Supplementary Material for:

# Dynamical Approach to Multi-Equilibria Problems Considering Debye–Hückel Theory of Electrolyte Solutions. Concentration Quotients as a Function of Ionic Strength

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**Table S1** Comparison of experimental and computed pH values

| Multi-Equlibria System | | Ref. [35][a] | | Our calculations | | | | | | Ref. [36] method | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $pH_{exp}$ | $pH_{con}$ $I = 0$ | $pH_{con}$ $b = 0$ G'berg[b] | $pH_{con}$ $b = 0.2$ Davies | $pH_{con}$ $b = 0.1$ Davies | $pH_{act}$ $b = 0$ G'berg[b] | $pH_{act}$ $b = 0.2$ Davies | $pH_{act}$ $b = 0.1$ Davies | $pH_{con}$ $b = 0.1$ Davies | $pH_{act}$ $b = 0.1$ Davies |
| Acetate buffer | | | | | | | | | | | |
| HAc $(mol \cdot L^{-1})$ | NaAc $(mol \cdot L^{-1})$ | | | | | | | | | | |
| 0.0926 | 0.0074 | 3.6 | 3.68 | 3.60 | 3.60 | 3.60 | 3.63 | 3.63 | 3.63 | 3.60 | 3.64 |
| 0.088 | 0.012 | 3.8 | 3.90 | 3.80 | 3.80 | 3.80 | 3.84 | 3.84 | 3.84 | 3.80 | 3.85 |
| 0.082 | 0.018 | 4.0 | 4.10 | 3.98 | 3.99 | 3.99 | 4.03 | 4.03 | 4.03 | 3.99 | 4.04 |
| 0.0736 | 0.0264 | 4.2 | 4.32 | 4.17 | 4.18 | 4.18 | 4.23 | 4.23 | 4.23 | 4.18 | 4.25 |
| 0.061 | 0.039 | 4.4 | 4.57 | 4.40 | 4.41 | 4.40 | 4.46 | 4.47 | 4.46 | 4.40 | 4.48 |
| 0.051 | 0.049 | 4.6 | 4.74[e] | 4.56 | 4.57 | 4.56 | 4.63 | 4.64 | 4.63 | 4.56 | 4.65[d] |
| 0.04 | 0.06 | 4.8 | 4.94 | 4.74 | 4.75 | 4.74 | 4.81 | 4.82 | 4.82 | 4.74 | 4.84 |
| 0.0296 | 0.0704 | 5.0 | 5.14 | 4.92 | 4.94 | 4.93 | 5.00 | 5.02 | 5.01 | 4.93 | 5.03 |
| 0.021 | 0.079 | 5.2 | 5.34 | 5.11 | 5.13 | 5.12 | 5.19 | 5.21 | 5.20 | 5.12 | 5.23 |
| 0.0176 | 0.0824 | 5.4 | 5.43 | 5.20 | 5.22 | 5.21 | 5.29 | 5.30 | 5.30 | 5.21 | 5.32 |
| 0.0096 | 0.0904 | 5.6 | 5.73 | 5.50 | 5.52 | 5.51 | 5.59 | 5.60 | 5.59 | 5.51 | 5.62 |
| Citric acid titration | | | | | | | | | | | |
| Citric acid $(mol \cdot L^{-1})$ | NaOH $(mol \cdot L^{-1})$ | | | | | | | | | | |
| 0.2 | 0.02 | 2.15 | 2.29 | 2.19 | 2.19 | 2.19 | 2.25 | 2.25 | 2.26 | 2.17 | 2.24 |
| 0.2 | 0.04 | 2.39 | 2.56 | 2.43 | 2.44 | 2.43 | 2.50 | 2.50 | 2.52 | 2.40 | 2.48 |
| 0.2 | 0.06 | 2.58 | 2.77 | 2.61 | 2.62 | 2.62 | 2.69 | 2.70 | 2.72 | 2.57 | 2.67 |
| 0.2 | 0.08 | 2.75 | 2.95 | 2.77 | 2.78 | 2.77 | 2.86 | 2.86 | 2.88 | 2.72 | 2.83 |
| 0.2 | 0.10 | 2.89 | 3.11 | 2.91 | 2.92 | 2.91 | 3.00 | 3.01 | 3.03 | 2.86 | 2.98 |
| 0.2 | 0.12 | 3.04 | 3.26 | 3.04 | 3.05 | 3.04 | 3.14 | 3.15 | 3.17 | 2.98 | 3.11 |

| 0.2 | 0.14 | 3.18 | 3.42$^e$ | 3.16 | 3.18 | 3.17 | 3.27 | 3.29 | 3.31 | 3.11 | 3.24$^c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.2 | 0.16 | 3.32 | 3.59 | 3.29 | 3.31 | 3.30 | 3.41 | 3.42 | 3.44 | 3.23 | 3.38 |
| 0.2 | 0.18 | 3.46 | 3.76 | 3.41 | 3.45 | 3.43 | 3.54 | 3.56 | 3.58 | 3.36 | 3.51 |
| 0.2 | 0.20 | 3.59 | 3.94 | 3.54 | 3.58 | 3.56 | 3.67 | 3.70 | 3.71 | 3.48 | 3.64 |
| 0.2 | 0.22 | 3.75 | 4.13 | 3.66 | 3.71 | 3.68 | 3.80 | 3.83 | 3.84 | 3.60 | 3.76 |
| 0.2 | 0.24 | 3.90 | 4.30 | 3.77 | 3.83 | 3.80 | 3.92 | 3.96 | 3.96 | 3.72 | 3.88 |
| 0.2 | 0.26 | 4.03 | 4.46 | 3.87 | 3.95 | 3.91 | 4.03 | 4.09 | 4.08 | 3.83 | 4.00 |
| 0.2 | 0.28 | 4.14 | 4.61 | 3.97 | 4.06 | 4.02 | 4.14 | 4.21 | 4.19 | 3.94 | 4.12 |
| 0.2 | 0.30 | 4.27 | 4.76 | 4.07 | 4.18 | 4.13 | 4.24 | 4.32 | 4.30 | 4.05 | 4.23 |
| 0.2 | 0.32 | 4.37 | 4.91 | 4.17 | 4.29 | 4.23 | 4.35 | 4.44 | 4.41 | 4.16 | 4.34 |
| 0.2 | 0.34 | 4.50 | 5.06$^e$ | 4.27 | 4.41 | 4.34 | 4.45 | 4.56 | 4.53 | 4.27 | 4.45$^c$ |
| 0.2 | 0.36 | 4.62 | 5.22 | 4.37 | 4.54 | 4.45 | 4.56 | 4.69 | 4.64 | 4.38 | 4.57 |
| 0.2 | 0.38 | 4.74 | 5.40 | 4.47 | 4.66 | 4.57 | 4.67 | 4.82 | 4.76 | 4.50 | 4.69 |
| 0.2 | 0.40 | 4.87 | 5.58 | 4.57 | 4.79 | 4.68 | 4.78 | 4.95 | 4.88 | 4.62 | 4.81 |
| 0.2 | 0.42$^c$ | 4.98 | 5.77 | 4.68 | 4.93 | 4.80 | 4.88 | 5.09 | 5.00 | 4.74 | 4.94 |
| 0.2 | 0.44 | 5.11 | 5.94 | 4.78 | 5.06 | 4.92 | 4.99 | 5.22 | 5.12 | 4.86 | 5.06 |
| 0.2 | 0.46 | 5.21 | 6.11 | 4.88 | 5.20 | 5.04 | 5.10 | 5.36 | 5.24 | 4.99 | 5.19 |
| 0.2 | 048$^c$ | 5.34 | 6.27 | 4.99 | 5.34 | 5.16 | 5.21 | 5.50 | 5.36 | 5.11 | 5.32 |
| 0.2 | 0.50 | 5.49 | 6.43 | 5.10 | 5.48 | 5.29 | 5.33 | 5.65 | 5.49 | 5.25 | 5.45 |
| 0.2 | 0.52 | 5.63 | 6.59 | 5.23 | 5.64 | 5.43 | 5.46 | 5.80 | 5.64 | 5.40 | 5.60 |
| 0.2 | 0.54$^c$ | 5.80 | 6.78 | 5.38 | 5.83 | 5.60 | 5.61 | 5.99 | 5.81 | 5.57 | 5.77 |
| 0.2 | 0.56$^c$ | 6.02 | 7.01$^e$ | 5.57 | 6.06 | 5.82 | 5.81 | 6.22 | 6.02 | 5.79 | 5.99$^c$ |
| 0.2 | 0.58$^c$ | 6.33 | 7.36 | 5.89 | 6.41 | 6.15 | 6.14 | 6.57 | 6.36 | 6.13 | 6.34 |
| 0.2 | 0.59$^c$ | 6.51 | 7.68 | 6.20 | 6.74 | 6.47 | 6.45 | 6.89 | 6.67 | 6.45 | 6.66 |

Units of $b$, L·mol$^{-1}$

[a]Experimental data for citric acid titration reported to two digits, see Table 10.9 in ref. [3]. Experimental data for acetic acid buffer reported to one digit, see Table 10.18 in ref. [35]

[b] G'berg = Güntelberg

[c]Ionic strength values are given in Fig. 4. The $I$ values allow the determination of the highest pH values for which the above data and the graphs in Fig. 3 are within the recommended limits of the respective approximations

[d]Values computed with the Baeza–Baeza method, that are also presented in the ref. [36]

[e]The calculated value shown exactly matches the corresponding value presented in ref. [36]
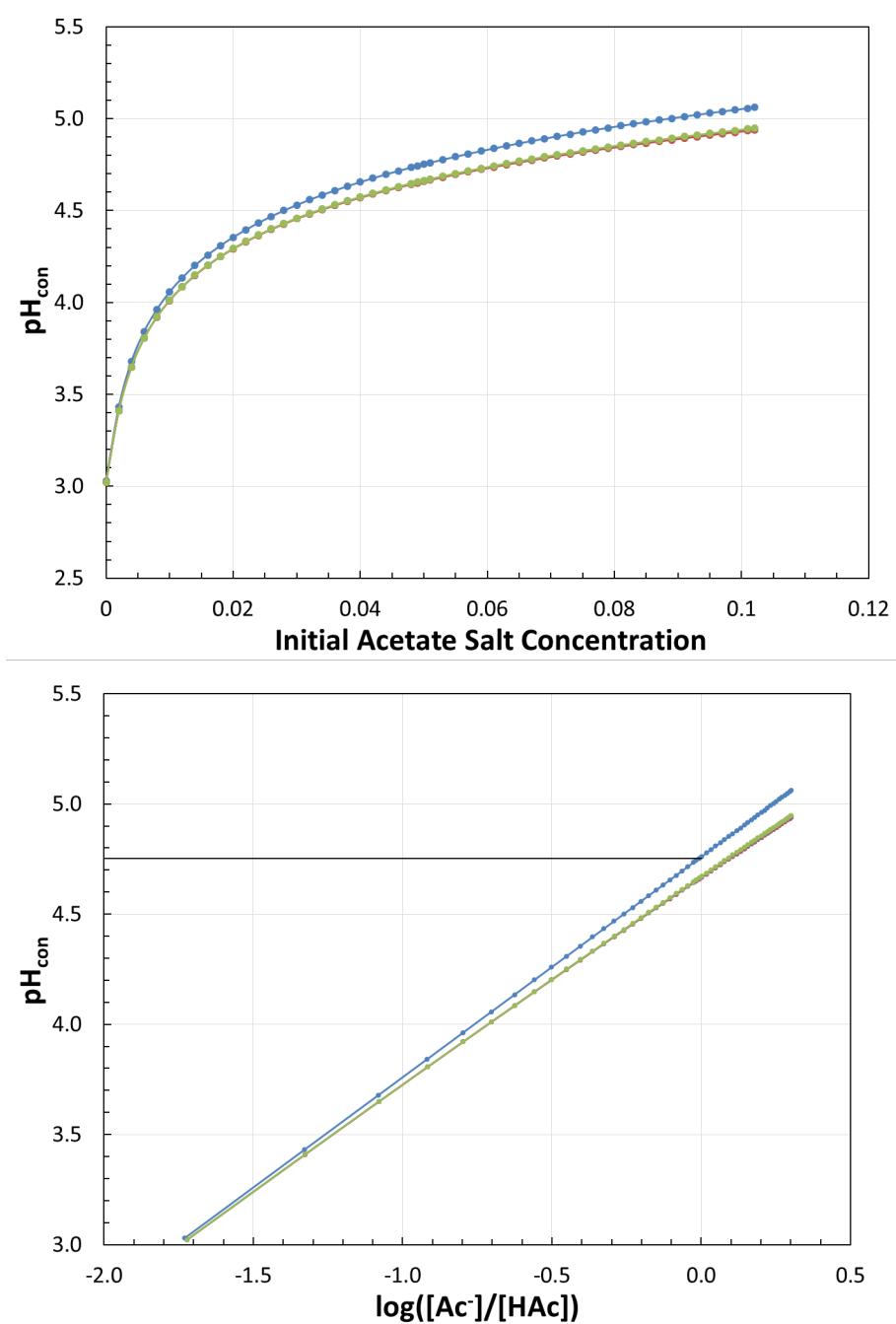
**Fig. S1** Computed $pH_{con}$ values of acetate-buffered acetic acid. Top plot: $pH_{con}$ as a function of the amount of added acetate. Bottom plot: $pH_{con}$ as a function of $\log_{10}([Ac^-]/[HAc]) = -\log_{10}([HAc]/[Ac^-])$. Line color represents different approximations to Debye–Hückel (DH) theory: $I = 0$ (blue, $pH_{con} = 4.76 + \log_{10}([Ac^-]/[HAc])$), Güntelberg (red, $pH_{con} = 4.6638 + 0.9371 \cdot \log_{10}([Ac^-]/[HAc])$), and Davies with $b = 0.1$ L·mol$^{-1}$ (purple, $pH_{con} = 4.6668 + 0.9403 \cdot \log_{10}([Ac^-]/[HAc])$) or $b = 0.2$ (green, $pH_{con} = 4.6698 + 0.9434 \cdot \log_{10}([Ac^-]/[HAc])$
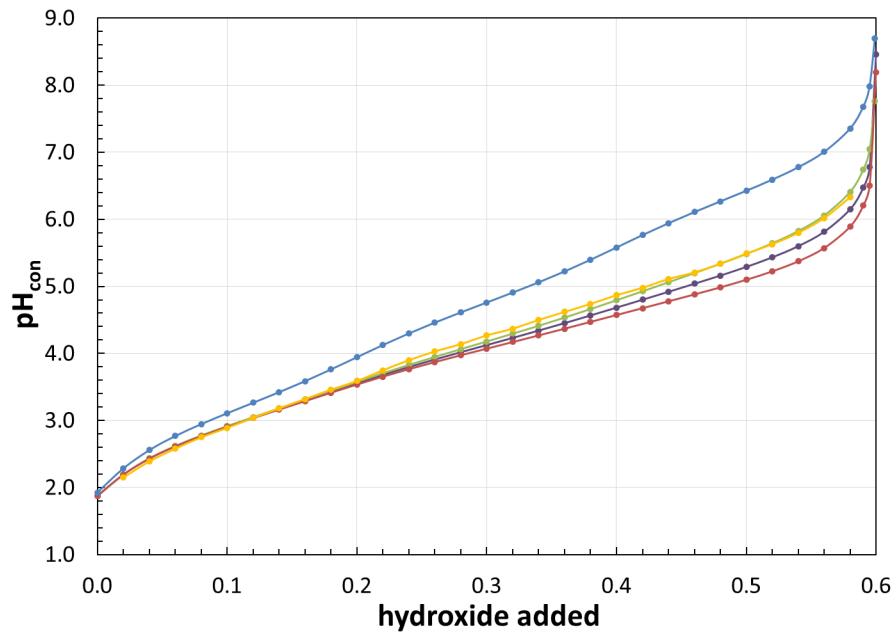
**Fig. S3** Computed $pH_{con}$ values of hydroxide titration of $0.2$ mol·L$^{-1}$ citric acid as a function of the amount of added hydroxide of the same concentration. Experimental data are shown in orange, and otherwise line color represents various approximations to the Debye–Hückel (DH) theory: $I = 0$ (red), Güntelberg (green), Davies with $b = 0.1$ L·mol$^{-1}$ (purple) or $b = 0.2$ L·mol$^{-1}$ (blue)
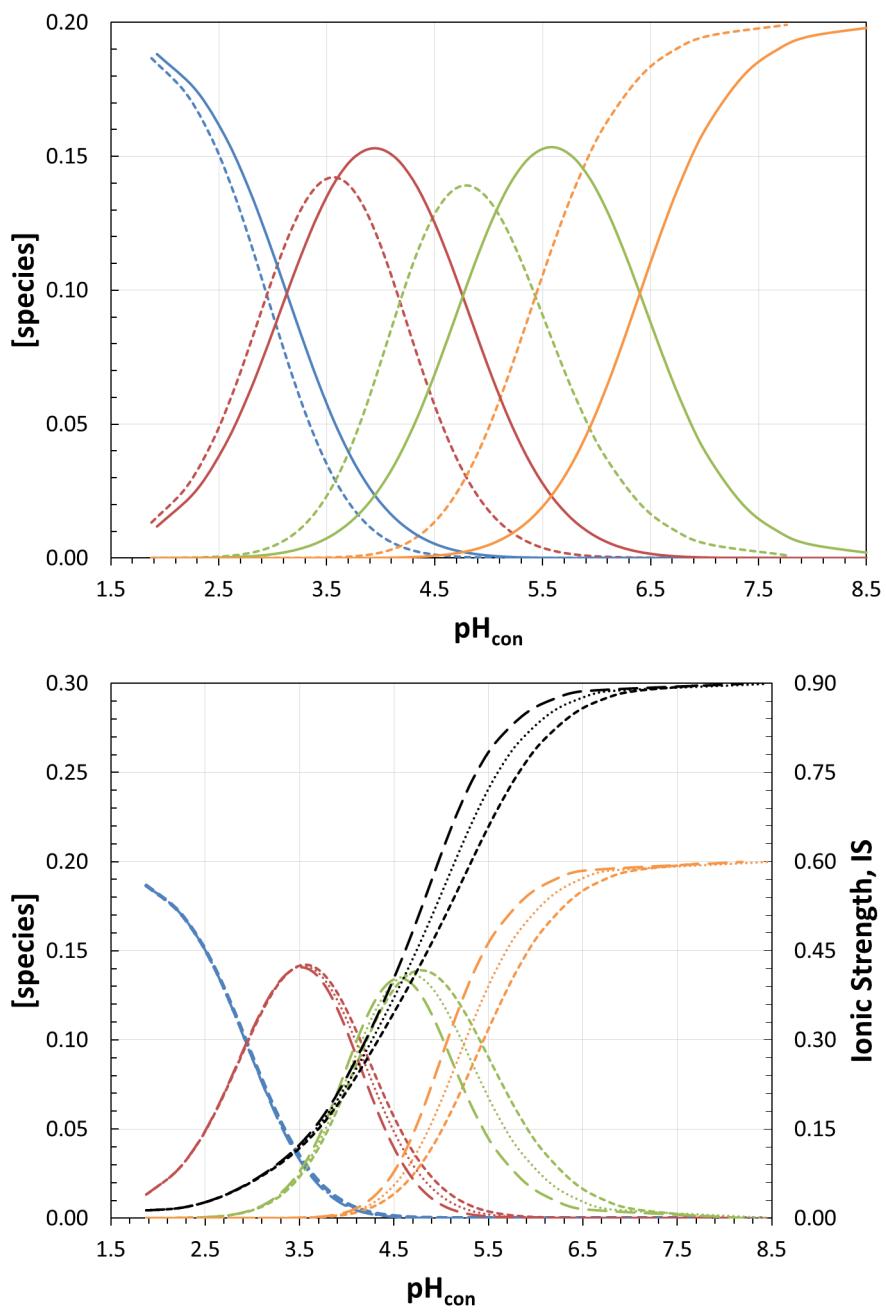
**Fig. S5** Species concentrations in hydroxide titration of 0.2 mol·L$^{-1}$ citric acid. Concentration of H$_3$A (blue), H$_2$A$^-$ (red), HA$^{2-}$ (green) and A$^{3-}$ (orange) as a function of pH$_{con}$. Line style represents approximations to the Debye–Hückel theory: $I = 0$ (solid), Güntelberg (long dash), Davies with $b = 0.1$ L·mol$^{-1}$ (dotted) or $b = 0.2$ L·mol$^{-1}$ (short dash). Top plot: ionic strength effect on concentrations. Bottom plot: effect of different DH approximations as function of concentration. Black curves show ionic strength calculated from the three DH methods
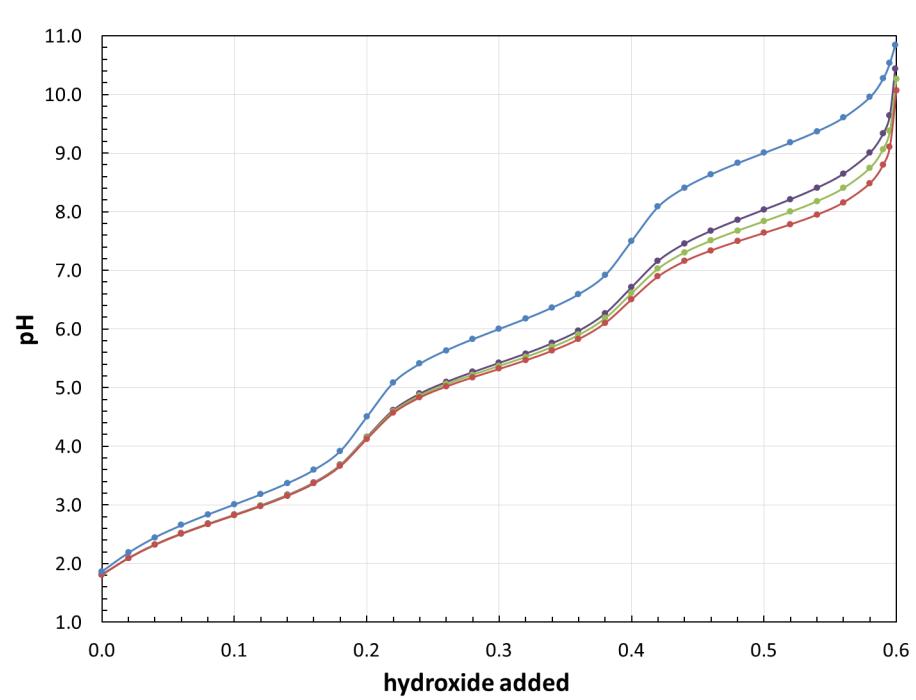
**Fig. S7** Hydroxide titration of a 0.2 mol·L$^{-1}$ triprotic model acid with p$K_a$ values of 3, 6, and 9. pH as a function of added amount of hydroxide ion of the same concentration. Line color represents various approximations to the Debye–Hückel (DH) theory: $I = 0$ (blue), Güntelberg (red), and Davies with $b = 0.1$ L·mol$^{-1}$ (purple) or $b = 0.2$ L·mol$^{-1}$ (green)
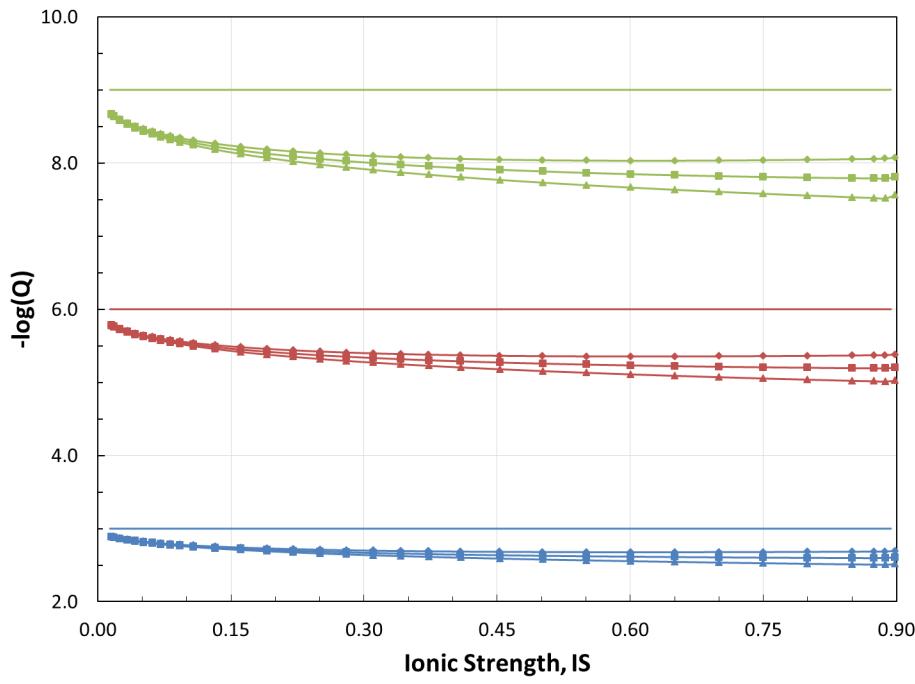
**Fig. S8** Hydroxide-titration of a 0.2 mol·L$^{-1}$ triprotic model acid. Negative logarithm of concentration quotient {$-\log_{10}(Q)$} as a function of ionic strength ($I$) with $Q = K_a^I =$ [H$^+$][B$^-$]/[HB]. Line colors identify the acid dissociation number: first (blue), second (red), and third (green) dissociation. Marker shape represents the DH approximation method: $I = 0$ (no marker), Güntelberg (triangle), and Davies with $b = 0.1$ L·mol$^{-1}$ (circle) or $b = 0.2$ L·mol$^{-1}$ (square)
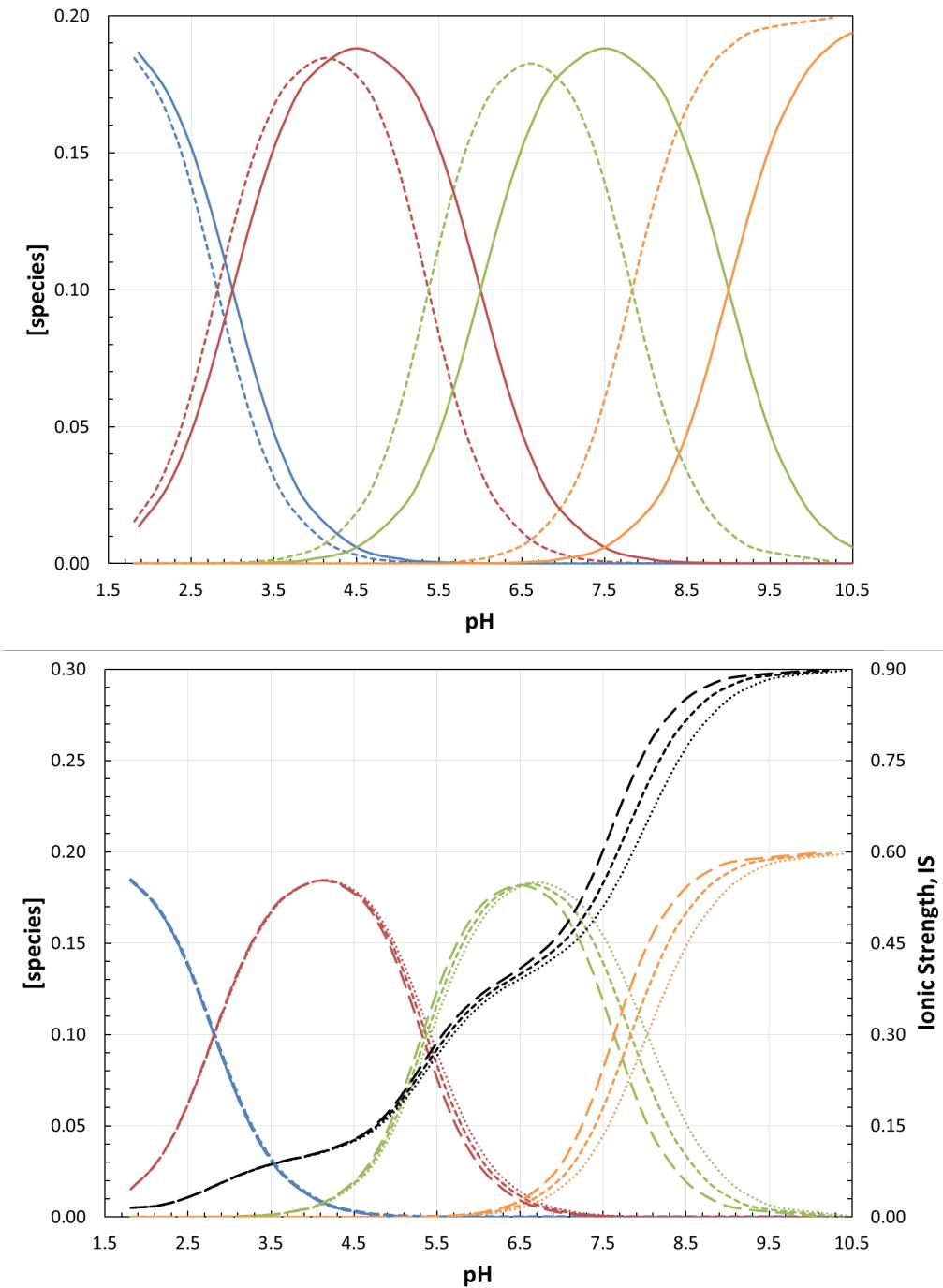
**Fig. S9** Hydroxide titration of 0.2 mol·L$^{-1}$ triprotic model acid with p$K_a$ values of 3, 6, and 9. Concentration of H$_3$A (blue), H$_2$A$^-$ (red), HA$^{2-}$ (green) and A$^{3-}$ (orange) as a function of the pH of the solution. Line style represents various approximations to the Debye–Hückel (DH) theory: $I = 0$ (solid), Güntelberg (long dash), Davies with $b = 0.1$ L·mol$^{-1}$ (dotted) or $b = 0.2$ L·mol$^{-1}$ (short dash). Top plot: ionic strength effect on concentrations. Bottom plot: effect of different

DH approximations on concentrations. Black curves show the ionic strength calculated from the three different DH methods