Impact of Electrostatics on the Chemodynamics of Highly Charged Metal–Polymer Nanoparticle Complexes

Jérôme F. L. Duval,*†,‡,§ José Paulo S. Farinha,§ and José P. Pinheiro||

1Laboratoire Interdisciplinaire des Environnements Continentaux (LIEC), Université de Lorraine, UMR 7360, 15 avenue du Charmois, Vandœuvre-lès-Nancy, F-54501, France
2Laboratoire Interdisciplinaire des Environnements Continentaux (LIEC), CNRS, UMR 7360, 15 avenue du Charmois, Vandœuvre-lès-Nancy, F-54501, France
§Centro de Química-Física Molecular and IN - Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, 1049-001 Lisboa, Portugal
||IBB/CBME, Departamento de Química e Farmácia, Faculdade de Ciencias e Tecnologia, Universidade do Algarve, Campus de Gambelas, 8005-139 Faro, Portugal

Supporting Information

ABSTRACT: In this work, the impact of electrostatics on the stability constant, the rate of association/dissociation, and the lability of complexes formed between Cd(II), Pb(II), and carboxyl-modified polymer nanoparticles (also known as latex particles) of radius ~ 50 nm is systematically investigated via electroanalytical measurements over a wide range of pHs and NaNO₃, electrolyte concentrations. The corresponding interfacial structure and key electrostatic properties of the particles are independently derived from their electrokinetic response, successfully interpreted using soft particle electrohydrodynamic formalism, and complemented by Förster resonance energy transfer (FRET) analysis. The results underpin the presence of an ~0.7−1 nm thick permeable and highly charged shell layer at the surface of the polymer nanoparticles. Their electrophoretic mobility further exhibits a minimum versus NaNO₃ concentration due to strong polarization of the electric double layer. Integrating these structural and electrostatic particle features with recent theory on chemodynamics of particulate metal complexes yields a remarkable recovery of the measured increase in complex stability with increasing pH and/or decreasing solution salinity. In the case of the strongly binding Pb(II), the discrepancy at pH > 5.5 is unambiguously assigned to the formation of multidentate complexes with carboxylate groups located in the particle shell. With increasing pH and/or decreasing electrolyte concentration, the theory further predicts a kinetically controlled formation of metal complexes and a dramatic loss of their lability (especially for lead) on the time-scale of diffusion toward a macroscopic reactive electrode surface. These theoretical findings are again shown to be in agreement with experimental evidence.

1. INTRODUCTION

Trace metals are a perennial issue among environmental threats, not only due to their increasing extraction, modification, and disposal by humans but also, in some particular cases, due to their adverse bio- and geochemical impacts.1 Upon entering an aquatic system, trace metal ions face a large variety of dissolved inorganic and organic ligands including nanoparticles, colloids, suspended matter, and living organisms.2 These (bio)ligands significantly differ in terms of size, chemical composition, form, and charge, thus resulting in metal complexes with a wide range of stabilities. Understanding the physicochemical processes that govern the distribution of trace metals among the various chemical species found in aquatic environments is a prerequisite for predicting their transport, bioavailability, and ecotoxicity.3−8 In view of the intrinsic nonequilibrium nature of environmental systems, a correct analysis of intertwined speciation and ecotoxicological effects of metals should further quantify the relative time scales pertaining to metal transport and to the chemodynamics of the complexes formed between metals and (bio)ligands.3−5,7,8

Until 2005, the kinetics of metal ion complexation by charged colloidal ligands in aquatic systems was essentially tackled on the basis of the Eigen mechanism proposed about 50 years ago.9 The latter consists of two steps: first, the formation of a precursor outer-sphere complex with a stability constant $K_{os}$ determined by electrostatic metal−colloid interactions treated at the Coulombic level, followed by the removal of water from the inner coordination sphere as the rate-limiting step. This approach basically discarded the colloidal nature of the reagents that where assimilated to complexing point charges homogeneously distributed in solution. As such, it oversimplified the chemodynamics of colloidal metal complexes
by overlooking (i) the confinement of the reactive (binding) sites over the surface/volume of the colloids (termed hard/soft colloids, respectively) and the corresponding consequences for the reactant transport, and (ii) the electric double layer and associated electrostatic features of the binding particle interface.

In 2005, Pinheiro et al. recognized the first shortcoming of the Eigen theory when applied to colloids. In agreement with experimental data, they derived an expression for the steady-state association/dissociation rate constants of hard colloidal metal complexes with explicit account of metal diffusion to/from the reactive sites located at the particle surface. The authors showed that depending on particle size, the formation rate constant of colloidal metal complexes could differ by several orders of magnitude from that obtained using the Eigen model. The fundamental difference is associated with the progression from a chemically controlled to a diffusion-controlled association of the metal upon increasing the size of the ligand from molecular to colloidal scales. This work triggered the more rigorous development of theory on speciation dynamics of metals in colloidal dispersions. In particular, much progress has now been achieved in rationalizing the impact of reactive site protonation, hydrodynamic flow conditions, particle electrostatics, heterogeneity in reactive sites, and nature of binding colloids ranging from hard, core−shell to porous types.

Although the above theoretical background has significantly improved our basic understanding of the processes limiting the overall kinetics of metal complex formation with colloids, we recognize that there is still a critical paucity of direct confrontation between theoretical prediction and experimental data. This is particularly true for evaluating the role played by particle electrostatics in the binding kinetics of colloids with metal ions and in further rationalizing the lability of the colloidal complexes when exposed to reactive surfaces like electrodes or microorganisms.

The objective of this work is to support the basis of previously reported theory for the impact of colloidal electric double layer on chemodynamics and lability of particulate metal complexes. For that purpose, the stability constant and steady-state lability degree of complexes formed between highly charged polymer nanoparticles of radius ~ 50 nm (also known as latex particle dispersions) and Cd(II) or Pb(II) metal ions are determined over a broad range of pH and background electrolyte concentration by means of ChronoPotentiometry (SSCP).

2. EXPERIMENTAL SECTION

Reagents. All electrolyte solutions and particle dispersions were prepared in ultrapure water from a Barnstead EasyPure UV system (resistivity > 18 MΩ cm). Cd(II) solutions were prepared from solid Cd(NO₃)₂ (Merck, p.a.), and those for Pb(II) from dilution of a certified standard (0.100 M Pb(NO₃)₂, Metehrohm). Indifferent background NaN₃ electrolyte solutions were prepared from solid NaN₃ (Merck, p.a.). Stock solutions of 0.1 M MES (2-(N-morpholino)ethanesulfonic acid) and MOPS (3-(N-morpholino)-propanesulfonic acid) buffers were prepared from the corresponding solid materials (Fluka, Microselect, >99.5%). Concentrated 0.1 M HNO₃ (Merck, suprapur) and NaOH (0.1 M standard, Merck) solutions were used to adjust solution pH. The carboxyl-modified polymer nanoparticles used in this work were kindly provided by J. Forcada (Universidad del País Vasco, Spain). A particle hydrodynamic diameter of 109 nm was measured by dynamic light scattering (DLS). Additional transmission electronic microscopy (TEM) analysis further indicates that 80% of the particles have a diameter in the range 92.5–97.5 nm (average 94 nm), thus confirming the DLS results.

Apparatus for Electrochemistry and Electrophorochemistry. An Ecochemie Autolab PGSTAT12 potentiostat was used in conjunction with a Metrohm 663VA stand. The three electrode configuration was adopted with a thin mercury film electrode (TMFE)-plated rotating glassy carbon (GC) disc (2 mm diameter, Metrohm) as the working electrode, a GC rod counter electrode, and a double junction Ag/AgCl KCl(3M) reference electrode, encased in a 0.1 M NaNO₃ solution. Measurements were performed at 23 °C. All electrochemical potentials mentioned in this work are indicated with respect to the potential of the above reference electrode. The electrophoretic mobility of the polymer nanoparticles was measured at room temperature as a function of solution pH and background electrolyte concentration by means of a Malvern Nanosizer ZS instrument equipped with polystyrene cuvettes (Malvern, DTS1061). A Denver Instrument (model 15) and a Radiometer analytical combined pH electrode, calibrated with standard NBS buffers, were employed to measure the pH of the solution.

Electrophoretic Mobility Measurements. The electrophoretic mobility of polymer nanoparticles was measured in batch over the 1–200 mM range in NaNO₃ electrolyte concentration and for pH values from 3.5 to 7. The electrolyte concentration was adjusted using 1 M NaNO₃, and the pH was fixed at 3.5 and 4.5 by means of 0.1 M HNO₃ from 5.0 to 6.5 using 0.1 M MES, and at 7.0 with 0.1 M MOPS.

Förster Resonance Energy Transfer (FRET). Because of its high sensitivity to energy donor−acceptor dye distance, FRET can be used to obtain nanometer-scale structural information for soft materials. Here we measured the fluorescence donor decay curves of rhodamine 6G (R6G, an energy donor) in dispersions of the polymer nanoparticles containing adsorbed R6G and malachite green (MG, a nonfluorescent energy acceptor). FRET from donor to acceptor dyes affects the fluorescence decay curves, from which we evaluate the distribution of dyes adsorbed at the polymer nanoparticles, which mimics the charge distribution at the particle/water interface. This donor/acceptor pair was chosen because R6G has a high quantum yield and a monoexponential fluorescence decay in aqueous solutions, while MG absorbs light in the region of R6G emission but is nonemissive itself.

Rhodamine 6G (R6G), 99% pure, and Malachite Green carbinol hydrochloride (MG), 85% pure, both purchased from Aldrich, were used as received because no trace of fluorescent impurities were detected in the fluorescence spectra of the dyes. Stock solutions of donor and acceptor were prepared in purified ultrapure water, from which we prepared mixtures with a constant 2 × 10⁻⁶ M concentration of donor (R6G) and acceptor (MG) concentrations in the range 2−14 × 10⁻⁶ M. The mixed solutions were equilibrated in 0.02% (w/w) polymer nanoparticle dispersions. Measurements were carried out at room temperature, first at pH 4 in 100 mM NaNO₃ electrolyte and second at pH 7 in 3 mM NaN₃ electrolyte, which corresponds to the
extreme solution compositions adopted in the electroanalytical measurements in terms of polymer nanoparticle charge.

Steady-state fluorescence and absorption spectra were measured using a Horiba Fluorolog 3 spectrophotometer and a Jasco V660 spectrometer, respectively, in both cases by means of 5 × 5 mm quartz cuvettes. Time-resolved fluorescence decays with picosecond resolution were obtained by the single-photon timing technique. The system consists of a Nd:YAG laser (Coherent Antares 76-s) that synchronously pumps a cavity damped DCM dye laser (Coherent model 700) delivering pulses of about 6 ps and variable repetition rate. The output from the DCM laser was frequency-doubled to 347 nm, and used to excite the donor, R6G. A microchannel plate photomultiplier (Hamamatsu R15560-1) was used to detect the fluorescence at 547 nm, selected by a monochromator. Intensity decay measurements were performed by alternated collection of impulse and decays with the emission polarizer set at the magic angle position. The instrumental response function (fwhm of 107 ps) was recorded slightly away from the excitation wavelength with a scattering dispersion. For the decays, a cutoff filter was mounted in front of the photomultiplier tube detector to minimize the interference due to scattered light. Emission light was passed through a depolarizer before reaching the monochromator (Jobin-Yvon HR320 with a 100 lines/mm grating) and detected using a Hamamatsu 2809U-01 microchannel plate photomultiplier. Each decay was recorded with around 16 000 counts in the channel of maximum intensity. The decay curves were analyzed using a nonlinear least-squares reconvolution method.25

SSCP and AGNES Measurements. The basic principles of Scanned Stripping Chronopotentiometry (SSCP)16–18 and Absence of Gradients and Nernstian Equilibrium Stripping (AGNES)19 techniques using thin mercury film rotating disk electrodes (TMF-RDE) have been extensively detailed in previous reports.16–19 For the sake of completeness, the basic formalisms associated to this steady-state (SSCP) and equilibrium (AGNES) metal speciation measurements are reported in Supporting Information. BRIelly, SSCP and AGNES are stripping techniques: first, metal ions are amalgamated in the working electrode (deposition step), and the concentration of amalgamated metal is then quantified during the stripping step. The key idea in AGNES measurements is that, during the deposition step, metal amalgamation in the working electrode is allowed to proceed until one reaches the equilibrium ratio value between the concentrations of oxidized and reduced metallic forms, similarly to measurements by ion selective electrode (ISE). AGNES then renders possible the evaluation of free metal ion concentration in solution as well as the dimensionless stability constant of metal–polymer nanoparticle complexes, hereafter denoted K*′, as detailed in Supporting Information. K*′ is defined by the product of the complex stability constant K′ by the concentration of ligands averaged over the sample solution volume, as further detailed in section 3.1.

SSCP curves are constructed from a series of measurements performed at different deposition potentials, E0 covering the situations where there is no metal reduction at the electrode, passing through the Nernstian equilibrium regime and exploring the potential region were all metal ions at the electrode surface are reduced (diffusion-limited faradaic current).19 The shift of the potential observed between the metal-only calibration and the signal obtained in the presence of colloidal ligands provides the value K*′ of the stability constant of metal–polymer nanoparticle complexes (Supporting Information). Experimental derivation of the lability degree of particulate metal complexes (section 3.1) can be further achieved by comparing the K*′ value computed from the aforementioned potential shift in the SSCP curves and that evaluated from the decrease of the characteristic electrolysis time in the plateau region reached at sufficiently negative E0 values,26 as detailed in Supporting Information.

SSCP and AGNES experiments were performed sequentially using the same cell. For SSCP, the deposition potential E0 was applied for a duration t0 = 45 s, during which metals accumulated at the working electrode. Once the accumulation step was completed, a high oxidizing stripping current, I = 5 × 10−6 A, was applied in quiescent solution until the potential reached a value sufficiently large as compared to that of the transition plateau (−0.3 V). The adopted I value corresponds to conditions of complete metal depletions inside the mercury film and it further avoids oxygen interference.27

In this study, AGNES measurements were performed by applying a deposition potential and waiting long enough to reach Nernstian equilibrium. Due to the nature of the electrode (large surface area as compared to sample solution volume), a waiting time of 240 s under 1000 rpm stirring condition, was sufficient to achieve Nernstian equilibrium conditions.

SSCP and AGNES experiments were carried out here with a 0.02% (w/w) polymer nanoparticle dispersion with the following solution compositions (a) 10−6 M concentration of Cd2+ ions and a 6–100 mM background NaNO3 electrolyte concentration at pH values in the range 6.0–7.0, and (b) 10−6 M concentration of Pb2+ ions and a 10–100 mM background NaNO3 electrolyte concentration at pH values in the range 5.0–6.0. The pH range adopted for the electroanalytical experiments eliminates the possible formation of interfering cadmium and lead hydroxide complexes. The lowest pH values selected in this work (6.0 for Cd2+ and 5.0 for Pb2+) correspond to the conditions where binding of metals to particles could be acceptably detected. The preparation of the working electrode used in SSCP and AGNES experiments is detailed in the next section.

Preparation of the Thin Mercury Film Electrode for Electroanalytical Measurements. The glassy carbon (GC) disc was polished with an alumina slurry (grain size 0.3 μm, Metrohm) and sonicated in pure water for 60 s in order to obtain a renewed electrode surface. An electrochemical pretreatment was subsequently carried out according to a multicyle voltammetric scanning (50x) between −0.8 and +0.8 V at 0.1 V s−1, in NH4Ac-HCl solution. These polishing and electrochemical pretreatments were repeated daily. The thin mercury film was then prepared ex situ in 0.24 mM mercury(II) nitrate in nitric acid 0.01 M (pH 1.9) by electrodeposition at −1.3 V during 420 s and a rotation rate of 1000 rpm. The charge associated to the deposited mercury was calculated by integration of the linear sweep stripping peak of mercury. The electrolyte solution used for that purpose was ammonium thiocyanate 5 mM (pH 3.4). The stripping step was initiated at −0.15 V and ended at +0.4 V. A film thickness of 25 nm was estimated from at least three replicate measurements (RSD < 3%). When not in use, the glassy carbon electrode was stored dry in a clean atmosphere.

3. THEORY

3.1. Chemodynamics of Colloidal Metal Complexes: Association/Dissociation Rate Constants, Stability Constant, and Lability. Let us consider a dispersion of core–shell (or soft) particles consisting of an ion- and solvent-impermeable core of radius a and a permeable charged soft surface layer of characteristic thickness d (Figure 1). The polar coordinate system is defined in Figure 1, and the particle radius is denoted r = a + d. The particles are positioned according to a Kuwabara cell representation where each particle is surrounded by a virtual cell of radius rc = rαβ−1/3 with β being the particle volume fraction.24 The particles shell carries a single type of ligands L of charge zL (zL = −1 and L = −COO− in this study). The distribution of the local concentration of ligands at the shell/electrolyte solution interface, c(r), is given by:

\[
\frac{c(r)}{c_L} = f(r) = \frac{1}{1 + 10^{pK_{tu} - \phi} \exp(z_L \phi \mu/z_L)}
\]

(1)

where f is a radial function corresponding to the diffuse density distribution of polymer segments that carry the charged ligands across the shell layer.13,20,25 The function f decreases with r, and sufficiently far from the interface formed between the shell and the electrolyte medium, it satisfies the condition \( f \rightarrow 0 \). In the case of homogeneous polymer segment distribution across the shell, f is identified with the step-function \( f(r < a) = 1 \) and \( f(r \geq a) = 0 \). For a diffuse segment density profile, the
The particle shell contains charged ligands $L$ (carboxylate groups) and indifferent negatively charged groups $I$ (sulfonate) at concentrations much lower than that of $L$ (see section 4). The particles are distributed according to a Kuwabara cell model of radius $r_s$. Under the conditions of interest in this work, the cell radius $r_s$ is much larger than the reciprocal Debye length $1/\kappa$ and the steady-state metal diffusion layer thickness. The figure is not to scale. See text for further details.

**Complex Association/Dissociation Rate Constants.** The soft colloidal ligand particles described above are dispersed in an aqueous medium containing a symmetrical salt indifferent background electrolyte of bulk concentration $c^m$. We consider the situation where the particle-double medium double layer is completely relaxed; that is, the anion/cation distributions within and outside the soft particle have reached Boltzmann equilibrium. Metal ions (M) of valence $z_M$ ($z_M = +2$ in this study) are introduced into the medium at initial bulk concentration far below the background electrolyte concentration ($c^m \ll c^m$), the time scale of the chemical reaction (Figure 1)

$$M + L \rightarrow \text{ML}$$

where $k_0$ is the rate constant (in $s^{-1}$) for water loss from the inner coordination sphere of the local ML complex and $K_{aw}$ (mol$^{-1}$ m$^3$) is the stability constant for the local outer sphere ML complex as determined by the Fuoss-Debye-Hückel equation

$$K_{aw} = 4\pi N_A a_k^3 \alpha_m \gamma^2 e \left[ 1 - \alpha_m \left( 1 + \alpha_m \right) \right] \left( 4\pi \varepsilon_0 \varepsilon_r k_0 T a_k \right) / 3$$

where $\varepsilon_0$ and $\varepsilon_r$ are the dielectric permittivity of vacuum and relative dielectric permittivity of the medium, respectively. The principal (chemical) stability constant $K$ (mol$^{-1}$ m$^3$) of the ML complex within the particle shell is defined by $K = k_0/k_b$. Following a previously adopted strategy, it may be shown that the effective kinetic rate constant $k^*_{ML}$ (mol$^{-1}$ m$^{-3}$ s$^{-1}$), relevant at the scale of the whole sample solution volume, for the formation of ML complex between M and charged core–shell particles (Figure 1) is given by (Supporting Information)

$$k^*_{ML} = \frac{k_0}{1 + k_b \psi L \beta_L / (4\pi \varepsilon_0 D_M c_p)}$$

where $D_M$ is the diffusion coefficient of M, $\beta_L = \exp(-z_M q_L r_s / 5r_s) / (5r_s)$ is the Boltzmann factor evaluated at the particle surface, $\psi L = 4\pi \int_0^{\infty} \frac{r_c(r)}{V_c} dr / V_c$ is the ligand concentration smeared-out over the Kuwabara unit cell volume of radius $r_s$ and volume $V_c = 4\pi r_s^3 / 3$, $c_p = 1 / V_c$ is the particle number concentration, and $\alpha_m = \int_0^{\infty} r^2 \exp \left[ \frac{z_M q_L (r / 5r_s)}{5r_s} \right] dr$ is the factor expressing the acceleration in the diffusion of M, from the bulk solution to the particle surface, upon crossing the electrostatic potential profile $\psi(r)$.

The rate constant $k_a$ is generally in agreement with the Eigen mechanism, that is,

$$k_a = K_{aw} k_w$$

where $k_w$ is the rate constant (in $s^{-1}$) for water loss from the inner coordination sphere of the local ML complex and $K_{aw}$ (mol$^{-1}$ m$^3$) is the stability constant for the local outer sphere ML complex as determined by the Fuoss-Debye-Hückel equation

$$K_{aw} = 4\pi N_A a_k^3 \alpha_m \gamma^2 e \left[ 1 - \alpha_m \left( 1 + \alpha_m \right) \right] \left( 4\pi \varepsilon_0 \varepsilon_r k_0 T a_k \right) / 3$$

where $\varepsilon_0$ and $\varepsilon_r$ are the dielectric permittivity of vacuum and relative dielectric permittivity of the medium, respectively. $a_k$ is the geometrical center-to-center distance between M and L, $q_L$ is the charge center-to-center distance between M and L, $\kappa$ is the reciprocal screening Debye layer $\kappa = (2z^2 F^2 c^m / (\varepsilon_0 \varepsilon_r RT))^{1/2}$, and $N_A$ is the Avogadro number. In line with previous work, we set $a_k = a_{CL} = 0.5$ nm. The limit of eq 4 and 5 when applied to rapidly dehydrating Pb2+ is further discussed in section 4.4.
In the other extreme where M transport limits the rate of colloidal metal complex formation (i.e., \( k_p \rho_i^2 \beta_j / (4 \pi r_p D_M a_{\text{eff}}) \gtrsim 1 \)), we have

\[
k^*_{\text{s}} / k_a = 1 / (k_p \rho_i^2 / (4 \pi r_p D_M a_{\text{eff}}) \beta_j) \quad (7)
\]

Equations 6 and 7 correspond to cases where the formation of metal–particle complexes is rate-limited by reaction kinetics and by metal transport dynamics, respectively.

**Complex Stability Constants.** Under the underlying validity of eq 3, the stability constant \( K \equiv k_{\text{fl}}^* / k_{\text{diff}} \) (mol\(^{-1}\) m\(^3\)) for the colloidal metal complex is connected to the intrinsic stability constant \( K_\text{fi} \) of the locally formed ML complex by the relationship\(^{13} \)

\[
K^* / K = \frac{V_c}{V_i} \int_a^\infty r^2 \exp(-z\alpha r/z) \, dr / \left[ \frac{V_i}{V_c} \int_0^\infty r^2 \exp(-z\alpha r/z) \, dr \right] \quad (8)
\]

where \( r_* \) is defined in Figure 1 and \( V_i \) is the volume of the particle shell layer. The term in the right-hand side of eq 8 may be interpreted as the ratio between the equilibrium \( M \) and derived from the rate constant \( k_\text{fl}^* \) or static when the rates of these volume reactions are fast or slow, respectively.\(^{33,34} \) For the former situation, we further distinguish nonlabile and labile complexes, that is, cases where the metal binding solely through the electrostatics. Their covalent binding is negligible, since, like all conjugated bases of strong acids \((pK_a = 1.74)\), they do not easily share their valence electrons. This is confirmed by our electroanalytical measurements (section 4.3) that do not reveal significant metal binding in the pH range where particle charge density is solely fixed by sulfonate groups. Equation 10 applies under the condition where the characteristic distance between the charged groups carried by the particle is well below the Debye length, which is satisfied for sufficiently low electrolyte concentrations \( c \). The boundary conditions associated with eq 10 express the absence of charge at the particle core surface and the electroneutrality of the bulk medium.\(^{20,39} \) The searched electrophoretic mobility \( \mu \) of the particle then satisfies the Taylor expansion\(^{39} \)

\[
h(r \to \infty) = \mu r / 2 + O(1/r) \quad (11)
\]

where the radial function \( h \) depends on the potential distribution \( y(r) \) and defines the electroosmotic flow field profile \( \vec{u}(\vec{r}) \) developed around/within the soft particle via

\[
\vec{u}(\vec{r}) = (-2h(r)E \cos \theta / r, \ (d(rh(r))/dr)E \sin \theta / r, 0) \quad (12)
\]

with \( \vec{r} = (r, \theta, \phi) \) the coordinate system specified in Figure 1 and \( E \) being the magnitude of the applied electric field. The
hydrodynamic function \( h \) is obtained from the solution of the coupled nonlinear Navier–Stokes–Brinkman equation, continuity equation for steady incompressible flow and continuity equations for all mobile ions present in the system.\(^{20}\) This set of equations expresses the friction force exerted by the shell layer on the electroosmotic flow, and it accounts for the possible radial distribution of polymer segment density from the particle surface to the outer electrolyte solution (via the function \( f \) introduced in eqs 1 and 10). In particular, the friction force depends on the so-called (nominal) softness parameter \( \lambda_o \) of the permeable polymeric shell, with \( 1/\lambda_o \) being the Brinkman length. In the limit \( 1/\lambda_o \rightarrow 0 \), there is no flow penetration within the shell while the limit of free draining shell is reached for \( 1/\lambda_o \rightarrow \infty \). The set of governing electrostatic and electrodynamics equations was numerically solved using the COLSYS package\(^{40}\) where the solution is assimilated to polynomial function estimated on an auto-adaptive spatial grid. As argued in previous reports,\(^{20,38,39,41–52}\) the concept of zeta potential has no physical basis for soft particles.

4. RESULTS AND DISCUSSION

4.1. Evidence of a Thin Shell Layer at the Polymer Nanoparticles Surface from FRET. Donor fluorescence decay curves of 2 wt % polymer nanoparticle dispersions containing different ratios of adsorbed R6G and MG were measured at room temperature, at pH 4 in 100 mM NaNO3 electrolyte and at pH 7 in 3 mM NaNO3, (Figure 2A and B, respectively). The data were analyzed by the distribution method for FRET in spherical nanodomains considering a Poisson distribution of adsorbed dyes per particle.\(^{21,53}\) This allowed us to obtain the distribution of dyes adsorbed at the particle surface, a distribution that, in turn, follows the searched polymer segment density distribution profile at the particle–water interface. The latter profile was rationalized from a modification of the density distribution expression by Helfand and Tagami for interfaces in strongly segregated polymer systems, with \( f(r) = \{0.5\pi\delta \times \cosh(2(r - R_s)/\delta)\}^{-1} \).\(^{21,54}\) Adjustment of the model to data requires two fitting parameters: \( \delta \), that controls the shape of the density profile,\(^{21}\) and a normalization factor for the fluorescence intensity decay curves. The equivalent hard-sphere radius \( R_s \) in the expression of \( f(r) \) was measured by dynamic light scattering (\( R_s = 54.5 \) nm), and the number of acceptor molecules in the shell was independently calculated from the mass balance of adsorbed MG. The critical Förster distance was further kept fixed to the experimental value \( R_0 = 6.8 \) nm,\(^{24}\) the encounter radius was set at \( R_e = 0.5 \) nm,\(^{21,24}\) and the dipole–dipole relative orientation parameter at \( \langle \chi^2 \rangle = 0.476 \), which corresponds to randomly oriented dipoles that are immobile on the time-scale of the energy transfer.\(^{24}\) A donor lifetime of \( \tau_D = 4.3 \) ns was independently obtained from particle dispersions containing only R6G, whose fluorescence decay curves were in line with a single-exponential function.

The decay fluorescence curves depicted in Figure 2A,B were successfully reconstructed using the formalism published elsewhere\(^{21,24,25}\) and detailed in Supporting Information. While maintaining constant the average number of donor molecules per particle, the fitting procedure was applied to all data collected for different donor/acceptor concentration ratios in order to obtain the distribution of donor adsorbed at the particle surface under the various concentration ratios tested (Figure 2C). It is found that \( \delta \) remains approximately constant for all acceptor concentrations and that \( \delta \) further hardly varies in the pH range 4–7 and electrolyte concentrations range 3–100 mM, with \( \delta = (0.5 \pm 0.1) \) nm and \( \delta = (0.78 \pm 0.04) \) nm obtained at pH 4 with 100 mM NaNO3 and pH 7 with 3 mM NaNO3, respectively. The shell layer thickness extending outside the equivalent hard-sphere radius \( R_s = 54.5 \) nm that includes 90% of all the dyes adsorbed at the nanoparticle surface is \( d = 1.3 \times \delta \), which corresponds to 0.7 and 1 nm over the pH and ionic strength conditions examined in panels (A) and (B), respectively.

![Figure 2. Time-resolved fluorescence decay curves of R6G (5 × 10^{-7} M) in a 2 wt % suspension of polymer nanoparticles (obtained for an excitation wavelength \( \lambda_{exc} = 340 \) nm, and collected at \( \lambda_{em} = 547 \) nm) at (A) pH = 4, 100 mM NaNO3, (B) pH = 7, 3 mM NaNO3, in the absence of MG (dark orange, monoeponential decay) and in the presence of MG at the concentrations 2 × 10^{-6} M (green); 4 × 10^{-6} M (purple); 6 × 10^{-6} M (blue); 1.0 × 10^{-5} M (orange); and 1.4 × 10^{-5} M (gray). (C) Typical normalized polymer segment density profiles \( f(r) \) (normalization to 1 at \( r = 53 \) nm) at the particle/water interface as calculated from fitting the donor fluorescence decay curves for all tested concentrations of acceptor (Supporting Information). Parameter values: \( \delta = (0.5 \pm 0.1) \) nm at pH = 4, 100 mM NaNO3, and \( \delta = (0.78 \pm 0.04) \) nm at pH = 7, 3 mM NaNO3. The shell layer thickness that includes 90% of all the dyes adsorbed at the nanoparticle surface is \( d = 1.3 \times \delta \), which corresponds to ca. 0.7 and 1 nm over the pH and ionic strength conditions examined in panels (A) and (B), respectively.

4.2. Electrokinetics of Polymer Nanoparticles. In order to determine the electrostatic properties of the present polymer nanoparticles electrophoretic mobility measurements (\( \mu \)) were performed on dilute dispersions according to the procedure detailed in section 2. Results are collected in Figure 3 over the pH range 3.5–6.9 and for NaNO3 electrolyte concentrations in the range 1 mM to 200 mM. At pH 3.5, it is observed that \( \mu \) increases in magnitude with decreasing salt concentration, in line with the decrease of the screening of the particle charge by
ions present in the medium. For sufficiently large values of electrolyte concentration, \( \mu \) asymptotically reaches a constant nonzero plateau value (as noticed from the plot of \( \mu \) versus \( c_\infty \) in a linear scale, not shown). This electrokinetic property is the characteristic signature of the presence of an ion- and water-permeable polyelectrolytic shell layer at the particle surface.\(^{20,38,39,41-43,46,48,51}\) It confirms the core–shell nature of the investigated polymer nanoparticles, as independently revealed by the FRET measurements detailed in section 4.1.

With increasing solution pH, at fixed \( c_\infty \), \( |\mu| \) increases as a result of the increase in particle charge, following the deprotonation of carboxylic groups in the shell layer. The electrokinetic data further highlight a nonmonotonous dependence of \( \mu \) on salt concentration with the apparition of a minimum in mobility at \( c_\infty \sim 10 \text{ mM} \). This minimum becomes increasingly marked with increasing pH from 5 to 6.9. As extensively detailed elsewhere,\(^{38}\) two explanations may be advanced for the origin of the observed minimum in \( \mu \) at low electrolyte concentrations:

(i) Upon increase of the solution pH at fixed low \( c^\infty \), the repulsion between the charges located in the particle shell becomes significant, which leads to a swelling of the polymer surface layer. This swelling is accompanied by the broadening of the diffuse distribution of polymer segments from the particle core surface to the outer electrolyte medium, resulting in an increased friction exerted by the particle coating on the electroosmotic flow. In turn, the particle electrophoretic mobility decreases with decreasing \( c^\infty \) at sufficiently large pH values. This process has been theoretically and experimentally evidenced in various reports mentioned in ref 38.

(ii) At sufficiently large pH and low \( c^\infty \), the polarization of the electric double layer (EDL) at the particle/solution interface becomes important. The corresponding noncoincidence of the centers of counterion charge and particle charges generates an electric field whose direction is opposite to that of the applied field. This induced field counteracts the migration of the particle and it thus reduces particle electrophoretic mobility.\(^{20,48,51}\) The EDL polarization phenomenon is very well-known in the field of electrokinetics of both hard particles (i.e., particle deprived of polymeric surface layer), and soft particles that exhibit at their surface an ion- and water-permeable shell layer. EDL polarization comes into play for highly charged particles at sufficiently low electrolyte concentrations.

In order to quantitatively determine the electrostatic properties of the polymer nanoparticles and discriminate between processes (i) and (ii) on the origin of the minimum in their electrophoretic mobility \( \mu \), we attempted to consistently reconstruct the electrokinetic data on the basis of the soft particle electrokinetic theory outlined in §3.2. The required particle core radius \( a \) and the estimated value for the shell layer thickness \( d \) are independently obtained from DLS/TEM and FRET measurements, respectively \((a \approx 50 \text{ nm} \text{ and } d = 1.3 \times \delta \approx 0.7 \text{ nm})\). The remaining unknown parameters are the types and amounts of dissociable charges and their density within the particle shell, the associated mean dissociation pK values and the Brinkman length \( 1/\lambda_o \).
with literature, for this type of polymer nanoparticles, the main source of charges stems from the dissociation of carboxylic groups, that is, the groups that, once deprotonated, bind metal ions $M$ ($L = \text{COO}^-$ in section 3.1 and in eq 10). As detailed in section 4.3, the dependence of the stability constant $K^* = K^0 \rho_i^*$ (eq 8) on pH is strongly governed by the searched $pK_a$ via eqs 1, 8, and 10. Analysis of experimental $K^* = K^0 \rho_i^*$ data collected under different conditions of pH and salt concentration eventually leads to $pK_a = 6.1$ (see section 4.3). This value is in good agreement with that reported in literature.55

Taking into account the above values of $a_i$, $pK_a$, and the estimated value for $d$ provided by FRET analysis, the electrokinetic data displayed in Figure 3 could be reconstructed remarkably well using $d = 0.9 \pm 0.2$ nm and introducing sulfonate charged groups ($1 \equiv -\text{SO}_3^-$ in eq 10) known to be present at polymer nanoparticle surface.55 Under the pH conditions adopted in the electrokinetic experiments, the strong acids $\text{SO}_3\text{H}$ are fully dissociated ($pK_a < 3.5$). In addition, we find that the Brinkman length $1/\lambda_a$ is systematically comparable to the shell layer thickness $d$ for pH in the range 3.5–6, reflecting a significant electroosmotic flow penetration within the particle polymer coating. At pH $= 6.9$, the dependence of $\mu$ on $c^\infty$ is consistent with $1/\lambda_a = 0.25$ nm, which suggests a “solidification” of the polymer coating with increasing significantly the particle charge following deprotonation of carboxylic groups ($pK_a = 6.1$). Oshima recently showed that this “solidification effect” is relevant for highly charged soft particles whose electrokinetic properties may be similar to those expected for hard rigid particles (with low $1/\lambda_a$) under conditions where intrashell potentials are very large.56 As a last remark, we found that, regardless of the pH and ionic strength conditions examined, the mobility $\mu$ of polymer nanoparticles is not very sensitive to the diffuseness in polymer segment density distribution, so that data could be recovered using a step-function-like profile for the radial density distribution $f$ involved in eq 10. As shown in previous theoretical work on electrokinetics of soft surface layers, this poor-dependence of $\mu$ on the interfacial polymer segment density gradient is explained by the significant flow penetration length $1/\lambda_a$ as compared to the shell layer thickness.56,57 This renders the friction force exerted by the particle on the flow quasi-insensitive to details in polymer segment distribution at the particle/electrolyte solution interface. As a result, the minima in mobility $\mu$ discussed above originate from the large amount of charges carried by the particles and from the ensuing EDL polarization taking place at sufficiently low $c^\infty$ and large solution pH. Quantitatively, the searched values for the density of sulfonate and carboxylic groups in the particle shell as derived from the analysis of $\mu$ over 2 orders of magnitude in $c^\infty$ and nearly 4 pH units are $c^\infty_L = 190$ mM $\pm 10\%$ and $c^\infty_r = 2 \times 10^3$ mM $\pm 10\%$, respectively.

As an intermediate conclusion, we note that the dependence of $\mu$ on pH and salt concentration for polymer nanoparticles is consistent with a characteristic shell layer thickness $d = 0.9 \pm 0.2$ nm (using a step-function like profile for $f$), and with the following protolytic features and density of the (metal-binding) carboxylate groups $L$, $pK_a = 6.1$ and $c^\infty_L = 2 \times 10^3$ mM $\pm 10\%$. At this stage of the analysis, the electrostatic potential distribution $y(r)$ was derived at the shell/solution interface is known from eq 10 over the pH range 3.5–6.9 and over the salt concentration range 1–200 mM. The so-obtained $y(r)$ remains further unchanged upon introduction of metal ions in the particle dispersion essentially because the conditions of large excess of ligands over metals (i.e., $c^\infty_M \ll c^\infty_e$) and large excess of indifferent ions over metals (i.e., $c^\infty_M \ll c^\infty_e$) are systematically satisfied within the framework of this study.

The molecular dimension we found for the surface layer surrounding the particle core $(d = 0.9 \pm 0.2$ nm) deserves some additional comments. It is comparable to the size of carboxylate or sulfonate groups, which means that latex particles may be effectively viewed as hard particles carrying charges distributed at their very surface. Within the mean-field PB theory, the electrostatic potential profile derived at the shell/solution interface is similar to that obtained for a planar distribution of the particle charges for $kd < 1$. This condition is basically verified for the electrolyte concentration values adopted in this work. At sufficiently large electrolyte concentrations, the spatial separation between particle charges and the dimension of charged groups become necessarily comparable to the Debye layer thickness. A refined molecular evaluation of $y(r)$ would then require that we account for charges discretization and size. Although this refinement is not included here (within the PB-based electrostatic model), we found that it still adequately captures, at a quantitative level, the impact of electrostatics on metal–nanoparticle complex stability (section 4.3) for $c^\infty$ values ranging from 1 to 100 mM. This is due to the high charge density of the particles and the corresponding dense packing of the ionogenic groups at their surface, which in turn validates the smeared-out approximation for charge distribution made within PB theory. Undoubtedly, further electrostatic modeling would be needed to better define the transition between electrostatic properties of hard spheres (planar distribution of charges) and those of core particles surrounded by shell of molecular dimensions. Such modeling is beyond the scope of this paper, and, in a first order approximation, polymer nanoparticles effectively behave here as hard particles from an electrostatic point of view.

The presence of a soft (permeable) shell layer around the particles (confirmed by FRET data analysis) is however required for appropriate understanding of their electrokinetic properties, in particular their constant mobility value reached at large electrolyte concentrations. This is done by introducing an effective characteristic length for the flow penetration within the shell ($1/\lambda_a$) that is of the order of $d$. A comparison between our electrokinetic modeling and results issued from molecular electrohydrodynamic simulations within the shell layer would be most welcome to guarantee the validity of standard Navier–Stokes–Brinkman equations for permeable surface layers with thickness of the order of one nanometer or below. To the best of our knowledge, the theoretical framework for such simulations is not yet available. However, the matching between the soft surface layer thickness found from electrokinetics and from FRET suggests the adequacy of our effective hydrodynamic approach applied to a shell of molecular dimension. There are numerous literature examples that illustrate the success of this approach for understanding hydrodynamic flow profiles at rough surfaces.18

With regard to their metal binding features, the polymer nanoparticles investigated here may be viewed as hard particles essentially because the shell layer dimension does not allow for a complete hosting of metal ions. In turn, there is no significant concentration gradient within the shell, which is in line with one of the assumptions underlying the validity of eq 3.

Having in mind the above elements, the measured impact of electrostatics on the stability constant and on the chemo-dynamic and lability properties of metal–polymer nanoparticle...
complexes is quantitatively investigated in the next section with use of eqs 3, 8, and 9.

4.3. Thermodynamic Stability Constant of Cd(II)–Polymer and Pb(II)–Polymer Nanoparticle Complexes. The Case of Cd(II)–Polymer Nanoparticle Complexes. As mentioned in section 2, SSCP and AGNES measurements allow for a direct evaluation of the (dimensionless) stability constant $K^{*'} = K^* \rho_{L}^0$ of colloidal metal complexes as detailed in the Supporting Information.18,19 $K^{*'}$ values are collected in Figure 4 for Cd(II)–polymer nanoparticles as a function of pH in the range 6–7 for different values of NaNO$_3$ concentrations $c^0$.

![Figure 4](image.png)

Figure 4. Dependence of the dimensionless stability constant $K^{*'} = K^* \rho_{L}^0$ of Cd(II)–polymer nanoparticle complexes on NaNO$_3$ electrolyte concentration and pH. $c^0 \rightarrow \infty$ (a), $c^0 = 100$ mM (b), 60 mM (c), 30 mM (d), 11 mM (e), and 6 mM (f). Symbols: experiments. Dotted lines: theory (eqs 8 and 10). Electrostatic and particle dimension parameters: as in Figure 3. Other model parameters: $K = 10.5 \pm 0.5$ mol$^{-1}$ m$^3$. The solid line shows the slope of unity for a linear dependence of log($K^{*'}$) on pH (eq 14). Total Cd(II) concentration: 10$^{-6}$ M.

It is observed that the logarithm of $K^{*'}$ increases quasi-linearly with pH while log($K^{*'}$) vs pH curves are translated upward in Figure 4 with decreasing $c^0$. The theoretical reconstruction of $K^{*'} = K^* \rho_{L}^0$ necessitates the computation of the constant $K^*$ defined by eq 8 and the evaluation of the volume-averaged concentration of carboxylate groups $\rho_{L}^0 = 4\pi \int_0^\infty c_L(r) \, dr / V_L$ (where $c_L(r)$ is defined by eq 1) for the various sets of pH and electrolyte concentration adopted in Figure 4. To that end, the potential profile $y(r)$ involved in eqs 1 and 8 is obtained from eq 10, with use of the $p_{K_{s,L}}$, $c_L^0$, $a$, $d$, and $f$ quantities evaluated in section 4.2. Given these elements, the recovery of the $K^{*'}$ data displayed in Figure 4 with use of eqs 1 and 8 only requires the adjustment of the intrinsic (chemical) stability constant $K$ of the locally formed ML complex. Results depict a remarkable agreement between experiments and theory with $K = 10.5 \pm 0.5$ mol$^{-1}$ m$^3$ (Figure 4). The consistency of the analysis is reflected by the single $K$ value that is, within experimental error, independent of pH and $c^0$. In order to appreciate the impact of electrostatics on $K^{*'}$, the predicted dependence of $K^{*'}$ under infinite particle charge screening condition ($c^0 \rightarrow \infty, y(r) \rightarrow 0$) is given in Figure 4 (curve a) obeying the same value of $K = 10.5$ mol$^{-1}$ m$^3$).

Comparing this dependence to that obtained at finite $c^0$, indicates that, even at 100 mM NaNO$_3$ concentration and pH = 6, electrostatics still significantly affects $K^{*'}$. This is due to the contribution of the dissociated sulfonate groups in maintaining a high interfacial electric field under pH conditions where dissociation of carboxylic groups is limited.

The dependence of $K^{*'}$ on pH and $c^0$ is very well captured by theory in case of Cd(II)–polymer nanoparticle complexes. In order to further justify the quasi-linear increase of log($K^{*'}$) with pH, we further derive below approximate analytical expressions of $K^{*'}$. In the limit $\kappa d \ll 1$ reached at sufficiently low $c^0$, the potential distribution within the shell layer is nearly constant so that $y(a \leq r \leq b) \approx y_o$ where $y_o$ is the particle surface potential that depends both on pH and $c^0$. Then, combining eqs 1 and 8 with the expression of $\rho_{L}^0$, we obtain for dilute dispersions ($\kappa r_o \gg 1$) and step-function-like distribution $f(r)$:

$$
\log(K^{*'}) \approx \log(V_K c_L^0 / V_c) + \log\left\{ \exp\left( -z a y_o^* / z \right) \right\} /
\left( \left[ 1 + 10^{pK_a - pH} \exp\left( z a y_o^* / z \right) \right] \times \left[ 1 + V_c \exp\left( -z a y_o^* / z / V_c \right) \right] \right) \tag{13}
$$

For pH $\ll pK_a$, the magnitude of $y_o$ is governed by $c^0$ and by the sole sulfonate charge in the shell. Under such condition, $y_o$ is essentially independent of pH. For the polymer nanoparticles carrying a high density of sulfonate and for pH $\ll pK_a$, we have $\exp(z a y_o^* / z) \gg 10^{pK_a - pH}$ and eq 13 reduces to

$$
\log(K^{*'}) \approx \log\left( V_K c_L^0 / V_c \right) / \left( 1 + V_c \exp\left( -z a y_o^* / z / V_c \right) \right) - \frac{1}{z} \ln(10) (z_M + z_o) y_o^* + pH - pK_L \tag{14}
$$

Equation 14 reveals that in the pH range pH $\ll pK_a$ under the condition $\kappa d \ll 1$, log($K^{*'}$) linearly increases with pH with a slope equal to unity. This behavior agrees with the exact numerical computations performed for Cd(II)–polymer nanoparticle complexes at pH $< 6$ (data not shown), and it is confirmed by the analysis of the log($K^{*'}$) data collected for Pb(II)–polymer nanoparticle complexes in the pH range 5–6, as discussed later (Figure 5). The variation of log($K^{*'}$) with pH will necessarily deviate from that given by eq 14 as soon as $y_o$ becomes pH-dependent (eq 13). This is typically the case for Cd(II)–polymer nanoparticle complexes in the pH range 6–7 where dissociation of carboxylic groups comes into play ($pK_L = 6.1$). The associated increase in $V_L$ then enhances the increase of log($K^{*'}$) with pH as compared to that predicted from eq 14, which is illustrated in Figure 4. In line with experimental data, $y_L$ increases with decreasing $c^0$ at fixed pH, thus resulting in an increase of log($K^{*'}$), as verified from inspection of the approximate analytical eqs 13 and 14. Under conditions where $y_o \rightarrow 0$, electrostatics do not impact $K^{*'}$, and eq 13 simplifies into log($K^{*'}$) $\sim$ log($V_K c_L^0 / V_c$) $- \log(1 + 10^{pK_a - pH})$, where we used the inequality $V_c / V_L \ll 1$ valid for dilute suspensions. The plateau reached by $K^{*'}$ at pH $\gg pK_a$ under the conditions leading to $y_o \rightarrow 0$ (curve a in Figure 4) identifies to $V_K c_L^0 / V_c$. We verified that the theoretical results depicted in Figure 4 were not affected when introducing some diffuseness in the polymer segment density distribution $f(r)$. This feature, analogously observed in conductivity analysis of charged soft thin films,27 is explained by the dependence of $K^{*'}$ on potential-dependent terms that are integral-averaged over the entire particle soft surface layer region (eq 8).
Comparison with the Thermodynamic Stability for Pb(II)–Polymer Nanoparticle Complexes. The variations of the dimensionless stability constant \(K^{*}\) with pH and \(c^\infty\) measured for Pb(II)–polymer nanoparticle complexes are shown in Figure 5. Qualitatively, the dependence of \(K^{*}\) on pH and \(c^\infty\) is similar to that discussed for Cd(II)–polymer nanoparticle complexes. Following the strategy detailed in the previous section, we attempted to recover the experimental data using the particle structure and electrostatic parameters independently derived from electrokinetics (section 4.2) and appropriate adjustment of the intrinsic chemical stability constant. The results given in Figure 5 show a very good agreement between experiments and theory at pH < 5.5 over the tested range of \(c^\infty\) with \(K = 4.9 \times 10^3\) mol\(^{-1}\) m\(^3\). As expected, this intrinsic K value is significantly larger than that obtained for Cd(II)–polymer nanoparticle complexes, in line with the stronger binding strength of Pb(II) as compared to that of Cd(II). For pH > 5.5, that is, with significantly increasing the amount of charged metal-binding sites across the particle shell, the theory systematically underestimates \(K^{*}\) or, equivalently, the amount of Pb(II) bound to the particle shell. In view of the remarkable matching between experiments and theory for Cd(II)–polymer nanoparticle complexes (Figure 4), it is very unlikely that the discrepancy observed for lead originates from an (electrostatic) heterogeneity in the carboxylate binding sites as a result of a broad distribution in associated dissociation pH\(_A\) values. Instead, we hypothesize at pH > 5.5 a 1:n (n ≥ 1) binding of lead to carboxylic groups located along a given polymer chain or belonging to adjacent chains, thus resulting in ML\(_n\) complexes. The corresponding K values would then be larger than those obtained at pH < 5.5 due to stronger binding, and they would lead to larger \(K^{*}\) than those estimated from eq 8 for a 1:1 metal–L binding stoichiometry. More quantitative conclusions would necessitate the nontrivial implementation of metal binding heterogeneity in theory for chemodynamics of colloidal metal complexes.

**4.4. Chemodynamics and Lability of Cd(II)–Polymer and Pb(II)–Polymer Nanoparticle Complexes.** As outlined in section 3.1, the magnitude of the ratio \(k_s^*/k_s\) reflects the extent at which the overall formation of metal–particle complexes is rate-limited by metal (conductive-diffusion) transport dynamics and local reaction kinetics between M and L. Figure 6 shows the variations of \(k_s^*/k_s\) computed from eq 3 for Cd(II)–polymer and Pb(II)–polymer nanoparticle complexes under the pH and ionic strength conditions tested in the electroanalytical experiments. It is emphasized that the quantities involved in eq 3 could all be evaluated from the key polymer nanoparticle electrostatic parameters determined from electrokinetics. In addition, we draw attention on the fact that \(k_s^*/k_s\) depends on pH and \(c^\infty\) via the kinetic constant \(k_f\) (eqs 4 and 5), the volume-averaged ligand concentration \(\rho_s^*\), the Boltzmann factor \(\beta_s\), and the conductive-diffusion term \(f_{\text{diff}}\).

Overall, two main conclusions may be drawn from Figure 6. First, \(k_s^*/k_s\) decreases with increasing pH at fixed \(c^\infty\) essentially because \(\rho_s^*\) increases as a result of significant dissociation of the carboxylic groups. Second, \(k_s^*/k_s\) increases with decreasing \(c^\infty\) at fixed pH due to the strong increase of \(\beta_s\) in the numerator of eq 3. The metal diffusion layer thickness is significantly larger than the Debye length and the particle shell layer thickness.

This explains the moderate variation of \(\beta_s\) with varying solution pH. Overall, decreasing \(c^\infty\) thus favors a kinetic limitation of particulate metal complex formation. A similar effect is found with increasing pH after adequate normalization of the complex formation rate constant \(k^*\) by the pH-dependent ligands concentration \(\rho_s^*\) (panels C and D in Figure 6). This normalization is required in order to properly compare chemodynamic features of complexes whose concentrations in charged metal-binding sites are significantly different (in particular with varying solution pH).

An important feature is that \(k_s^*/k_s\) for Cd(II)–polymer nanoparticle complexes is larger than that for Pb(II)–polymer nanoparticle complexes under given pH and \(c^\infty\) conditions. This marked transport-limitation for Pb(II)–polymer nanoparticle complex formation is explained by the larger \(k_s^*\) (and thus larger \(k_f\), see eq 4) for Pb(II) as compared to Cd(II). Stated differently, the kinetic formation of local ML complexes is faster in the case of lead, so that Pb(II)–polymer nanoparticle binding is more significantly rate-limited by metal transport to/from the binding particles. The effect of electrostatics on \(k_s^*/k_s\) may be further apprehended upon comparing the results obtained for finite \(c^\infty\) with those for \(c^\infty\rightarrow\infty\) where \(k_s^*/k_s\) reduces to \(k_s^*/k_s = \{1 + \rho_s^* c_f V,/[4\pi\varepsilon D_s(1 + 10^{\phi_s^*\text{pH}})]\}^{-1/2}\) (Figure 6, dotted lines). The positioning of the curve obtained for \(c^\infty\rightarrow\infty\) with respect to that evaluated for finite \(c^\infty\) is explained by the corresponding variations of \(\rho_s^*\) and \(\beta_s\) with pH.

Using the above \(k_s^*/k_s\) results, the lability \(L^*\) of the metal–polymer nanoparticle complexes was evaluated by means of eq 9 as a function of pH and \(c^\infty\) (Figure 7). Let us start analyzing the situation for Cd(II)–polymer nanoparticle complexes (Figure 7A). At low pH values, the dependence of \(L^*\) on pH is dominated by that of \(k_s^*/k_s\)^1/2 so that \(L^*\) increases with pH (see the pH-dependence of \(k_s^*/k_s\) in Figure 6C,D) as a result of the corresponding increase in particle charge density. With increasing pH, the complete dissociation of carboxylic groups is gradually approached and the term \((k_s^*/k_s)\) involved in eq 9 becomes less dependent on solution pH (Figure 6C,D). In turn, the variation of \(L^*\) with further increasing pH becomes
predominately governed by that of $K^*'$ (Figure 4). After examining the $K^*'$-dependent terms in eq 9, it comes that $3^*$ decreases with increasing pH. The above nonmonotonous evolution of $L^*$ with pH is further in agreement with the $c^\infty$-dependent trends depicted in Figure 7. At a fixed low pH corresponding to partial charge dissociation, $L^*$ increases with decreasing $c^\infty$. In this pH range, we have indeed $K^*tí»1$, and the dependence of $L^*$ on $c^\infty$ is dictated by that of $(ka^*L)$1/2. At sufficiently large pH values, the variation of $L^*$ with $c^\infty$ becomes controlled by that of $K^*'$, which explains the decrease

Figure 6. Theoretical dependence of the ratio $ka^*/ka$ (eq 3−5) on salt concentration and pH for (A) Cd(II)−polymer nanoparticle complexes and (B) Pb(II)−polymer nanoparticle complexes. In panels (C) and (D), the quantity $ka^*L$ is given for Cd(II)−polymer nanoparticle complexes and Pb(II)−polymer nanoparticle complexes, respectively. The meaning of the letters (a)−(f) in panels (A)/(C) and (B)/(D) is identical to that in Figures 4 and 5, respectively. Model parameters as in Figures 4 and 5, with $a_g = a_{cc} = 0.5$ nm,10 and in panel (A) $D_M = 7.3 \times 10^{-10}$ m−2 s−1, $k_w = 3 \times 10^9$ s−1,31 and in panel (B) $D_M = 9.85 \times 10^{-10}$ m−2 s−1, $k_w = 7 \times 10^9$ s−1.

Figure 7. Theoretical dependence of the lability $L^*$ (eq 9) on salt concentration and pH for (A) Cd(II)−polymer nanoparticle complexes and (B) Pb(II)−polymer nanoparticle complexes. The meaning of the letters (a)−(f) in panels (A) and (B) is identical to that in Figures 4 and 5, respectively. The dotted vertical lines mark the pH window accessible by electroanalytical measurements (Figures 4 and 5). Model parameters: as in Figure 6 with, in addition, $D_M = 4.62 \times 10^{-12}$ m−2 s−1 (obtained from dynamic light scattering measurement) and $\omega = 157$ s−1. For the sake of readability, the critical lability value $L^* \sim 1$ marking the frontier between labile ($L^* \gg 1$) and nonlabile ($L^* \ll 1$) particulate metal complexes is indicated. The vertical blue lines represent the range of lability values $L^*$ estimated from experiments via eq 9 for three sets of pH and ionic strength conditions specified in the text. See text for further details.
of $L^*$ with decreasing $c^\infty$ in this pH range. Figure 7A shows that the pH position for the minimum in $L^*$ is shifted to the left with decreasing $c^\infty$. This shift originates from the impact of electrostatics on the dissociation of carboxylic groups: the lower $c^\infty$, the larger the potential (in magnitude) within the particle shell, and the earlier dissociation shows up with increasing pH (eq 1). The situation for Pb(II)–polymer nanoparticle complexes is similar to that detailed above for Cd(II)–polymer nanoparticle complexes (Figure 7B). The major difference is that the dependence of $L^*$ on pH and $c^\infty$ is now systematically dominated by $K^*$, whose value is 1–2 orders of magnitude larger than for Cd(II)–polymer nanoparticle complexes under given pH and $c^\infty$ conditions (Figures 4 and 5). As a result, $L^*$ for Pb(II)–polymer nanoparticle complexes monotonously decreases with increasing pH and with decreasing $c^\infty$.

The most important feature revealed by Figure 7 is that, within the pH window accessible in electroanalytical experiments, an increase of the potential distribution at the polymer nanoparticle/solution interface following an increase in pH and/or a decrease in $c^\infty$ results in a loss of lability for both Cd(II)–polymer and Pb(II)–polymer nanoparticle complexes. This lability loss is most significant for Pb(II)–polymer nanoparticle complexes, as judged from the respective magnitudes of $L^*$ for Cd(II)–polymer and Pb(II)–polymer nanoparticle complexes, for example, in the pH range 6–7. As a remark, Figure 7B necessarily underestimates the lability loss of the Pb(II)–polymer nanoparticle complexes at high pH because the applied theory leads to lower $K^*$ as compared to values obtained from experiments under such pH condition (Figure 5). Overall, electrostatics favors a kinetically limited supply of metal species at the electrode. This property is relevant at the scale of the volume reactions taking place in the vicinity of the macroscopic electrode surface. It is the direct pendant of the impact of electrostatics on the formation of metal–polymer nanoparticle complexes, as discussed via the examination of the ratio $k^d/k^c$ in Figure 6.

The loss of lability predicted by Figure 7 at sufficiently low $c^\infty$ and large pH values is qualitatively in agreement with $L^*$ data independently derived from SSCP curves following the procedure in the Supporting Information. In detail, SSCP-lability diagnosis indicates that Cd(II)–polymer nanoparticle complexes are nonlabile under the condition {pH = 7, $c^\infty$ = 6 mM} ($L^*$ = 1.4–5.2), and Pb(II)–polymer nanoparticle complexes are nonlabile at {pH = 6, $c^\infty$ = 20 mM} ($L^*$ = 1.9–7.3) and at {pH = 6, $c^\infty$ = 10 mM} ($L^*$ = 2.6–8.1) (see Figure 7, blue lines). For all other sets of pH and $c^\infty$ values experimentally tested, we found that both Cd(II)–polymer and Pb(II)–polymer nanoparticle complexes are fully labile. It is emphasized that the experimental estimation of $L^*$ is subject to a large error that is connected to the evaluation of the reaction layer thickness $\mu$, introduced in section 3.1 (eq 9). This is especially true for metal complexes whose $L^*$ is evaluated under conditions that correspond to the onset of lability loss.

It is noted that the loss of lability for Pb(II)–polymer nanoparticle complexes is experimentally “detected” at lower pH and larger $c^\infty$ values than for Cd(II)–polymer nanoparticle complexes. This qualitative trend is again in agreement with theory (Figure 7), as revealed upon comparative inspection of the theoretical $L^*$ data for Cd(II)–polymer and Pb(II)–polymer nanoparticle complexes with respect to the limit $L^*$ = 1 under given pH and $c^\infty$ conditions. As a last comment, we note that the application of the Eigen mechanism for rapidly dehydrating ions like Pb$^{2+}$ (eqs 4 and 5) may be questionable. Indeed, data from the literature suggest that the rate of diffusive supply of metals with high $k_d$ plays a role in limiting the overall complexation process of such metals. Recognizing this potential limitation of our treatment for estimating the kinetic constant $k_d$ in the case of Pb$^{2+}$, the estimated labilities of nanoparticle–Pb$^{2+}$ complexes are then necessarily overestimated.

The decrease of the metal complex lability due to electrostatics is however still adequately captured here at a qualitative level via the electrostatic potential-dependent terms involved in $k^d$ (eq 3). An additional complication stems from the impact of the Boltzmann accumulation of metals in the electric double layer outside the thin-layer shell surrounding the particle. In turn, only a fraction of the diffusive supply flux of metals leads to accumulated metals at the particle surface. However, this correction (that would lead to lower labilities) is rather marginal here, since under all conditions tested in this work the extension of the double layer represents ≈20% of the particle radius at most.

5. CONCLUSIONS

The results reported in this work demonstrate the strong impact of electrostatics on the kinetic parameters pertaining to the formation of metal–(charged) nanoparticle complexes and on their lability. The conclusions are supported by experimental data collected for Cd(II), Pb(II), and highly charged complexing polymer nanoparticles over a wide range of pH and electrolyte concentration conditions. The key electrostatic features of the particles are independently evaluated on the basis of refined analysis of their electrophoretic response, taking into account morphological shell details obtained by FRET. The dependence of the complex stability constant on pH and electrolyte concentration, as derived from electroanalytical measurements, is then shown to be in agreement with predictions from recent theoretical formalism on chemodynamics of charged colloidal metal complexes. Namely, electrostatics favors a kinetic control of the dissociation of nanoparticulate metal complexes and a reduction of their lability when exposed to a macroscopic metal-consuming surface. A rigorous account of electrostatics further allows a clear appreciation of the impact of chemical heterogeneity in metal binding on the stability, lability, and chemodynamic complex properties. This is done here upon comparing results obtained for Cd(II)–particle and Pb(II)–particle complexes.

The work highlights the importance of considering the physicochemical medium composition to appropriately evaluate the dynamic features of particulate metal complexes in the vicinity of a metal-consuming biosurface (e.g., a microorganism), here mimicked by an electrode. In particular, any evaluation of adverse ecotoxicological impact of metal complexes should necessarily integrate the physicochemical parameters affecting both metal speciation (chemodynamics) and metal flux supply from the medium (lability). In that respect, results reported in this study demonstrate the requirement for a careful account of electrostatics in metal-toxicity risk assessment. This recommendation is particularly important for predicting metal toxicity in aquatic media with different salt contents, for example, fresh waters and marine ecosystems.
ASSOCIATED CONTENT

Supporting Information
Detailed information for (i) the evaluation of $K^{**}$ from AGNES and SSCP electroanalytical measurements, (ii) the lability-diagnosis from SSCP data, (iii) the derivation of eq 3 in the main text, and (iv) the FRET analysis of the fluorescence decay curves displayed in Figure 2. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: jerome.duval@univ-lorraine.fr.

Author Contributions
J.F.L.D. and J.P.P. equally contributed to this work.

Notes
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LIST OF MAIN SYMBOLS

- $a$ particle core radius
- $a_b$ geometrical center-to-center distance between M and L
- $a_c$ charge center-to-center distance between M and L
- $c^*_I$ bulk concentration of indifferent ionogenic groups I in the particle shell
- $c^*_L$ bulk concentration of ligands L in the particle shell
- $c_L(r)$ local concentration of ligands L in the particle shell
- $c_M$ concentration of metals M in the bulk solution
- $c_n$ particle number density
- $c_{li}$ concentration of indifferent ions in the bulk solution
- $d$ thickness of the shell surrounding the particle core
- $D_M$ metal diffusion coefficient
- $D_p$ particle diffusion coefficient
- $D^f$ effective diffusion coefficient of metal M for the evaluation of the lability of metal–nanoparticle complex (eq 9)
- $f(r)$ function pertaining to the density distribution of polymer segments that carry the charged ligands in the particle shell
- $f_d$ factor expressing the acceleration in the diffusion of M from the bulk solution to the particle surface upon crossing the electrostatic potential profile
- $I$ pertains to the indifferent ionogenic groups located in the particle shell (sulfonate in this study)
- $J_{zl}$ diffusive flux of ML complexes at a macroscopic metal-consuming interface
- $J_{zl}$ dissociation kinetic flux of ML complexes at a macroscopic metal-consuming interface
- $J_T$ total flux of metals at a macroscopic metal-consuming interface
- $k_i$ kinetic constant for the local association of metal M with charged binding site L
- $k_a^*$ effective kinetic constant for the association of metal M with charged binding site L whose concentration is smeared-out over the sample solution volume
- $k_d$ kinetic constant for the local dissociation of complex between metal M and charged binding site L
- $k_a^*$ effective kinetic constant for the dissociation of metal–nanoparticle complex
- $k_w$ rate constant for water loss from the inner coordination sphere of the local ML complex
- $K = k_w/k_d$ stability constant for local ML complex
- $K^*$ = $k_a^*/k_d$ stability constant for metal–nanoparticle complex
- $K^{**}$ dimensionless stability constant for metal–nanoparticle complex defined by $K^{**} = K^*/K_w$
- $K_w$ stability constant for the local outer sphere ML complex as determined by the Fuoss–Debye–Hückel equation (eq 5)
- $L^*$ lability of metal–nanoparticle complex
- $L$ charged binding site
- $M$ metal ion
- $ML$ complex between metal and binding site
- $pK_i$ mean protonation constant for indifferent groups I in the particle shell
- $pK_{li}$ mean protonation constant for binding sites L in the particle shell
- $r$ radial coordinate
- $r_c$ radius of the Kuwabara unit cell
- $r_p = a + d$ particle radius
- $R_e$ radius of equivalent hard sphere
- $V_c$ volume of the Kuwabara unit cell
- $V_p$ volume of the particle shell
- $y(r)$ dimensionless electrostatic potential at the position r
- $z$ valence of ions from indifferent background electrolyte
- $z_i$ valence of I
- $z_L$ valence of L
- $z_M$ valence of M
- $\beta$ Boltzmann surface factor
- $\delta$ parameter that controls the shape of the polymer segment density profile at the shell/solution interface
- $\delta$ effective metal diffusion length scale (involved in eq 9)
- $e = D_p/D_M$ ratio between diffusion coefficients of particle and metal (involved in eq 9)
- $\phi$ particle volume fraction
- $\kappa$ reciprocal Debye layer thickness
- $1/\lambda_o$ length scale for the penetration of electroosmotic flow within the particle shell
- $\mu$ electrophoretic mobility
- $\mu_e$ reaction layer thickness (involved in eq 9)
- $\psi(r)$ electrostatic potential
- $\rho_{li}^*$ ligand concentration averaged over the Kuwabara unit cell volume of radius $r_c$

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