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Development of W/WO$_3$ sensors for the measurement of pH in an emulsion polymerization system

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Abstract

This paper describes the development of a rugged pH sensor that can be used to monitor hydrogen ion activity in an emulsion polymerization system under demanding reaction conditions. To inhibit deposition of the latex onto the sensor surface, a sensor was chosen to have the same surface charge as that on the latex particles at the pH of the emulsion system. An analysis of *pzc* (pH of zero charge) of the emulsion latex, as inferred from the zeta potential, the expected pH of the latex, and the known *pzc* values for various metal oxides, indicated that the W/WO$_3$ electrode should be a viable pH sensor for the particular latex system of interest. It was concluded that the *pzc* values for both the latex and the pH sensor would lie below the expected pH of the latex, rendering the surfaces of both systems negatively charged. Coulombic repulsion should therefore inhibit the deposition of latex particles onto the pH sensor surface, thereby avoiding possible interference with the pH-determining reactions. Measurement of the W/WO$_3$ sensor potential against a Ag/AgCl, KCl (sat.) reference electrode has shown that the sensor potential varies linearly with pH over a wide pH range, as established by various borate buffers, at temperatures of 25 °C, 70 °C and 130 °C. The slope of the potential versus pH correlation at each temperature is slightly less than the theoretical value indicated by the Nernst equation for a system at electrochemical equilibrium. This deviation, which has been noted in previous work on the W/WO$_3$ sensor in homogeneous aqueous systems, is attributed to the fact that the sensor is not strictly at equilibrium, but instead displays a mixed potential. The W/WO$_3$ sensor can be accurately calibrated over the conditions that exist in the latex system explored in this work and, while no independently measured pH data are available for the latex at elevated temperatures, the value determined by the W/WO$_3$ sensor is consistent with expectations. To our knowledge, this work represents the first measurement of proton activity in a latex system under polymerization reaction conditions.

1. Introduction

Monitoring a polymerization reaction usually involves measuring the temperature, pressure, depletion of monomer, and/or build-up of polymer. However, for those polymerization reactions that involve hydrogen ion, the pH is often the key variable that should be controlled and monitored. The reluctance to monitor pH frequently stems from the fact that the reaction medium is under extreme conditions of temperature and/or pressure, rendering 'off-the-shelf' pH monitors ineffective. The aim of the present work was to develop the necessary techniques for measuring pH more quantitatively under typical emulsion polymerization conditions.

Knowledge of the pH of the emulsion during polymerization is desirable, because the pH affects the stability of the final latex and because the activity of hydrogen ion (or hydroxide ion) may effect the reaction rate. The emulsion polymerization in our study was carried out at temperatures and pressures much higher than ambient. Furthermore, the probe must not become fouled by latex particles adhering to the electrochemically active surface, as fouling would interfere with the potential-determining equilibria. These two requirements led us to rule out conventional glass bulb-type and transistor-type electrodes for this application, because these conventional electrodes are limited in their service temperature and pressure and because they are prone to fouling. Also, latex particles tend to block the frits (liquid junctions) of conventional reference electrodes, with the result that high impedance develops at the interface between the reference electrode internal solution and the external environment.

The working principle adopted in selecting the most appropriate pH sensor is that deposition of the latex onto the sensor surface should be avoided, so that the pH-determining equilibria are not impacted by deposition of the latex particles. A metal/metal oxide couple that has the same sign of the surface charge as the latex of interest, under the expected measurement conditions, should be selected. This condition requires that the pH of zero charge (*pzc*) of *both* the metal oxide and the latex be either greater than or less than the pH of the latex solution. It was found that the *pzc* of the latex used in this study was very small (negative zeta potential to low pH values). Accordingly, we required a metal/metal oxide pH sensor having a *pzc* that is also small, so that the *pzc* of both the sensor and the latex would be smaller than the pH of the latex solution. Based on this criterion, the only suitable system appears to be W/WO_3 (*pzc* 2.5), which has been extensively studied in the past in homogeneous aqueous systems under conditions that are significantly more severe than those that exist in the latex [1]. Thus, according to the rationale developed above, both the latex particles and the W/WO_3 electrode surface will be negatively charged at the expected pH of the latex and hence deposition of latex particles onto the sensor surface should be inhibited by coulombic repulsion.

The work described in this paper demonstrates the feasibility of performing pH measurements in latex environments at elevated temperatures and pressures. The work consisted of measuring the voltage of the W/WO_3 sensor in a series of buffer solutions over a wide pH range and then measuring the voltage of the sensor in the latex. The measured pH was then compared with the expected pH to judge the viability of the sensor system. The experiments were carried out at temperatures of 25 °C, 70 °C and 130 °C with the first two sets being carried out at pressures close to ambient and the latter at a pressure of over 500 psi. The principal innovation of the work described here is the selection of a pH sensor having an appropriate *pzc*, in order to avoid latex deposition.

2. Experimental details

Three tungsten wires were oxidized in a natural gas (CH_4) flame for 2, 5 and 10 min, in order to produce a black film of tungsten oxide on the electrode surface. The rest of the wire, except the sensor end (W/WO_3) and the opposite end (connected to the voltmeter), was covered with a heat-shrinkable PTFE tube. Since pH measurements under ambient conditions in standard buffer solutions that were performed with sensors that had been oxidized for different times showed similar results, only the 5 min-fired tungsten/tungsten oxide electrode was employed in the high temperature, high pressure studies.

A Ag/AgCl, KCl (sat.) electrode functioned as the reference electrode for the potential (pH) measurements. A silver wire was anodized for 18 h in a 0.1 M HCl solution at a current density of 5 mA cm^{-2} using a Schlumberger/Solartron 1286 electrochemical interface, resulting in the formation of a thick AgCl film on the silver surface. The Ag wire was then sealed into a PTFE tube with the sensor part (Ag/AgCl) in contact with a saturated KCl solution. A heat-shrinkable, PTFE tube was used to contain the saturated KCl solution, with one end covering a porous ZrO_2 plug (for electrolytic contact with the test environment) and the other end covering the Ag wire sealed into a PTFE tube, from which part of the Ag wire was exposed for connection to the voltmeter.

Standard buffer solutions were prepared from Aldrich ACS-grade reagents and conductivity grade water (Milli-Q system, 18.2 MΩ cm). The compositions of the solutions were 0.1 M NaOH, 0.5 M H_3BO_3 + 0.2 M NaOH, 0.5 M H_3BO_3 + 0.05 M NaOH, 0.75 M H_3BO_3 + 0.02 M NaOH and 1 M H_3BO_3. The pH values for these solutions at room temperature were measured using a Fisher Scientific pH meter. The pH of each solution at each of the test temperatures was also calculated using an equilibrium solution model.

The apparatus used for the high-temperature, high-pressure pH measurements is shown schematically in Figure 1(a) and (b). Nitrogen gas was provided from a tank at 150 bar (2200 psi) and a Messer S145-2 piston gas regulator was used to control the gas pressure in the measurement system. An additional pressure gauge provided pressure readings for the closed system; the readings proved to be very close to those of the gas regulator. A slow flow of nitrogen was maintained through the system via a check valve in order to prevent the back-distillation of water into the nitrogen cylinder. The Omega heating system that was used to control the cell temperature included a thermocouple, a heating tape, and a proportional temperature controller. The thermocouple, the W/WO_3 electrode, and the Ag/AgCl reference electrode were sealed into three ends of the cross (Figure 1(b)) using Conax MPG-125-A-V packing glands. The upper branch of the cross (Figure 1(b)) was connected to the pressure gauge. The reference solutions and the latex filled the cross except for the branch connected to the pressure gauge, which contained high-pressure nitrogen gas. All the tube/cross connections were Swagelok products. A Keithley 2182 voltmeter was employed to record the potential differences between the W/WO_3 electrode and the Ag/AgCl reference electrode in the buffer solutions and in the latex.

3. Results and discussion

Considerable work has been reported in the past on measuring pH at elevated temperatures and pressures [1–6], with the highest reported temperature being 528 °C [6]. Generally, these measurements have employed M,M_xO_y/ZrO_2(Y_2O_3) or W/WO_3 sensors, or even glass membranes, in homogeneous aqueous sys-

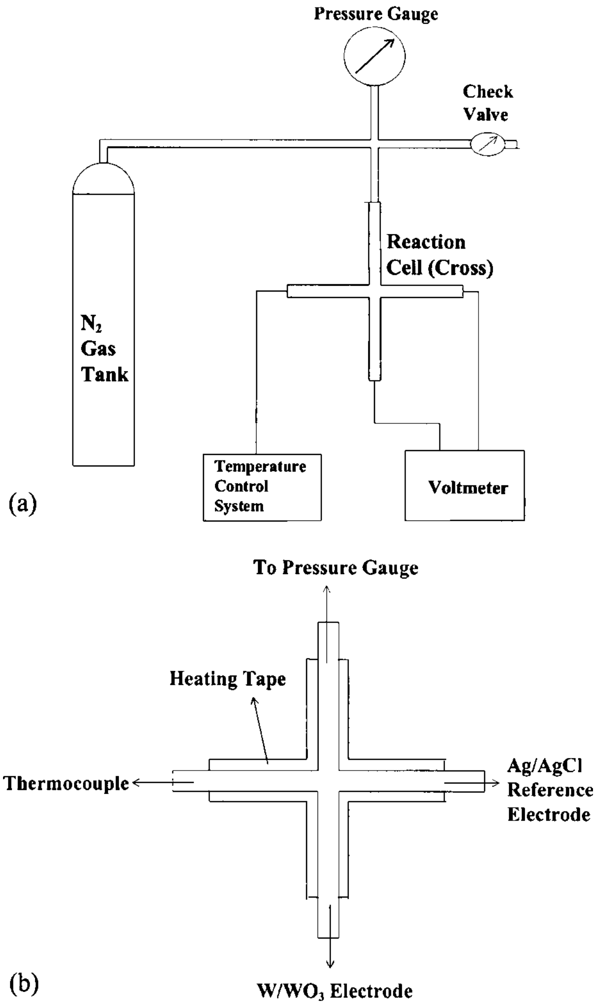

Fig. 1. The high temperature, high-pressure pH measurement system (a) and a closer look at the reaction cell (cross) containing the electrodes (b).

tems, where fouling of the sensor surface by a second phase is not an issue. However, a previous attempt to utilize the first of these pH sensors in a geothermal environment was only partially successful [7], because of fouling of the sensor surface by silica and other minerals. A similar potential for fouling exists in latex environments and it might be expected that the function of the sensor would be severely compromised. Thus, the strategy outlined above of selecting a sensor that has a surface charge of the same sign as that of the latex particles was aimed entirely at inhibiting fouling.

To our knowledge, this paper reports the first *in situ* measurement of pH in a latex system under typical reaction conditions. Thus, a plot of the W/WO_3 sensor potential against calculated pH for the five borate buffers and the latex at 25 °C is shown in Figure 2. The plot is linear, as expected from the Nernst equation, and the pH indicated for the latex (3.44) is close to the expected value of about 3.5. Similar plots were produced when the sensor potential was plotted against the measured pH. The calculated and measured pH values are in good agreement as shown by the correlation displayed in Figure 3, with the line indicating a perfect 1:1 correlation. From this plot we conclude that the variance between the measured and calculated pH is less than 0.1, and this residual is probably attributable to activity coefficient effects. (Note that the hydrogen ion activity coefficient is taken into account in the calculated pH, whereas the measured pH is a comparison against standard buffers using a glass electrode. This latter measurement procedure does not incorporate the activity coefficient of H^+ *per se*).

Plots of the W/WO_3 sensor potential against calculated pH at the higher temperatures of 70 °C and 130 °C are shown in Figures 4 and 5, with Figure 5 displaying replicate measurements under the most demanding experimental condition. Again, excellent linearity is observed at 70 °C and for each of the five runs conducted at 130 °C, as predicted by the Nernst equation, with the indicated pH of the latex being in

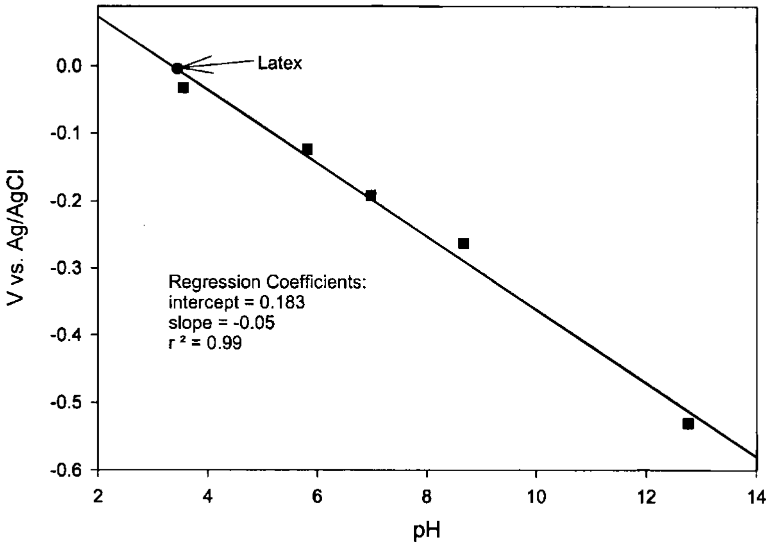

Fig. 2. Plot of W/WO_3 sensor potential against calculated pH for borate buffers and the latex at 25 °C.

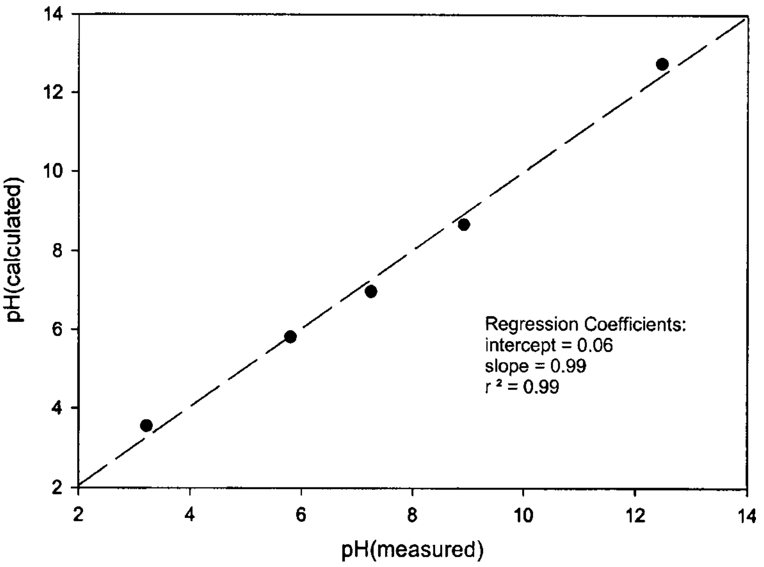

Fig. 3. Correlation of calculated pH with measured pH at 25 °C.

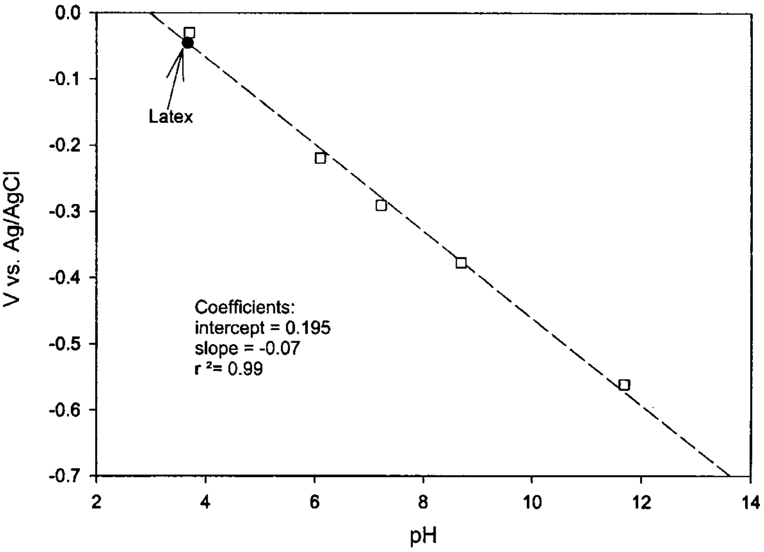

Fig. 4. Plot of W/WO_3 sensor potential against calculated pH for borate buffers and the latex at 70 °C.

reasonable agreement for the five runs (3.86, 3.77, 4.04, 3.98 and 4.16, respectively, for the 130 °C case). The differences among these five runs may result from concentration changes in the buffer solutions and the latex at high temperatures, resulting from the distillation of water through the check valve (Figure 1(a)), and perhaps also from small differences in temperature.

Figure 6 presents cell temperature and the corresponding sensor potential data as a function of the measurement time over a period of 3 h. In spite of fluctuations in the temperature (closed circles), the potential (open squares) remains stable, and hence the W/WO_3 sensor is judged to be viable for measuring pH in the latex system under the selected operating conditions.

For a pH sensor at equilibrium, the Nernst equation predicts that the slope of the potential versus pH plot should be 2.303 RT/F, where R is the gas constant and F is Faraday's constant. Substituting values of $R = 8.314$ kJ K^{-1} $kmol^{-1}$ and $F = 96\,487$ C mol^{-1}, we obtain theoretical values for the slope of 0.059, 0.068 and 0.080 V at 25, 70 and 130 °C, respectively. From the experiments, we recorded average slopes of 0.054, 0.066 and 0.075 V at these same temperatures. The standard deviation of the slopes is 0.0018 V. The experimental slopes are slightly below the theoretical values, as was previously reported [1] for this sensor in homogeneous borate buffer solutions. However, deviation from equilibrium theory is to be expected, because the W/WO_3 sensor is not an equilibrium system, but rather displays a mixed potential resulting from a balance between a partial anodic process ($W + 3\,H_2O \rightarrow WO_3 + 6\,H^+ + 6e^-$) and a partial cathodic reaction (e.g., $H^+ + e^- \rightarrow 1/2\,H_2$) occurring at the sensor surface. Nevertheless, we have shown in

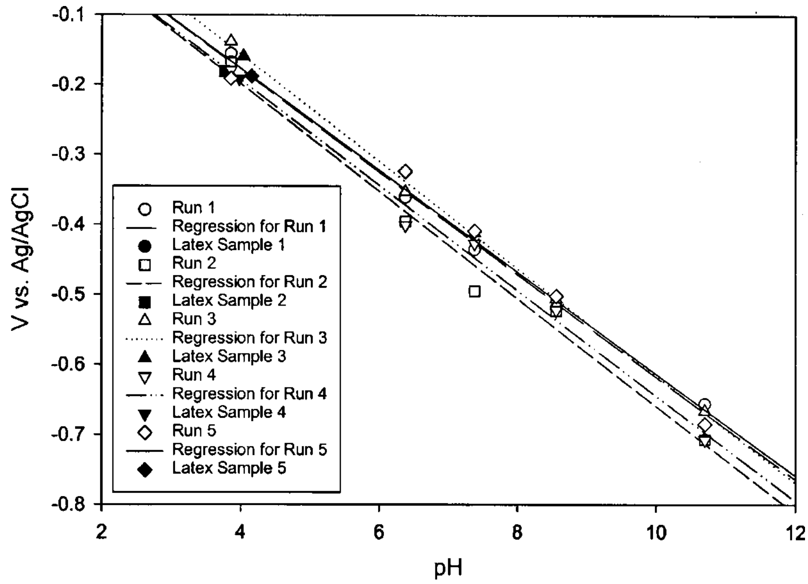

Fig. 5. Plot of W/WO$_3$ sensor potential against calculated pH for borate buffers and the latex at 130 °C (all 5 runs).

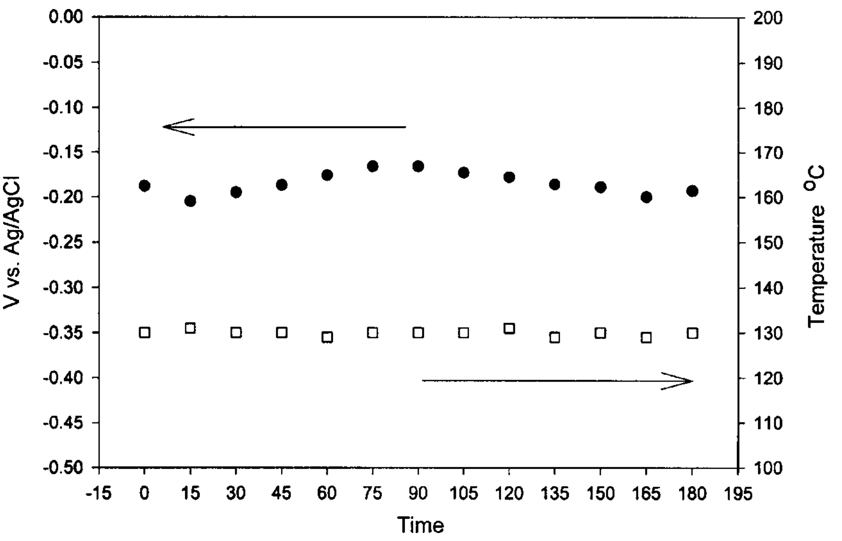

Fig. 6. Plot of W/WO$_3$ sensor potential and cell temperature against measurement time for the latex at 130 °C lasting for 3 h.

this work, and elsewhere [1], that the W/WO$_3$ electrode responds consistently as a pH sensor, that it can be accurately calibrated using standard buffers, and that it can be employed to measure pH in a heterogeneous latex system.

4. Summary and conclusions

The work reported here may be summarized as follows:

(i) An analysis of *pzc* (pH of zero charge) of a latex system of interest, as inferred from the zeta potential, the expected pH of the latex, and the known *pzc* values for various metal oxides, indicated that the W/WO$_3$ electrode should be a viable pH sensor for measuring pH. It was concluded that the *pzc* of both the latex and the pH sensor would lie below the expected pH of the latex, rendering the surfaces of both systems negatively charged. Coulombic repulsion should therefore inhibit the deposition of the latex particles on to the pH sensor surface, thereby avoiding possible interference with the pH determining equilibria.

(ii) Measurement of the W/WO$_3$ sensor potential against a Ag/AgCl, KCl (sat.) reference electrode has shown that the sensor potential varies linearly with pH over a wide pH range, as established by various borate buffers, at temperatures of 25, 70 and 130 °C. The slope of the potential against pH correlation at each temperature is slightly less than the theoretical value indicated by the Nernst equation for a system at electrochemical equilibrium. This deviation, which has been noted in previous work [1], is attributed to the fact that the sensor is strictly not at equilibrium, but instead displays a mixed potential.

(iii) The W/WO$_3$ sensor can be accurately calibrated over the conditions described in this work. Measurement of pH for our latex system is now possible without the limitations associated with commercially available pH sensors.

(iv) While no independently measured pH data were available for the latex at elevated temperatures, the value determined by the W/WO$_3$ sensor is consistent with the expected values.

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