Supporting Information for "Modeling ion binding to humic substances: Elastic polyelectrolyte network model"

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Figures S1 and S2 show fittings to the proposed model of acid-base titration data for several fulvic and humic acids, detailed in Tables 1 and 2 of the main article. Figure S3 shows additional results of humic volume as a function of pH. Figure S4 shows results for linear expansion ($\varphi_2^{-1/3}$). Figure S5 shows additional results for dimensionless Donnan potential (Ψ). Figure S6 shows results for merging of different proton binding curves on a single master curve. Appendix A gives a short account of Ohshima soft particle model. Appendix B contains a short account of Flory's statistical polymer network model. Appendix C gives details of the derivation of the electrostatic contribution to the swelling free energy. Finally, Appendix D compares volume predictions of this work with Donnan volume results from present models.

The citation numbers correspond to the references of the main text.

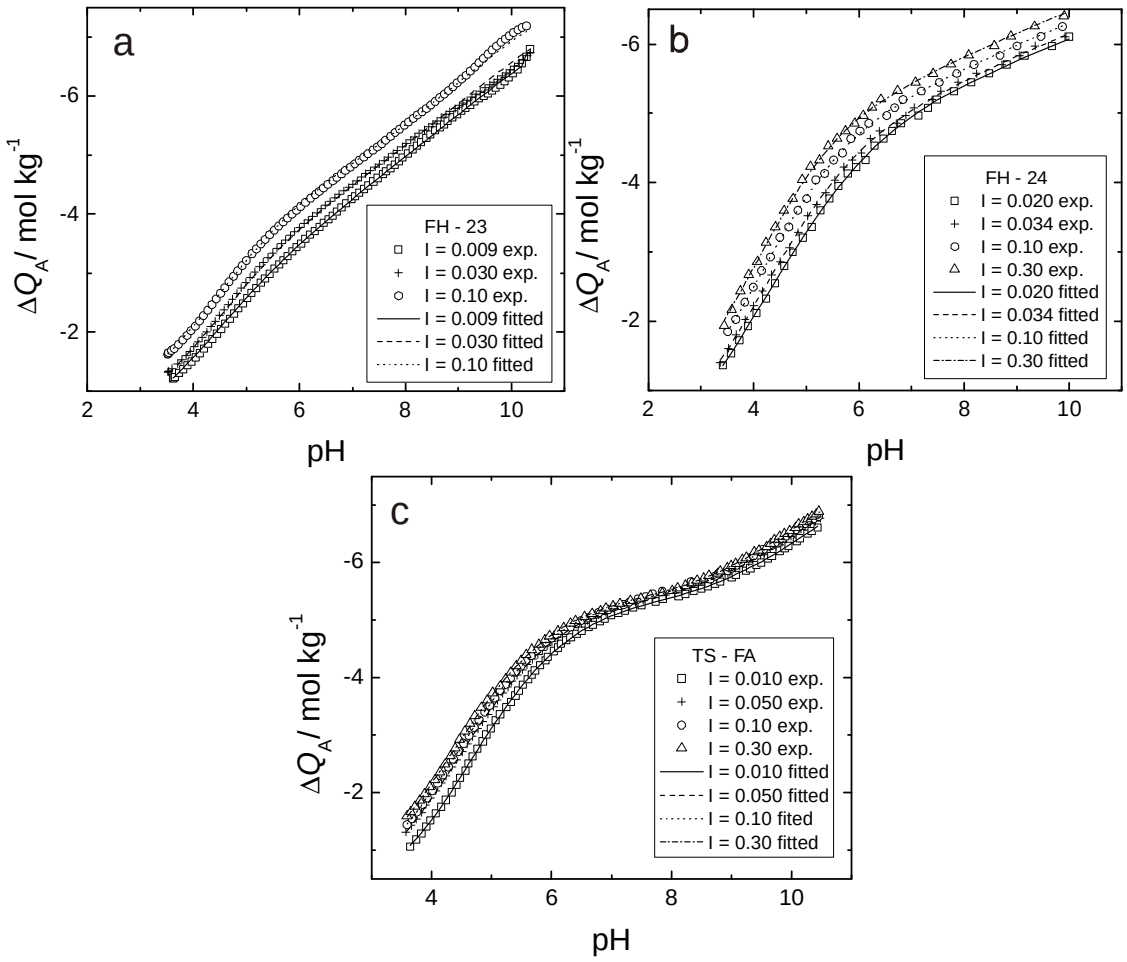


Figure S1. Model fitting result for fulvic acids: Laurentian soil (a), PUFA (b) and Toledo soil (c). Symbols indicate experimental results, lines are fitted curves. Ionic strengths are in molar units.

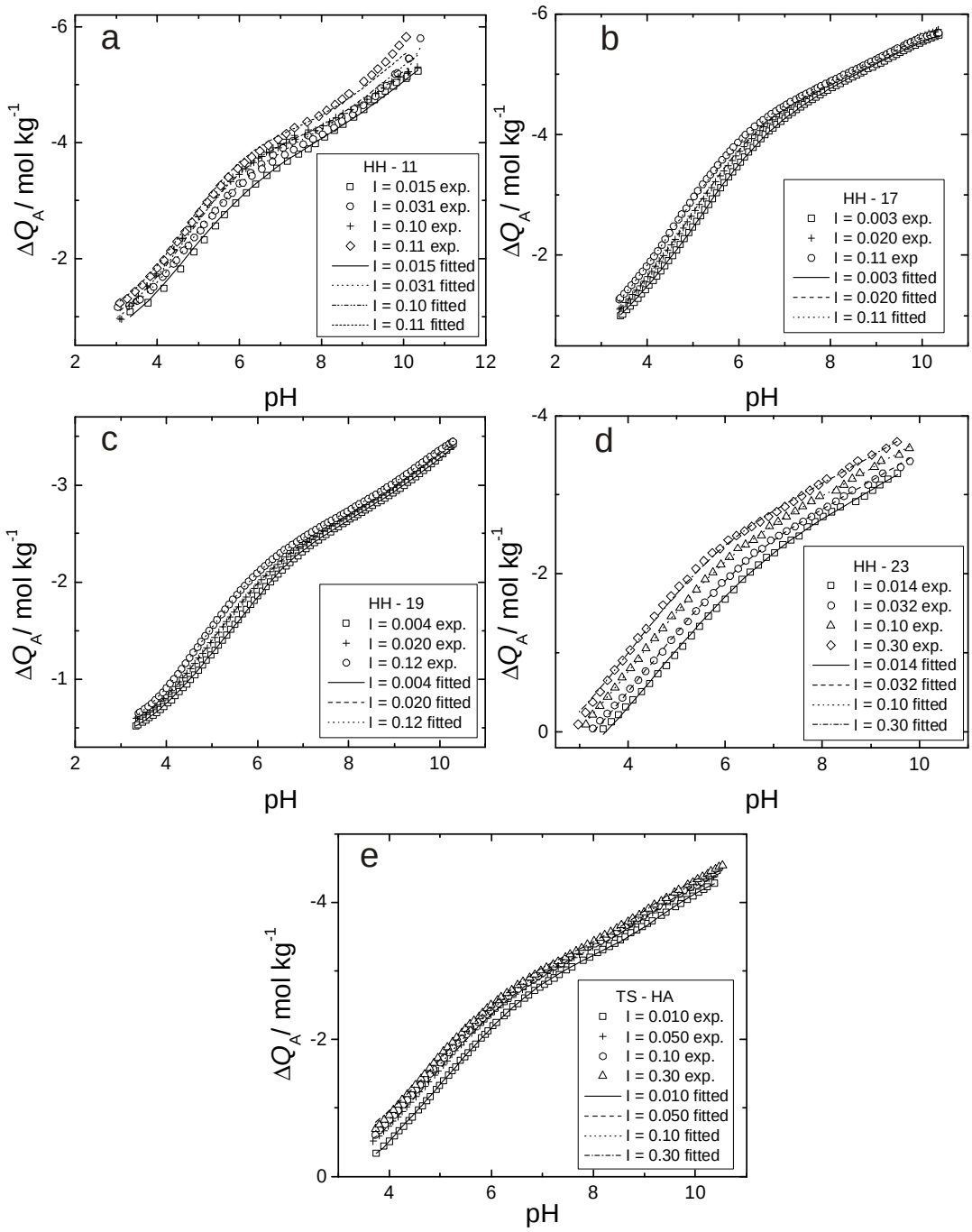


Figure S2. Model fitting result for humic acids: Elliot silt loam HA (a), Shitara Black HA (b), Tongbersven Forest HA (c) PUHA (d), and Toledo soil HA (e). Symbols indicate experimental results, lines are fitted curves. Ionic strengths are in molar units.

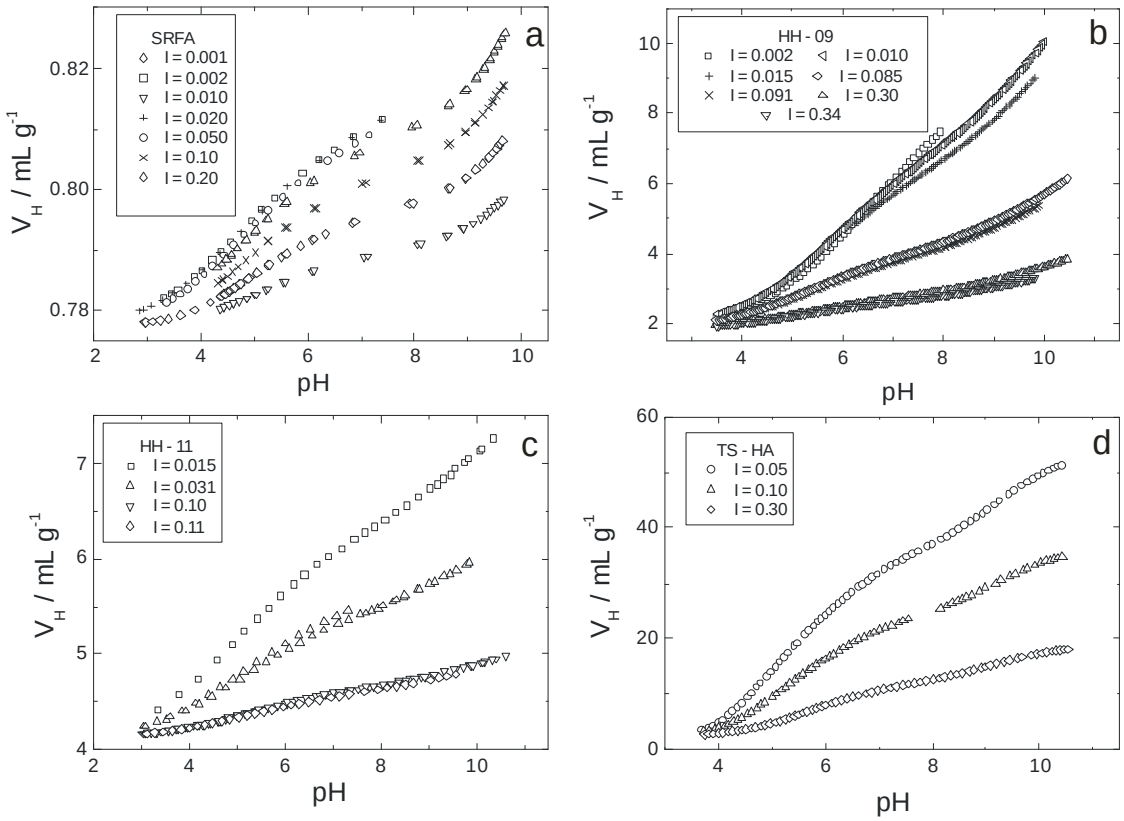


Figure S3. Total humic volume as a function of pH from EPN model results: (a) Suwannee River FA; (b) Purified Peat HA (PP-HA); (c) Eliot silt loam HA; (d) Toledo soil HA. Ionic strengths are in molar units.

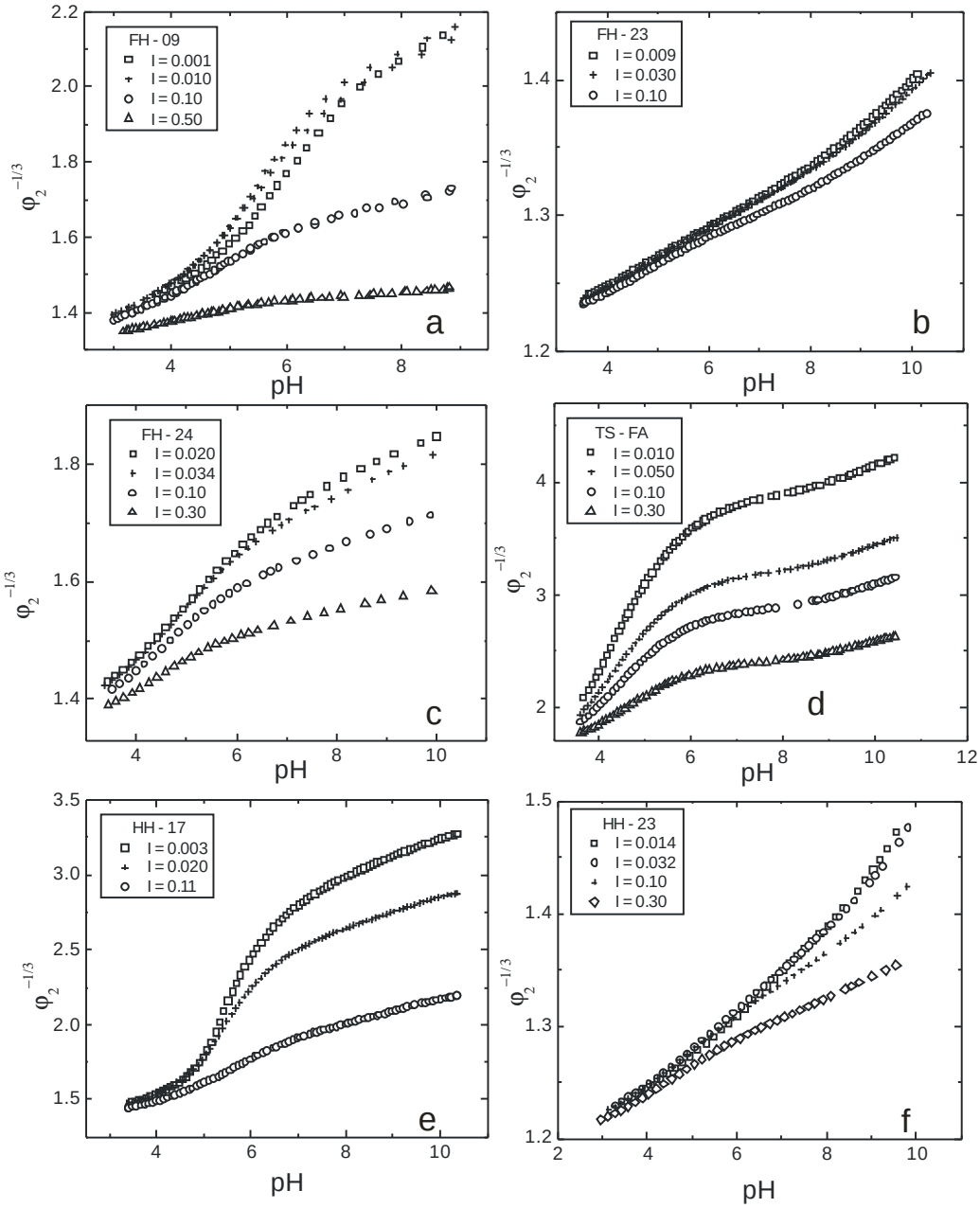


Figure S4. Model results for linear expansion of humic particles as a function of pH for different ionic strengths. (a) Lake Drummond FA; (b) Laurentian soil FA; (c) PUFA; (d) Toledo Soil FA; (e) Shitara Black HA; (f) PUHA. Ionic strengths are in molar units.

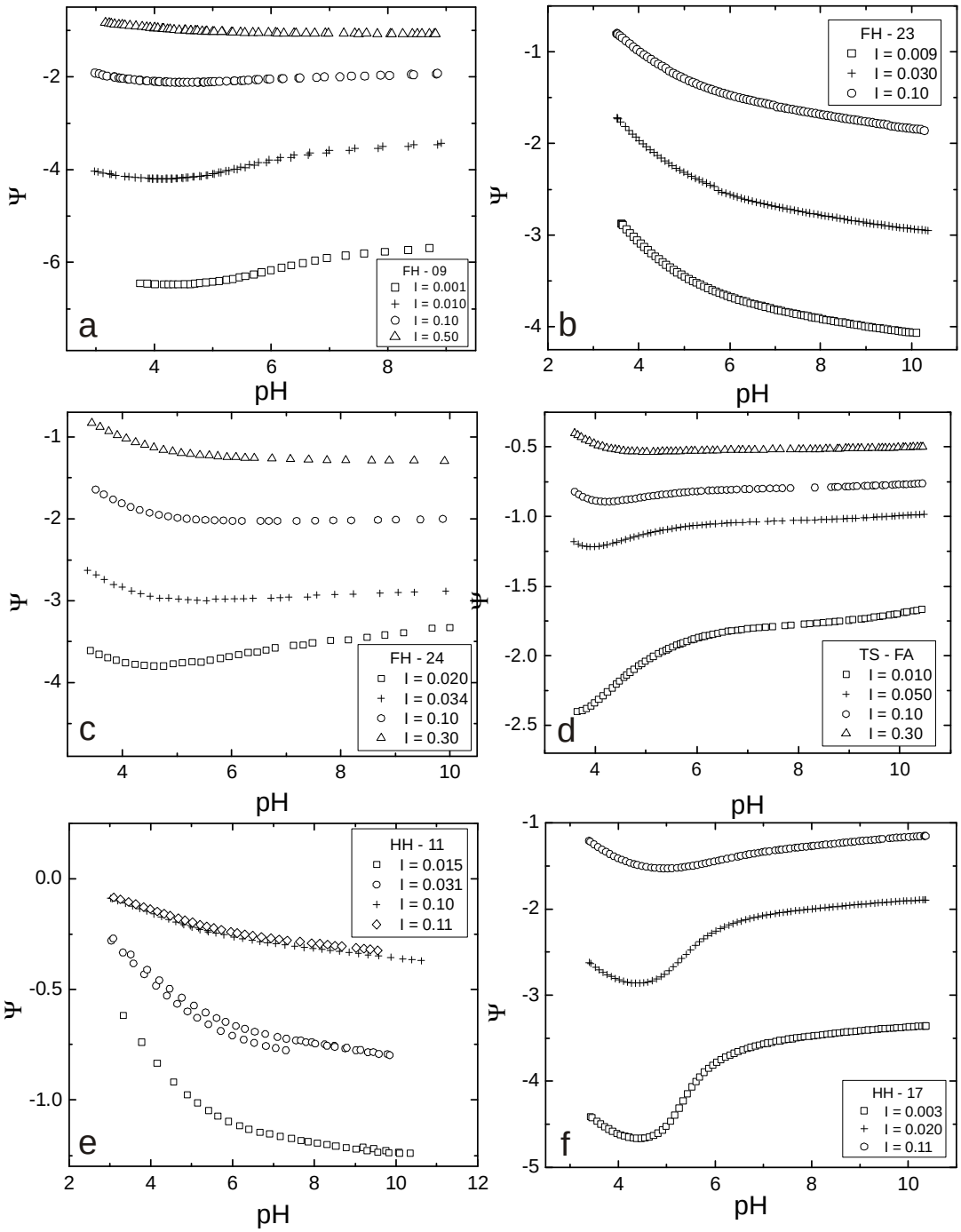


Figure S5 (start). Model results for dimensionless Donnan potential of humic particles as a function of pH for different ionic strengths. (a) Lake Drummond FA; (b) Laurentian soil FA; (c) PUFA; (d) Toledo soil FA; (e) Elliot silt loam HA; (f) Shitara Black HA. Ionic strengths are in molar units.

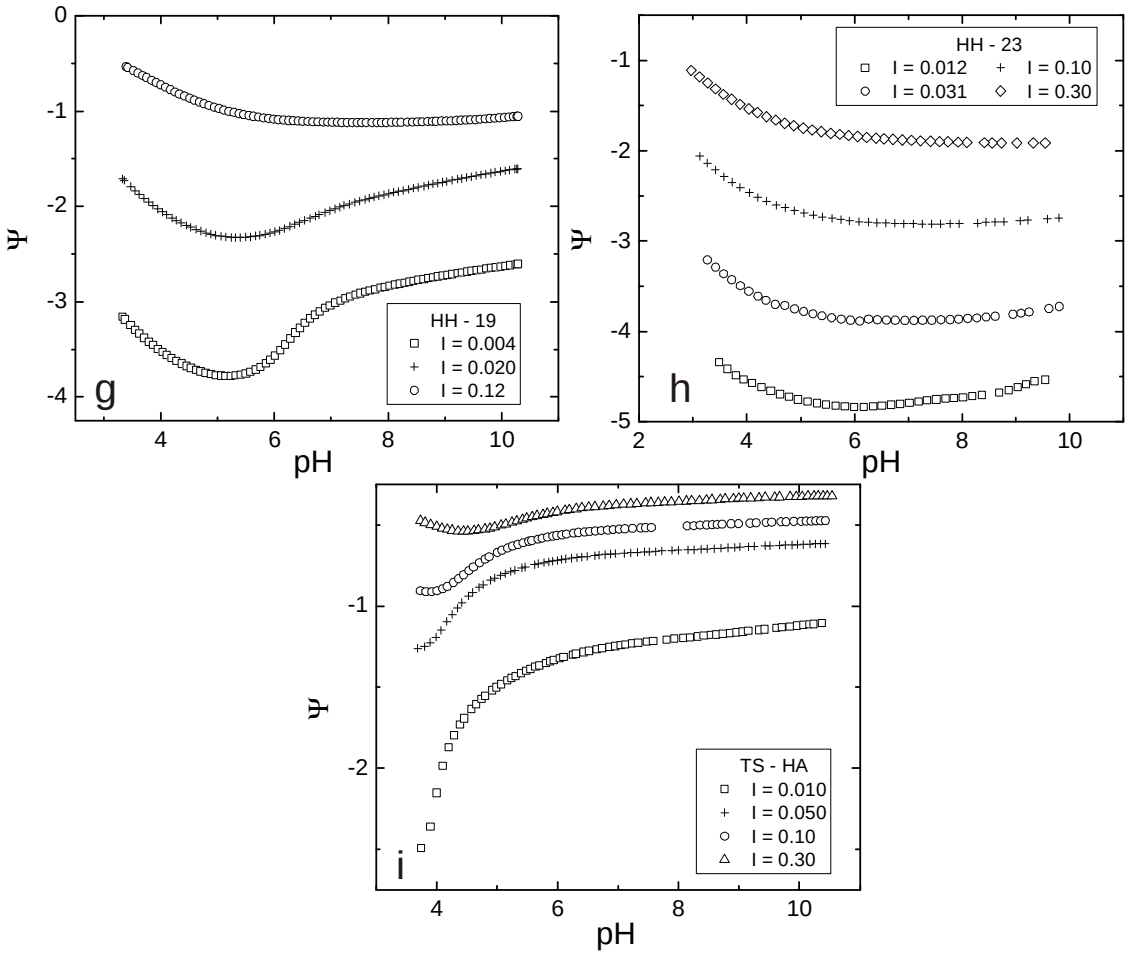


Figure S5 (end). Model results for dimensionless Donnan potential of humic particles as a function of pH for different ionic strengths. (g) Tongbersven Forest HA; (h) PUHA; (i) Toledo Soil HA. Ionic strengths are in molar units.

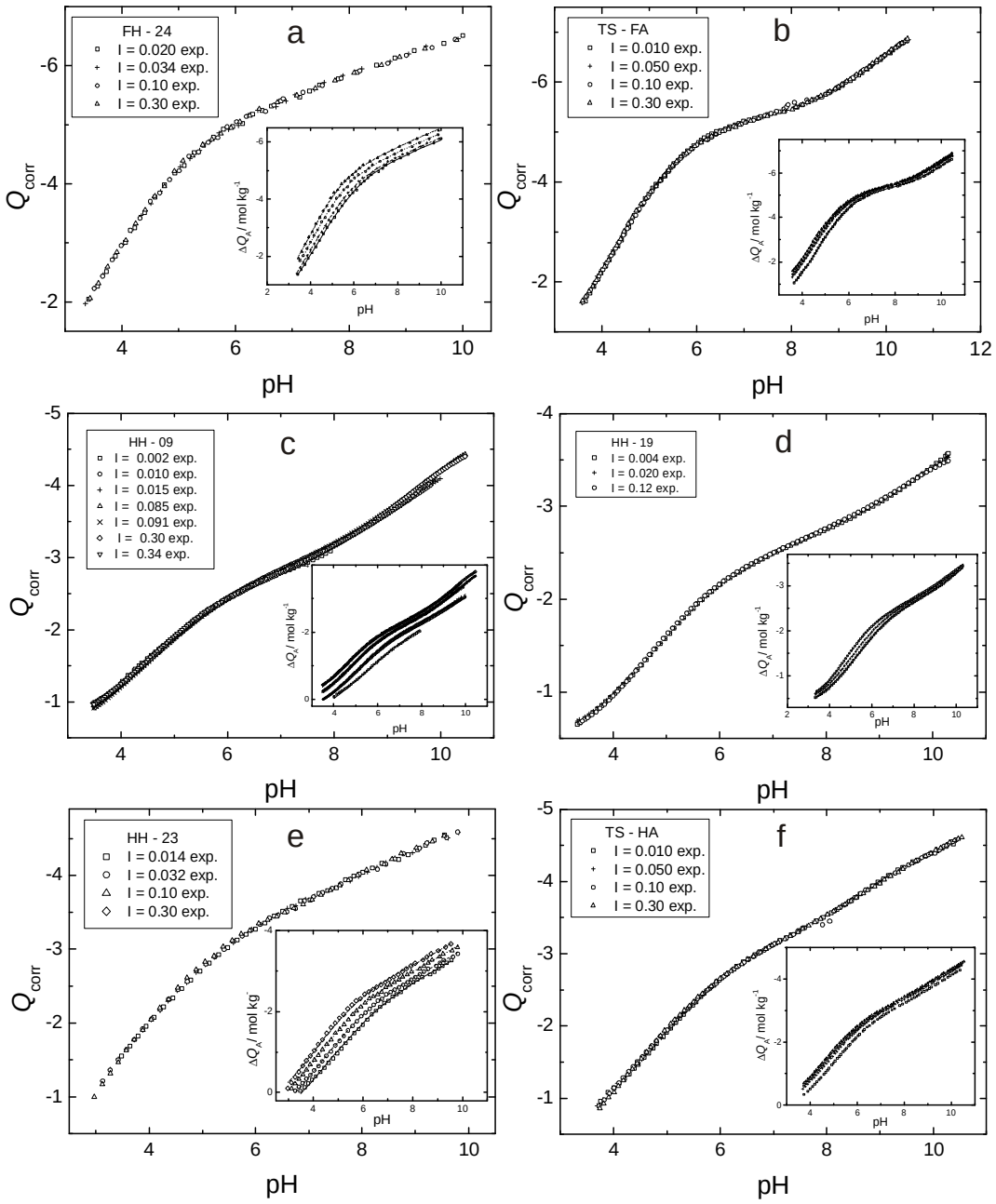


Figure S6. Verification of the convergence to a single curve (master curve) upon correction for electrostatic effects. The insets show the original data. (a) PUFA; (b) Toledo Soil FA; (c) PPHA; (d) Tongbersven Forest HA; (e) PUHA; (f) Toledo Soil HA. Ionic strengths are in molar units.

APPENDIX A

Ohshima soft particle model

Ohshima and coworkers (Ref. 33 of the main text, and references therein) developed a partially penetrable particle model, termed soft particle model (SPM). In this model, the particle is assumed to be composed of an impenetrable core and a layer (surface charge layer) which can be charged and penetrable by the electrolyte solution. The potential profile is schematized in Fig. 2 of the main text. If the thickness of the soft layer is much larger than the Debye length, then a non planar particle can be treated approximately in the one-dimensional case. Assuming that the internal core is uncharged, solution of the Poisson-Boltzmann equation for a plate-like particle (plane surface) with appropriate boundary conditions leads, for a symmetrical *z*-*z* electrolyte of concentration *c*, to the following expression for the Donnan potential

$$\psi_{\mathrm{D}} = \frac{RT}{zF}\operatorname{arcsinh}\left(\frac{\rho}{2zcF}\right) \tag{A1}$$

and the surface potential is given by

$$\psi_0 = \psi_{\mathrm{D}} - \left(\frac{RT}{zF}\right)\tanh\left(\frac{zF\psi_{\mathrm{D}}}{2RT}\right) \tag{A2}$$

The potential profile inside the soft particle is obtained from the transcendental equation:

$$\kappa' x = \operatorname{sgn}(y_0)\int_{y}^{y_0} \frac{dy}{\left[2(\cosh y - \cosh y_{\mathrm{D}}) - \frac{\rho}{zc}\left(y - y_{\mathrm{D}}\right)\right]^{1/2}} \tag{A3}$$

where

$$\kappa' = \sqrt{\frac{2z^2F^2c}{\varepsilon_r'\varepsilon_0 RT}} \tag{A4}$$

is the Debye inverse length inside of the surface layer with relative permittivity ε_r'; ε_0 is the vacuum permittivity. As an alternative to eq. (A3), approximate expressions (for low ψ values) can be derived for the potential inside and outside the particle:

$$\psi(x)=\begin{cases}\psi_0 e^{-\kappa x} & x>0\\ \psi_D+(\psi_0-\psi_D)\exp\left[\kappa' x\sqrt{1+\left(\frac{\rho}{2cF}\right)^2}\right] & x\le 0\end{cases} \qquad \text{(A5)}$$

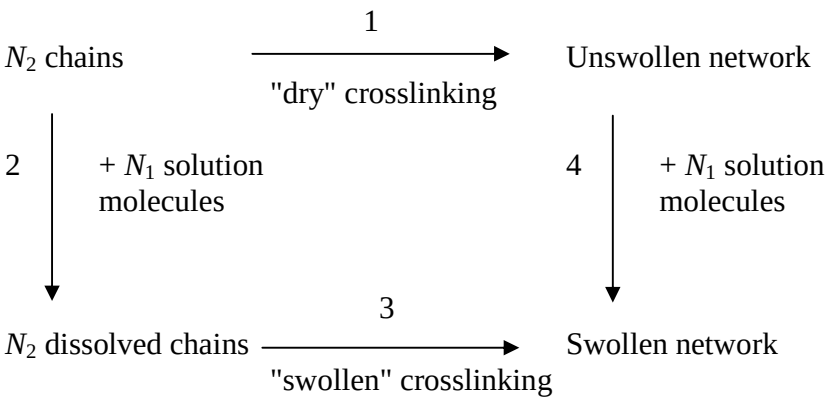
where κ is the Debye inverse length outside the particle, which differs from (A4) only in the bulk solution relative permittivity ε_r instead of ε_r'.

APPENDIX B

Flory model for the swelling of network structures

In this model, developed in Ref. 40, the network is assumed to be composed of N_2 linear chains. These chains are linked at the ends; at each crosslink point there are, on average, f_P chains bounds. Thus, f_P represents the network connectivity: f_P = 2 means that two chains converge at each point, effectively resulting in no crosslinking; on the other hand, f_P = 4 can be regarded as if a C atom at the crosslink point is fully bonded to different chains.

The entropy of swelling is obtained considering the following cycle:



The swelling entropy is that of step 4, that is

$$\Delta S_4 = \Delta S_2 + \Delta S_3 - \Delta S_1 \qquad \text{(B1)}$$

Step 1 consist in the assemblage of the chain elements in $2N_2/f_P$ groups. Considering the probability for a given chain end to be surrounded by f_P -1 other ends within the volume element $\Delta\tau$, it is found that

$$\Delta S_1 = 2k\frac{f_P - 1}{f_P}\ln\left(\frac{2N_2\Delta\tau}{Ve}\right) \qquad \text{(B2)}$$

where k is the Boltzmann constant and V the total volume. The entropy of mixing in step 2 is

$$\Delta S_2 = -k\left(N_1\ln\varphi_1 + N_2\ln\varphi_2\right) \qquad \text{(B3)}$$

The entropy of step 3 is similar to that of step 1, but allowing for dilation of the chain most probable displacement length, resulting in

$$\Delta S_3 = kN_2\left[2\frac{f_P - 1}{f_P}\ln\left(\frac{2N_2\Delta\tau}{V'e}\right) - \frac{3}{2}\left(\varphi_2^{-2/3} - 1\right) - \ln\varphi_2\right] \qquad \text{(B4)}$$

where V' is the total volume for the swollen network, with $V/V' = \varphi_2$. Replacing (B2-B4) in (B1) results in

$$\Delta S_4 = -k\left[N_1\ln\varphi_1 + \frac{3N_2}{2}\left(\varphi_2^{-2/3} - 1\right) + \frac{2N_2}{f_P}\ln\varphi_2\right] \qquad \text{(B5)}$$

The first term within brackets in (B5) is the mixing entropy, so that the deformation entropy is the remainder, resulting in eq. (6) in the main text.

APPENDIX C

Electrostatic contribution to the free energy following Hill[41]

Assuming that in the Poisson-Boltzmann equation border effects can be neglected, the Donnan potential is given as a function of the charge density by eq (10) of the main text:

$$\psi_D(\rho) = \frac{RT}{F}\,\mathrm{arcsinh}\left(\frac{\rho}{2I(1-\varphi_2)}\right) \qquad \text{(C1)}$$

The electrostatic contribution to the free energy is obtained by considering that the network, initially dry and uncharged, is first swollen by the electrolyte solution and then gradually charged to the full charge density keeping V and the c_i constant. Thus,

$$\Delta F_{el} = \int_0^1 \psi_D(\rho\lambda) ZF d\lambda = ZRT\left[\mathrm{arcsinh}\left(\frac{\rho}{2I(1-\varphi_2)}\right) - \sqrt{1+2\left(\frac{2I(1-\varphi_2)}{\rho}\right)} + \frac{2I(1-\varphi_2)}{\rho}\right] \qquad \text{(C2)}$$

as in eq (11) of the main text.

APPENDIX D

Comparison with Donnan-Volume models

The present Donnan volume, V_D, models involve the calculation of a volume such that the electroneutrality condition is fulfilled. The NICA-Donnan model[4,5,15,23] assumes that V_D is function only of the ionic strength:

$$\log V_D = b(1 - \log I) - 1 \qquad \text{(D1)}$$

where b is an adjustable parameter. For the case of purified Aldrich HA (PAHA, HH-18), Milne et al.[15] report b = 0.69; with this value, V_D ranges from 2.4 L kg^{-1} at I = 0.1 M to 57.5 L kg^{-1} at I = 0.001 M, independent of pH. Whereas at high I eq. (D1) gives reasonable values, at the lower ionic strengths it results in quite high volumes, a fact already known.[5,15,20] Companys et al.[20] gave a somewhat similar expression:

$$V_D = cI^{-b} \quad \text{(D2)}$$

with b and c being adjustable parameters. For PAHA Companys et al.[20] report b = 0.40 and c = 10 kg^{-1} (mol L)$^{1/2}$, which results in V_D values ranging from 25 to 158 L kg^{-1} for the same range of I, values still higher than those of eq. (D1). Companys et al. also proposed a different expression, which for a 1-1 electrolyte reads:

$$V_D = \frac{1}{4a\sqrt{I + a^2Q^2}} \quad \text{(D3)}$$

where a is an adjustable parameter. Eq. (D3) predicts that V_D will *decrease* with a Q (that is, pH) increase, opposite to what is found here and in other studies (Avena et al.[38] and references therein). Companys et al. report a = 0.030 kg (mol L)$^{-1/2}$ for PAHA; with this value, eq. (D3) predicts values similar to (D2) for the usual range of I and Q. It should be remarked that V_D is the volume required to fulfill the overall electroneutrality equation, so it is expected to be greater than V_H; however, the results for the lower I range seem to be excessively large. The opposite behavior of the variation of the Donnan volume with the charge in eq. (D3) is due to the different correction of Donnan models at high charges (high pH) with respect to the polyelectrolyte correction made by a impenetrable rigid sphere model for HA, in accordance with other approximate models as, for example, the Marinsky-Mijayima et al. model.[42-44]