pH Impact on Inhibitor Performance

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Abstract

Water treatment chemists have long observed that some scale inhibitors function better at high rather than low pH, and that some inhibitors have little, if any, activity at very low pH. Examples would be the effectiveness of polyacrylic acid at high pH as a calcium carbonate inhibitor, as in ash sluice and some mining applications; mediocre performance near a neutral pH, as in cooling water applications; and very low activity in an acid pH range, as in gypsum control in the pH range from 2 to 4. This article provides a framework for evaluating relative inhibitor activity using dissociation profiles for common inhibitors and calculating the distribution of inhibitor species versus pH. The use of dissociation constants for inhibitors provides a valuable tool for matching inhibitors to a specific application range pH, and as an aid in scale inhibitor selection. It can also provide a tool for evaluating and comparing new molecules. The article, and the concept of active versus inactive (or less active) inhibitor forms, offers explanations for what appeared to be anomalies during the modeling of inhibitor performance data, and field observations. These anomolies included:

- Why is the minimum dosage requirement for calcium phosphate inhibition by some polymers so much lower than the requirement for others?
- Why does the addition of pH as a variable for correlation dramatically improve the correlation coefficient (niceness of fit) for some inhibitors, even for scales whose solubility is, for all practical purposes, independent of pH?
- Why can many phosphonates' performance in the cooling water pH range be modeled without incorporating inhibitor speciation or pH as a variable?

Background

The impact of pH and protonation state on treatment efficacy is observed in many areas of water treatment. Chlorination provides an example, with the protonated form of hypochlorous acid being observed to have much more biocidal activity than the dissociated alkaline hypochlorite form. Adsorption studies of inhibitors used as squeeze treatments in oil field applications provide another example of the efficacy of dissociated versus protonated inhibitor forms.[1] In some cases, such as bromination, the impact of dissociation state on efficacy is arguably negligible.

Similar observations have been made concerning the impact of pH and protonation state on efficacy in the case of scale inhibition by phosphonates and polymers.[2–5]

Scale inhibitors dissociate like other acids as in Equation 1:

H-Inhibitor <--> H$^+$ + Inhibitor $^-$ (1)

with a dissociation constant that might be generalized as:

Ka = {H$^+$} {Inhibitor$^-$}/{H-Inhibitor} (2)

and a pK$_a$ defined as:

pK$_a$ = - log10(K$_a$) (3)

By definition, pK$_a$ is the pH where 50% of the acid for a given dissociation step will be in the protonated form and 50% will be in the dissociated form. Knowing the pK$_a$ for the final dissociation step of an inhibitor can be critical when the dissociated and protonated forms have significantly different efficacy as inhibitors. A conservative method for employing the dissociation state is to assume that the dissociated inhibitor concentration for the final step is the active species.

Understanding the impact of pH upon the relative efficacy of an inhibitor can be key to providing the optimum inhibitor dosage and in assuring that the minimum effective active inhibitor is present.

In the simplest case, an inhibitor may have almost 100% efficacy in a pH range where it is almost completely dissociated and close to 0% efficacy in a pH range where the inhibitor is almost completely protonated. This scenario has been reported for simple phosphonates such as HEDP (1-hydroxylethylidene-1,1-diphosphonic acid). Profiles comparing the protonation state and inhibitor efficacy for the simple phosphonates indicate that the final dissociation constant (pK$_a$) is a controlling factor with minor, if any, contribution from lower dissociation states, as shown in Figure 1.

In a more complex case, such as HDTMPA [hexa-methylenediamine-tetra(methylenephosphonic) acid], the various protonation states appear to have significant efficacy, so their combined efficacy is greater than might be expected based on experience with a simpler inhibitor.

Griffiths et al.[2] developed dissociation profiles for common phosphonates and compared them to inhibition studies over the same pH range. They summarized their laboratory results for simple phosphonates as follows:

"The general trend… is an improvement in performance with increasing pH. The improvement runs parallel to the titration curve with full activity occurring only at a pH value that approaches the final phosphonic acid pK$_a$ value."[2]

Figures 1–3 profile the protonation state (fraction) for the phosphonates HEDP, ATMP [aminotris(methylene phosphonic) acid], and HDTMPA versus pH. The red lines depict the active form.
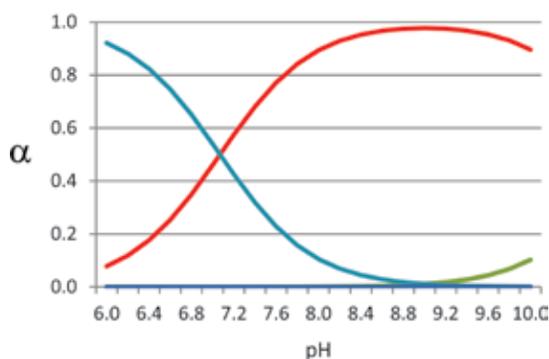
Figure 1: HEDP Distribution of Species
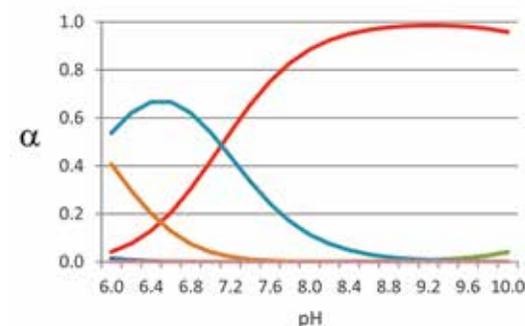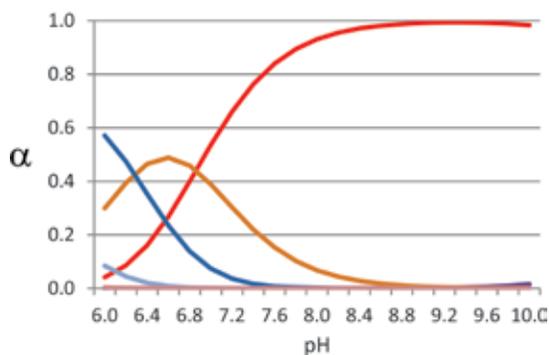

Figure 2: ATMP Distribution of Species

Figure 3: HDTMPA Distribution of Species

It is significant to note that the lower pK_a or the final dissociation step for these phosphonates results in a high percentage of the inhibitor being in the active, dissociated state in the typical cooling water pH range.

pH has a similar impact on polymer dosages for scale inhibition. The first time the author encountered the need to correct the dosages and models for speciation was when developing a model for calcium phosphate scale inhibition by AA-AMPS (copolymer of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid).

The data of minimum effective dosage versus saturation ratio and temperature was developed at three distinct pH values in the cooling water range of 7.0 to 9.0 .

Three distinct scatter plots resulted from the first model attempted—a correlation of dosage as a function of driving force, induction time, and temperature.

Dosage = f(SR,time,temperature)   (4)

Where:
• SR is the ion association model saturation ratio for tricalcium phosphate.
• Dosage is the active AA-AMPS concentration in the test solution.
• Temperature is the absolute temperature °K.
• Time is the last time before failure.

Figure 4 profiles the distribution of species for the AA-AMPS copolymer. The pK_a for its final dissociation step is at a significantly higher pH than the comparable pK_a's for the phosphonates profiled in Figures 1–3. The red line indicates the high activity dissociated form.

Figure 4: AA-AMPS Distribution of Species
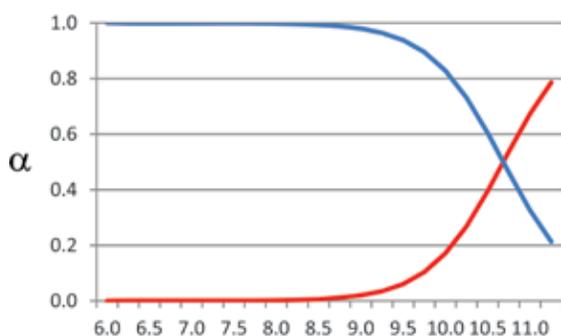
It can be seen that only a small percentage of the copolymer is in the active form (red line) in the typical cooling water pH range of 7 to 9, while a majority of the phosphonate concentration is in the active form for the same pH range.

Figure 5 profiles the predicted versus observed values for this correlation with a low coefficient of definition (R^2) of 0.31.

Figure 5: Copolymer Model Uncorrected for Protonation
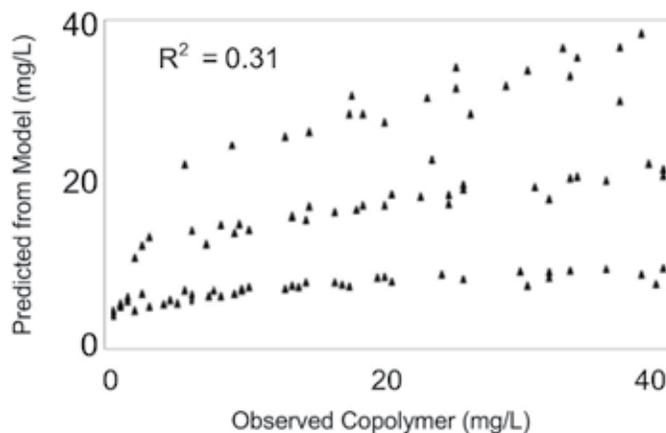
Adding pH to the parameters modeled reduced the scatter plot to one zone and increased the correlation to an R^2 of 0.81, as depicted in Figure 6. pH had a negative coefficient, indicating that dosage, when treated independently of saturation ratio, decreased with increasing pH.[6,7] The pH factor in this case followed the dissociation fraction and corrected for the speciation at the various pHs studied.

Figure 6: Copolymer Model Corrected Using pH
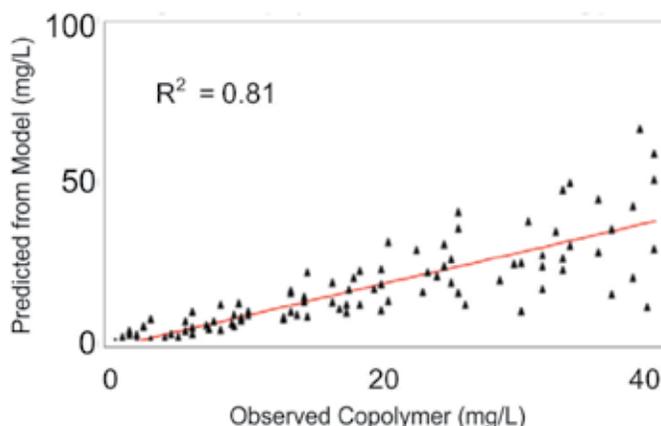
The final correlation calculated the speciation of the inhibitor and used the active concentration of the unprotonated form, rather than the total polymer dosage. Figure 7 depicts the correlation improvement when the dissociated inhibitor concentration is used for the model.

Figure 7: Copolymer Model Corrected Using pK_a
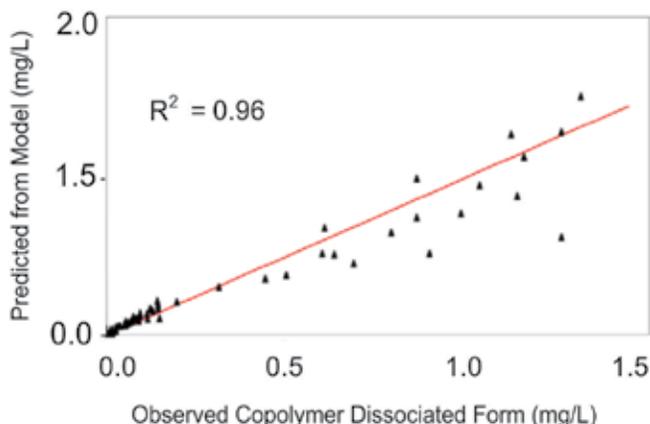
Application

A knowledge of inhibitor speciation and activity versus pH is useful in selecting and matching inhibitors to a specific application. It is also useful for developing performance tests to create inhibitor performance models against specific scales and for optimizing dosages.

Evaluating a terpolymer with the addition of the final dissociation constant resolved another polymer performance riddle. Laboratory data for the performance of a terpolymer seemed almost too good. The polymer performed at approximately one-fifth of the dosage of AA-AMPS copolymer under comparable conditions. Yet, the model developed initially for the polymer using the relationship of equation 4 yielded R-squared correlation coefficient of only 0.02 (Figure 8). Adding pH as a variable increased the correlation coefficient to an acceptable value for experimental data. Using the dissociated inhibitor form in the model, as calculated from the terpolymer's pK_a, increased the correlation coefficient to 0.99 (Figure 9). The performance increase might be attributed to the decrease in pK_a from 10.5 for the copolymer to 9.7 for the terpolymer.

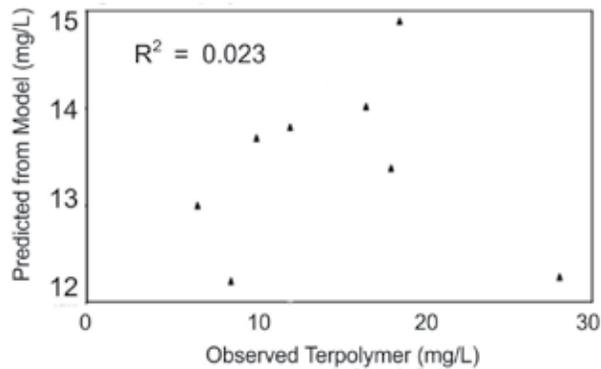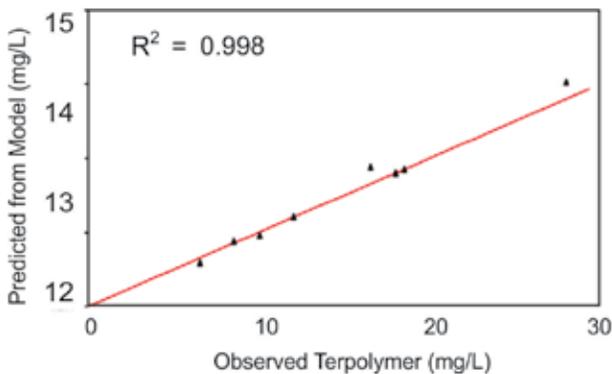Figure 8: Terpolymer Model Uncorrected for Protonation

Figure 9: Corrected for Protonation State Using pK_a

Selecting Inhibitors

Knowledge of dissociation profiles is useful in selecting inhibitors for an application. For a low pH application, select an inhibitor with a low pK_a, preferably below or within the pH range for the application. This ensures that the maximum amount of inhibitor will be in the active form in the application pH range.

Optimizing Dosages

Tomson et al.[6] recommend the use of a factor to correct dosage models for the active specie concentration expected. They incorporated the correction into models for minimum effective dosage. For example, if the minimum effective dosage calculated from a model is Dmin, and the alpha (fraction) for the final dissociation species is α, the use dosage, D_{use}, would be:

$$D_{use} = D_{min} / \alpha \qquad (5)$$

For optimized dosage D_{min} of 1.0 mg/L and a dissociation fraction α of 0.8, this reduces to:

$$D_{use} = 1.0 / 0.8 \text{ or } 1.25 \text{ mg/L} \qquad (6)$$

This method provides a simple, reasonably conservative approach to correcting for active species versus total inhibitor concentration. It assumes that the final dissociation species is the only active material.

Developing New Models

Ideally, the experimental design for developing inhibitor models[5] would allow the researcher to calculate the relative efficacy of each inhibitor form in relation to the final dissociated form. An experimental design with a broad range of pH and saturation ratios would allow the researcher to calculate the relative efficacy for each significant specie from the inhibitor dissociation profile.

Once the relative efficacies are calculated, the dosage model expands to:

$$D_{use} = D_{min} / (\alpha_1 {}^*eff_1 + \alpha_2 {}^*eff_2 + \dots \alpha_n {}^*eff_n) \quad (7)$$

This equation reduces to equation 5 when only the final dissociated form is significant.

Summary

pH can affect the efficacy of scale inhibitors. Some species of inhibitors are more active than others. The dissociated form, at the highest pH, tends to be the active specie. An understanding of the relative efficacy of inhibitor species versus pH can greatly improve models developed for calculating the minimum effective dosage, and for selecting the optimum inhibitor for a specific application.

Further Work

Laboratory studies are planned to develop dissociation profiles for commercial phosphonates and polymeric scale inhibitors, followed by inhibitor optimization studies over a broad pH range. The objective of the application research is to quantify the impact of pH on the efficacy of commercial inhibitors, with initial tests studying $BaSO_4$, $CaSO_4$, and $CaCO_3$ inhibition. This article provides background information and the rationale for the work. ᨏ

References

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