Derivation of the pK_a-equations for fitting of absorption data

1 Two species: AH and A^- ≙ one pK_a-value

Consider the following acid-base equilibrium:

$$AH \overset{K_1}{\rightleftharpoons} A^- + H^+ \quad , \text{with } K_1 = \frac{[A^-]\cdot[H^+]}{[AH]}$$

Both species, AH and A^-, show an UV absorption δ:

$$\delta_{total}\cdot([AH]+[A^-]) = \delta_{AH}\cdot[AH]+\delta_A\cdot[A^-]$$

Taking both equations together gives the following expression:

$$\delta_{total}\cdot\left(\frac{[A^-]\cdot[H^+]}{K_1}+[A^-]\right) = \delta_{AH}\cdot\frac{[A^-]\cdot[H^+]}{K_1}+\delta_A\cdot[A^-]$$

$$\Leftrightarrow \delta_{total}\cdot\left(\frac{10^{-pH}}{10^{-pK_1}}+1\right) = \delta_{AH}\cdot\frac{10^{-pH}}{10^{-pK_1}}+\delta_A$$

$$\Leftrightarrow \boxed{\delta_{total} = \frac{\delta_A+\delta_{AH}\cdot 10^{pK_1-pH}}{1+10^{pK_1-pH}}}$$

2 Three species: AH_2, AH^-, and A^{2-} ≙ two pK_a-values

Consider the following acid-base equilibria:

$$AH^- \overset{K_1}{\rightleftharpoons} A^{2-} + H^+ \quad , \text{with } K_1 = \frac{[A^{2-}]\cdot[H^+]}{[AH^-]} \quad \Leftrightarrow \quad [AH^-] = \frac{[A^{2-}]\cdot[H^+]}{K_1}$$

$$AH_2 \overset{K_2}{\rightleftharpoons} AH^- + H^+ \quad , \text{with } K_2 = \frac{[AH^-]\cdot[H^+]}{[AH_2]} \quad \Leftrightarrow \quad [AH_2] = \frac{[A^{2-}]\cdot[H^+]^2}{K_1K_2}$$

All species, AH_2, AH^- and A^{2-}, show an UV absorption δ:

$$\delta_{total}\cdot([AH_2]+[AH^-]+[A^{2-}]) = \delta_{AH2}\cdot[AH_2]+\delta_{AH}\cdot[AH^-]+\delta_A\cdot[A^{2-}]$$

Taking all three equations together gives the following expression:

$$\delta_{total}\cdot\left(\frac{[A^{2-}]\cdot[H^+]^2}{K_1K_2}+\frac{[A^{2-}]\cdot[H^+]}{K_1}+[A^{2-}]\right) = \delta_{AH2}\cdot\frac{[A^{2-}]\cdot[H^+]^2}{K_1K_2}+\delta_{AH}\cdot\frac{[A^{2-}]\cdot[H^+]}{K_1}+\delta_A\cdot[A^{2-}]$$

$$\Leftrightarrow \delta_{total}\cdot\left(\frac{10^{-2pH}}{10^{-(pK_1+pK_2)}}+\frac{10^{-pH}}{10^{-pK_1}}+1\right) = \delta_{AH2}\cdot\frac{10^{-2pH}}{10^{-(pK_1+pK_2)}}+\delta_{AH}\cdot\frac{10^{-pH}}{10^{-pK_1}}+\delta_A$$

$$\Leftrightarrow \boxed{\delta_{total} = \frac{\delta_A+\delta_{AH}\cdot 10^{pK_1-pH}+\delta_{AH2}\cdot 10^{pK_1+pK_2-2pH}}{1+10^{pK_1-pH}+10^{pK_1+pK_2-2pH}}}$$

3 Four species: AH_3, AH_2^-, AH^{2-}, and A^{3-} ≙ three pK_a-values

Consider the following acid-base equilibria:

$$AH^{2-} \overset{K_1}{\rightleftharpoons} A^{3-} + H^+ \quad \text{, with } K_1 = \frac{[A^{3-}]\cdot[H^+]}{[AH^{2-}]} \quad <=> \quad [AH^{2-}] = \frac{[A^{3-}]\cdot[H^+]}{K_1}$$

$$AH_2^- \overset{K_2}{\rightleftharpoons} AH^{2-} + H^+ \quad \text{, with } K_2 = \frac{[AH^{2-}]\cdot[H^+]}{[AH_2^-]} \quad <=> \quad [AH_2^-] = \frac{[A^{3-}]\cdot[H^+]^2}{K_1K_2}$$

$$AH_3 \overset{K_3}{\rightleftharpoons} AH_2^- + H^+ \quad \text{, with } K_3 = \frac{[AH_2^-]\cdot[H^+]}{[AH_3]} \quad <=> \quad [AH_3] = \frac{[A^{3-}]\cdot[H^+]^3}{K_1K_2K_3}$$

All species, AH_3, AH_2^-, AH^{2-} and A^{3-}, show an UV absorption δ:

$$\delta_{total}\cdot([AH_3]+[AH_2^-]+[AH^{2-}]+[A^{3-}]) = \delta_{AH3}\cdot[AH_3]+\delta_{AH2}\cdot[AH_2^-]+\delta_{AH}\cdot[AH^{2-}]+\delta_A\cdot[A^{3-}]$$

Taking all three equations together gives the following expression:

$$\delta_{total}\cdot\left(\frac{[A^{3-}]\cdot[H^+]^3}{K_1K_2K_3}+\frac{[A^{3-}]\cdot[H^+]^2}{K_1K_2}+\frac{[A^{3-}]\cdot[H^+]}{K_1}+[A^{3-}]\right)$$

$$= \delta_{AH3}\cdot\frac{[A^{3-}]\cdot[H^+]^3}{K_1K_2K_3}+\delta_{AH2}\cdot\frac{[A^{3-}]\cdot[H^+]^2}{K_1K_2}+\delta_{AH}\cdot\frac{[A^{3-}]\cdot[H^+]}{K_1}+\delta_A\cdot[A^{3-}]$$

$$<=> \delta_{total}\cdot\left(\frac{10^{-3pH}}{10^{-(pK_1+pK_2+pK_3)}}+\frac{10^{-2pH}}{10^{-(pK_1+pK_2)}}+\frac{10^{-pH}}{10^{-pK_1}}+1\right)=\delta_{AH3}\cdot\frac{10^{-3pH}}{10^{-(pK_1+pK_2+pK_3)}}+\delta_{AH2}\cdot\frac{10^{-2pH}}{10^{-(pK_1+pK_2)}}+\delta_{AH}\cdot\frac{10^{-pH}}{10^{-pK_1}}+\delta_A$$

$$<=> \quad \boxed{\delta_{total} = \frac{\delta_A+\delta_{AH}\cdot10^{pK_1-pH}+\delta_{AH2}\cdot10^{pK_1+pK_2-2pH}+\delta_{AH3}\cdot10^{pK_1+pK_2+pK_3-3pH}}{1+10^{pK_1-pH}+10^{pK_1+pK_2-2pH}+10^{pK_1+pK_2+pK_3-3pH}}}$$

4 Assume two pK_a-values are (nearly) equal, e.g. pK_1 and pK_2

$$=> \quad \boxed{\delta_{total} = \frac{\delta_A+\delta_{AH}\cdot10^{pK_1-pH}+\delta_{AH2}\cdot10^{2pK_1-2pH}+\delta_{AH3}\cdot10^{2pK_1+pK_3-3pH}}{1+10^{pK_1-pH}+10^{2pK_1-2pH}+10^{2pK_1+pK_3-3pH}}}$$

5 And so on...