Supporting Information

for the manuscript

Rigorous Physicochemical Framework for Metal Ion Binding by Aqueous Nanoparticulate Humic Substances: Implications for Speciation Modeling by the NICA-Donnan and WHAM Codes

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The Supporting Information comprises 5 pages, and includes an outline of the Ohshima formalism for the electrophoretic mobility of soft charged particles, description of the procedures used to obtain the intrinsic stability constants for metal ion binding by nanoparticulate complexants, Table S1 with definitions of the parameters used in the CCD-based model, Figure S1 showing the intraparticulate speciation of Cd species associated with Aldrich HA, Figure S2 showing the double logarithmic plot of $\overline{K}_{\mathrm{int}}$ *vs.* θ_{M} and SSCP waves for Cd(II) and Cu(II) complexes with FA, and a list of the references cited in the SI.

Ohshima Formalism for the Electrophoretic Mobility of Soft Charged Particles

The rigorous theory for electrophoresis of hard (ion-impermeable) particles, valid for any ratio between the particle radius, r_{p}, and the Debye layer thickness in the bulk medium, κ^{-1}, was established in the late 70's by O'Brien and White.[1] The key electrokinetic quantity obtained from experimental data by such a theory is the particle zeta-potential, *i.e.* the potential located at the slip plane separating the stagnant liquid layer surrounding the particle from the 'bulk' mobile liquid phase.[2] The zeta-potential is converted to particle surface charge density by means of Gouy-Chapman theory or more sophisticated double layer representations.[3] However, the basic concept of a zeta-potential is not applicable to soft NPs due to the absence of a discrete slip plane at the interphase they form with the electrolytic medium (see ref 4 and references cited therein). The formalisms for electrokinetics of soft particles differ according to their treatment of electrostatics, in particular their ability to apply to thin double layer cases ($\kappa r_{\mathrm{p}} \leq 1$),[5-8] or to the degree of sophistication in integrating particle backbone material distribution which impacts on both the electrostatic and hydrodynamic flow field distributions and, in turn, the particle electrophoretic mobility, μ.[7-9] The model by Ohshima[5] has been successfully employed to determine the electrostatic surface properties of various particles, including microgels, erythrocytes, and bacterial surfaces.[4,6] Specifically, the electrophoretic mobility μ of soft particles that meet the conditions for establishment of a Donnan phase, *i.e.* $\kappa r_{\mathrm{p}} >> 1$, reads as:

$$\mu = \frac{\rho_{\mathrm{p}}}{\eta \lambda_{\mathrm{o}}^2} + \frac{\varepsilon}{\eta} \frac{\psi_{\mathrm{o}} \kappa_{\mathrm{p}}^{-1} + \psi_{\mathrm{D}} \lambda_{\mathrm{o}}^{-1}}{\kappa_{\mathrm{p}}^{-1} + \lambda_{\mathrm{o}}^{-1}} \qquad \text{(S1)}$$

where ρ_{p} represents the net density of charges (in C m^{-3}) carried by the soft NP (and assumed to be homogeneously distributed therein), $1/\kappa_{\mathrm{p}}$ the intraparticulate Debye layer thickness, $1/\lambda_{\mathrm{o}}$ the characteristic penetration length of the electroosmotic flow within the soft NP, ε and η are the permittivity and dynamic viscosity of the electrolyte medium, respectively, ψ_{o} corresponds to the NP surface potential, and ψ_{D} to the

Donnan potential. The parameters ψ_D, ψ_o and $1/\kappa_p$ all depend on the space charge density ρ_p and on the electrolyte concentration according to:

$$\psi_D = \frac{RT}{F}\operatorname{asinh}\left(\frac{\rho_p}{2Fc_1^*}\right) \tag{S2}$$

$$\psi_o = \psi_D - \frac{RT}{F}\tanh\left(\frac{F\psi_D}{2RT}\right) \tag{S3}$$

$$\kappa_p = \kappa\left\{\cosh\left(\frac{F\psi_D}{RT}\right)\right\}^{1/2} \tag{S4}$$

which are written here for a 1-1 electrolyte with concentration c_1^*.

In agreement with experimental data, Ohshima's model quantitatively describes how the particle mobility μ decreases in magnitude with increasing solution ionic strength due to particle charge screening. Most remarkably, it demonstrates that the mobility μ of soft Donnan particles (Figs. 1A-B in main text), unlike that of hard particulate systems (Fig. 1C in main text), asymptotically reaches a non-zero plateau value at sufficiently large electrolyte concentrations, which is a direct consequence of their defining ion permeability features.[4,6,7]

Computation of $\overline{K}_{int}$ Values

The expression for the intrinsic stability constant $\overline{K}_{int}$ is given as eq 15 in the main text, and repeated here for convenience:

$$\overline{K}_{int} = \frac{c_{MS}}{c_M c_S} \tag{S5}$$

where c_{MS}, c_M and c_S are the *local* average concentrations of inner-sphere complexes, free metal ion and reactive sites in the particle body, respectively. In the present case, the total intraparticulate concentration of reactive sites, $c_{S,t}$, corresponds to the concentration of charged sites and $c_S = c_{S,t} - c_{MS}$.

For small NPs, with $\kappa_p r_p \approx 1$, c_M is obtained from $\overline{f}_{B,M} c_M^*$, where c_M^* is the concentration of the free metal ion in the bulk solution and $\overline{f}_{B,M}$ is the Boltzmann factor for M^{2+} computed via the mean-field Poisson-Boltzmann approach based on the *equilibrated* potential profile over the intraparticulate and relevant extraparticulate zones. See ref 10 for details. The smeared-out concentration of metal ions associated with the NP, $\bar{c}_{M,b}$, simply corresponds to the difference between the total metal ion concentration in the dispersion and the free metal ion concentration in the bulk solution. The intraparticulate concentration of all forms of M associated with the particle (= c_M + c_{MS}) is given by $\bar{c}_{M,b}$ divided by the aqueous particle volume fraction in the dispersion; subsequent subtraction of c_M yields c_{MS}.

For large NPs, with $\kappa_p r_p >> 1$, the CCD electrostatic model is used to compute the intraparticulate speciation in the intraparticulate double layer (DL) and Donnan volume.[11] The defining parameters are given in Table S1. In practice, an iterative process is used to determine the intraparticulate speciation. In a first step, the particle-associated M is distributed to satisfy the electrostatic demands of counterion condensation and Donnan partitioning, and the remaining M is ascribed to inner-sphere complexes, MS. The presence of MS in the DL reduces the net charge therein, and thus the proportion of condensed ions is correspondingly decreased. Accordingly, the initial intraparticulate metal speciation is iterated with respect to the concentrations of inner-sphere complexes c_{MS} versus condensed metal ions in the DL zone $c_{M,cond}^{DL}$ until a consistent intraparticulate distribution over the Donnan bulk and DL zone is attained. Typically *ca.* 4 iterations are required to obtain consistent values for c_{MS} and $c_{M,cond}^{DL}$.

Table S1. CCD-Based Model Parameters Defining the Intraparticulate Metal Speciation in Highly Charged, Soft Nanoparticulate Complexants[a]

M(II) species	Intraparticulate double layer	Donnan volume	Governing physicochemical features
Free M	$c_{\mathrm{M}}^{\mathrm{DL}} = \overline{f}_{\mathrm{B,M}}^{\mathrm{DL}} c_{\mathrm{M}}^{*}$	$c_{\mathrm{M,f}}^{\mathrm{D}} = \overline{f}_{\mathrm{B,M}}^{\mathrm{D}} c_{\mathrm{M}}^{*}$	Donnan
Condensed M	$c_{\mathrm{M,cond}}^{\mathrm{DL}} = \overline{f}_{\mathrm{C}} c_{\mathrm{S}}^{\mathrm{DL}}$	0[b]	Counterion condensation
Inner-sphere MS[c]	$c_{\mathrm{MS}} = \overline{K}_{\mathrm{int}} c_{\mathrm{S}} c_{\mathrm{M}}$		Covalent binding

[a] The concentrations are denoted by superscript D or DL for local intraparticulate concentrations in the pertaining part of the particle volume; the superscript * denotes the free metal ion concentration in the bulk solution. The condensation limit for 2+ counterions in the DL with $\rho = \overline{\rho}_{\mathrm{DL}}$ is denoted by $\overline{f}_{\mathrm{C}}$.

[b] In the high charge density regime, with $\kappa_{\mathrm{p}} r_{\mathrm{p}} >> 1$, counterion condensation is confined to the intraparticulate double layer shell. See main text.

[c] See eq S5.

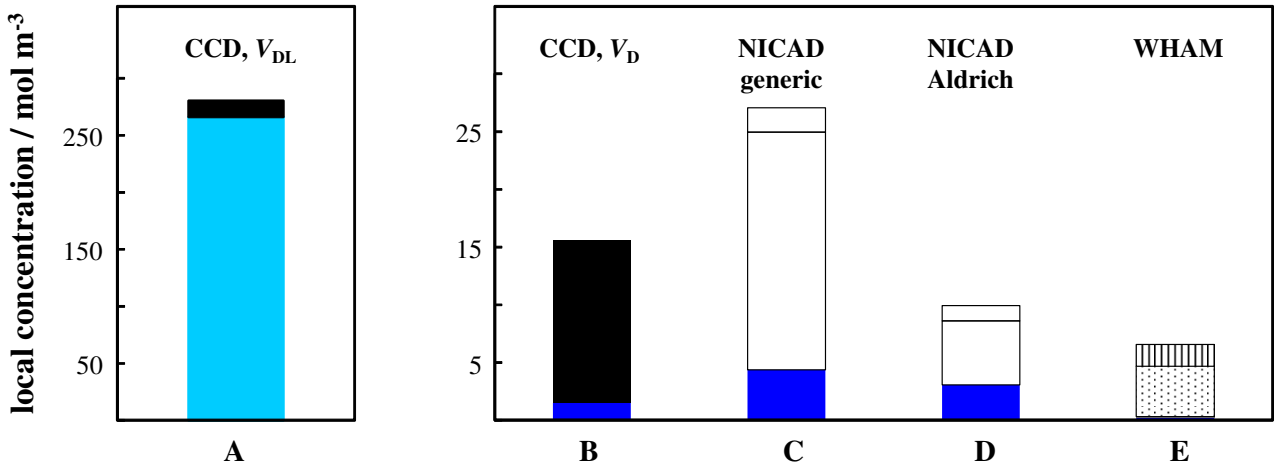

Figure S1. Intraparticulate speciation of Cd species associated with Aldrich HA, for a total Cd concentration of 4.6×10^{-3} mM and an HA concentration of 50.5 g m^{-3}, in 10 mM KNO_3 at pH 6. Data correspond to the local concentrations determined via the (A) CCD model, intraparticulate double layer: condensed M (pale blue) and inner-sphere complexes (solid black); (B) CCD model, Donnan volume: free M (dark blue) and inner-sphere complexes (solid black); (C) and (D) NICA-Donnan model using (c) generic and (d) Aldrich optimised parameters: free M (dark blue) and inner-sphere complexes with nominal carboxylic groups (diagonal stripes) and phenolic groups (horizontal stripes); and (E) WHAM: free M (dark blue) and inner-sphere complexes that are monodentate (solid dark grey), bidentate (black dots), and tridentate (vertical black stripes).

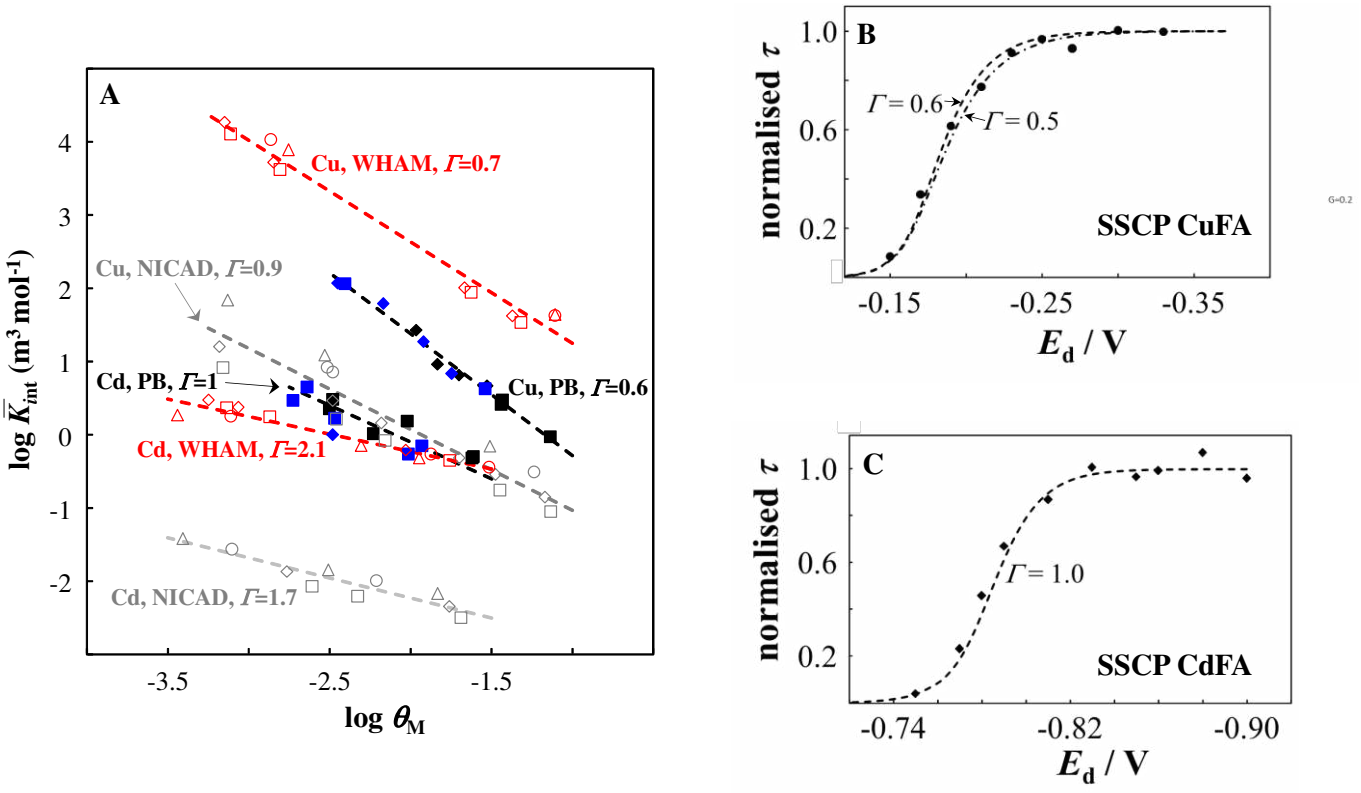

Figure S2. (A) Intrinsic stability constant, log $\overline{K}_{int}$, as a function of the degree of inner-sphere complex formation, log θ_M, for Cd(II) and Cu(II) complexes with FA. The mean-field Poisson-Boltzmann (PB)-based results were obtained from experimental data for SRFA,[10] obtained in 10 mM KNO_3 (solid black squares), 100 mM KNO_3 (solid black diamonds), 3.33 mM $Ca(NO_3)_2$ (solid blue squares), and 33.33 mM $Ca(NO_3)_2$ (solid blue diamonds). The NICAD-Donnan computations were done using the generic parameters for FA,[12,13] and c_{MS} was taken as the sum of the complexes with the nominal carboxylic and phenolic sites. For WHAM, c_{MS} was taken as the sum of the mono-, bi-, and tri-dentate complexes. The computations with both speciation codes were performed for the background electrolytes 10 mM KNO_3 (NICA-Donnan: open grey squares; WHAM: open red squares), 100 mM KNO_3 (NICA-Donnan: open grey diamonds; WHAM: open red diamonds), 3.33 mM $Ca(NO_3)_2$ (NICA-Donnan: open grey circles; WHAM: open red circles), and 33.33 mM $Ca(NO_3)_2$ (NICA-Donnan: open grey triangles; WHAM: open red triangles). The SSCP waves[10] for (B) CuFA and (C) CdFA correspond to the experimental (solid diamonds) and computed curves for the indicated Γ values (curves) of the normalised reoxidation time, τ, as a function of deposition potential, E_d. The experimental data correspond to $\bar{c}_{M,b} / \bar{c}_{S,t} \approx 0.03$ for Cu and 0.01 for Cd, and were measured in $Ca(NO_3)_2$ electrolyte at pH 6 and an ionic strength of 100 mol m^{-3} for CuHA and 10 mol m^{-3} for CdHA.

References

(1) O'Brien, R. W.; White, L. R. Electrophoretic mobility of a spherical colloidal particle. *J. Chem. Soc. Faraday Trans. II.* **1978**, *74*, 1607-1626.

(2) Delgado, A. V.; González-Caballero, F.; Hunter, R. J.; Koopal, L. K.; Lyklema, J. Measurement and interpretation of electrokinetic phenomena. *J. Colloid Interf. Sci.* **2007**, *309*, 194-224.

(3) Lyklema, J. Electric double layers. In: *Fundamentals of Colloid and Interface Science.* Academic Press: New York, pp. 3.1-3.232.

(4) Duval, J. F. L.; Gaboriaud, F. Progress in electrohydrodynamics of soft microbial particle interphases. *Curr. Opinion Coll. Interf. Sci.* **2010**, *15*, 184-195.

(5) Ohshima, H. Electrophoresis of soft particles. *Adv. Colloid Interf. Sci.* **1995**, *62*, 189-235.

(6) Duval, J. F. L. Electrophoresis of soft colloids: basic principles and applications. In: *Environmental Colloids and Particles: Behaviour, Separation and Characterisation*. Wilkinson, K. J. and Lead, J. R. (Vol. Eds), IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, Vol. 10, Buffle, J. and van Leeuwen, H. P. (Series Eds), John Wiley & Sons Ltd: Chichester, 2007, pp. 315-344.

(7) Hill, R. J.; Saville, D. A.; Russel, W. B. Electrophoresis of spherical polymer-coated particles. *J. Coll. Interf. Sci.* **2003**, *258*, 56-74.

(8) Duval, J. F. L.; Ohshima, H. Electrophoresis of diffuse soft particles. *Langmuir* **2006**, *22*, 3533-3546.

(9) Martin, J. R. S.; Bihannic, I.; Santos, C.; Farinha, J. P. S.; Demé, B.; Leermakers, F. A. M.; Pinheiro, J. P.; Rotureau, E.; Duval, J. F. L. Structure of multiresponsive brush-decorated nanoparticles: a combined electrokinetic, DLS, and SANS study. *Langmuir* **2015**, *31*, 4779-4790.

(10) Town, R. M.; Duval, J. F. L.; van Leeuwen, H. P. The intrinsic stability of metal ion complexes with nanoparticulate fulvic acids. *Environ. Sci. Technol.* **2018**, *52*, 11682-11690.

(11) Town, R. M.; van Leeuwen, H. P. Intraparticulate speciation analysis of soft nanoparticulate metal complexes. The impact of electric condensation on the binding of Cd^{2+}/Pb^{2+}/Cu^{2+} by humic acids. *Phys. Chem. Chem. Phys.* **2016**, *18*, 10049-10058.

(12) Milne, C. J.; Kinniburgh, D. G.; van Riemsdijk, W. H.; Tipping, E. Generic NICA-Donnan model parameters for metal-ion binding by humic substances. *Environ. Sci. Technol.* **2003**, *37*, 958-971.

(13) Milne, C. J.; Kinniburgh, D. G.; Tipping, E. Generic NICA-Donnan model parameters for proton binding by humic substances. *Environ. Sci. Technol.* **2001**, *35*, 2049-2059.