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Spectroscopic pH Measurement for High Temperatures, Pressures and Ionic Strength

B. Raghuraman, G. Gustavson, O. C. Mullins, and P. Rabbito
Schlumberger-Doll Research, Ridgefield, CT 06877

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The optical spectroscopic technique using pH sensitive dyes has been extended to measure pH in high-temperature, pressure, and ionic strength environments. Lack of standard calibrating buffers for these conditions necessitated a two-step process for development of this technique. The first step involved chemical equilibrium modeling to predict pH values of simple buffer salt systems at high temperatures, pressures and ionic strengths. The second step involved using these modeled buffer solutions as calibration solutions for the dye chemistry and equilibrium dissociation constant. Optical spectra of dye in these buffer solutions were used to calibrate the dye equilibrium dissociation constant. Results are presented for 293°K to 373°K temperature range, 0.101325–65.5 MPa pressure range and 0–3 mol/kg water ionic strength range. Once the dye equilibrium dissociation constant has been characterized, pH of unknown solutions can be obtained from their dye spectra. This method has been successfully employed for high-temperature and high-pressure measurements of oilfield waters. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3257–3265, 2006

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Accurate measurement of pH is important in several diverse fields, such as process control, reaction equilibrium and kinetics, environmental research to monitor seawater chemistry and natural water quality, biomedical research and in oilfields. The International Union of Pure and Applied Chemistry (IUPAC) has issued guidelines for the standard potentiometric technique for pH measurements. These methods and calibrating standards are, however, recommended only for 278–323°K, 0.101325 MPa and ionic strengths below 0.1 mol/kg water.[1] The reasons for these measurement constraints are the uncertainty in liquid junction potential and reference electrode stability at high temperatures, pressures and ionic strength and the lack of calibrating standards. Many chemical reactions and processes require pH monitoring and control at extreme conditions of pressure, temperature and salinity. In oilfield applications, accurate pH measurements require that they be made at downhole wellbore conditions with fluids in their native state at high temperatures (typically 323–473°K), high pressures (typically 30 to 100 MPa), and high ionic strengths (typically 0.5–5 mol/kg water). pH is a key parameter whose accurate measurement at downhole wellbore conditions is critical in understanding formation fluid water chemistry to predict corrosion and scale potential in well tubing and surface facilities.

Spectroscopic measurement of pH with very high accuracy using pH-sensitive dyes is a well-established laboratory technique for ambient conditions since the early 1900's.[2,3] More recently, this technique has been shown to improve precision for seawater pH measurements.[4] Using equimolal tris buffers for total pH scales, dye equilibrium dissociation constant was characterized at 0.101325 MPa pressure as a function of temperature (293°K to 303°K) and salinity over the narrow salinity range characteristic of seawater (30 to 37 salinity range corresponding to ionic strengths of ~0.53 to 0.66 mol/kg water). Yao and Byrne[5] have also applied this technique for freshwater pH measurements, where potentiometric methods can prove to be problematic. Using phosphate buffers, the dye equilibrium

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Correspondence concerning this article should be addressed to B. Raghuraman.

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dissociation constant was characterized at 0.101325 MPa pressure as a function of temperature (283°K to 303°K) and ionic strength (0 to 0.016 mol/kg water). The Davies equation, which is valid at these low ionic strengths, was used to calculate the activity coefficients. Martz et al.[6] describe an autonomous spectroscopic pH sensor for *in situ* measurements of natural waters that have low ionic strengths ($\sim$0.01 mol/kg water) and temperature range of 277–293°K. These references cite the advantages of the spectroscopic technique with respect to low-drift, reproducibility, and rapidness of the measurement as compared to the standard glass electrodes. Furthermore, since the measurement depends only on the molecular properties of the indicator dyes, once the dye equilibrium dissociation constants have been characterized, it eliminates the need for calibration prior to every measurement.

The works cited earlier allow implementation of the spectroscopic technique at close to ambient conditions and narrow ionic strength intervals corresponding to either seawater or fresh water conditions. They overcome the problems associated with glass electrode measurements that arise from poor reproducibility, and drifts of liquid junction potentials encountered at both very low and very high ionic strengths. Measurements of pH of standard buffers at high temperature and pressure using hydrogen electrode and glass electrode have been reported,[7,8] but again the liquid junction instability results in uncertainties in the measurement. Furthermore, pressure balancing needs and liquid junctions make it practically inconvenient to use this set up for routine measurements in high-pressure, high-temperature systems. Boreng et al.[9] describe a solid-state electrode for high-temperature and high-pressure pH measurement. However, while the liquid junction uncertainty is eliminated, the pH is measured relative to sodium activity that must be independently determined to get the absolute pH.

In this article we show how the spectroscopic pH measurement technique can be applied over much broader ranges of temperature, pressure and ionic strengths. Dye equilibrium dissociation constants have been calibrated for temperatures to 373°K, pressures to 65.5 MPa and ionic strengths in the 0 to 3 mol/kg water range. These procedures can be used to extend the calibration to even higher temperatures, pressures and ionic strengths. The lack of a standard pH measurement technique at these conditions means that there are no pH standards to calibrate any technique being developed for these conditions. Standard pH calibration buffers are available only at 0.101325 MPa pressure in the 273–323°K temperature range and for the 0.05–0.1 mol/kg water ionic strength range. These buffer solutions are simple salt-water systems whose reactions have been well characterized over a range of conditions. We, therefore, use chemical equilibrium modeling to predict their pH values for the broader temperature, pressure and ionic strength range of interest. We then show how we use these pH values to calibrate the dye technique for these extreme conditions. Once these dyes are characterized, they can be used to measure pH of unknown solutions without any calibration requirements prior to each measurement. These advantages make this a potentially attractive pH measurement technique at conditions where standard potentiometric techniques can be problematic.

Experimental

All spectra were measured with a Cary 500 UV-Visible-NIR spectrometer. Custom interface optics relayed the optical beam from the spectrometer to a high-pressure, high-temperature optical cell. High-pressure stainless steel ports in the optical cell were used to fill and pressurize the cell with the solution whose spectra was to be measured. For temperature control, the optical cell was placed in an oven and temperatures were recorded using a thermocouple inserted into a thermal well in the optical cell. Once the optical cell reached the set temperature, an additional hour was given to ensure sample temperature had steadied at desired value. A high-pressure syringe pump (ISCO 100DM) was used for pressure control to 68.9 MPa. All spectra were baseline corrected prior to analysis.

Spectra were measured for pure de-ionized water, standard buffer solutions and solutions of phenol red dye (concentrations in the range of 1.0×10^{-5} to 8.2×10^{-5} mol/kg water) in buffers. Temperature was varied in the range 293–373°K with a constant pressure of 0.965 MPa maintained to stay well above the vapor pressure of water in this temperature range to ensure that no vaporization occurred. Pressure effects were studied in the range of 0.1 to 65.5 MPa.

NIST certified standard buffer solutions or buffer powders were obtained from Fisher Scientific. Phenol red sodium salt (Fisher Scientific) was purchased as solid powder and solutions of desired strengths were prepared.

Theory

Measurement at ambient conditions. pH indicator dyes are weak acids, and their dissociation equilibrium can be represented as shown

$$A \Leftrightarrow B + H^+ \tag{1}$$

The fraction of the dye existing in the acid (A) and base (B) form depends on the pH of the solution. The individual spectra of these two forms are different and, hence, the measured dye spectra (which is a mole-fraction weighted combination of the acid and base spectra) changes as the fraction of each form changes with pH. The pH is calculated using the following equation

$$pH = pK_a + \log\frac{\gamma_B}{\gamma_A} + \log\frac{[B]}{[A]} \tag{2}$$

where $pK_a = -\log K_a$; K_a is the thermodynamic equilibrium constant for the dye dissociation (Eq. 1), and is a function of temperature and pressure; $[A]$, $[B]$ are the concentrations of the acid, base form of the dye in the dye-sample mixture, respectively; and γ_A, γ_B are activity coefficients of the acid and base forms of the dye, and a function of temperature, pressure and ionic strength of solution.

This equation is more commonly written as

$$pH = pK_a' + \log\frac{[B]}{[A]} \tag{3}$$

where

$$pK'_a = -\log\left(K_a \frac{\gamma_A}{\gamma_B}\right) \quad (4)$$

Because pK'_a includes the activity coefficients, it is no longer only a function of pressure and temperature, but also a function of ionic strength.

For any given pH, the dye spectrum is a mole fraction weighted linear combination of the acid-only and base-only spectra. Using a two-wavelength measurement, one can determine the concentration ratio of base-to-acid form as below

$$C_T = [A] + [B] \quad (5)$$

$$OD^{\lambda 1} = \varepsilon_A^{\lambda 1} l[A] + \varepsilon_B^{\lambda 1} l[B] \quad (6)$$

$$OD^{\lambda 2} = \varepsilon_A^{\lambda 2} l[A] + \varepsilon_B^{\lambda 2} l[B] \quad (7)$$

$$ODR_{\lambda 1}^{\lambda 2} = \frac{OD^{\lambda 2}}{OD^{\lambda 1}} \quad (8)$$

$$\frac{[B]}{[A]} = \frac{ODR_{\lambda 1}^{\lambda 2}}{\varepsilon_B^{\lambda 2}/\varepsilon_A^{\lambda 1}} \frac{\left(1 - \frac{\varepsilon_A^{\lambda 2}}{\varepsilon_A^{\lambda 1}} \frac{1}{ODR_{\lambda 1}^{\lambda 2}}\right)}{\left(1 - \frac{\varepsilon_B^{\lambda 1}}{\varepsilon_B^{\lambda 2}} ODR_{\lambda 1}^{\lambda 2}\right)} \quad (9)$$

where OD^{λ_i} is the optical density measured at wavelength λ_i; l is optical path length; C_T is total dye concentration in solution-dye mixture; $\varepsilon_A^{\lambda i}$, $\varepsilon_B^{\lambda i}$ are molal absorption coefficients at wavelength λ_i for A, B, respectively; and $ODR_{\lambda 1}^{\lambda 2}$ is optical density ratio as defined in Eq. 8.

The base-to-acid concentration ratio can also be obtained by regression using spectral OD values at more than two wavelengths of the dye spectra when available.

Equations 3 and 9 may now be combined to give

$$pH = pK'_a + \log\left(\frac{ODR_{\lambda 1}^{\lambda 2}}{\varepsilon_B^{\lambda 2}/\varepsilon_A^{\lambda 1}} \frac{\left(1 - \frac{\varepsilon_A^{\lambda 2}}{\varepsilon_A^{\lambda 1}} \frac{1}{ODR_{\lambda 1}^{\lambda 2}}\right)}{\left(1 - \frac{\varepsilon_B^{\lambda 1}}{\varepsilon_B^{\lambda 2}} ODR_{\lambda 1}^{\lambda 2}\right)}\right) \quad (10)$$

The individual spectra of pure acid and base forms of the dye are obtained from dye solutions in extreme pH values (about 3 to 4 units away from the pK'_a) where the dye exists only in the acid or base form. These end point spectra are used to determine the molal absorption coefficients in Eq. 10. Estimation of pK'_a can be done by least-squares fit of Eq. 10 with spectroscopically measured $ODR_{\lambda 1}^{\lambda 2}$ values of the dye in various standard buffer solutions of known pH. Once pK'_a is determined, pH of an unknown solution may be obtained from the spectra of the dye in that solution.

The procedure outlined above needs calibration solutions of known pH to characterize pK'_a. Calibration at higher temperatures, pressures and ionic strengths is difficult since there are no standard pH buffer solutions for these conditions. In the next section, we describe how chemical equilibrium modeling of buffers can be used to obtain pH calibration solutions for these conditions.

Calibration pH references for high-temperature, pressure and ionic strength. pH values measured as per IUPAC procedures have been assigned for primary standard buffers to 323°K.[1] Chemical equilibrium of these buffer salt solutions in the temperature range 273–323°K have been modeled[10,11] using reaction equilibrium constants and Debye-Huckel and Pitzer activity coefficient models.[12,13] Good agreement of calculated pH values with the IUPAC assigned values has been reported.

Buffer solutions are typically mixtures of simple acid-salt systems in water. The reaction equilibria of these acid-salt systems have generally been well characterized at high temperatures.[12] The effect of pressure on these reactions has also been studied.[12,14] The effect of ionic strength on the equilibria is through the ion-activity coefficients which can be obtained from activity coefficient models, such as Debye-Huckel for low-ionic strengths, and the Pitzer equations at higher ionic strengths.[12,13] We have used these equilibrium reaction parameter characterizations reported in literature to model these systems to high-temperature, pressure and ionic strength conditions. This allows calculation of pH of standard buffers at these conditions, a prerequisite for calibration and testing of any new pH measurement technique being developed. For background information on general principles of modeling aqueous reaction equilibria and activity coefficients, the reader is referred to Langmuir[12] and Stumm and Morgan.[15] Phosphate buffers are useful for characterizing the phenol red dye used in this study, and so we will describe the procedure for getting high-temperature and pressure calibration references by using these buffers as an example. For the ionic strength calibration references, the Debye-Huckel or Pitzer activity coefficient model can be used for ionic strengths below 0.1 mol/kg water.[16] At higher ionic strengths, we will use reported pH values that have been calculated with chemical equilibrium models based on the Pitzer activity coefficient model.[17]

Phosphate buffers. Standard phosphate buffers are mixtures of potassium and sodium phosphate salts.[1] The salt is fully dissociated, while the weak phosphoric acid has two dissociation equilibria

$$\mathrm{H_3PO_4} \leftrightarrow \mathrm{H^+} + \mathrm{H_2PO_4^-} \quad Ka_1 \quad (11)$$

$$\mathrm{H_2PO_4^-} \leftrightarrow \mathrm{H^+} + \mathrm{HPO_4^{2-}} \quad Ka_2 \quad (12)$$

$$\mathrm{KH_2PO_4} \rightarrow \mathrm{K^+} + \mathrm{H_2PO_4^-} \quad (13)$$

$$\mathrm{Na_2HPO_4} \rightarrow 2\mathrm{Na^+} + \mathrm{HPO_4^{2-}} \quad (14)$$

$$\mathrm{H_2O} \leftrightarrow \mathrm{H^+} + \mathrm{OH^-} \quad Kw \quad (15)$$

Equilibrium relations for the reactions are given by

$$Ka_1 = \frac{a_{\mathrm{H^+}} a_{\mathrm{H_2PO_4^-}}}{a_{\mathrm{H_3PO_4}}} = \frac{\gamma_{\mathrm{H^+}} \gamma_{\mathrm{H_2PO_4^-}}}{\gamma_{\mathrm{H_3PO_4}}} \frac{[\mathrm{H^+}][\mathrm{H_2PO_4^-}]}{[\mathrm{H_3PO_4}]} = f(T, P) \quad (16)$$

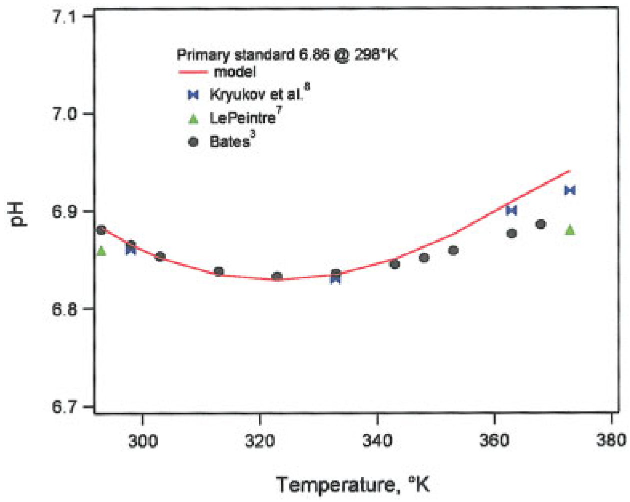

Figure 1. Variation of pH of primary standard phosphate buffer (pH = 6.86 @ 298°K and 0.101325 MPa) with temperature.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$Ka_2 = \frac{a_{H^+}a_{HPO_4^{2-}}}{a_{H_2PO_4^-}} = \frac{\gamma_{H^+}\gamma_{HPO_4^{2-}}}{\gamma_{H_2PO_4^-}}\frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = f(T, P) \quad (17)$$

$$Kw = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}} = \frac{\gamma_{H^+}\gamma_{OH^-}}{\gamma_{H_2O}}\frac{[H^+][OH^-]}{[H_2O]} = f(T, P) \quad (18)$$

Phosphate balance is obtained by equating total initial phosphate added to system in the form of salts and acids to sum of phosphates from all different phosphate containing species at equilibrium

$$[KH_2PO_4]_0 + [Na_2HPO_4]_0 = [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] \quad (19)$$

Total alkali-metal balance is obtained from total initial salt added to system

$$[KH_2PO_4]_0 + 2[Na_2HPO_4]_0 = [K^+] + [Na^+] \quad (20)$$

The electroneutrality equation is given by

$$[H^+] + [K^+] + [Na^+] = 2[HPO_4^{2-}] + [H_2PO_4^-] + [OH^-] \quad (21)$$

where Ka_1, Ka_2 are acid dissociation constants; Kw is water dissociation constant; P is pressure; T is temperature; a is activity; γ is activity coefficient; [] is concentration of a species; and $[]_0$ is initial concentration of a species.

All concentrations are expressed in molality units (mol/kg water). The Deby-Huckel model is used for activity coefficients, and is valid for ionic strength below 0.1 mol/kg water. An iterative numerical procedure is used to solve this set of equations to calculate pH ($= -\log [H^+]$) for any temperature or pressure.

High-temperature calibration references. The variation of the reaction equilibrium constant with temperature can be derived from thermodynamic principles. It has been measured for a number of reactions, and is well described by the following general equation[12]

$$\log K = A + BT + \frac{C}{T} + D \log T + ET^2 + \frac{F}{T^2} + GT^{1/2} \quad (22)$$

where A through G are empirical constants and T is the temperature in Kelvin.

Using the reported values of these constants for phosphate buffers,[12] one can solve Eqs. 16–21 to get the pH variation of phosphate buffers with temperature.

Figure 1 plots temperature dependence of pH 6.86 primary standard phosphate buffer and compares model results with reported experimental data. There is some deviation (0.02 to 0.05 units) at higher temperatures beyond 343°K, but these are of the same order as the deviation among the experimental data sets. Note that the reported data use electrode measurements, and because of inherent uncertainties of the liquid junction and reference electrode at high-temperatures, are not necessarily the best standard for comparisons for model predictions.

High-pressure calibration references. Byrne and Laurie[14] have reviewed the influence of pressure on chemical equilibria in aqueous systems. The effect of pressure on equilibrium constant can be derived from thermodynamic principles[12]

$$RT \ln\left(\frac{K_P}{K_{P_0}}\right) = -\Delta V^0(P - P_0) + 0.5\Delta k^0(P - P_0)^2 \quad (23)$$

where ΔV^0 is difference between the partial molal volumes of products and reactants in their standard states; Δk^0 is difference in partial molal isothermal compressibilities between products and reactants in their standard state; R is ideal gas constant; P

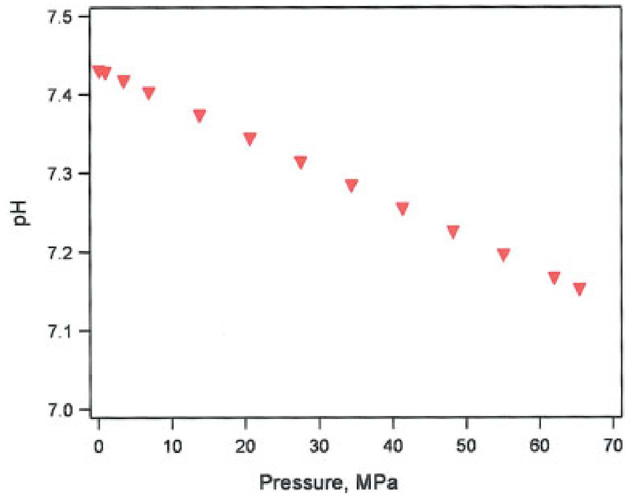

Figure 2. Modeled effect of pressure at 293°K on pH of primary standard phosphate buffer (pH = 7.429 @ 293°K and 0.101325 MPa).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 1. Model Predicted pH Values for Primary Standard Phosphate Buffer (pH = 7.429 @ 293°K and 0.101325 MPa)

Ionic Strength (mol/kg)	pH Model
0.01	7.6822*
0.02	7.6233*
0.05	7.5230*
0.1	7.4290
0.15	7.3490**
0.2	7.3020**
0.3	7.2270**
0.4	7.1670**
0.6	7.0740**
0.8	6.9990**
1.1	6.9070**
2.1	6.6820**
3.1	6.5160**

*Using Debye-Huckel.
**Reference [17].

is pressure; and P_0 is pressure at standard state, typically, 0.101325 MPa.

This equation is claimed to give good fit to experimental equilibrium data to 200 MPa. Beyond 200 MPa, Δk^0 can also become a function of pressure.

We have applied this equation to the pH 7.4 primary standard phosphate buffer using partial molal volume and compressibility changes reported in literature[14,18,19] for the first and second phosphoric acid dissociation reactions, and the water dissociation reaction. Pressure dependence of density and dielectric constant has been calculated using correlations in literature[19,20] and incorporated in the calculation of activity coefficients. Figure 2 plots the predicted effect of pressure on the pH of this standard buffer at 293°K. The change in pH going from atmospheric pressure to 67.1 MPa is about 0.25 units.

Ionic strength calibration references. The phosphoric acid dissociation constants Ka_1, Ka_2 are a function of only temperature and pressure, and not affected by ionic strength. However, the activity coefficients that appear in the chemical equilibrium relations are a strong function of ionic strength. While the Debye-Huckel model for activity coefficient is valid for low-ionic strengths (<0.1 mol/kg water), the Pitzer equations are valid over a wide range going to 6 mol/kg water, and have been extensively employed in the past two decades to describe such equilibria. Chemical equilibrium of pH 7.4 primary standard phosphate buffer has been modeled using the Debye-Huckel activity coefficient model for ionic strengths below 0.1 mol/kg water (Table 1). For higher-ionic strengths, reported pH values based on the Pitzer activity coefficient model have been used.[17] Table 1 shows that increasing the ionic strength from 0.1 to 3.1 mol/kg water at 293°K and 0.101325 MPa causes pH of primary standard phosphate pH 7.4 buffer to fall by about 0.9 units.

The procedure outlined above may be used for any buffer chosen for calibration of pH sensitive dyes.

Results and Discussions

Having obtained calibration buffer pH values over the desired range of temperature, pressure and ionic strength values, the pK'_a of any pH indicator dye may now be characterized for this range using the calibration procedure outlined earlier for ambient conditions. Before selecting a dye for pH measurement at high-temperature, it is important to check for potential degradation of the dye or loss in pH sensitivity at these conditions. Phenol red belongs to the class of sulfonaphtalein indicators that have been used successfully by several investigators[4–6] for ambient pH measurements. Phenol red dye was boiled at 373°K in solutions containing common aqueous phase salts and no degradation was observed. The dye solution was also cooked at 423°K for several hours, and its pH sensitivity was found to be preserved. This dye was thus selected as a suitable indicator for high-temperature pH measurement.

pK'_a as a function of temperature. Using the set up described in the experimental section, phenol-red spectra in several standard buffer solutions were obtained for temperatures in

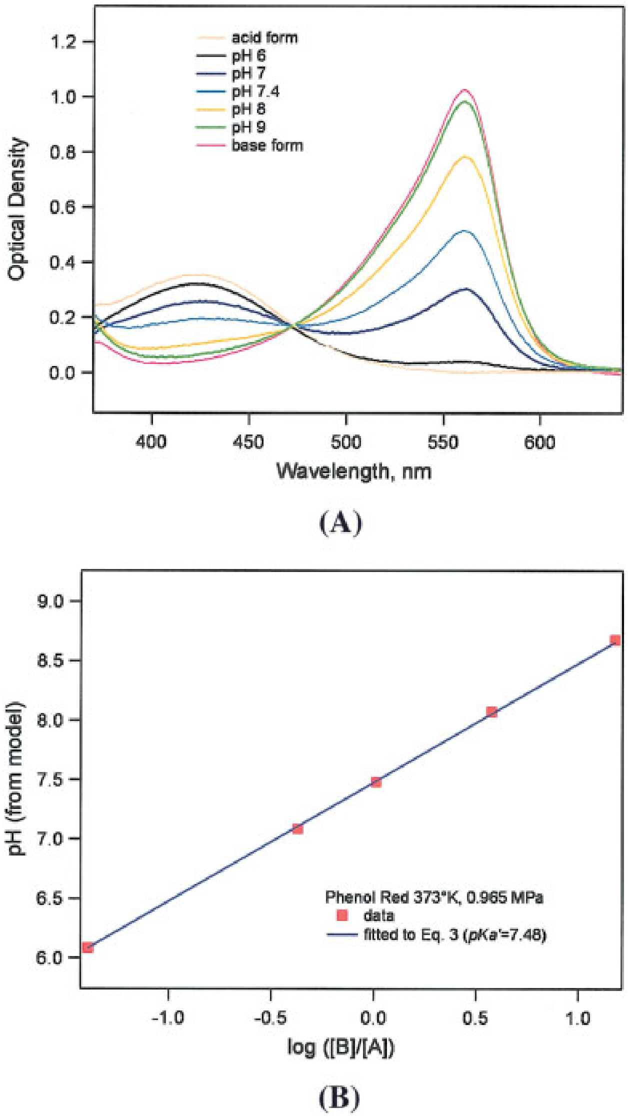

Figure 3. (A) Phenol-red spectra in various buffer solutions at 373°K; (B) calculating pK'_a for phenol red at 373°K.

The pH values in Figure 3A refer to the buffer pH values at standard conditions (293°K and 0.101325 MPa). The acid form spectrum is obtained in a pH 4 buffer and the base form spectrum in pH 12. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

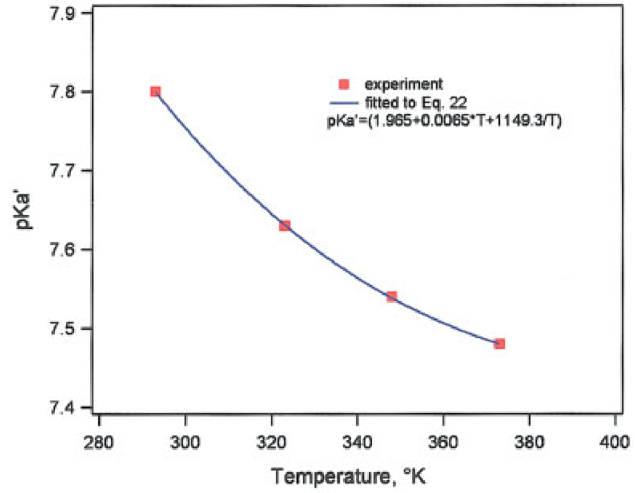

Figure 4. Temperature dependence of pK$'_a$ for phenol red at 0.965 MPa, and 0.1 mol/kg water.

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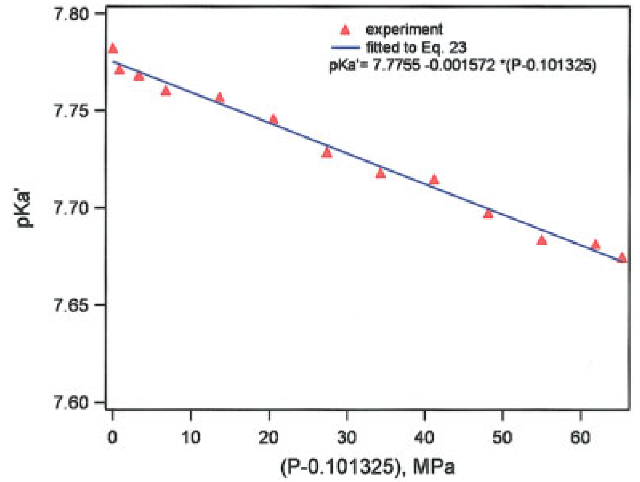

Figure 5. Pressure dependence of pK$'_a$ for phenol red at 293°K, and 0.1 mol/kg water.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the range of 293°K to 373°K. The pressure was maintained at 0.965 MPa to prevent flashing of the water phase at high-temperatures. Figure 3a shows the spectra of phenol red in various buffer solutions at 373°K and 0.965 MPa pressure and 0.1 mol/kg water ionic strength. Figure 3b plots the model predicted pH value for each buffer at this temperature and pressure vs. the log ($[B]/[A]$) obtained from the spectral data. Using Eq. 3, the value of pK'_a at 373°K is determined to be 7.48 (intercept at log $([B]/[A]) = 0$). In a similar manner, pK'_a values were determined at other temperatures as well. Eq. 22 can be used to model the temperature dependence of the dye equilibrium dissociation constant (Figure 4). Note that this fitted equation is valid for the temperature range 293°K to 373°K at 0.965 MPa, and 0.1 mol/kg water ionic strength.

pK'_a as a function of pressure. Phenol-red spectra in primary standard phosphate buffer (pH 7.429 @ 293°K and 0.101325 MPa) were obtained as a function of pressure from 0.101325 to 65.5 MPa at 293°K. At each pressure, the base to acid fraction was obtained from the spectra, and using the model predicted pH values for the buffer in Eq. 3, the pK'_a was calculated. Figure 5 shows a good linear fit of pK'_a vs. pressure at 293°K. If we use Eq. 23 to describe the pressure dependence, it implies that Δk^0 is close to zero. From the slopes, one can estimate ΔV^0 to be -10.96 cm^3/mol at 293°K. Note that the change in pK'_a is of the order of 0.1 unit over this large pressure range. Similar changes were observed even at higher temperatures. The effect of pressure on reaction equilibrium constants has in general not been as widely studied as the effect of temperature. Consequently, the uncertainty in modeling the pressure variation of buffer equilibria, and in the calculation of the high-pressure pH calibration reference values is more than that for temperature effects. The small effects of pressure seen here, suggest that one could choose to ignore the effect of pressure on pK'_a of phenol red in pH measurement for targeted accuracies of 0.1 pH unit, as uncertainties could be expected to be of that order.

pK'_a as a function of ionic strength. Phenol red spectra were obtained in pH 7.4 primary standard phosphate buffer adjusted to varying ionic strengths (0.01 to 3 mol/kg water) by dilution with deionized water and/or by addition of NaCl salt at 293°K and 0.101325 MPa pressure. Using model predicted pH values, and the base to acid ratio obtained from laboratory spectra, one can determine the pK'_a from Eq. 3. Figure 6 plots pK'_a as a function of ionic strength. Note that as ionic strength increases by an order of magnitude from 0.3 to 3.1 mol/kg water, the pK'_a is relatively insensitive to ionic strength and changes only by 0.035 units.

We have used the Pitzer model of activity coefficients to derive an equation to fit the pK'_a as a function of ionic strength.

Equation 4 can be rewritten as

$$pK'_a = pK_a + \log\left(\frac{\gamma_B}{\gamma_A}\right) \qquad (24)$$

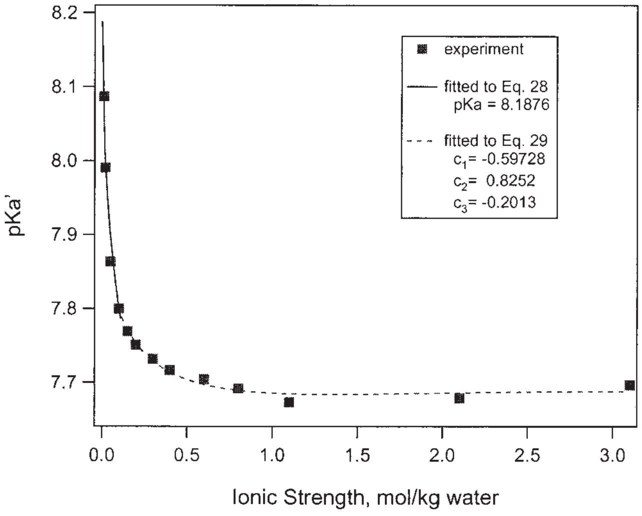

Figure 6. Ionic strength dependence of pK$'_a$ for phenol red at 293°K, and 0.101325 MPa.

Since pK_a is independent of ionic strength, the functional dependence of pK'_a on ionic strength should be the same as the functional dependence of log (γ_B/γ_A).

The Pitzer model equation for the activity coefficient of ions is given by[13,19]

$$\ln \gamma_i = z_i^2 f_\gamma + P_i(B, \Phi, C, \psi, m_c, m_a, z) \tag{25}$$

P_i represents the Pitzer group of functions with binary and ternary ion interaction parameters, and f_γ is a modified Debye-Huckel term given by

$$f_\gamma = \frac{-A_\phi \sqrt{I}}{1 + b\sqrt{I}} - \frac{2A_\phi}{b} \ln(1 + b\sqrt{I}) \tag{26}$$

where A_ϕ is Debye-Huckel parameter; b is universal constant = 1.2 (kg/mol)$^{0.5}$; B, Φ are Pitzer binary ion interaction parameters and a function of I; C, ψ are Pitzer ternary ion interaction parameters; I is ionic strength, mol/kg water; m_c, m_a are cation, anion concentrations, mol/kg water; and z is electric charge on ion.

Using this model with z_A equal to -1, and z_B equal to -2, the difference in the logarithm of the activity coefficients for the base and acid form of the dye in Eq. 24 may be written as

$$\begin{aligned} pK'_a - pK_a &= (\log \gamma_B - \log \gamma_A) \\ &= \frac{1}{2.303}\Bigg[\frac{-3A_\phi\sqrt{I}}{1 + b\sqrt{I}} - \frac{6A_\phi}{b}\ln(1 + b\sqrt{I}) \\ &\quad + P_B(B, \Phi, C, \psi, m_c, m_a, z) - P_A(B, \Phi, C, \psi, m_c, m_a, z)\Bigg] \end{aligned} \tag{27}$$

A rigorous calibration for the ionic strength effect on pK'_a would require a comprehensive set of measurements in single, and mixed electrolytes to determine the relevant dye acid and dye base interaction parameters with all other ions expected in water solutions where we want to measure pH. Since our first application of this technique was targeted to formation waters in oil fields that are generally dominated by sodium and chloride ions, we narrowed the calibration matrix by using only sodium chloride salt to adjust ionic strength in our calibrating solutions (Figure 6).

For dilute solutions with ionic strengths up to 0.1 mol/kg water, Pitzer ion interaction terms are expected to be small. We, hence, assume that for low ionic strengths below 0.1 mol/kg water, Eq. 27 can be simplified to a limiting form with only the modified Debye-Huckel term

$$pK'_a - pK_a = \frac{-0.5055\sqrt{I}}{1 + 1.2\sqrt{I}} - 1.94 \log(1 + 1.2\sqrt{I}) \tag{28}$$

where we have used b equal to 1.2 (kg/mol)$^{0.5}$ and A_ϕ equal to 0.388 at 293°K and 0.101325 MPa.

Using this equation to fit the experimentally estimated pK'_a for this ionic strength range, the true dissociation constant, pK_a is determined to be 8.1876 units at 293°K and 0.101325 MPa for phenol red (Figure 6). This is a function of only temperature and pressure and independent of ionic strength.

For the higher ionic strength range ($I > 0.1$ mol/kg water), the Pitzer ion interaction terms in the functions P_B and P_A of Eq. 27 have to be considered. We take advantage of the fact that for calibrating the dye pK'_a as a function of ionic strength, we only need the difference in the log of the individual activity coefficients of the base and acid form. Thus, the Pitzer ion interaction effects appear as a difference of the functions P_B and P_A in Eq. 27. Since the dye forms have a similar molecular structure, and are also similar in size, it may be reasonable to expect that their interaction parameters with the other ions are similar and terms that involve differences in dye interaction parameters will be negligible. Furthermore, the dye molal concentrations (in the range of 10^{-5} to 10^{-4} mol/kg water) are three to four orders of magnitude lower than the main ions Na^+ and Cl^- in the aqueous solution. Hence, terms that include the molality of the dye will also be negligible. One can examine the Pitzer equations to determine the dominating terms in Eq. 27 and use the functional forms of their ionic strength dependence to fit the data in the higher ionic strength range at 293°K and 0.010325 MPa (Figure 6)

$$\begin{aligned} pK'_a - 8.1876 &= \frac{-0.5055\sqrt{I}}{1 + 1.2\sqrt{I}} + c_1 \log(1 + 1.2\sqrt{I}) \\ &\quad + \frac{c_2}{2}(1 - (1 + 2\sqrt{I} + 2I)\exp(-2\sqrt{I})) + c_3 \end{aligned} \tag{29}$$

Measuring pH of unknown samples at high temperature, pressure and ionic strength. The dependence of pK'_a on temperature, pressure and ionic strength obtained from our calibration experiments are summarized below:

For T = 293°K–373°K; P = 0.965 MPa, I = 0.1 mol/kg water

$$pK'_a = \left(1.965 + 0.0065 * T + \frac{1149.3}{T}\right) \tag{30}$$

For T = 293°K; P = 0.101325–65.5 MPa, I = 0.1 mol/kg water

$$pK'_a = 7.7755 - 0.001572(P - 0.101325) \tag{31}$$

For T = 293°K; P = 0.101325 MPa, I = 0–0.1 mol/kg water

$$pK'_a - 8.1876 = \frac{-0.5055\sqrt{I}}{1 + 1.2\sqrt{I}} - 1.94 \log(1 + 1.2\sqrt{I}) \tag{32}$$

For T = 293°K; P = 0.101325 MPa, I = 0.1–3.0 mol/kg water

$$\begin{aligned} pK'_a - 8.1876 &= \frac{-0.5055\sqrt{I}}{1 + 1.2\sqrt{I}} - 0.59728 \log(1 + 1.2\sqrt{I}) \\ &\quad + \frac{0.8252}{2}(1 - (1 + 2\sqrt{I} + 2I)\exp(-2\sqrt{I})) - 0.2013 \end{aligned} \tag{33}$$

Our first target application for this method is for pH measurement of formation waters at high temperatures and pressures in oilfields. These waters typically have ionic strengths greater than 0.1 mol/kg water. Eq. 30 can be used first to determine pK'_a at the desired temperature, and an ionic strength of 0.1 mol/kg water. From Eq. 33 one can calculate the difference between pK'_a at any ionic strength and 0.1 mol/kg water at 293°K. Given the relative insensitivity of pK'_a to ionic strength in this range, we assume that this difference is independent of temperature and pressure and, hence, apply it to account for the ionic strength effect at the desired temperature. One can then use Eq. 31 to apply a shift due to the pressure effect. Again we assume that because of the relative insensitivity of pK'_a to pressure, the pressure effect is independent of temperature and ionic strength. Future work in our laboratory will focus on testing the validity and limitations of these assumptions.

Accurate pH measurement is critical to estimate the corrosion and scaling potential of formation waters in oilfields, and predict compatibility of waters that may be commingled from different zones or wells. Because gases and solids can come out of solution as downhole samples are transported to surface laboratories, it is important to measure pH downhole with the formation water in its native condition at reservoir temperature and pressure. The lack of such a robust measurement today requires large safety margins to be applied in selecting appropriate corrosion resistant materials and this impacts field development economics. A downhole pH measurement, even with target accuracies of the order of 0.1 units, would have a huge impact in terms of savings in cost of material chosen for corrosion resistance or in planning for scale treatment and mitigation.

To overcome the limitation that single dyes are sensitive only in a limited pH range we have also developed dye mixture formulations that allow extended range pH measurements at high temperature, pressure and ionic strength.[21]

The dye technique has been successfully applied for in-situ downhole pH measurements of formation water in high-temperature and high-pressure oil wells in the North Sea.[21] To validate these measurements, water samples from these wells were also collected and brought to the surface. These samples were flashed to ambient conditions, followed by laboratory analysis of the gas phase by gas chromatography, and a complete ion analysis of the water phase. These were used as inputs to a predictive model that simulated the chemical equilibrium of these samples and calculated the downhole pH. The *in situ* measurements of pH at reservoir conditions agreed well with the simulated values over a wide range of temperatures, pressures and ionic strengths.[21]

Conclusions

The use of pH sensitive dyes offers an alternative method of measuring pH at high-temperature, pressure and ionic strength conditions, where the IUPAC recommended electrode techniques are not valid. We have developed a calibration procedure for these dyes that uses chemical equilibrium models to get pH values of calibrating buffers for these conditions. Any uncertainties in parameters used in the thermodynamic models for calculating calibration references will impact the accuracy of the measurement. Such uncertainties will be inherent in the calibration process for any pH technique being developed for these conditions, and are not specific to the spectroscopic method using dyes. As thermodynamic models at high-temperatures, pressures and ionic strengths evolve and databases of Pitzer coefficients become more consistent, the calibrating buffer pH values can be revised and the dye calibration updated to improve target accuracies. The advantage of using such dyes is that, unlike potentiometric methods, the dye measurement depends only on the molecular properties of the pH sensitive dyes and once the dye equilibrium dissociation constant has been characterized, it eliminates the need for calibration prior to every measurement. This technique has been successfully applied for pH measurement of formation waters in the oilfields.

Literature Cited

1. Buck RP, Rondini S, Covington AK, Baucke FGK, Brett CMA, Camoes MF, Milton MJT, Mussini T, Naumann R, Pratt KW, Spitzer P, Wilson GS. Measurement of pH, Definition, Standards, and Procedures, *Pure & Appl. Chem.* 2002;74(11):2169–2200.
2. Vogel AI. *Text-Book of Quantitative Inorganic Analysis.* 3rd ed. John Wiley & Sons. 1961.
3. Bates R. *Determination of pH: Theory and Practice.* John Wiley & Sons: New York; 1964.
4. Clayton TD, Byrne RH. Spectrophotometric Seawater pH Measurements: Total Hydrogen Ion Concentration Scale Calibration of m-Cresol Purple and At-Sea Results, *Deep-Sea Research.* 1993;40(10): 2115–2129.
5. Yao W, Byrne RH. Spectrophotometric Determination of Freshwater pH Using Bromocresol Purple and Phenol Red, *Environ. Sci. Technol.* 2001;35:1197–1201.
6. Martz TD, Carr JJ, French CR, DeGrandpre MD. A Submersible Autonomous Sensor for Spectrophotometric pH Measurements of Natural Waters, *Anal. Chem.* 2003;75:1844–1850.
7. LePeintre MM. Mesure Du pH Sous Pression et a Temperature Elevee, *Bull. Soc. Franc. Electr.* 1960;8:584.
8. Kryukov PA, Perkovets VD, Stardostiva LI, Smolyakov BS. In *pH Measurement: Fundamentals, Methods, Applications, Instrumentation.* Galster, H.; VCH Publishers: New York, 1991; 60.
9. Boreng R, Schmidt T, Vikane O, Tau LA, Dybdahl B, Dale T, Thowsen O. Downhole measurement of pH in Oil & Gas Applications by use of a Wireline Tool, *SPE European Formation Damage Conference.* May 13–14: The Hague, The Netherlands: 2003; Paper SPE 82199.
10. Lito MJG, Camoes MF, Ferra MIA, Covington AK. Calculation of reference pH Values for Standard Solutions from the Corresponding Acid Dissociation Constants, *Analytica Chimica Acta.* 1990;239:129–137.
11. Camoes MF, Lito MJ, Ferra MIA, Covington AK. IUPAC, Consistency of pH Standard Values with the Corresponding Thermodynamic Acid Dissociation Constants, *Pure & Appl. Chem.* 1997;69(6):1325–1333.
12. Langmuir D. *Aqueous Environmental Geochemistry,* Prentice-Hall: New Jersey; 1997.
13. Pitzer KS. *Activity Coefficients in Electrolyte Solutions.* 2nd ed. CRC Press: Florida; 1991: Chapter 3.
14. Byrne RH, Laurie SH. IUPAC, Influence of Pressure on Chemical Equilibria in Aqueous Systems-With Particular Reference to Seawater, *Pure & Appl. Chem.* 1999;71(5):871–890.
15. Stumm W; and Morgan JJ. *Aquatic Chemistry.* 3rd ed. John Wiley & Sons: New York. 1996.
16. Partanen JI, Minkkinen PO. Equations for Calculation of the pH of Buffer Solutions Containing Sodium or Potassium Dihydrogen Phosphate, Sodium Hydrogen Phosphate, and Sodium Chloride at 25°C, *J. Solution Chem.* 1997;26(7):709–727.

17. Tishchenko PY, Bychkov AS, Pavlova GY, Chichkin RV, Standardization of pH measurements with the Use of the Pitzer Method and Phosphate Buffer, *Russian J. Phys. Chem.* 1998;72(6):935–943.
18. Surdo AL, Bernstrom K, Jonsson CA, Millero FJ. Molal Volume and Adiabatic Compressibility of Aqueous Phosphate Solutioins at 25°C, *J. Phys. Chem.* 1979;83(10):1255–1262.
19. Kaasa B. Prediction of pH, mineral precipitation and multiphase equilibria during oil recovery, PhD Thesis. *Norwegian University of Science and Technology*, Trondheim, Norway, 1998.
20. Kell GS. Thermal Expansivity, and Compressibility of Liquid Water from 0° to 150°: Corrections and Tables for Atmospheric Pressure and Saturation Reviewed and Expressed on 1968 Temperature Scale, *J. Chem. Eng. Data.* 1975;20(1):97–105.
21. Raghuraman B, O'Keefe M, Eriksen KO, Tau LA, Vikane O, Gustavson G, Indo K. Real-Time Downhole pH Measurement Using Optical Spectroscopy, SPE International Symposium on Oilfield Chemistry. Feb 2–4: Houston; 2005: Paper SPE 93057.

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