b]	(0.8164 ± 0.01)	(0.1060 ± 0.01)
250	1.0432	0.587	1.02	0.4274 ± 0.01	0.4210 ± 0.01
		0.468	1.29	0.5076 ± 0.01	0.3942 ± 0.01
		0.354	1.76	0.5993 ± 0.01	0.3396 ± 0.01
		0.229	2.89	0.6513 ± 0.01	0.2253 ± 0.01
		0.102	(7.72)[b]	(0.8104 ± 0.01)	(0.1050 ± 0.01)
275	1.0388	0.552	1.01	0.4570 ± 0.01	0.4517 ± 0.01
		0.457	1.24	0.4916 ± 0.01	0.3950 ± 0.01
		0.336	1.75	0.5977 ± 0.01	0.3425 ± 0.01
		0.232	2.62	0.6683 ± 0.01	0.2555 ± 0.01
		0.103	(6.35)[b]	(0.8035 ± 0.01)	(0.1265 ± 0.01)
300	1.0432	0.517	7.32	0.4497 ± 0.01	0.4410 ± 0.01
		0.421	3.64	0.5135 ± 0.01	0.4043 ± 0.01
		0.325	2.77	0.6042 ± 0.01	0.3541 ± 0.01
		0.215	2.15	0.6552 ± 0.01	0.2449 ± 0.01
		0.096	(1.70)[b]	(0.8093 ± 0.01)	(0.1275 ± 0.01)

[a] Error limits are standard deviations of the parameters obtained from the regression

[b] Points not used in the regression

In light water, the ionization constants of boric acid, shown in Fig. 2, are very similar to those of β-naphthol. This suggests that β-naphthol is a suitable colorimetric pH indicator for determining the ionization constant of boric acid in heavy water, using the experimental methods described in Refs. [8, 9]. The measurements involved preparing $B(OD)_3/B(OD)_4^-$ buffers, acid and base solutions with known relative concentrations of β-naphthol, then measuring their UV-visible spectra, exactly as described above for the $D_2PO_4^-/DPO_4^{2-}$ buffers. The difference is that the ionization constant of boric acid in heavy water is unknown. The accurate expressions for $\log_{10} K$ and $\Delta \log_{10} K$ for β-naphthol reported in Sect. 4 (Eqs. 16a and 16b), allowed us to determine the equilibrium aquamolalities of $H^+(aq)$ and $D^+(aq)$ from which the ionization constants of boric acid could be determined. The experimental conditions, solution compositions, and the fitted values of parameters k and l, are listed in Tables 9 and 10, along with the corresponding values of m_{aq,H^+} and m_{aq,D^+} derived from them.

Table 10 The fitting parameters 'k' and 'l' obtained from regression of Eq. 12,[a] $B(OD)_3(aq) + D_2O(l) \leftrightarrows B(OD)_4^-(aq) + D^+(aq)$

t/°C	Concentration ratio, D	Buffer ratio	Indicator ratio	Parameter, k	Parameter, l
225	0.9165	2.109	0.40	0.3089 ± 0.01	0.7715 ± 0.01
		1.676	0.48	0.3545 ± 0.01	0.7315 ± 0.01
		1.190	0.66	0.4411 ± 0.01	0.6645 ± 0.01
		0.646	1.21	0.5810 ± 0.01	0.4791 ± 0.01
		0.220	3.80	0.7890 ± 0.01	0.2078 ± 0.01
250	0.9125	4.040	(0.23)[b]	(0.1772 ± 0.01)	(0.7743 ± 0.01)
		3.350	(0.26)[b]	(0.2036 ± 0.01)	(0.7749 ± 0.01)
		0.910	0.82	0.4831 ± 0.01	0.5889 ± 0.01
		0.524	1.42	0.5766 ± 0.01	0.4064 ± 0.01
		0.208	3.73	0.8264 ± 0.01	0.2216 ± 0.01
275	0.9165	1.761	0.45	0.3349 ± 0.01	0.7465 ± 0.01
		1.450	0.53	0.3763 ± 0.01	0.7103 ± 0.01
		1.068	0.69	0.4510 ± 0.01	0.6551 ± 0.01
		0.608	1.20	0.5778 ± 0.01	0.4816 ± 0.01
		0.213	3.47	0.7826 ± 0.01	0.2258 ± 0.01
300	0.9125	3.171	(0.35)[b]	(0.2612 ± 0.01)	(0.7455 ± 0.01)
		2.654	(0.38)[b]	(0.2849 ± 0.01)	(0.7421 ± 0.01)
		0.823	0.93	0.5332 ± 0.01	0.5721 ± 0.01
		0.490	1.50	0.6071 ± 0.01	0.4045 ± 0.01
		0.199	3.61	0.8341 ± 0.01	0.2313 ± 0.01

[a] Error limits are standard deviations of the parameters obtained from the regression

[b] Points not used in the regression

Values of $\log_{10} K$ for boric acid ionization in H_2O and D_2O, and the resulting values of $\Delta \log_{10} K$ are tabulated in Tables 11–13. The values of $\log_{10} K$ are plotted as a function of temperature in Fig. 5, along with the low-temperature results of Edwards et al. [22] and Gold and Lowe [23], respectively. The light-water results agree with literature values from high-temperature potentiometric titrations [19, 20], to within the combined experimental uncertainties ($\pm 0.1 \log_{10}$ units). In addition to the uncertainties associated with the experimental precision, listed in Tables 11 and 12, the results for boric acid in both H_2O and D_2O also include systematic errors due to the uncertainty in the values of the acid dissociation constants for β-naphthol. From the standard errors in Tables 5 and 6, we estimate these additional uncertainties in $\log_{10} K$ for reaction 17 to be no more than $\pm 0.05 \log_{10}$ units.

Table 11 Experimental values for equilibrium constants for boric acid hydrolysis in H_2O, $B(OH)_3(aq) + H_2O(l) \leftrightarrows B(OH)_4^-(aq) + H^+(aq)$

$t/°C$	$-\log_{10} K_{\mathrm{NapOH}}$[a]	$I/\mathrm{mol{\cdot}kg^{-1}}$	Buffer ratio	Indicator ratio	$-\log_{10} Q$	$-\log_{10} K$	avg. $(-\log_{10} K)$[c]
225	8.90	0.0420	0.622	1.03	9.09	9.09 ± 0.02	9.08 ± 0.02
		0.0387	0.504	1.29	9.09	9.09 ± 0.02	
		0.0327	0.362	1.84	9.08	9.08 ± 0.02	
		0.0264	0.246	2.86	9.06	9.06 ± 0.03	
		0.0148	0.108	(7.70)[b]	(8.98)	(8.98 ± 0.05)	
250	8.98	0.0422	0.587	1.02	9.21	9.21 ± 0.01	9.19 ± 0.02
		0.0381	0.468	1.29	9.20	9.20 ± 0.01	
		0.0329	0.354	1.76	9.19	9.19 ± 0.02	
		0.0259	0.229	2.89	9.16	9.16 ± 0.03	
		0.0143	0.102	(7.72)[b]	(9.09)	(9.09 ± 0.06)	
275	9.09	0.0420	0.552	1.01	9.35	9.35 ± 0.01	9.33 ± 0.02
		0.0387	0.457	1.24	9.34	9.34 ± 0.01	
		0.0327	0.336	1.75	9.33	9.33 ± 0.01	
		0.0264	0.232	2.62	9.31	9.31 ± 0.01	
		0.0148	0.103	(6.35)[b]	(9.28)	(9.28 ± 0.02)	
300	9.25	0.0422	0.517	1.02	9.54	9.54 ± 0.01	9.52 ± 0.02
		0.0381	0.421	1.27	8.73	9.53 ± 0.01	
		0.0329	0.325	1.71	9.51	9.51 ± 0.01	
		0.0259	0.215	2.68	9.50	9.50 ± 0.01	
		0.0143	0.096	(6.35)[b]	(9.47)	(9.47 ± 0.02)	

[a] Calculated from Eq. 16 of this work

[b] Not included in the average due to the higher indicator ratio

[c] Uncertainty limits are standard errors (precision). An uncertainty of ±0.05 due to the systematic errors in the values of $-\log_{10} K_{\mathrm{NapOH}}$ should be added when estimating the accuracy of these data. Units: aquamolal, $m_{\mathrm{aq}} = \text{mol-solute}/(55.509\text{mol-solvent}) = \mathrm{mol{\cdot}(kg\text{-}H_2O)^{-1}}$

6 Discussion

Values of the deuterium isotope effect on the ionization constants of β-naphthol and boric acid, $\Delta \log_{10} K$, are plotted as a function of temperature in Fig. 6, along with the values for $D_2PO_4^-(aq)$ from Mesmer and Herting [6], corrected to the aquamolal scale. At 25 °C, the value for all three species, $\Delta \log_{10} K \approx -0.6$, is consistent with most other simple acids which typically lie in the range $-0.7 < \Delta \log_{10} K < -0.2$. The magnitude of the deuterium isotope effect for $H_2PO_4^-(aq)$ falls from $\Delta \log_{10} K = -0.62$ to $\Delta \log_{10} K = -0.47$ as the temperature rises above 125 °C, then remains almost constant. Although the temperature range of our measurements is more limited, the new results

Table 12 Experimental values for equilibrium constants for boric acid hydrolysis in D_2O,[a] $B(OD)_3(aq) + D_2O(l) \leftrightarrows B(OD)_4^-(aq) + D^+(aq)$

t/°C	$-\log_{10} K_{NapOD}$[a]	I_{aq}	Buffer ratio	Indicator ratio	$-\log_{10} Q$	$-\log_{10} K$	avg. $(-\log_{10} K)$[c]
225	9.29	0.0680	2.109	0.40	9.37	9.37 ± 0.01	9.38 ± 0.01
		0.0644	1.676	0.48	9.38	9.38 ± 0.01	
		0.0583	1.190	0.66	9.40	9.40 ± 0.01	
		0.0467	0.646	1.21	9.40	9.40 ± 0.01	
		0.0255	0.220	3.80	9.37	9.37 ± 0.01	
250	9.38	0.0802	4.040	(0.23)[b]	(9.42)	(9.42±0.04)	9.51 ± 0.01
		0.0774	3.350	(0.26)[b]	(9.44)	(9.44±0.03)	
		0.0541	0.910	0.82	9.51	9.51 ± 0.01	
		0.0434	0.524	1.42	9.51	9.51 ± 0.01	
		0.0244	0.208	3.73	9.50	9.50 ± 0.02	
275	9.52	0.0680	1.761	0.45	9.63	9.63 ± 0.02	9.65 ± 0.01
		0.0644	1.450	0.53	9.64	9.64 ± 0.02	
		0.0583	1.068	0.69	9.66	9.66 ± 0.01	
		0.0467	0.608	1.20	9.66	9.66 ± 0.02	
		0.0255	0.213	3.47	9.65	9.65 ± 0.02	
300	9.73	0.0802	3.171	(0.35)[b]	(9.69)	(9.69±0.08)	9.86 ± 0.01
		0.0774	2.654	(0.38)[b]	(9.72)	(9.72±0.07)	
		0.0541	0.823	0.93	9.85	9.85 ± 0.03	
		0.0434	0.490	1.50	9.87	9.87 ± 0.03	
		0.0244	0.199	3.61	9.88	9.88 ± 0.03	

[a] Calculated from Eq. 16 of this work

[b] Not included in the average due to the high buffer ratio

[c] Uncertainty limits are standard errors (precision). An uncertainty of ±0.05 due to the systematic errors in the values of $-\log_{10} K_{NapOD}$ should be added when estimating the accuracy of these data. Units: aquamolal, $m_{aq} = \text{mol} \cdot (1.1117\ \text{kg-D}_2\text{O})^{-1}$

for β-naphthol and boric acid appear to show a similar trend. Results for acetic acid from our laboratory, which will be reported in a subsequent publication, show similar behavior. Recent work by Trevani et al. [15] has successfully modeled the deuterium isotope effects on standard partial molar volumes under hydrothermal conditions with both a Born model and a corresponding-states treatment. These new results for $\Delta \log_{10} K$ are the beginning of a program to develop a more comprehensive understanding of deuterium isotope effects on solvation and ionization at extremes of temperature and pressure.

Table 13 Comparison with experimental $\log_{10} K$ values for boric acid in the aquamolal standard state, $B(OH)_3(aq) + H_2O(l) \leftrightarrows B(OH)_4^-(aq) + H^+(aq)$

t/°C	p/MPa	$-\log_{10} K$ (expt.)	$-\log_{10} K$ (fit at p_{sat})[a]	$-\log_{10} K$ (lit.)
$-\log_{10} K$ (in H_2O)				
25	0.10	–	9.27	9.27 [b]
225	4.00	9.08	9.08	
250	5.00	9.19	9.18	
275	7.00	9.33	9.33	
300	10.00	9.52	9.52	
$-\log_{10} K$ (in D_2O)				
25	0.10	–	9.79	9.79 [b]
225	4.00	9.38	9.39	
250	5.00	9.51	9.50	
275	7.00	9.65	9.66	
300	10.00	9.86	9.88	
$-\Delta \log_{10} K$				
25	0.10	–	0.52	0.52 [b]
225	4.00	0.30	0.31	
250	5.00	0.32	0.31	
275	7.00	0.32	0.33	
300	10.00	0.35	0.35	

[a] Calculated values from Eq. 16

[b] Literature data from Edwards et al. [22]

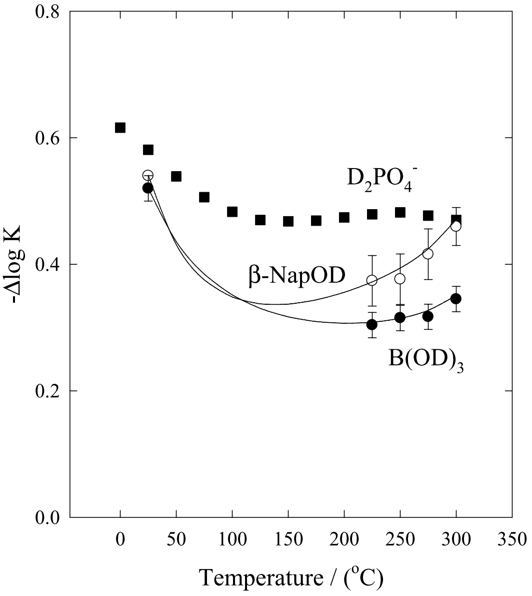


Fig. 6 The temperature dependence of pK for β-naphthol, boric acid and $H_2PO_4^-$ (aq). Symbols represent experimental data points from this work, and Mesmer and Herting [6] corrected to the aquamolality scale. Low-temperature results for β-naphthol and boric acid are from Wehry and Rogers [11] and Edwards et al. [22], respectively

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