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Kinetic Features of Metal Complexes with Polysaccharide Colloids: Impact of Ionic Strength

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The dynamic features of metal binding by a gel-like polysaccharide, carboxymethyldextran (CMD), are investigated by stripping chronopotentiometry (SCP). This technique measures the diffusive flux properties of the metallic species in the ligand dispersion as defined by their concentration, mobility, and lability. Cadmium(II) forms only 1:1 complexes with CMD, the lability of which is well described by Eigen mechanism principles, that is, the removal of a water molecule from the inner hydration sphere of the metal ion is limiting the complex formation rate. Lead(II) and copper(II), however, also form intramolecular bidentate complexes with CMD, which requires a conformational reorganization of the polymeric chain. The reorganization process appears to be the rate-limiting step of the overall complexation reaction, which takes place on a time scale of hours. The influence of ionic strength on the rate of bidentate complex formation is insignificant. In contrast, its impact on the stability of the monodentate complex follows the corresponding Donnan potential of the soft CMD particle.

1. Introduction

The distribution, fate, and bioavailability of heavy metal pollutants in natural waters are strongly influenced by dissolved organic matter (DOM) acting as a chelating agent.[1−3] Most of this DOM is present in the form of soft and permeable colloidal particles,[4] which play an important role in the so-called sink/source functioning of ecosystems. Therefore, evaluation of the bioavailability of the metal requires knowledge of (i) the equilibrium distribution over its various complexes as well as (ii) the labilities of these species.[5,6] The dynamic features of colloidal metal complexes are influenced by the hydrodynamic and electrostatic properties of the particulate ligands, that is, their nature and spatial distribution, as well as the distribution of the binding sites and charge density. Consequently, the lability of colloidal metal complexes is generally overestimated by classical approaches pertaining to homogeneous ligand solutions.[7] A recent theory to describe the dynamics and lability of colloidal metal complexes[8] accounts for the restricted localization of ligands within the body of the particles and the hydrodynamic consequences of their softness. The expression for the rate constant of complex formation between such colloids and metal ions is corrected for diffusion of the metal ion to/from the particle. In certain cases, the diffusive transport of metal within the soft colloidal particles may also take part in the kinetics of complexation and influence the lability of such complexes. Moreover, if the particle is highly charged and the ionic strength is rather low, then the rate of formation of the precursor outer-sphere complexes may decrease and even become rate-limiting for metals with very high dehydration rate constants.[9]

It has been shown that variation of the electrolyte concentration in the bulk medium can lead to non-negligible changes in the electrohydrodynamic properties of soft matters, for example, the electrostatic potential and the binding site distribution through swelling or shrinking process.[10−12] In light of this experimental evidence, the theory developed by Duval et al. for soft colloids has been recently extended to investigate the influence of ionic strength on the lability criterion and complex stability constant.[13] Nevertheless, to our knowledge, there are no experimental reports that deal with the influence of ionic strength on the electrostatics and dynamic features of metal complex formation with soft colloids.

In the case of polymeric colloids, the formation of metal complexes with higher coordination numbers may involve conformational changes that impact the thermodynamic strength as well as the kinetics of the complexation. Binding of metal can induce a more compact macromolecular structure via intramolecular bridging, as, for example, often observed with water-soluble polyelectrolytes.[14,15] In the case of the polysaccharide carboxymethyldextran (CMD), a previous study[16] has shown that the dynamic speciation of Pb(II) depends on macromolecular conformational changes that may have a dramatic impact on the kinetics of complex formation and lability. It was demonstrated that the rate-limiting step in the formation of the intramolecular bidentate Pb(LL) is the formation of the pertaining intermediate outer-sphere complex. In the present study, we investigate binding of lead(II), copper(II), and cadmium(II) by CMD at different ionic strengths and characterize the role of electrostatics in the formation of their monodentate and intramolecular bidentate complexes.

2. Material and Methods

2.1. Reagents. All solutions were prepared in ultrapure water (Milli-Q). Pb(II) and Cd(II) solutions were obtained from dilution of a certified standard (0.100 M Metrohm). Cu(II) solutions were prepared from solid cupric nitrate (Fluka, purity 99%). The ionic strength is set with $NaNO_3$ (Fluka, trace select). Stock solutions of MES (2-(*N*-morpholino)-ethanesulfonic acid) buffers were prepared from the solids (Fluka, Microselect,

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>99.5%). Diluted HNO_3 solutions (Merck suprapure) were used to adjust the pH.

CMD was prepared from dextran produced by bacteria of the species *Leuconostoc mesenteroides*. This neutral polysaccharide was obtained from Amersham Biosciences (Uppsala, Sweden). For further information regarding the preparation of CMD and its characterizations, see refs 16 and 17. In this study, the mean molar mass $\overline{M_n}$ of the CMD used is 460 000 g/mol, and its degree of substitution, d_S, that is, the fraction of carboxylated glucosidic groups, is 37%. Polysaccharide solutions were prepared with filtered (0.22 μm) Milli-Q water 24 h prior to experiments and subsequently stored at 4 °C. Protolytic titrations were previously performed[17] to determine the degree of deprotonation as a function of pH and ionic strength (10 and 100 mM). The diffusion coefficient of the CMD, D_{CMD}, obtained from dynamic light scattering measurements[16] is equal to 8.9×10^{-12} m^2/s. To study metal speciation, SCP measurements were performed at pH 6.2 using MES buffer. Under these conditions, essentially all carboxylic groups are deprotonated.

2.2. Apparatus. An Ecochemie Autolab type II potentiostat was used in conjunction with a Metrohm 663 VA stand. The electrometer input impedance of this instrument is >100 GΩ. The working electrode was a Metrohm multimode mercury drop electrode (surface area 4.0×10^{-7}m^2, Merck mercury, p.a.). The auxiliary electrode was glassy carbon, and the reference electrode was a calomel electrode encased in a 0.1 M KNO_3 salt bridge. The glass wall of the cells used in these experiments is coated with a polystyrene film to reduce trace metal adsorption by cell walls.[18]

2.3. Measurement Procedure. The technique of depletive stripping chronopotentiometry (SCP) consists of a deposition step, during which metal ions are reduced and accumulated in the electrode volume, followed by a quantification step where the accumulated metal is reoxidized by the application of a constant current. The analytical signal (the stripping time τ) is a measure of the accumulated metal, which is directly correlated with the pertinent species concentration in solution. The deposition step is carried out at the specified deposition potential E_d for a time, t_d, of 60 s. The stripping current, I_s, of 1×10^{-9} Å is applied in quiescent solution until the potential reaches a value well past the reoxidation transition plateau. The magnitude of I_s is low enough to warrant conditions of complete depletion for which the product $I_s\tau$ is a constant.[19] The limiting transition time, τ^*, is related to the total amount of metal accumulated during the deposition step for deposition potentials in the limiting current region of the metal/complex system. The experiments are run as follows. A solution is made up from 20 mL of pure water, 5 μL of HNO_3 and the appropriate amount of 1 M $NaNO_3$ to fix the ionic strength and left under argon bubbling for 2 h to remove oxygen; an argon blanket is maintained during measurements. Metal is then added in the form of $Pb(NO_3)_2$, $Cu(NO_3)_2$, or $Cd(NO_3)_2$, and a reference measurement is performed, yielding the metal-only signal, τ^*_M. Together with a given quantity of CMD solution, 200 μL of buffer (MES: 2-(*N*-morpholino) ethanesulfonic acid) is added to maintain the pH at 6.1 to 6.2. Metal-to-ligand ratios R (= $c_{M,t}/c_{L,t}$), where $c_{L,t}$ is the total (smeared-out) carboxylate concentration in moles per unit volume of dispersion and $c_{M,t}$ is the total metal concentration, were set to 0.03 with $c_{M,t}$ fixed at $\sim 3 \times 10^{-7}$ M. The progress of the metal complexation process is followed via the SCP signal of the complex system denoted as τ^*_{M+L} as a function of bulk equilibration time. We checked the uncertainty in τ^*_{M+L}/τ^*_M experimentally by performing the measurements in triplicate and it is found to be ~10% on average.

A series of SCP measurements over a range of deposition potentials, E_d, yields the full SSCP waves that are essential in the basic kinetic analysis. (See Section 3.2.)

3. Dynamic Speciation Analysis of Metal/CMD Complexes

3.1. Complexation Process. For low-molar-mass ligands, the rate of formation of metal complex species is generally consistent with the Eigen mechanism in which the formation of a precursor outer-sphere complex between the metal and the ligand is followed by the rate-limiting removal of water from the inner coordination sphere of the metal.[20] The overall rate constant of complex formation k_a is thus determined by k_w (rate constant of water substitution) and K_{os} (the stability constant for the intermediate outer-sphere complex). For successive complexes ML to ML$_n$, k_a is written as

$$k_{a,n} = k_{w,n} K_{os,n} \tag{1}$$

expressing that each association rate constant $k_{a,n}$ derives from the stability constant of the corresponding outer-sphere complex and the rate constant for release of the pertaining H_2O molecule.

Macromolecular multisite ligands may form intramolecular multidentate metal complexes involving more than one ligand site. This may require internal conformational changes that could slow down the overall kinetics of complex formation. In the particular case of CMD, we have observed the formation of two types of complexes, ML and M(LL), where (LL) denotes the coupling of two carboxylate ligands from the same CMD macromolecule. Contrary to the Eigen scheme, in the case of M(LL), the rate of formation of the precursor outer-sphere complex is the rate-limiting step.[16] Therefore, for a divalent metal ion and ligand site L^-, the reaction $ML^+ + L^- \rightleftarrows M(LL)$ is mechanistically formulated as

$$ML(H_2O)_5^+ + L^- \xrightarrow{k_{conf}} ML(H_2O)_5 \cdot L \overset{K_{ex}}{\rightleftarrows} M(LL)(H_2O)_4 + H_2O \tag{2}$$

where k_{conf} is the rate constant of the macromolecular reconformation process leading to the outer-sphere complex, $\cdot$ denotes an outer-sphere complex, and K_{ex} is the stability constant of the inner-sphere H_2O/L ligand exchange equilibrium (K_{ex} = [M(LL)(H$_2$O)$_4$]/[ML(H$_2$O)$_5 \cdot$L]).

Reaction 2 implies that equilibration between ML(H$_2$O)$_5 \cdot$L and M(LL)(H$_2$O)$_4$ is fast compared with the outer-sphere formation, and hence the overall rate constant for M(LL) formation is dependent only on k_{conf} and K_{ex}

$$k_{a,1-1} = k_{conf}\frac{K_{ex}}{1 + K_{ex}} \tag{3}$$

On a time scale t, the complex system is dynamic or static if the rates for the 3D association/dissociation reactions are fast or slow, respectively

$$\begin{tikzcd} & \gg 1 \ \text{dynamic} \\ k_{d,n}\,t,\ k'_{a,n}\,t \arrow[ur] \arrow[dr] & \\ & \ll 1 \ \text{static} \end{tikzcd} \tag{4}$$

with $n = 1$ or $1{-}1$ and $k'_{a,n}$ defined for conditions of excess of ligand as

$$k'_{a,n} = k_{a,n}c_{L,t} \quad \text{and} \quad k'_{a,n}/k_{d,n} = K'_n = K_n c_{L,t} \tag{5}$$

where K_n is the stability constant of ML_n and $c_{L,t}$ is the total ligand site concentration. Dynamic complexes fully maintain equilibrium in the bulk solution, whereas, at the other extreme, static ones are unable to maintain/restore equilibrium to any significant extent. Dynamic complexes contribute to an overall metal flux to an extent depending on the relative magnitudes of their diffusive and kinetic fluxes, ranging from fully labile (diffusion control) to nonlabile (kinetic control).[5,21]

If the metal/CMD system is subjected to electrodic reduction, then the free metal ion M^{2+} is reduced to metal M^0

$$\begin{tikzcd} M + L \arrow[r, shift left, "k_{a,1}"] \arrow[d, shift left, "ne^-"] & ML{+}L \arrow[l, shift left, "k_{d,1}"] \arrow[r, "k_{a,1\text{-}1}"] & M(LL) \\ M^0 \arrow[u, shift left] & & \end{tikzcd} \tag{6}$$

where the dissociation of M(LL) into ML is inherently slow. Under the usual conditions, the time scale of the electrochemical technique is much shorter than $1/k_{a,1-1}$, and hence the 1:2 complexes do not significantly contribute to the overall flux of metal from the bulk solution toward the electrode. Then, the flux is controlled by the diffusional transport of M and ML only, and the interconversion between these two species is governed by the rate constants $k_{a,1}$ and $k_{d,1}$. The 1:1 complexes of Pb(II), Cu(II), and Cd(II) with CMD have been shown to be labile on the effective time scale of SCP (order of 1 s).[16]

3.2. Dynamic Speciation Analysis by Stripping Chronopotentiometry. In SCP with a spherical electrode, the limiting deposition current for any degree of complex lability is given by[22]

$$I_d^* = \frac{nFA\bar{D}c^*_{M,t}}{\delta}\left(\frac{1+K'}{1+\mu K'/\bar{\delta}}\right) \tag{7}$$

where $\bar{D}$ is the effective diffusion coefficient for coupled diffusion of labile complex species and free metal, $c^*_{M,t}$ is the sum of free and labile species in the bulk solution, n is the number of electrons involved in the metal ion reduction process, F is the Faraday constant, A is the electrode area, μ is the reaction layer thickness, and $\bar{\delta}$ is the diffusion layer thickness.

$\bar{D}$ is defined as

$$\bar{D} = \frac{c_M D_M + \sum_{i=1}^{n} c_{ML_i} D_{ML_i}}{c_{M,t}} \tag{8}$$

where D_M and D_{ML_i} are the diffusion coefficients of the metal and the complex ML_i, respectively. For macromolecular multisite ligands and low metal-to-ligand ratio, D_{ML_i} can be assumed to be essentially equal to the diffusion coefficient of the macromolecule itself.

The measured signal in SCP is the limiting transition time, τ^*, which is proportional to the limiting deposition current, I_d^*. For depletive SCP, we then have[23]

$$\tau^* = \frac{I_d^* t_d}{I_s} \tag{9}$$

where t_d is the deposition time and I_s is the oxidizing strip current. For labile complexes, the signal τ^*_{M+L} is given by

$$\frac{\tau^*_{M+L}}{\tau^*_M} = \left(\frac{\bar{D}}{D_M}\right)^{(1-\alpha)}\left(\frac{c_M + c_{ML}^{labile}}{c_{M,t}}\right) \tag{10}$$

α is a parameter related to the hydrodynamic nature of the mass transport in the system; its value is set to 1/3. (See ref 24.)

Thermodynamic complex stability constants, K, can be retrieved from the SSCP wave from the shift in the half-wave deposition potential, $\Delta E_{d,1/2}$, irrespective of the degree of lability of the system

$$\ln(1 + K') = -(nF/RT)\Delta E_{d,1/2} - \ln(\tau^*_{M+L}/\tau^*_M) \tag{11}$$

A lability diagnosis can be evaluated by the comparison between $K'(\Delta E_{d,1/2})$ value obtained from eq 11 and $K'(\Delta\tau^*)$ issue from eq 10 with only M and ML species. The reader is referred to refs 25 and 26 for more detail.

3.3. Stripping Chronopotentiometry Analysis of Metal/Carboxymethyldextran Complexes. An ongoing decrease in τ^* as a function of bulk equilibration time generally reflects the formation of successive complex species. For the ligand CMD, it has been shown that the formation of M(LL)-type complexes with association rate constants on the order of 10^{-3} to 10^{-4} s (not SCP-labile) is the origin of the slow kinetic step observed.

The kinetic differences between ML and M(LL) allow the experimental complex formation curve to be divided into two parts. On the time scale of observation of M(LL) formation, the complexation process $M + L \rightleftarrows ML$ is instantaneous. Therefore, the initial part corresponds to a quasi-instantaneous decrease in the signal due to ML formation. The stability constant K_{ML} determines the apparent initial value in the long-time scale fitting of the M(LL) formation. Therefore, for $t \to 0$, we have $\tau^*_{M+L}/\tau^*_M \to (\bar{D}/D_M)^{(1-\alpha)}$. (See eq 10.) The variation in M(LL) concentration with time is then directly obtained from the experimental data τ^*_{M+L}/τ^*_M on the basis of applicability of eq 10 and realizing that $c_{M(LL)}$ equals $c_{M,t} - (c_M + c_{ML}^{labile})$.

Integration of the rate of formation of M(LL) leads to an exponential variation of $c_{M(LL)}$ with time[16]

$$c_{M(LL)}(t) = c^{eq}_{M(LL)}(1 - \exp(-k_{app}t)) \tag{12}$$

where $c_{M(LL)}$ is the concentration of M(LL), $c^{eq}_{M(LL)}$ is the concentration of M(LL) at equilibrium, and k_{app} is the apparent M(LL) formation rate given by

$$k_{app} = \frac{k_{a,1-1}}{1 + \frac{1}{K'_{ML}}} + k_{d,1-1} = k_{a,1-1}\left[\frac{K_{M(LL)} + K'_{ML} + 1}{K_{M(LL)}(K'_{ML} + 1)}\right] \tag{13}$$

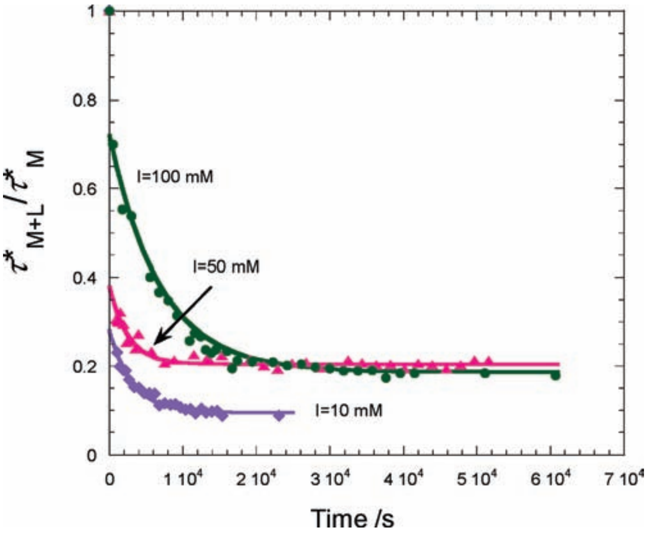

Figure 1. Normalized SCP reoxidation signal as a function of bulk equilibration time for Pb(II)/CMD$^{37\%}_{T500}$ at pH 6.2 and at different ionic strengths (I = 10, 50, and 100 mM NaNO$_3$). Solid points correspond to experimental data, and the fit (line) corresponds to the pertaining K_{ML}, $K_{M(LL)}$, and k_{conf} values given in Table 1.

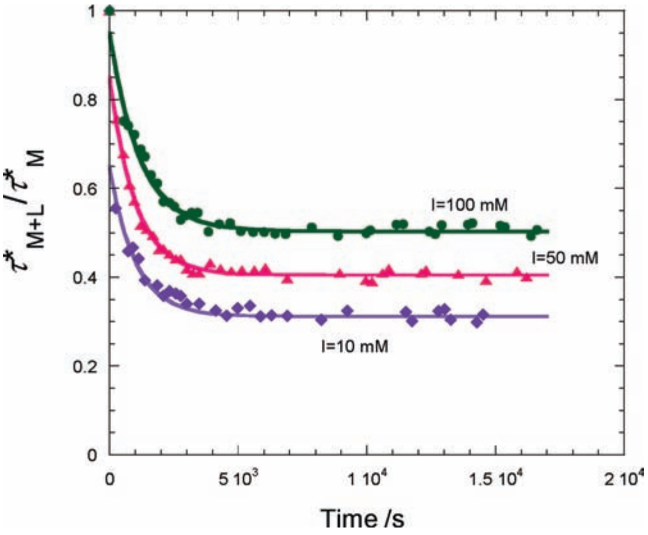

Figure 2. Normalized SCP reoxidation signal as a function of time for Cu(II)/CMD$^{37\%}_{T500}$ at pH 6.2 and at different ionic strengths (I = 10, 50, and 100 mM NaNO$_3$). Solid points correspond to experimental data, and the fit (curve) corresponds to the pertaining K_{ML}, $K_{M(LL)}$, and k_{conf} values given in Table 1.

4. Results and Discussion

The kinetics of CMD complex formation for three heavy metal ions, Pb(II), Cu(II), and Cd(II), was investigated at different ionic strengths in the range from I = 10 to 100 mM. The results for Pb and Cu show comparable M(LL) complex formation kinetics on a time scale of hours, with Cu somewhat faster than Pb (Figures 1 and 2). The experimental data are fitted to eq 12 following the procedure explained in Section 3.3. In contrast, for Cd, no slow equilibration process is observed at all; apparently, there is only fast 1:1 complex formation. Moreover, the results for Cd(II) at I = 50 and 100 mM show no sign of complexation. A significant variation of $\tau^*_{Cd+L}/\tau^*_{Cd}$ is observed only at 10 mM (where K' is sufficiently high), and hence the case of Cd is treated only for this ionic strength.

4.1. Formation of ML. ***4.1.1. Case of Pb and Cu.*** The decrease in the signal within the first seconds of bulk solution equilibration is attributed to fast formation of the monodentate complex ML. Ensuing values of $K_{ML}(\Delta\tau^*)$ for Pb and Cu are given in Table 1. $K_{ML}(\Delta\tau^*)$ for Cd is also given for comparison. At I = 10 mM, the stability of metal ion complexes with CMD carboxylate groups follows the order Pb > Cu > Cd. This trend is generally observed for organically bound carboxylates.[27,28] For Pb and Cu, the decrease in ionic strength from 100 to 10 mM leads to an increase in the value of K_{ML} by 0.7 to 0.8 log units. The dependence of K_{ML} on I can be partially attributed to the change in the activity coefficient of the species in solution. The values of log γ_M for $z = 2$ are -0.44 at I = 100 mM and -0.18 at I = 10 mM.[29] However, the variation of the activity coefficients is not sufficient to explain the change in stability constants in this ionic strength range. Apparently, additional polyelectrolyte effects play a role in the binding of metal ions by the charged polycarboxylate chains. The charge spacing between two adjacent CMD carboxylates is ~1.2 nm,[30] which is quite comparable to the Debye–Huckel screening length, κ^{-1}, at 50 and 10 mM (i.e., 1.4 and 3 nm, respectively, in water at 25 °C). In the studied range of ionic strengths,[17] the CMD polysaccharide is a random coil and can be modeled as a soft, charged colloidal particle with (i) an approximately uniform segment distribution (high molar mass) and (ii) a stepwise Donnan-type potential variation across the colloid/solution interface. This assumption is supported by previous electrokinetic experiments[17] showing that at $I \geq 10$ mM, the Duval–Ohshima model[31] for a homogeneous soft particle is in good agreement with experimental data for the CMD particle.

The dimensionless Donnan potential is given by

$$y^D = \sinh^{-1}\left(\frac{\rho_0}{2c_\infty F}\right) \tag{14}$$

where ρ_0/F is the space charge density due to carboxylate groups, equal to -16.2 mM for CMD$^{37\%}_{T500}$, F is the Faraday constant, and c_∞ is the 1:1 bulk electrolyte concentration.

Therefore, the apparent stability of a complex ML inside the spherical ligand volume is

$$K_{ML,app} = K_{int} \cdot \exp(-z_M y^D) \tag{15}$$

where K_{int} is the intrinsic stability constant for which the Donnan effect is insignificant ($y^D \rightarrow 0$) and z_M is the charge number of the metal ion. The intrinsic stability constant is obtained from the extrapolation of experimental values of $K_{ML}(\Delta\tau^*)$ to $y^D = 0$: log $K_{int,Pb}$ is then equal to 4.6 and log $K_{int,Cu}$ is equal to 4.0. Results are given in Table 1, and eq 15 gives a good estimation of the experimental values within the uncertainties. We emphasize, however, that below ionic strengths of 10 mM, K_{ML} values can no longer be extrapolated by means of the simple step-function type modeling of the interface. The Debye length κ^{-1} then is no longer small compared with the particle radius, which necessitates consideration of the profiles of both charge density and polymer segment density across the diffuse interface.[31]

4.1.2. Case of Cd. The absence of the slow kinetic step for cadmium (for the given pH and ionic strength conditions) leads us to conclude that only CdL is formed. Consequently, we employed the SSCP technique to estimate the stability constant from the shift of the half-wave deposition potential, $\Delta E_{d,1/2}$, which is known to give reasonably good approximation over a large range of labilities.[18,25,32] Results for different metal-to-

TABLE 1: Values of Constants Obtained by Means of the Fit of Experimental Data Using Equation 12 for $\mathrm{CMD}^{37\%}_{\mathrm{T500}}$ and the Three Metal Ions Pb, Cu, and Cd with $K_{\mathrm{ML}} = c_{\mathrm{ML}}/c_{\mathrm{M}}{*}c_{\mathrm{L}}$ Expressed in l mol^{-1} and $K_{\mathrm{M(LL)}} = c_{\mathrm{M(LL)}}/c_{\mathrm{ML}}$ the Stability Constants of ML and M(LL), Respectively[a]

metal	ionic strength (mM)	log $K_{\mathrm{ML}}(\Delta\tau^*)$	y^D	log $K_{\mathrm{ML,app}}$	log $K_{\mathrm{M(LL)}}$	$k_{\mathrm{a,1-1}}$ (s^{-1})	$k_{\mathrm{d,1-1}}$ (s^{-1})	k_{conf} (s^{-1})
Pb	10	5.5 ± 0.2	-0.74	5.3 ± 0.1	0.3 ± 0.2	2.5×10^{-4}	1.1×10^{-4}	3.6×10^{-4}
	50	5.1 ± 0.2	-0.16	4.8 ± 0.1	0.3 ± 0.2	3.2×10^{-4}	1.5×10^{-4}	4.8×10^{-4}
	100	4.7 ± 0.1	-0.08	4.7 ± 0.1	0.9 ± 0.1	2.8×10^{-4}	3.8×10^{-5}	3.0×10^{-4}
Cu	10	5.0 ± 0.2	-0.74	4.7 ± 0.1	0.35 ± 0.2	1.1×10^{-3}	4.8×10^{-4}	1.6×10^{-3}
	50	4.5 ± 0.2	-0.16	4.2 ± 0.1	0.7 ± 0.2	2.4×10^{-3}	4.7×10^{-4}	2.8×10^{-3}
	100	4.3 ± 0.1	-0.08	4.1 ± 0.1	0.7 ± 0.1	2.0×10^{-3}	3.6×10^{-4}	2.3×10^{-3}
Cd	10	4.8						

[a] $K_{\mathrm{ML,app}}$, the apparent stability constant of ML, is calculated from eq 15, and y^{D} is the dimensionless Donnan potential. $k_{\mathrm{a,1-1}}$ and $k_{\mathrm{d,1-1}}$ are the respective association and dissociation rate constants for M(LL), and k_{conf} is the rate constant of the conformation step. The experiments are performed at pH 6.2, $I = 10$, 50, and 100 mM $\mathrm{NaNO_3}$, and at room temperature. The total concentration of metal is 3×10^{-7} M.

TABLE 2: Values of Constants Obtained by Means of the Fit of Experimental Data Using Equation 12 for Pb/$\mathrm{CMD}^{37\%}_{\mathrm{T500}}$ at Different Metal-to-Ligand Ratios, R, with the Same Constants As Those Described in Table 1[a]

metal	R	log K_{ML}	log $K_{\mathrm{M(LL)}}$	$k_{\mathrm{a,1-1}}$ (s^{-1})	$k_{\mathrm{d,1-1}}$ (s^{-1})	k_{conf} (s^{-1})
Pb	0.01	4.2 ± 0.1	0.8 ± 0.1	6.1×10^{-4}	9.5×10^{-5}	6.9×10^{-4}
	0.1	5.2 ± 0.1	1.0 ± 0.1	3.6×10^{-4}	3.8×10^{-5}	3.9×10^{-4}
	0.3	5.4 ± 0.1	1.1 ± 0.1	4.3×10^{-4}	3.2×10^{-5}	4.6×10^{-4}

[a] Experiments are performed at pH 6.2, $I = 100$ mM $\mathrm{NaNO_3}$, and at room temperature. The total concentration of lead is 3×10^{-7} M.

TABLE 3: Stability Constants for Cadmium and CMD at Different Ratios $R = c_{\mathrm{L,t}}/c_{\mathrm{M}}$[a]

metal	R	K'_{ML} ($\Delta\tau$)	K'_{ML} (ΔE)	$c_{\mathrm{L},t}$ (M)	log K_{ML} (ΔE)
Cd	0.01	1.95	1.56 ± 0.22	3.26×10^{-5}	4.7
	0.03	0.77	0.71 ± 0.14	1.11×10^{-5}	4.8
	0.1	0.42	0.15 ± 0.10	3.70×10^{-6}	4.6

[a] $K'(\Delta E)$ values are obtained from eq 11, and $K'(\Delta\tau^*)$ values are obtained from equation 10. The experiments are performed at pH 6.2, $I = 100$ mM $\mathrm{NaNO_3}$, and at room temperature.

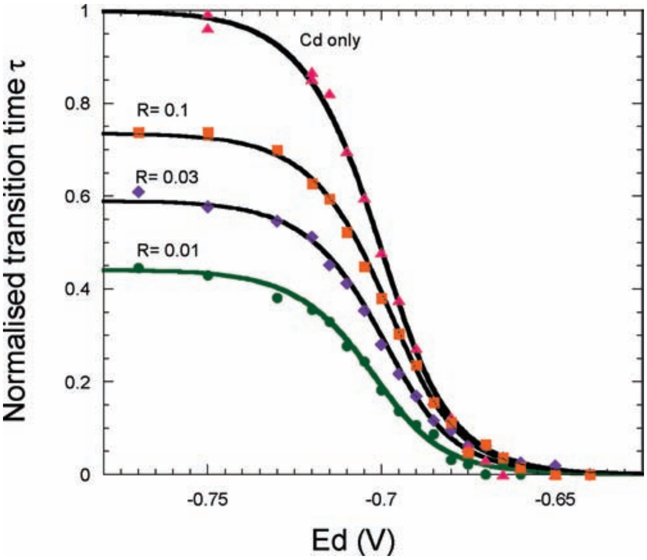

Figure 3. Experimental and fitted SSCP waves for Cd/$\mathrm{CMD}^{37\%}_{\mathrm{T500}}$ at different metal-to-ligand ratio R. Experimental curves were measured for 3.1×10^{-7} M Cd(II) in 10 mM $\mathrm{NaNO_3}$ at pH 6.2. Fitted waves (full curve) were calculated according to ref 25 with the parameters: $D = 7 \times 10^{-10}$ m s^{-1}, $A = 4 \times 10^{-7}$ m^2, $V = 2.4 \times 10^{-11}$ m^3, $\delta \approx 3 \times 10^{-5}$ m (varying with R), $t_{\mathrm{d}} = 60$ s, $I_{\mathrm{s}} = 1 \times 10^{-9}$ A, and the respective K_{ML} values and ligand concentrations given in Table 3.

ligand ratios (Table 3) are quite consistent, with a stability constant for the 1:1 complex of log $K_{\mathrm{Cd/CMD}} = 4.8$.

The comparison between the K values derived from the shift in $E_{\mathrm{d,1/2}}$ and from τ^* provides information on the lability of the Cd/CMD complexes on the time scale of the SCP experiments. Both values of K' are given in Table 3. For the experiments performed at different metal-to-ligand ratios, the results obtained from the change in τ^* give the same K'_{ML} values (within the error). Therefore, it can be concluded that the CdL complexes remain quite SCP-labile under the experimental conditions. Labile behavior of Cd complexes with colloidal carboxylate ligands was also verified with carboxylated latex nanospheres.[25] The lability of Cd/CMD as evaluated by the SSCP method (Figure 3) and the fact that K_{CdL} for the 1:1 complexes is not very much smaller than K_{PbL} and K_{CuL} over the ionic strength range covered (Table 1) support our previous assumption that 1:1 complexes formed with Pb and Cu are also labile at $I > 10$ mM. We thus conclude that ML species are labile, whereas M(LL) remain nonlabile or inert on time scales far beyond that of the formation of ML.

4.2. Formation of M(LL). The slow process of formation of M(LL) species occurs only with copper and lead; Cd(LL) is not produced in a significant proportion. At equilibrium, Cu(LL) is formed at ~50% of the total metal species and Pb(LL) is formed at 70–80%. It has been shown that 1:2 complexes of Cd(II) with acetate are considerably less stable than those of Pb(II).[33] This disparity is due to differences in electronic structure of the metal ion leading to different strengths of multiple carboxylate complex formation.[34]

The stability constants for Pb(LL) and Cu(LL) obtained from the curve fittings using eq 12 are given in Table 1. Because the equilibration between M and ML is fast compared with that between M(LL) and ML, we can write

$$K_{\mathrm{M(LL)}} \equiv \frac{c_{\mathrm{M(LL)}}}{c_{\mathrm{ML}}} = \frac{c_{\mathrm{M(LL)}}}{K_{\mathrm{ML}} c_{\mathrm{M}} c_{\mathrm{L,t}}} \qquad (16)$$

showing that, for given concentrations of $c_{\mathrm{L,t}}$, c_{M}, and $c_{\mathrm{M(LL)}}$, $K_{\mathrm{M(LL)}}$ is inversely proportional to K_{ML}. We showed above that K_{ML} decreases with increasing ionic strength. Equation 16 illustrates why $K_{\mathrm{M(LL)}}$ values do not decrease with increasing ionic strength but in fact show a slight tendency to increase. In addition, by changing the concentration of ligand (Table 2), no influence on the stability constant of Pb(LL) is observed as long as the concentration of ligand is in sufficient excess.

The values of k_{conf} for different ionic strengths are given in Table 1. The salt content practically does not affect the kinetics of M(LL) formation as the values of k_{conf} for the Pb(LL) and Cu(LL) formation are rather insensitive to variation in I. This is in basic contrast with conventional Eigen-type complex formation rate constants, which strongly depend on I via the stability of the intermediate outer-sphere complex.[9,29] Previously,[16] we performed experiments with CMD with differences in volume charge density, and no significant influence on the Pb(LL) formation rate constant was found. All together, the evidence supports the hypothesis that the slow formation of the bidentate complex is related to a specific rearrangement of the polymeric chain. Then, the rate-limiting step in the reconfiguration would be of a predominantly nonelectrostatic nature and hence insensitive to the salt concentration.

5. Conclusions

The experimental evidence shows that polyelectrolyte effects play a major role in the stability of 1:1 PbCMD or CuCMD complexes. At $I \geq 10$ mM, the stability constant, K_{ML}, can be predicted by a simple Donnan approximation of the electric potential inside the spherical CMD particle. In contrast, electrostatic effects have no apparent influence on either the kinetic rate of formation or the stability of the intramolecular bidentate M(LL) complex. Cadmium, which is known to have weak interaction with carboxylate ligands, exclusively forms 1:1 complexes with CMD at ionic strength below 10 mM.

According to the nature of the metal ion, the time-dependent characteristics of complex formation with CMD can vary from the order of nanoseconds, as predicted by the Eigen mechanism (see Cd case), to the order of hours because of the intramolecular rearrangements involved (see Pb and Cu cases). Similarly, the lability degree of the eventual metal complexes, as determined by SCP, ranges from fully labile 1:1 complexes to nondynamic bidentate Pb(LL) and Cu(LL) species.

Recently, considerable efforts have been made to analyze the dynamic metal speciation features of ligands contained in soft diffuse (bio)interfaces and (bio)colloidal dispersions.[13] The present work on a polysaccharide model colloid demonstrates that the kinetic features of such colloidal complexes may span enormous time windows that vary with the type of metal and the physicochemical conditions of the medium. This finding is important for metal complexation by soft environmental colloids, for example, in the framework of modeling the sink/source functioning of ecosystems, and the prediction of the temporal spread of colloid-bound pollutants.

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