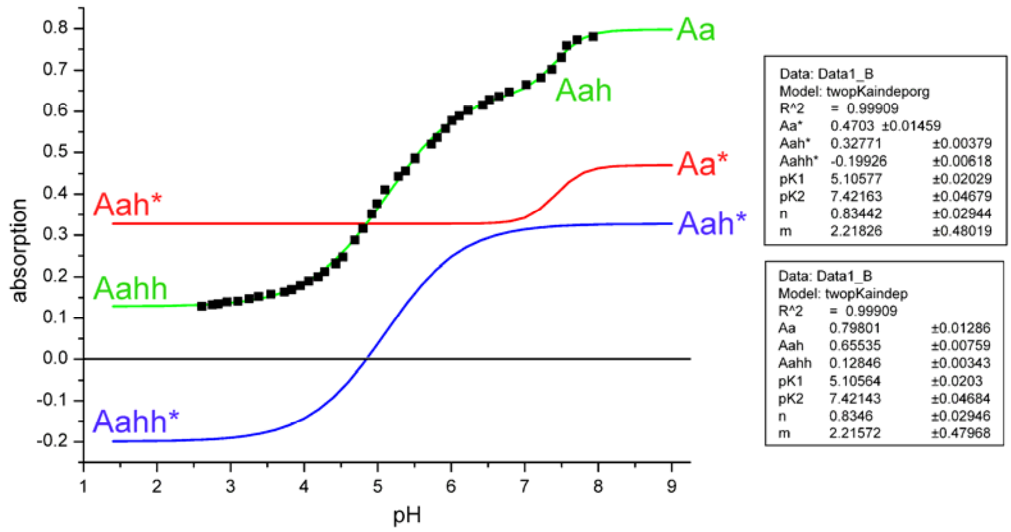
Derivatisation of eqation for fitting of pH titration curve with two independent pK_a values



Application of the "normal" setting of the equation as derived in E. Freisinger (2007), *Inorg. Chim. Acta*, 360, 369-380:

$$A_{total} = \frac{A_{Aah*} + A_{Aahh*}10^{n(pK_1 - pH)}}{1 + 10^{n(pK_1 - pH)}} + \frac{A_{Aa*} + A_{Aah*}10^{m(pK_2 - pH)}}{1 + 10^{m(pK_2 - pH)}}$$

(equation twopKaindeporg)

yields the green curve in the Figure above, but absolute values for the single absorption steps are different than those resulting from a curve fit with the equation derived from two dependent pK_a values (see Lit above).

What is the reason for this? Well, the equation for two independent pK_a values consists of two independent terms, each describing one acid-base equilibrium. The first term results in the blue curve, while the second one gives the red curve. Only the sum of both describes the green curve.

What to do to get "comparable" absorption values? Well, one possibility is to shift the curve along the y axis so that Aahh* becomes Aahh obtained with the equation for two dependent pK_a values. Alternatively, this shift can be incorporated into the equation as follows:

1) Aah* = 0.5 Aah (as Aah* + Aah* result in Aah)

2) Aah – Aahh = Aah* – Aahh* (i.e. the steps have always the same "height")

$\Rightarrow$ Aahh* = Aahh – 0.5 Aah

3) Aa – Aah = Aa* – Aah* (i.e. the steps have always the same "height")

$\Rightarrow$ Aa* = Aa – 0.5 Aah

Putting 1 – 3 into the equation above, we obtain the following, which describes the same green curve depicted above, but yielding values as with the equation for two dependent pK_a values:

$$A_{total} = \frac{0.5A_{Aah} + (A_{Aahh} - 0.5A_{Aah})10^{n(pK_1 - pH)}}{1 + 10^{n(pK_1 - pH)}} + \frac{A_{Aa} - 0.5A_{Aah} + 0.5A_{Aah}10^{m(pK_2 - pH)}}{1 + 10^{m(pK_2 - pH)}}$$

(equation twopKaindep)