Determining Percent Active Biocide as a Function of pH

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Acids in an aqueous environment exist in a dissociation equilibrium given by equation (1). The side of the reaction that is favored for a given system is determined by the pH of the system, and described by a number called the *acid dissociation constant*.

$$HA \rightleftharpoons A^- + H^+ \tag{1}$$

Since this acid dissociation constant relates the pH of the system to the concentrations of all acids and bases present in the system, if we know its value and the pH of the system, we can determine the concentrations of the acids and bases present.

This is important because many biocides are weak acids, but only the undissociated (HA) form of the biocide works as an active biocide. If we can generate a graph of percent active (undissociated) biocide versus pH, we can determine the maximum pH to run a produce flume, poultry chiller, or the like, before we start losing efficacy due to dissociation. Alternatively, if we prefer an even higher pH, the chart will allow us to determine what percentage of excess biocide needs to be fed such that we maintain the level of active biocide we require.

As a starting point, we'll use the Henderson-Hasselbach equation, which relates the pH of a solution to the ratio of molar concentrations of species present at equilibrium and the logarithm of the acid dissociation constant (the *pKa*) as follows:

$$\mathrm{pH} = \mathrm{pKa} + \log_{10}\left(\frac{[A^-]}{[HA]}\right) \tag{2}$$

Rearranging to get the ratio of species on its own

$$\mathrm{pH} - \mathrm{pKa} = \log_{10}\left(\frac{[A^-]}{[HA]}\right) \tag{3}$$

$$10^{\mathrm{pH}-\mathrm{pKa}} = 10^{\log_{10}\left(\frac{[A^-]}{[HA]}\right)} \tag{4}$$

$$10^{\mathrm{pH}-\mathrm{pKa}} = \frac{[A^-]}{[HA]} \tag{5}$$

However, what we want to graph is mass percent of species, not molar ratios. So we need to relate these two concepts for both species present. First we expand the right side of equation (5) based on the definition of molar concentration:

$$\frac{[A^-]}{[HA]} = \frac{\dfrac{\text{mol } A^-}{\cancel{L}}}{\dfrac{\text{mol } HA}{\cancel{L}}} \tag{6}$$

$$= \frac{\text{mol } A^-}{\text{mol } HA} \tag{7}$$

And noting that

$$\text{moles} = \left(\frac{\text{moles}}{\cancel{\text{grams}}}\right)(\cancel{\text{grams}}) \tag{8}$$

$$= \left(\frac{1}{\text{molar mass}}\right)(\text{grams}) \tag{9}$$

Equation (7) becomes

$$\frac{[A^-]}{[HA]} = \left(\frac{\text{g } A^-}{\text{g } HA}\right)\left(\frac{\mathrm{mm}_{HA}}{\mathrm{mm}_{A^-}}\right) \tag{10}$$

where mm_{HA} and mm_{A^-} are the molar masses of species HA and A^-, respectively. Now plugging equation (10) into equation (5), we get

$$10^{\mathrm{pH}-\mathrm{pKa}} = \left(\frac{\text{g } A^-}{\text{g } HA}\right)\left(\frac{\mathrm{mm}_{HA}}{\mathrm{mm}_{A^-}}\right) \tag{11}$$

$$\frac{\text{g } A^-}{\text{g } HA} = \left(\frac{\mathrm{mm}_{A^-}}{\mathrm{mm}_{HA}}\right)\left(10^{\mathrm{pH}-\mathrm{pKa}}\right) \tag{12}$$

We take a basis of 100 grams ($\text{g } A^- + \text{g } HA = 100$) so we can equate grams to percent in equation (12):

$$\frac{\%\ A^-}{\%\ HA} = \left(\frac{\mathrm{mm}_{A^-}}{\mathrm{mm}_{HA}}\right)\left(10^{\mathrm{pH}-\mathrm{pKa}}\right) \tag{13}$$

And noting that since

$$\% A^- + \% HA = 100 \tag{14}$$

$$\% A^- = 100 - \% HA \tag{15}$$

We now plug equation (15) into (13) to obtain

$$\frac{100 - \% HA}{\% HA} = \left(\frac{\mathrm{mm}_{A^-}}{\mathrm{mm}_{HA}}\right)\left(10^{\mathrm{pH}-\mathrm{pKa}}\right) \tag{16}$$

The last (and arguably most difficult) step is to solve for % HA:

$$\%HA = \frac{10^{2+\mathrm{pKa}}\mathrm{mm}_{HA}}{10^{\mathrm{pH}}\mathrm{mm}_{A} + 10^{\mathrm{pKa}}\mathrm{mm}_{HA}} \tag{17}$$

Since pKa, mm_{HA}, and mm_{A} are constants, equation (17) gives mass percent of HA (the active, undissociated bioside) relative to the sum of both biocide species as a function of pH of the system. Figure 1 gives curves based on this equation for several representative weak-acid biocides.

Figure 1 represents the practical purpose of this paper; by interpreting it we can determine how much usable biocide we have as a function of the pH of the system. The left axis represents weight % of a particular species relative to the sum of all biocide species present in the solution, while the bottom axis covers the range of pHs over which the speciation varies. Now for an example: if we want to know how much of our PAA is available at a pH of 7.5, first we find 7.5 on the bottom axis, and the draw a vertical line up until it intersects the PAA curve. Then draw a horizontal line from that point to the left axis - where it intersects this axis tells you the percent of your PAA concentration is available for antimicrobial action. In this case, we have a little more than 83% of our PAA in the undissociated form. Again, what this means practically is that if your test kit reads 200 ppm PAA at a pH of 7.5, you can expect the same biocidal efficacy as a solution of 167 ppm PAA that was at a pH of 6 or less. This same procedure can be applied to any line in the chart.

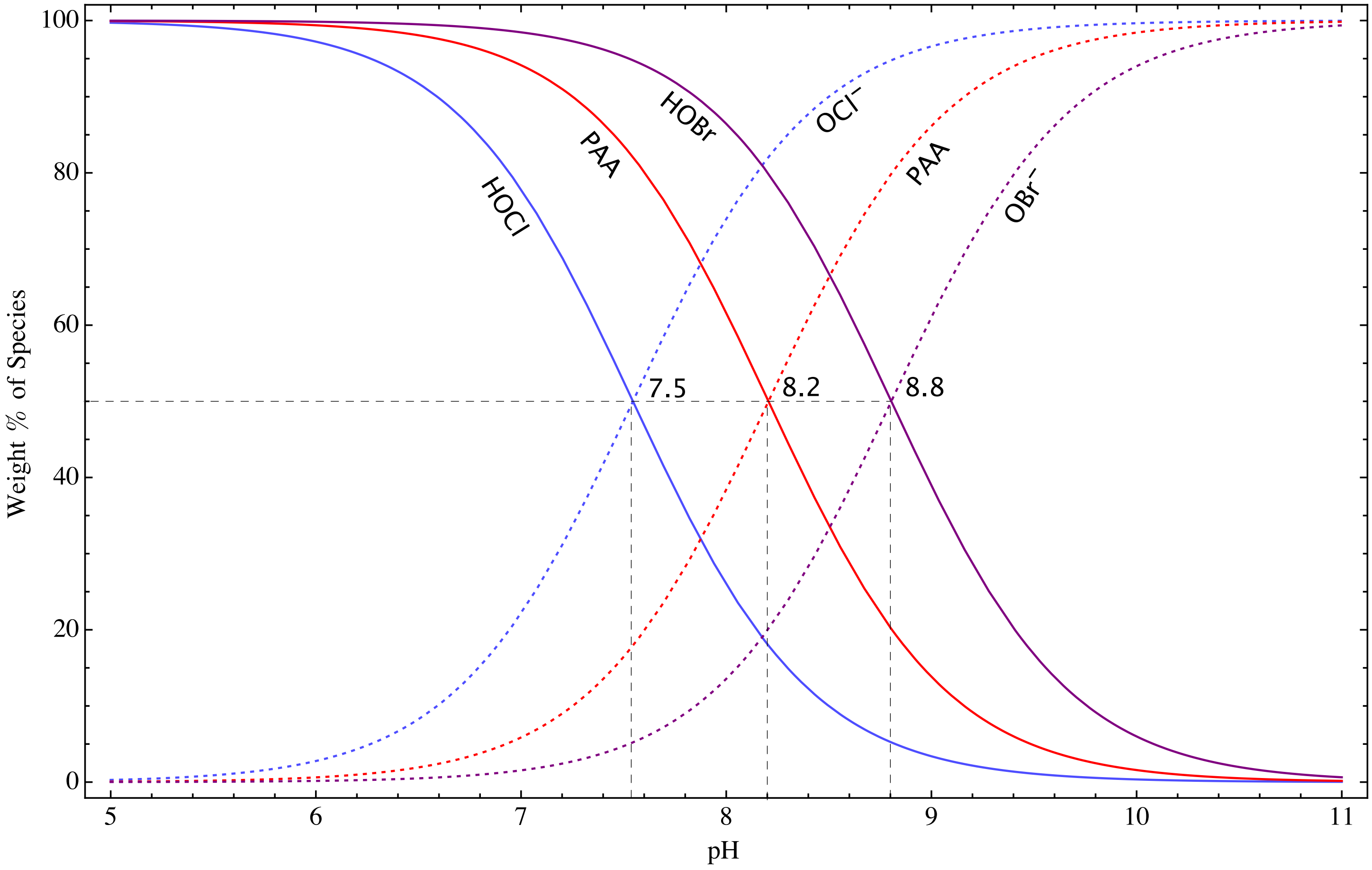

Figure 1: Sample speciation curves for three representative biocides. HOCl is common sodium hypochlorite bleach, PAA is peracetic acid such as Perasan® or BioSide HS-15%, and HOBr is hypobromous acid from a source such as HB2®. The pKa vaues of each biocide are listed at the 50% level.