Supporting Information for:

The Poisson–Boltzmann model for implicit solvation of electrolyte solutions: Quantum chemical implementation and assessment via Sechenov coefficients

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I. Extrapolation for Debye–Hückel model

We used a linear extrapolation to zero excess charge for all converged data points (box sizes 15-35 Å) for Debye lengths of 3 Å, see Figure S1.

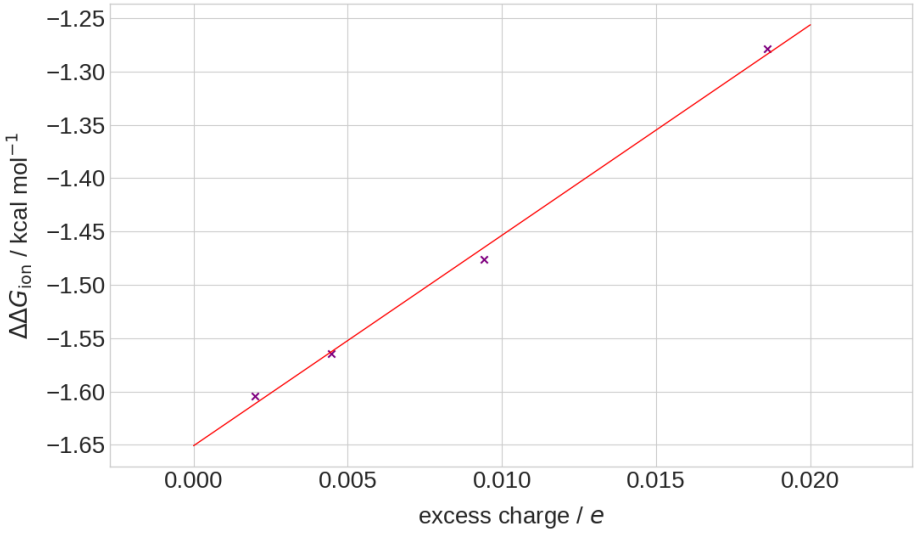

FIG. S1. Linear extrapolation of the Debye–Hückel model results for $\lambda = 3$ Å and an ion radius of $a = 2$ Å for all converged data points. The example shows the result for $\epsilon = 20$ and $l = 0.25$ Å, which is extrapolated to -1.651 kcal/mol.

For Debye lengths of 5 Å (Figure S2) we linearly extrapolate only the last four data points corresponding to box sizes of 35-50 Å, as these data points form a linear regime, which is not the case for smaller box sizes at this Debye length.

The ion contribution to the solvation free energy is not linear for the larger excess charges present for Debye lengths of 25 Å, corresponding to very low electrolyte concentrations. We empirically found that a fit to the simple polynomial expression

$$\Delta\Delta G_{\text{ion}}(x) = \Delta\Delta G_{\text{ion}}(x = 0) + bx^4 \tag{1}$$

with x being the excess charge, $\Delta\Delta G_{\text{ion}}(x = 0)$ being the extrapolated solvation free energy at zero excess charge, and an additional fitting parameter b allows a reasonably accurate extrapolation in this regime. The extrapolated region is much larger (see Figure S3) as for the shorter Debye lengths such that the reduced accuracy compared to the analytical results is not surprising. In future work we will assess variable grid spacing that allows us to use

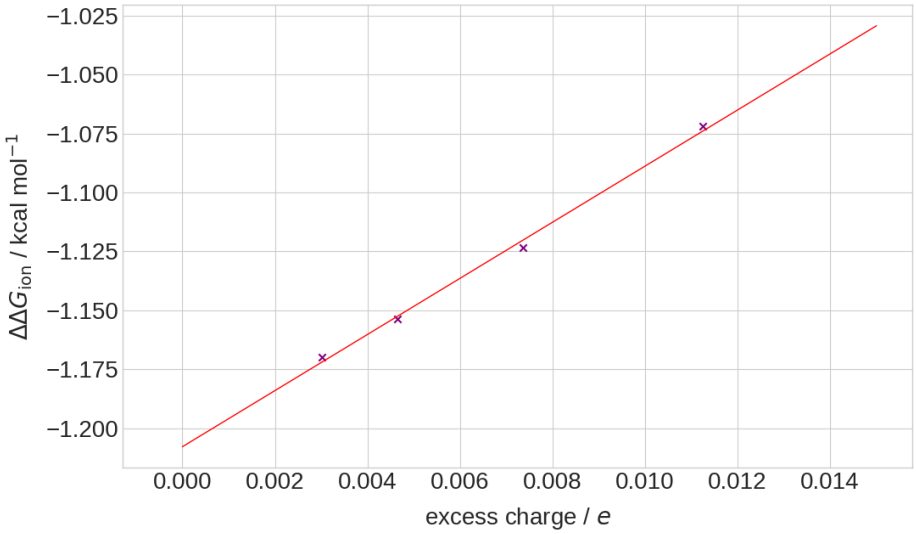

FIG. S2. Linear extrapolation of the Debye–Hückel model results for $\lambda = 5$ Å and an ion radius of $a = 2$ Å for all data points in the linear regime (large box sizes). The example shows the result for $\epsilon = 20$ and $l = 0.25$ Å, which is extrapolated to -1.208 kcal/mol.

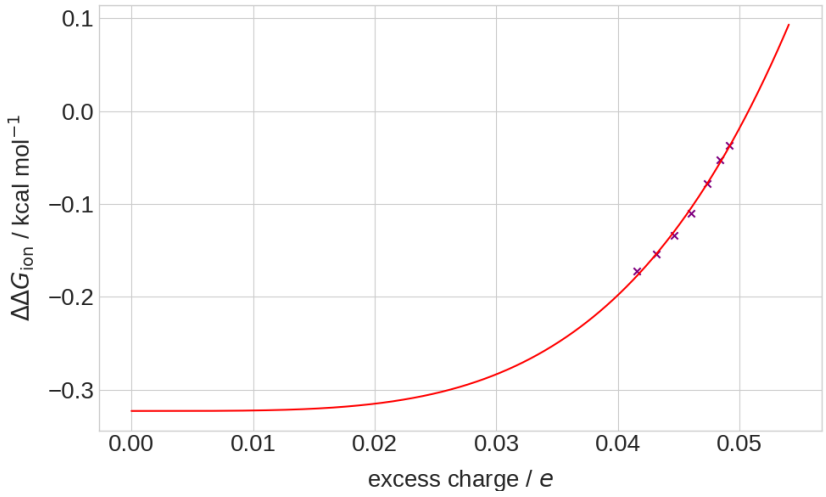

FIG. S3. Polynomial extrapolation of the Debye–Hückel model results for $\lambda = 25$ Å and an ion radius of $a = 2$ Å for all data points. The example shows the result for $\epsilon = 20$ and $l = 0.25$ Å, which is extrapolated to -0.323 kcal/mol.

much larger simulation boxes so that the linear regime can be reached also for these long Debye lengths.

II. Identification of optimal grid density

TABLE S1. Solvation free energy from the pure Onsager model (no electrolyte) with varying grid density factor f defined as the interpolation length l divided by the grid spacing s. Results are shown for a dipole moment of 0.76 D, an ion radius of $a = 1.0$ Å, and a dielectric permittivity of $\epsilon = 80.0$. The analytical solution is $E = -26.073$ kcal mol^{-1}.

points	grid spacing s [Å]	l [Å]	$f = l/s$	E [kcal mol^{-1}]	ΔE [kcal mol^{-1}]
153	0.0327	0.25	7.7	-27.296	-1.223
153	0.0327	0.125	3.8	-26.581	-0.508
153	0.0327	0.1	3.1	-26.431	-0.358
153	0.0327	0.05	1.5	-26.681	-0.608
305	0.0164	0.1	6.1	-26.479	-0.406
305	0.0164	0.05	3.1	-26.211	-0.138
305	0.0164	0.025	1.5	-26.674	-0.601

We define a grid density factor f as the interpolation length l divided by the grid spacing s as a measure for the average number of points along one axis in the interpolation region. Table S1 shows a smooth convergence to the analytical solution with decreasing interpolation length and grid spacing. However, for grid density factors below 3 (less than 3 points per axis in the interpolation region), the results get less accurate. Our implementation hence requires a minimum grid spacing of $l/3$ as stated in the main text.