714 *J. Chem. Eng. Data* **2010,** *55,* 714–722

On the Complexation of Cu(II) and Cd(II) With Polycarboxyl Ligands. Potentiometric Studies With ISE-H^+, ISE-Cu^{2+}, and ISE-Cd^{2+}

Concetta De Stefano,[†] Antonio Gianguzza,*[,‡] Alberto Pettignano,[‡] Silvio Sammartano,[†] and Salvatore Sciarrino[‡]

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Salita Sperone 31, I-98166, Messina (Vill. S. Agata), Italy, and Dipartimento di Chimica Inorganica e Analitica “Stanislao Cannizzaro”, Università di Palermo, Viale delle Scienze, I-90128, Palermo, Italy

The interaction of Cu^{2+} and Cd^{2+} ions with polyacrylates (PAA, 2 kDa and 100 kDa), polymetacrylate (PMA, 5.4 kDa), and alginate (AA, 70 kDa to 100 kDa) was studied by potentiometry, using ISE-Cu^{2+}, ISE-Cd^{2+}, and ISE-H^+ electrodes. The investigations were performed in $NaNO_3$ aqueous solutions, in the ionic strength range $0.10 \leq I\ (\text{mol}\cdot\text{L}^{-1}) \leq 0.75$, at $T = 298.15$ K. The “diprotic-like model” was used to explain the acid−base behavior of the polycarboxylates under investigation (for this model, the monomeric unit of the polyelectrolyte is considered as a dicarboxylate). The results give evidence for the formation of the ML species in all the systems investigated. In addition, the MLH species was found in the M-PAA, (2 and 100) kDa, and M-PMA, 5.4 kDa ($M = Cu^{2+}$ and Cd^{2+}). The values of stability constants of complex species obtained by ISE-H^+ and by ISE-Cu^{2+} and ISE-Cd^{2+} electrodes are in excellent agreement. Measurements carried out at different ionic strengths allowed us to evaluate the dependence of formation constants on ionic strength by using an extended Debye−Hückel type equation and to calculate the formation constants at infinite dilution. At $I = 0.1\ \text{mol}\cdot\text{L}^{-1}$, $\log K_{(M+L)}$ ranges from 5.67 (PMA, 5.4 kDa) to 3.63 (AA, 70 kDa to 100 kDa) for copper(II) and from 4.60 (PAA, 100 kDa) to 3.07 (AA, 70 kDa to 100 kDa) for cadmium(II) complexes. This stability is quite similar to that shown by low molecular weight dicarboxylates. The specific interaction coefficients for all the species involved in the complexation model were also calculated by using the specific interaction ion theory (SIT). The stability data of species formed were used to quantitatively define the sequestering capacity of the synthetic and naturally occurring polycarboxylates considered. The value of pL_{50} (i.e., the total ligand concentration necessary to bind 50 % of the metal ion) is reported for each metal−ligand system.

Introduction

Metal complexation by polycarboxylic ligands has been widely investigated in light of its use in different technical applications such as water and wastewater treatment, heavy metal removal in contaminated sites, metal recovery, etc. In particular, polyacrylates and polymethacrylates are used as flocculants in drinking water production, as scale inhibitors, as dispersants in papermaking, and as basic components in ion-exchange polymer systems for metal ion sequestration.

The interaction of polyacrylates and polymethacrylates with metal ions has been extensively studied for many years[1−16] and is still the subject of investigation to define the complexation models and to have quantitative information on the possibility of using these synthetic polycarboxylates for metal ion removal. Different techniques, such as potentiometry,[17−23] spectrophotometry,[24] and voltammetry,[25−34] have been used in these investigations. In spite of the great interest in these systems and the number of articles, the quantitative data on stability of metal−polyacrylate/polymethacrylate complex species formed are not homogeneous, and often there is disagreement between them. The main reasons are ascribed to: (i) the different experimental conditions used by different authors, such as pH range, ionic strength, ionic medium, and the concentration ratio L/M which influences strongly the stoichiometry of species formed;[35] (ii) the electrostatic effects due to the nature and molecular weight of the polyelectrolyte under investigation (linear or cross-linked) and the model used to describe its acid−base behavior. Moreover, the dependence on ionic strength of metal−polycarboxylate formation constants was neglected, except in a few investigations.[27,36−40]

In this work, we report results of a study on the complex formation between copper(II) and cadmium(II) ions with polyacrylate [(2 and 100) kDa] and polymethacrylate (5.4 kDa) ligands in $NaNO_3$ ionic medium in the ionic strength range (0.1 to 0.75) $\text{mol}\cdot\text{L}^{-1}$. To compare the stability of metal complexes formed with synthetic and naturally occurring polycarboxylate ligands, investigations were also performed on the species formation of Cd^{2+} and Cu^{2+} ions with alginic acid (acidic polysaccharide copolymer of 1,4-linked β-D-mannuronic and α-L-guluronic acids) which is the main component of brown algae. Measurements were carried out by potentiometry using ISE-H^+ and ISE-Cu^{2+} and ISE-Cd^{2+} electrodes at 298.15 K.

For all the polycarboxylates investigated here, we used the protonation constants previously determined using a new model[36] according to which the monomer unit of the polyelectrolyte is considered as a dicarboxylate.

The measurements carried out at different ionic strengths allowed us to consider the dependence on ionic strength of formation constants by using a Debye−Huckel type equation, and the specific interaction parameters were calculated by the specific ion interaction theory (SIT).

---

* Corresponding author. E-mail: giang@unipa.it.
[†] Università di Messina.
[‡] Università di Palermo.

10.1021/je9004245 CCC: $40.75

Table 1. Experimental Conditions Used in the ISE-H^+ and ISE-Me^{2+} Measurements for Cu/Cd−PAA/PMA and AA Systems, in $NaNO_3$ and at T = 298.15 K

systems	I/mol·L^{-1} [a]	C_M [b]	C_L [b]	pH range	runs	points
			ISE-H^+ Measurements			
Cu−PAA 100 kDa	0.100	0.6	1.0	2.8 to 5.6	4	623
Cu−PAA 2 kDa	0.096 to 0.695	0.5 to 0.6	1.0	2.5 to 5.5	14	1062
Cu−PMA 5.4 kDa	0.105 to 0.712	0.5 to 0.6	1.2	2.5 to 7.5	16	1186
Cu−AA (70 to 100) kDa	0.101 to 0.672	0.5	0.3 to 0.8	3.0 to 5.0	14	941
Cd−PAA 100 kDa	0.097	1.0	1.0	3.8 to 5.7	7	513
Cd−PAA 2 kDa	0.102 to 0.708	1.0	1.0 to 1.2	2.3 to 6.3	29	2089
Cd−PMA 5.4 kDa	0.101 to 0.717	0.5 to 2.0	0.6 to 2.0	3.0 to 6.8	16	1319
Cd−AA (70 to 100) kDa	0.101 to 0.663	1.0	1.0	3.0 to 4.8	16	1249
			ISE-M^{2+} Measurements			
Cu−PAA 100 kDa	0.100	0.5	9.96[c]	4.1 to 5.1	4	292
Cu−PAA 2 kDa	0.102 to 0.729	0.3 to 1.0	6.60 to 7.14	4.9 to 5.8	21	484
Cu−PMA 5.4 kDa	0.100 to 0.723	0.55	8.72 to 8.96	4.6 to 5.9	20	782
Cu−AA (70 to 100) kDa	0.098 to 0.694	0.25 to 0.35	4.51 to 4.62	4.1 to 4.7	16	782
Cd−PAA 100 kDa	0.100	0.98	9.96	4.1 to 4.4	4	280
Cd−PAA 2 kDa	0.097 to 0.715	0.55 to 1.00	4.94 to 7.51	4.9 to 6.2	16	373
Cd−PMA 5.4 kDa	0.101 to 0.674	0.5 to 1.1	8.72	4.9 to 6.0	13	769
Cd−AA (70 to 100) kDa	0.098 to 0.702	1.0	5.00	4.9 to 5.2	12	683

[a] Effective ionic strength. [b] In mmol·L^{-1}. [c] Titrant solution.

A comparison of the stability constants of the different complex species obtained here with the data reported in the literature for the corresponding species is given.

From the stability data of the metal complex species formed, a trend of sequestering capacity of polycarboxylic ligands toward copper(II) and cadmium(II) ions was also obtained and discussed.

Experimental Section

Chemicals. Cadmium(II) nitrate tetrahydrate and copper(II) nitrate hydrate were analytical grade high purity (> 99.5 %) Aldrich products. Polyacrylates [PAA 2 kDa and PAA 100 kDa, this last 35 % (by weight) solution in water] and polymethacrylate [PMA sodium salt 5.4 kDa, 30 % (by weight) solution in water] were Fluka or Aldrich products. Commercial alginic acid (AA, molecular weight in the range 70 kDa to 100 kDa), extracted from *Macrocystis pyrifera*, with an average content of mannuronic (M) and guluronic (G) acids of (61 and 39) %, respectively, was supplied by Sigma (lot 60K1443). Ligand purity, checked by potentiometric titrations, and water content [(26 and 24) %, for PAA 2 kDa and AA 70 kDa to 100 kDa, respectively] estimated by thermogravimetric analysis were always taken into account. Hydrochloric or nitric acid and sodium hydroxide solutions were prepared by diluting concentrated Fluka ampules and standardized against sodium carbonate and potassium hydrogen phthalate, respectively. All the solutions were prepared using freshly prepared CO_2-free ultra pure water (R = 18 MΩ), and grade A glassware was always employed.

Apparatus and Procedure. Potentiometric titrations were carried out at (298.15 ± 0.1) K using an apparatus consisting of a model 654 Metrohm potentiometer, equipped with the electrodes used for the experiments, and a model 765 Metrohm motorized buret. The following electrodes were used: a combined glass electrode Ross type 8102 for ISE-H^+ measurements; a cadmium membrane electrode type 9448SC; and a cupric membrane electrode type 9429SC coupled with a double junction reference electrode Ross type 900200 for ISE-Cd^{2+} and ISE-Cu^{2+} measurements. The estimated precision is ± 0.15 mV and ± 0.003 mL for emf and titrant volume readings, respectively. The apparatus was connected to a PC, and automatic titrations were performed using a homemade computer program to control titrant delivery, data acquisition, and to check for emf stability. All titrations were carried out under magnetic stirring, and presaturated N_2 was bubbled through the purified solution to exclude O_2 and CO_2 inside. Two different procedures were employed to carry out potentiometric titrations. In the first, applied for ISE-M^{2+} measurements, 25 mL of titrand solution containing a known amount of Cu^{2+}or Cd^{2+} was titrated with a sodium salt solution of the polyelectrolyte used for the different systems, i.e., PAA, (2 or 100) kDa; PMA, 5.4 kDa; and AA, (70 to 100) kDa. Sodium nitrate was added in the titration vessel to obtain the pre-established values of ionic strength (I/mol·L^{-1} = 0.10, 0.25, 0.50, and 0.75). At the same time, the pH of titrand solutions was checked by using the combined ISE-H^+ glass electrode connected to another potentiometer.

In the second procedure, used for ISE-H^+ titrations, 25 mL of titrand solution containing known amounts of cupric or cadmium nitrate, the polyelectrolyte (PAA or PMA at different molecular weights) in its acidic form, nitric acid to adjust the pH of solution to ∼3, and sodium nitrate to obtain the pre-established value of ionic strength was titrated with standard sodium hydroxide solution. In the case of alginic acid, a different procedure was applied owing to the low solubility of the polyelectrolyte in its acidic form: the pH of titrand solution was adjusted to ∼7 by adding a known amount of sodium hydroxide to the titrand solution, and a standard solution of nitric acid was used as titrant. Further experimental details are given in Table 1.

To determine the formal potential $E°$ of the combined ISE-H^+ glass electrode, independent titrations of HNO_3 solutions were performed, for each experiment, with standard sodium hydroxide solutions in the same experimental conditions of ionic strength and temperature as the systems under investigation. For the experiments with ISE-M^{2+} membrane electrodes, the electrode calibration was performed by titrating a solution containing standard solutions of cupric or cadmium nitrate, at the same ionic strength ($NaNO_3$ medium) of the experiments.

Calculations. The following computer programs were used: BSTAC and STACO to refine all the parameters of an acid−base titration ($E°$, pK_w, liquid junction potential coefficient, j_a, analytical concentration of reagents) and to calculate the complex formation constants; ES4ECI to draw speciation diagrams and to calculate species formation percentages; LIANA to fit different equations. Details for the computer programs used in these laboratories in equilibrium analysis studies were already reported.[41]

All the complex formation constants refer to the general equilibrium

$$pM^{2+} + qL^{z-} + rH^{+} = M_pL_q(H)_r^{(2p-zq+r)} \qquad \beta_{pqr} \tag{1}$$

where $M^{2+} = Cu^{2+}$ or Cd^{2+} ion and L^{z-} = polyelectrolyte ligand (PAA (2 or 100) kDa, PMA 5.4 kDa, or AA (70 to 100) kDa) with z = effective charge of the polyelectrolyte.

The dependence of formation constants on ionic strength was taken into account by the following Debye–Hückel type equation

$$\log \beta = \log {}^{T}\beta - z^{*}0.51I^{1/2}/(1 + 1.5I^{1/2}) + CI \tag{2}$$

with

$$z^{*} = \Sigma(\text{charges})^2_{\text{reactants}} - \Sigma(\text{charges})^2_{\text{products}} \tag{2a}$$

where β is the conditional formation constant and ${}^{T}\beta$ is the formation constant at infinite dilution and C is a parameter dependent on I. Formation constants, concentrations, and ionic strengths are expressed in the molar ($mol \cdot L^{-1}$) scale.

Moreover, the specific ion interaction theory (SIT) approach was also used. According to this model, the formation constants can be expressed as

$$\log \beta_m = \log {}^{T}\beta_m - z^{*}0.51I^{1/2}(1 + 1.5I^{1/2}) + L(\varepsilon, I) \tag{3}$$

where β_m and ${}^{T}\beta_m$ are conditional and thermodynamic formation constants, respectively, and $L(\varepsilon, I)$ is a linear term dependent on ionic strength and on interaction coefficients ε. In the SIT approach, formation constants, concentrations, and ionic strengths are expressed in the molal ($mol \cdot kg^{-1}$ [H_2O]) scale. For the generic reaction reported in eq 3, the linear term in $NaNO_3$ ionic medium assumes the form

$$L(\varepsilon, I) = I[p\varepsilon(M^{2+}, NO_3^{-}) + q\varepsilon(L^{z-} + Na^{+}) + r\varepsilon(H^{+}, NO_3^{-}) - \varepsilon(M_pL_qH_r^{(2p-zq+r)}, Na^{+}) \tag{3a}$$

Further considerations must be made when the SIT equation is applied to the protonation equilibria of the polyelectrolytes which were investigated using the "diprotic-like model" (see hereafter section Protonation of Polyelectrolytes in Results and Discussion). In this case, the equation can be generically written as

$$L^{z-} + iH^{+} = H_iA^{(i-z)} \qquad \beta_i \tag{4}$$

where i is equal to 1 or 2 and z is the effective charge of polyelectrolytes.[36] In this case, the linear term $L(\varepsilon, I)$ of the SIT equation in $NaNO_3$ ionic medium is

$$L(\varepsilon,I) = I[\varepsilon(L^{z-} + Na^{+}) + n\varepsilon(H^{+}, NO_3^{-}) - \varepsilon(H_iL^{(i-z)}, Na^{+})] \tag{5}$$

The number of unknown parameters of eq 5 can be reduced considering the interaction coefficient $\varepsilon(H_iL^{(i-z)}, Na^{+})$ of the species $HL^{(1-z)}$ and $H_2L^{(2-z)}$ as a function of z^2[42] according to eq 5a

$$\varepsilon = \bar{\varepsilon} \cdot z^2 \tag{5a}$$

where $\bar{\varepsilon}$ is an empirical parameter which refers to mono- and diprotonated species of each polyelectrolyte investigated (numerical values of $\bar{\varepsilon}$ are reported as footnotes in Table 6 in the Dependence of Formation Constants on Ionic Strength section).

Results and Discussion

Protonation of Polyelectrolytes and Hydrolysis of Metals. In the complexation models of all the systems investigated, the protonation equilibria of polyelectrolytes and the hydrolysis of metal ions were considered. The protonation constants of polyacrylates, polymethacrylate, and alginate in $NaNO_3$ at different ionic strengths are reported in Table 2. These constants were determined by assuming the polyelectrolytes to be constituted of dicarboxylic monomeric units with the possibility to express their acid–base properties by only two protonation constants (K_1^H and K_2^H) and to make their protonation independent of the dissociation degree (α). We tested this model, namely, the Diprotic-like model, on a large number of synthetic and natural polyelectrolytes (polyacrylates, polymethacrylates, polyacrylate–comaleate at different molecular weights, synthetic and natural humic substances, and alginic acid).[36]

The results obtained using this new model were also compared with those obtained by other classical models, such as the three parameters model proposed by Högfeldt[43] and the modified Henderson–Hasselbalch equation proposed by Katschalsky,[44,45] according to which protonation constants are expressed as a function of the dissociation degree (α). The comparison shows a very good agreement between the results obtained, and this confirms the possibility of using the Diprotic-like model[36] in the studies of acid–base properties of polyelectrolytes with a reduced difficulty in data processing and with a negligible loss of accuracy in the calculation of protonation constants. The effective charges of the polyelectrolyte units, calculated using eq 2 for the dependence of protonation constants on ionic strength, are −3.0, −4.6, −4.4, and −3.5, for PAA 2

Table 2. Protonation Constants[a], According to the Diprotic-Like Model,[36] of PAA (2 and 100) kDa, PMA 5.4 kDa, and AA (70 to 100) kDa in $NaNO_3$ at Different Ionic Strengths and at T = 298.15 K

I / $mol \cdot L^{-1}$	$\log K_1^{Hb}$	$\log \beta_2^{Hb}$	I / $mol \cdot kg^{-1}$ [H_2O]	$\log K_1^{Hc}$	$\log \beta_2^{Hc}$
		PAA, 2 kDa			
0	6.42	11.3	0	6.42	11.3
0.10	5.69	10.05	0.10	5.69	10.04
0.25	5.56	9.79	0.25	5.55	9.78
0.50	5.40	9.56	0.51	5.39	9.54
0.75	5.32	9.42	0.77	5.31	9.40
		PAA, 100 kDa			
0.10	5.70	9.91	0.10	5.70	9.91
		PMA, 5.4 kDa			
0	7.44	13.28	0	7.44	13.28
0.10	6.537	11.554	0.10	6.534	11.549
0.25	6.267	11.140	0.25	6.262	11.130
0.50	6.051	10.820	0.51	6.043	10.804
0.75	5.951	10.681	0.77	5.940	10.658
		AA, (70 to 100) kDa			
0	5.18	7.93	0	5.18	7.93
0.10	3.499	6.42	0.10	3.496	6.41
0.25	3.247	6.008	0.25	3.242	5.999
0.50	3.135	5.896	0.51	3.127	5.880
0.75	3.060	5.743	0.77	3.049	5.720

[a] K_i^H refers to equilibrium $H_{i-1}L^{(i-z-1)} + H^{+} = H_iL^{(i-z)}$. [b] Molar concentration scale. [c] Molal concentration scale.

Table 3. Formation Constants[a] in the Molar Concentration Scale, of Cd^{2+}− and Cu^{2+}−L (L = PAA 2 kDa, PMA 5.4 kDa, and AA (70 to 100) kDa) Complex Species Calculated with ISE-M^{2+}(Cd^{2+}, Cu^{2+}) and ISE-H^+ in $NaNO_3$, at Different Ionic Strengths and at $T = 298.15$ K

ISE-Cd^{2+} or ISE-Cu^{2+} measurements			ISE-H^+ measurements		
I^b	log β_{110}	log β_{111}	I^b	log β_{110}	log β_{111}
		Cu−PAA, 100 kDa			
0.100	5.192 ± 0.008[c]	9.30 ± 0.01[c]	0.100	5.228 ± 0.007[c]	9.304 ± 0.007[c]
		Cu−PAA, 2 kDa			
0.102	4.745 ± 0.006	-	0.096	4.65 ± 0.01	9.33 ± 0.01
0.246	4.294 ± 0.002	-	0.235	4.282 ± 0.005	8.856 ± 0.003
0.491	4.052 ± 0.002	-	0.463	4.052 ± 0.004	8.383 ± 0.004
0.729	3.956 ± 0.002	-	0.694	3.956 ± 0.002	8.288 ± 0.004
		Cu−PMA, 5.4 kDa			
0.100	5.669 ± 0.003	10.68 ± 0.01	0.105	5.69 ± 0.03	10.70 ± 0.02
0.244	5.191 ± 0.006	10.19 ± 0.01	0.247	5.08 ± 0.02	10.07 ± 0.02
0.484	4.822 ± 0.005	9.68 ± 0.01	0.478	4.68 ± 0.01	9.61 ± 0.01
0.723	4.559 ± 0.003	9.36 ± 0.02	0.704	4.495 ± 0.004	9.44 ± 0.01
		Cu−AA, (70 to 100) kDa			
0.098	3.626 ± 0.001	-	0.101	3.586 ± 0.006	-
0.239	3.189 ± 0.001	-	0.249	3.22 ± 0.01	-
0.470	2.857 ± 0.002	-	0.493	2.85 ± 0.05	-
0.694	2.967 ± 0.003	-	0.727	2.90 ± 0.05	-
		Cd−PAA, 100 kDa			
0.100	4.604 ± 0.009	8.83 ± 0.01	0.100	4.690 ± 0.002	8.83 ± 0.01
		Cd−PAA, 2 kDa			
0.097	4.009 ± 0.005	-	0.102	3.94 ± 0.01	7.91 ± 0.03
0.236	3.621 ± 0.005	-	0.243	3.667 ± 0.005	7.59 ± 0.03
0.478	3.400 ± 0.001	-	0.476	3.35 ± 0.01	7.39 ± 0.05
0.715	3.202 ± 0.002	-	0.708	3.348 ± 0.004	7.37 ± 0.02
		Cd−PMA, 5.4 kDa			
0.101	4.22 ± 0.01	9.11 ± 0.03	0.101	4.104 ± 0.007	9.18 ± 0.01
0.234	3.832 ± 0.004	8.72 ± 0.01	0.247	3.726 ± 0.002	8.717 ± 0.009
0.456	3.43 ± 0.01	8.68 ± 0.01	0.486	3.400 ± 0.008	8.58 ± 0.01
0.674	3.30 ± 0.01	8.676 ± 0.001	0.717	3.33 ± 0.04	8.56 ± 0.01
		Cd−AA, (70 to 100) kDa			
0.098	3.072 ± 0.005	-	0.101	3.027 ± 0.004	-
0.239	2.432 ± 0.001	-	0.246	2.60 ± 0.01	-
0.471	2.160 ± 0.005	-	0.485	2.22 ± 0.02	-
0.702	2.112 ± 0.002	-	0.720	2.05 ± 0.03	-

[a] β_{pqr} refers to the equilibrium of eq 1. [b] mol·L^{-1}. [c] ± std. dev.

kDa, PAA 100 kDa, PMA 5.4 kDa, and AA (70 to 100) kDa, respectively.[36]

About the hydrolysis of metal ions, the following considerations can be made. The hydrolysis of cadmium(II), occurring at pH > 7 according to Baes and Mesmer,[46] can be neglected in the pH range investigated in our measurements. On the contrary, the hydrolysis of copper(II), starting from pH ∼ 5,[46] was considered in the complex formation model of Cu^{2+}−polyelectrolyte systems. We used in our calculations values of hydrolysis constants of Cu^{2+} in $NaClO_4$ medium[47] by considering that they should be very similar to those in $NaNO_3$. Nevertheless, calculations performed showed that also copper(II) hydrolysis is negligible in the pH range considered.

Complex Formation in the Cu^{2+}− and Cd^{2+}−Polyelectrolyte Systems. Tables 3 and 4 show the formation constants, in molar and molal concentration scales, of Cu^{2+}− and Cd^{2+}−polyelectrolyte complex species formed in the systems investigated at different ionic strengths in $NaNO_3$ ionic medium, obtained by ISE-H^+ and ISE-M^{2+} potentiometric measurements.

As can be seen, the values obtained using the two techniques are in excellent agreement, as confirmed also by the linear correlation reported in Figure 1 showing a slope of 0.995 ± 0.003 and a linear correlation coefficient $R = 0.9996$.

In all the systems investigated, the species ML is formed. A further species MLH was also found in the M-PAA (2 and 100) kDa and in the M-PMA 5.4 kDa systems. The formation of the monoprotonated species in these systems is consistent with the possibility of metal interaction with the partially protonated polyelectrolyte in the acidic pH range, according to the diprotic-like model adopted here to explain the acid−base behavior of polyelectrolytes. This species was not found in the Cu/Cd−AA (70 to 100) kDa systems since alginic acid is fully deprotonated in the pH range investigated.

As expected, the stability of Cu^{2+}−polyelectrolyte species is higher, almost one logarithm unit more (as log K), than the corresponding ones in the Cd^{2+}−polyelectrolyte systems (see Tables 3 and 4). A similar trend is also shown by copper(II) and cadmium(II) complex species with low molecular weight carboxylic ligands.[48] Moreover, the Cu^{2+} and Cd^{2+} alginate species show a stability lower than that of the corresponding polyacrylate and polymethacrylate species. This can be attributed to a lower density of carboxylic groups (D_{COOH}, expressed as mmol of COOH groups per gram of polyelectrolyte) in AA (70 to 100) kDa (5.7 mmol·g^{-1} of COOH groups) with respect to that of the other ligands: (14 and 11.6) mmol·g^{-1} of COOH groups for PAA (2 and 100) kDa and PMA 5.4 kDa, respectively.

Dependence of Formation Constants on Ionic Strength. Literature data on metal polyacrylate and polymethacrylate complex formation refer to measurements carried out mainly at one value of ionic strength, in particular 0.1 mol·L^{-1} in nitrate or chloride ionic media. However, since these studies are greatly

Table 4. Formation Constants[a] in the Molal Concentration Scale, of Cd^{2+}− and Cu^{2+}− L (L = PAA 2 kDa, PMA 5.4 kDa, and AA (70 to 100) kDa) Complex Species Calculated with ISE-M^{2+}(Cd^{2+}, Cu^{2+}) and ISE-H^+ in $NaNO_3$, at Different Ionic Strengths and at T = 298.15 K

ISE-Cd^{2+} or ISE-Cu^{2+} measurements			ISE-H^+ measurements		
I^b	log β_{110}	log β_{111}	I^b	log β_{110}	log β_{111}
Cu−PAA, 100 kDa					
0.100	5.189	9.29	0.100	5.225	9.300
Cu−PAA, 2 kDa					
0.103	4.742	-	0.097	4.65	9.32
0.249	4.289	-	0.237	4.278	8.847
0.500	4.044	-	0.471	4.045	8.366
0.748	3.945	-	0.711	3.945	8.267
Cu−PMA, 5.4 kDa					
0.100	5.666	10.67	0.106	5.69	10.69
0.246	5.186	10.18	0.250	5.07	10.06
0.492	4.814	9.66	0.486	4.67	9.61
0.741	4.548	9.34	0.721	4.484	9.42
Cu−AA, (70 to 100) kDa					
0.099	3.623	-	0.102	3.583	-
0.239	3.185	-	0.252	3.22	-
0.478	2.849	-	0.502	2.84	-
0.711	2.956	-	0.746	2.89	-
Cd−PAA, 100 kDa					
0.100	4.601	8.82	0.100	4.69	8.82
Cd−PAA, 2 kDa					
0.097	4.006	-	0.103	3.94	7.90
0.238	3.617	-	0.245	3.662	7.58
0.486	3.392	-	0.484	3.34	7.37
0.733	3.191	-	0.726	3.337	7.35
Cd−PMA, 5.4 kDa					
0.102	4.22	9.10	0.102	4.101	9.17
0.236	3.828	8.71	0.250	3.721	8.708
0.464	3.42	8.66	0.494	3.392	8.56
0.690	3.29	8.655	0.735	3.32	8.54
Cd−AA, (70 to 100) kDa					
0.098	3.069	-	0.102	3.024	-
0.241	2.428	-	0.249	2.60	-
0.479	2.152	-	0.494	2.21	-
0.719	2.101	-	0.738	2.04	-

[a] β_{pqr} refers to the equilibrium of eq 1. [b] $\text{mol}\cdot\text{kg}^{1-}[\text{H}_2\text{O}]$.

Table 5. Formation Constants of Complex Species at Infinite Dilution Together with Empirical Parameter C for the Dependence on Ionic Strength According to Equation 2 in $NaNO_3$ Ionic Medium, at T = 298.15 K

pqr	log ${}^{T}\beta_{pqr}{}^{a}$	C	z^*	σ^b
Cu−PAA, 2 kDa				
110	5.93 ± 0.02[c]	0.42 ± 0.03[c]	12	0.035
111	10.83 ± 0.02	0.11 ± 0.07	14	0.046
Cu−PMA, 5.4 kDa				
110	7.58 ± 0.03	0.42 ± 0.07	17.60	0.051
111	13.13 ± 0.01	0.78 ± 0.04	22.40	0.057
Cu−AA, (70 to 100) kDa				
110	5.05 ± 0.02	0.69 ± 0.06	14	0.070
Cd−PAA, 2 kDa				
110	5.25 ± 0.02	0.42 ± 0.06	12	0.044
111	9.37 ± 0.02	0.93 ± 0.04	14	0.011
Cd−PMA, 5.4 kDa				
110	6.06 ± 0.02	0.83 ± 0.05	17.60	0.010
111	11.42 ± 0.02	2.14 ± 0.06	22.40	0.009
Cd−AA, (70 to 100) kDa				
110	4.53 ± 0.03	0.26 ± 0.05	14	0.073

[a] β_{pqr} refers to the equilibrium of eq 1. [b] std. dev. on the fit. [c] std. dev. on the parameters.

Table 6. Protonation Constants[a] at Infinite Dilution of Polyelectrolytes Calculated with the SIT Model Equation 3 and Interaction Coefficients of HA and H_2A Species (with A = PAA 2 kDa, PMA 5.4 kDa, and AA (70 to 100) kDa), at T = 298.15 K

SIT coefficients	PAA, 2 kDa	PMA, 5.4 kDa	AA, (70 to 100) kDa
log $\beta_{011}{}^{b}$	6.36 ± 0.02[c]	7.48 ± 0.01[c]	4.22 ± 0.05[c]
log $\beta_{012}{}^{b}$	11.14 ± 0.02	13.23 ± 0.02	7.66 ± 0.05
$\varepsilon(A^{z-}, Na^+)$	0.14 ± 0.04	0.78 ± 0.03	0.50 ± 0.03
$\varepsilon(HA^{(1-z)}, Na^+)$	0.06[d]	0.64[d]	0.35[d]
$\varepsilon(H_2A^{(2-z)}, Na^+)$	0.01[d]	0.32[d]	0.13[d]
$\varepsilon(H^+, NO_3^-)$	0.07[e]		

[a] Molal concentration scale. [b] log β refers to equilibrium of eq 1. [c] std. dev. on the parameters. [d] Calculated by eq 5a with $\bar{\varepsilon} = 0.01$ for PAA 2 kDa; $\bar{\varepsilon} = 0.06$ for PMA 5.4 kDa; and $\bar{\varepsilon} = 0.05$ for AA (70 to 100) kDa. [e] Ref 47.

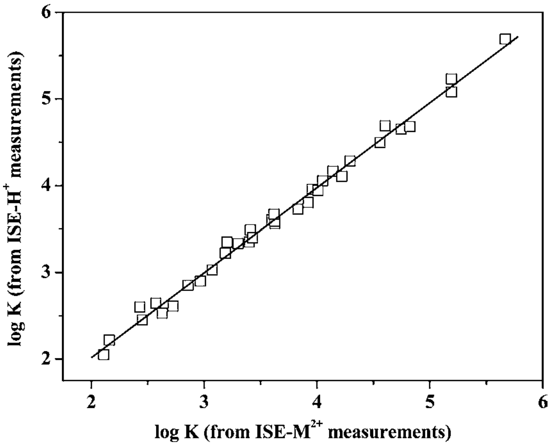

Figure 1. Correlation between the log K values (molar concentration scale) of complex species of the systems investigated, calculated by potentiometric ISE-H^+ and ISE-M^{2+} measurements, in $NaNO_3$ ionic medium, at different ionic strengths and at T = 298.15 K.

related to the possibility of using these polyelectrolytes in industrial and environmental applications, different ionic strengths, such as, for example, from (0.1 to 0.7) mol·L^{-1} for natural waters and wastewaters, should be considered. In this work, we carried out measurements at (0.1, 0.25, 0.5, and 0.75) mol·L^{-1} ionic strengths in $NaNO_3$ medium to evaluate the influence of ionic strength on the formation constants of all species formed in the systems investigated and also to calculate the formation constants at infinite dilution where the constants are independent of the medium used. The dependence of formation constants on ionic strength was studied by using two different approaches: an extended Debye−Hückel type equation (see eq 2) and the SIT model (see eq 3). Results obtained by using the Debye−Hückel approach are shown in Table 5 where thermodynamic formation constants (log ${}^{T}\beta_{pqr}$) of the complex species, together with the empirical parameters C of eq 2 and z^* of the species, are reported.

As an example, in Figure 2 is shown the dependence on ionic strength of log K of CuL (L = PAA 2 kDa, Figure 2a) and CdL (L = PMA 5.4 kDa, Figure 2b) species, obtained by ISE-H^+ and ISE-M^{2+} measurements, using the extended Debye−Hückel model. The value of C of eq 2 is fairly constant (see Table 5) for the different metal complex species in relation to the charge-difference parameter z^*: in fact, for the ratio C/z^* we have a mean value of 0.041 ± 0.015.

In Tables 6 and 7, we report the values (molal concentration scale) of polyelectrolyte protonation constants and stability constants at infinite dilution of Cu^{2+}− and Cd^{2+}−polyelectrolyte species according to the SIT model (see eq 3), together with the specific interaction coefficients ε. The interaction coefficients of mono- and diprotonated polyelectrolyte species with the sodium ion (Table 6) were calculated according to eq 5a, while

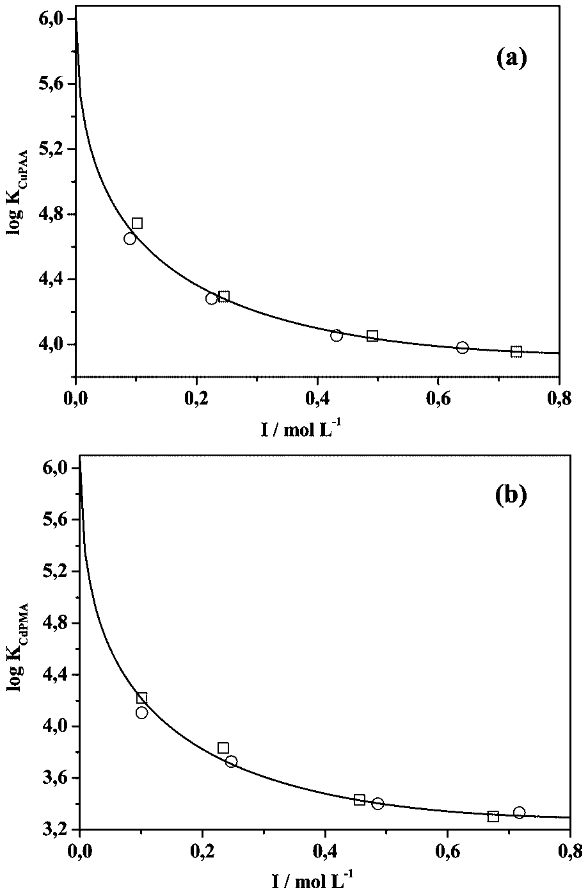

Figure 2. Dependence on ionic strength (according to the Debye–Hückel model, eq 2) of formation constants of Cu–PAA 2 kDa (a) and Cd–PMA 5.4 kDa (b) species in $NaNO_3$ at $T = 298.15$ K. Experimental data obtained with □, ISE-M^{2+} and ○, ISE-H^+ electrodes.

the specific interaction coefficients for $H^+{-}NO_3^-$, $Cd^{2+}{-}NO_3^-$, and $Cu^{2+}{-}NO_3^-$ species are taken from the literature.[49]

By comparing data obtained by the Debye–Hückel (Table 5) and SIT models (Tables 6 and 7), it is evident that each of the two approaches for the dependence on ionic strength of stability constants can be used successfully in the ionic strength range investigated. Both models give satisfactory results, as confirmed by the good fits on the experimental data which show also a very good accordance between them.

Quantitative Parameters for Sequestering Capacity of the Polyelectrolytes toward Cd^{2+} and Cu^{2+} Ions. The term "sequestration" is generally used when a metal ion is removed from the solution by absorption on a solid phase or gel. The aim of the process is to reduce the concentration of free metal ion and therefore its potential toxicity and bioavailability. In this light, metal complexation in solution can be considered a sequestering process since even in this case the concentration of free metal ion continues to reduce as much as the stability of metal complex species formed increases. This concept is widely used in chelation therapy to reduce the toxicity of metal ions in the human body, as well as in several industrial applications.

The stability data obtained for the complex species formed in all the systems investigated allowed us to quantitatively define the sequestration capacity of the polyelectrolytes toward Cd^{2+} and Cu^{2+} ions, by considering the amount of ligand necessary to bind the metal under fixed experimental conditions of pH, ionic medium, ionic strength, and temperature. To this end, we used a function Σ % vs pL, where Σ % represents the sum of the formation percentage of all the metal complex species formed at a certain pH value, and pL (L = ligand considered) is the $-\log\,[L]_{tot}$. The function can be expressed by the following equation already used successfully for other metal–ligand systems[50−54]

$$\Sigma\,\% = 100\cdot\left[\frac{1}{1 + e^{(pL - pL_{50})/S}} - 1\right] \qquad (6)$$

where pL_{50} is the ligand concentration necessary to bind (to remove) 50 % of the metal ion (Cd^{2+} or Cu^{2+}, in this case) and S is the slope in the flex of the sigmoidal curve. The pL_{50} is a helpful parameter which can be used to quantitatively define the metal sequestration capability of whatever ligand in the experimental conditions used.

The values of pL_{50} and S for the systems investigated, at $I = 0.1\ mol\cdot L^{-1}$ ($NaNO_3$ medium), at pH = 5, $T = 298.15$ K, and for trace cadmium(II) and copper(II) concentration ($C_{Cu^{2+}/Cd^{2+}} = 10^{-10}\ mol\cdot L^{-1}$) are reported in Table 8.

The corresponding plots for Cd^{2+} and Cu^{2+} ions are reported in Figures 3a and 3b, respectively.

In general, the pL_{50} value of a polycarboxylic ligand is strictly correlated to the following factors: (i) the density of the COOH groups in the molecule (D_{COOH}, see Table 8); (ii) the molecular weight of the polymer and the effective charge of the polyanion; (iii) the proton exchange capacity of the polycarboxylate in the pH range investigated; (iv) the tendency for hydrolysis of the metal ion involved in the complexation. The two last factors could significantly influence the speciation profile of the metal–ligand systems under investigation.

By taking into account these factors altogether, the trends for the sequestering capacity of the polyelectrolytes investigated toward copper(II) and cadmium(II) ions are as follows:

PAA 100 kDa > PMA 5.4 kDa > PAA 2 kDa > AA (70 to 100) kDa, for the copper(II) ion

and

PAA 100 kDa > PAA 2 kDa > AA (70 to 100) kDa > PMA 5.4 kDa, for the cadmium(II) ion

As expected, the PAA 100 kDa, having the highest COOH group density ($14\ mmol\cdot g^{-1}$) and the highest molecular weight among the polyelectrolytes considered, shows the best sequestering capacity toward both copper and cadmium ions in the experimental conditions used (see Table 8). Noteworthy is the behavior of AA (70 to 100) kDa: in spite of the low density of COOH groups in the molecule ($5.7\ mmol\cdot g^{-1}$), alginate shows a pL_{50} value similar to that of the other polyelectrolyte ligands and, in the case of the sequestration of Cd^{2+} ion, higher than the pL_{50} of PMA 5.4 kDa and very close to that of PAA 2 kDa. This can be attributed, in addition to the high average molecular weight, also to the more favorable binding properties of AA (70 to 100) kDa at the pH value considered in the pL_{50} calculations. In fact, at pH 5 the alginate, among the polyelectrolytes investigated, is the only one almost completely deprotonated (see protonation constants reported in Table 2) and, therefore, more ready to bind the metal ion.

Literature Data Comparison. From a careful evaluation of literature data, an evident disagreement can be noted between the results reported by different authors, especially owing to the different techniques [potentiometry (POT), direct current polarography (DCP), reverse pulse polarography (RPP), differential pulse anodic stripping voltammetry (DPASV), differential pulse polarography (DPP)] and experimental conditions used. This makes it very difficult to do a comparison between literature data and between these and our results. In spite of this difficulty, we will try to compare our results with some selected literature data on the Cu^{2+}–polyelectrolyte[15,17,19,27,28]

Table 7. Formation Constants[a] at Infinite Dilution of Polyelectrolytes Calculated with the SIT Model (Equation 3) and Interaction Coefficients of Cd^{2+}– and Cu^{2+}–PAA 2 kDa, –PMA 5.4 kDa, and –AA (70 to 100) kDa Complex Species at $T = 298.15$ K

	Cd–PAA, 2 kDa	Cd–PMA, 5.4 kDa	Cd–AA (70 to 100) kDa	Cu–PAA, 2 kDa	Cu–PMA, 5.4 kDa	Cu–AA, (70 to 100) kDa
$\log \beta_{110}$[b]	5.25 ± 0.02[c]	6.06 ± 0.02[c]	4.53 ± 0.03[c]	5.93 ± 0.02[c]	7.58 ± 0.03[c]	5.05 ± 0.02[c]
$\log \beta_{111}$[b]	9.38 ± 0.02	11.42 ± 0.02	-	10.82 ± 0.02	13.14 ± 0.02	-
$\varepsilon(MA^{(2-z)}, Na^+)$	-0.18 ± 0.06	0.04 ± 0.06	0.33 ± 0.05	-0.16 ± 0.05	0.46 ± 0.07	-0.08 ± 0.06
$\varepsilon(MAH^{(3-z)}, Na^+)$	-0.62 ± 0.05	-1.16 ± 0.06	-	0.22 ± 0.08	0.19 ± 0.05	-
$\varepsilon(Cd^{2+}, NO_3^-)$	0.09[d]					
$\varepsilon(Cu^{2+}, NO_3^-)$	0.11[d]					

[a] Molal scale. [b] $\log \beta_{pqr}$ refer to equilibrium of eq 1. [c] std. dev. on the parameters. [d] Ref 47.

Table 8. Sequestration Parameters of Equation 6[a] for Solutions Containing Trace Metal Concentration (10^{-10} mol·L^{-1} of Cd^{2+} or Cu^{2+} Ions), at pH = 5, in $NaNO_3$ Ionic Medium, at $I = 0.1$ mol·L^{-1} and at $T = 298.15$ K

systems	pL_{50}	systems	pL_{50}	D_{COOH}[b]	$-z$[c]
Cu–PAA, 100 kDa	4.443	Cd–PAA, 100 kDa	3.911	14 (PAA, 100 kDa)	4.6
Cu–PAA, 2 kDa	3.965	Cd–PAA, 2 kDa	3.125	14 (PAA, 2 kDa)	3.0
Cu–PMA, 5.4 kDa	4.147	Cd–PMA, 5.4 kDa	2.596	11.6 (PMA, 5.4 kDa)	4.4
Cu–AA, (70 to 100) kDa	3.571	Cd–AA, (70 to 100) kDa	3.012	5.7 (AA, 70 100 kDa)	3.5

[a] $S = 0.434$. [b] Effective charge of the polyelectrolyte. [b] mmol of COOH groups per gram of polyelectrolyte. [c] Effective charge.

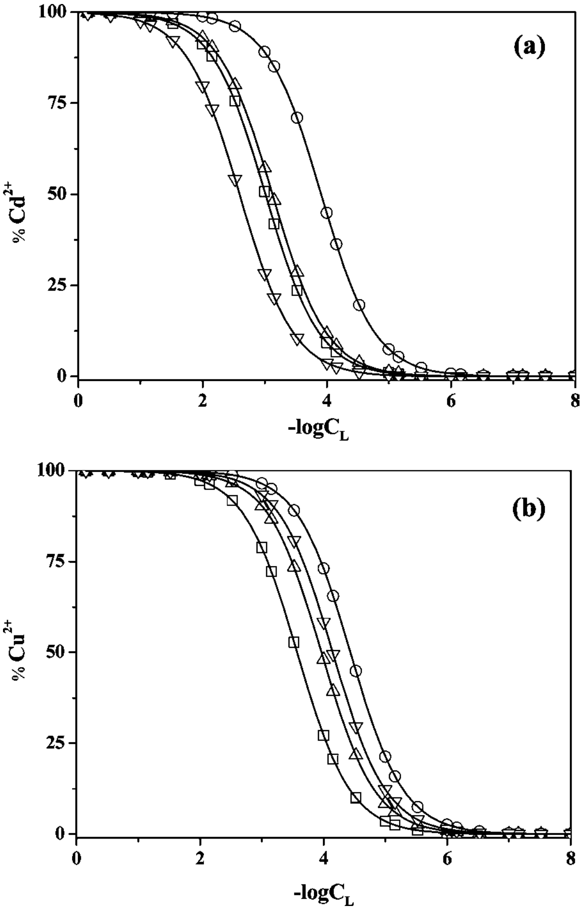

Figure 3. Percentage of Cd^{2+} (a) and Cu^{2+} (b) ions as sum of complex species with △, PAA 2 kDa; ○, PAA 100 kDa; ▽, PMA 5.4 kDa; and □, AA 70 – 100 kDa vs $-\log C_L$ in Cd^{2+} (a) and Cu^{2+} (b) –L systems at $I(NaNO_3) = 0.1$ mol·L^{-1} and at $T = 298.15$ K. Experimental conditions: $C_{Cd^{2+}-Cu^{2+}} = 10^{-10}$ mol·L^{-1} (trace), pH = 5.

and Cd^{2+}–polyelectrolyte[18,20,26] systems, shown in Tables 9 and 10. However, a comparison can be made only after the following aspects are considered: (i) almost all data reported in the literature are based on the Henderson–Hasselbalch model for protonation of polyacrylates and polymethacrylates considered, while we used the new protonation model, i.e., the diprotic-like model,[36] (see section Protonation of Polyelectrolytes), according to which also protonated metal complexes (MLH) have to be considered in the pH range where the polyelectrolyte is partially protonated; therefore, the $\log K_{ML}$ values reported in the literature are equivalent to our $\log \beta_{111} - \log K_{011}$, and the $\log \beta_{ML2}$ values of the literature correspond to our $\log K_{110}$ (the indexes of the constants refer to equilibrium of eq 1); (ii) the molecular weights of polyacrylates and polymethacrylates investigated here are lower (in some cases much lower) than those of the homologous polyelectrolytes considered in the literature; (iii) experimental conditions used by the different authors, in particular pH, ligand concentration, and ligand to metal ratios, are very heterogeneous and also differ from those used in this work. For a better reading, in Tables 9 and 10 we also report our results as mean values of formation constants obtained by ISE-H^+ and ISE-Cu^{2+}/Cd^{2+} measurements and opportunely modified, according to point (i) discussed above, to make them uniform with respect to those reported by other authors.

The log K values reported in Tables 9 and 10 are at the same ionic strength (0.1 mol·L^{-1}), in nitrate ionic medium. The main differences in the experimental conditions are the L/M ratio and the pH range investigated by the different authors. In spite of these differences, a good agreement among the $\log K_{ML}$ values ($M = Cu^{2+}$ and Cd^{2+}) is evident. For example, the value of 3.13 obtained in this work for the species Cd–PAA 100 kDa is comparable with the $3.0 \leq \log K_{ML} \leq 3.3$ reported by Morlay et al.[18,20] for PAA 250 kDa, PAA $3 \cdot 10^3$ kDa, and PAA cross-linked (MW not specified in the paper). Again, for the species Cu–PAA 2 kDa and Cu–PAA 100 kDa we obtain $\log K_{ML} =$ 3.64 and 3.60, respectively, in good agreement with $\log K_{ML}$ values ranging between 3.3 and 3.7 reported by Morlay et al.[17,19] for the species formed in the systems copper(II)–PAA (MW 250 and $3 \cdot 10^3$ kDa) and PAA cross-linked.

Diaz-Cruz et al.[27,28] report the formation constants of copper(II) complex species with PMA 26 kDa and PAA 230 kDa calculated at different dissociation degrees. In particular, for $\alpha = 0.3$ to 0.4 the authors give $\log K_{ML}$ values ranging from 4.29 to 4.87 for the Cu–PMA 26 kDa and from 3.7 to 4.2 for the Cu–PAA 230 kDa complex species, in good agreement with $\log K_{ML}$ values of 4.16 (for L = PMA 5.4 kDa) and of 3.60 (for L = PAA 100 kDa) obtained in this work.

The good accordance between the cited selected literature data and our results, obtained using the new diprotic-like model,[36] is a further confirmation on the possibility of using

Table 9. Some Literature Data for Complex Formation in the Cu−Polyacrylate and −Polymethacrylate Systems[a] at T = 298.15 K

polyelectrolyte	I/mol·L^{-1}	L/M ratio	pH range[b]	log K_{ML}	technique	ref
PAA, 2 kDa	0.1 ($NaNO_3$)	1 to 2	2.5 to 5.5	3.64[c]	POT. (ISE-H^+, ISE-Cu^{2+})	this work
PAA, 100 kDa	″	1 to 2	2.8 to 5.6	3.604[c]	″	″
PMA, 5.4 kDa	″	1 to 2	2.5 to 7.5	4.16[c]	″	″
PAA, 230 kDa	0.1 (KNO_3)	?	4.6 (α = 0.3)[d]	3.7 to 4.2	RPP, DPASV	28
PAA, 250 kDa	0.1 ($NaNO_3$)	6.3	3.5 to 7.5	3.4	POT. (ISE-H^+)	17
″	″	12.6	3.5 to 7.5	3.3	″	17
PAA cross-linked	0.1 ($NaNO_3$)	1.1 to 11.2	4 to 6	3.4 to 4.5	DPP	15
PAA cross-linked	0.1 ($NaNO_3$)	3.3	< 7.5	3.7	POT. (ISE-H^+)	19
″	″	8.3	″	3.6	″	19
PAA, $3\cdot10^3$ kDa	0.1 ($NaNO_3$)	3.1	3.5 to 7.5	3.6	POT. (ISE-H^+)	17
″	″	6.1	3.5 to 7.5	3.5	″	17
″	″	12.2	3.5 to 7.5	3.5	″	17
PMA, 26 kDa	0.1 (KNO_3)	?	α = 0.4[d]	4.29 to 4.87	DPP, DPASV	27

[a] Protonation constants of polyelectrolytes in the literature were calculated by the Henderson−Hasselbalch model. [b] pH range or pH value of the experiments. [c] log K_{ML} = log K_{111} − log K_{011} (indexes refer to eq 1); mean values of formation constants obtained from ISE-H^+ and ISE-Cu^{2+} measurements. [d] Dissociation degree of the polyelectrolyte.

Table 10. Some Literature Data for Complex Formation in the Cd−Polyacrylate and −Polymethacrylate Systems[a] at T = 298.15 K

polyelectrolyte	I/mol·L^{-1}	L/M ratio	pH range[b]	log K_{ML}	Technique	ref
PAA, 2 kDa	0.1 ($NaNO_3$)	1 to 2	2.3 to 6.3	2.22[c]	POT. (ISE-H^+, ISE-Cu^{2+})	this work
PAA, 100 kDa	″	1 to 2	3.8 to 5.7	3.13[c]	″	″
PMA, 5.4 kDa	″	1 to 2	3.0 to 6.8	2.64[c]	″	″
PAA, 250 kDa	0.1 ($NaNO_3$)	6.4	< 7.5	3.1	POT. (ISE-H^+)	18
″	″	12.9	< 7.5	3.0	″	18
PAA cross-linked	0.1 ($NaNO_3$)	3.4	2.8 to 6	3.2	POT. (ISE-H^+)	20
″	″	8.4	″	3.3	″	20
PAA, $3\cdot10^3$ kDa	0.1 ($NaNO_3$)	6.4	< 7.5	3.1	POT. (ISE-H^+)	18
″	″	12.9	″	3.0	″	18
PMA, 26 kDa	0.1 (KNO_3)	10	α = 0.8[d]	3.6 to 5.3	DCP, RPP, DPP, DPASV	26

[a] Protonation constants of polyelectrolytes in the literature were calculated by the Henderson−Hasselbalch model. [b] pH range or pH value of the experiments. [c] log K_{ML} = log K_{111} − log K_{011} (indexes refer to eq 1); mean values of formation constants obtained from ISE-H^+ and ISE-Cd^{2+} measurements. [d] Dissociation degree of the polyelectrolyte.

successfully this simpler model in investigating the acid−base properties of the polyelectrolytes.

No stability data on the complexation of alginic acid with Cu^{2+} and Cd^{2+} ions are reported in the literature, and no comparison can be made.

Conclusions

The binding capacity of natural and synthetic polycarboxylic polyelectrolytes toward Cd^{2+} and Cu^{2+} ions was studied by ISE-H^+ and ISE-M^{2+}potentiometric techniques. The results obtained by both techniques are in excellent agreement and allowed us to carry out measurements at different reagent concentrations and at different M/L ratios.

Both protonation of the ligands and metal hydrolysis were taken into account in the complexation model of the metal−polyelectrolyte systems investigated. The effective charge and the protonation constants of the polyelectrolytes considered here were calculated by a new model, the diprotic-like model, which allows us to define the acid−base properties of the polyelectrolytes in all the acidic pH range simply by two protonation constants. According to this model, the species MLH was found in the Cu/Cd−PAA/PMA systems at a pH value of 5, i.e., under conditions of partial protonation of the polyelectrolyte ligands. The same species was not found in the Cu/Cd−AA system owing to the total deprotonation of alginic acid under the same pH conditions.

From the investigations performed at different ionic strength, the formation constants at infinite dilution and interaction parameters were calculated by using both a Debye−Hückel type equation and the specific ion interaction theory (SIT) approaches.

On the basis of the stability data, the sequestration capacity of all the polyelectrolytes investigated toward copper(II) and cadmium(II) ions was calculated using a sigmoid function where the formation percentage of complex species is related to the pL_{50} parameter indicating the amount of ligand necessary to bind 50 % of metal ion in aqueous solution. The trend of sequestration is strictly dependent on the density of COOH groups in the polycarboxylate molecule. A rough dependence of the sequestering power on both the carboxylate density and effective charge can be expressed by the equation

$$pL_{50} = a + bD_{COOH}$$

For copper(II), we have pL_{50} (± 0.3) = 2.5 + 0.015D_{COOH} and for cadmium(II) pL_{50} (± 0.1) = 3.2 + 0.019D_{COOH}.

Literature Cited

(1) Wall, F. T.; Gill, S. Interaction of cupric ions with polyacrylic acid. *J. Phys. Chem.* **1954**, *58*, 1128–1130.
(2) Gregor, H. P.; Luttinger, L. B.; Loebl, E. M. Metal-polyelectrolyte complexes. I. The polyacrylic acid-copper complex. *J. Phys. Chem.* **1955**, *59*, 34–39.
(3) Gregor, H. P.; Luttinger, L. B.; Loebl, E. M. Metal-polyelectrolyte complexes. II. Complexes of copper with cross-linked polyacrylic and polymethacrylic acids. *J. Phys. Chem.* **1955**, *59*, 366–368.
(4) Kotliar, A. M.; Morawetz, H. Chelation of copper(II) with polyacrylic and polymethacrylic acid. *J. Phys. Chem.* **1955**, *77*, 3692–3695.
(5) Mandel, M.; Leyte, J. C. Interaction of poly(methacrylic acid) and bivalent counterions. I. *J. Polym. Sci.* **1964**, *2* (6), 2883–2899.
(6) Gustafson, R. L.; Lirio, J. A. Interaction of cross-linked polymethacrylic acid with polyvalent metal ions]. *J. Phys. Chem.* **1965**, *69* (9), 2849–2856.
(7) Leyte, J. C.; Zuiderweg, L. H.; van Reisen, M. A. spectroscopic study of binuclear copper complexes in aqueous poly(methacrylic acid) solutions. *J. Phys. Chem.* **1968**, *72* (4), 1127–1132.
(8) Gustafson, R. L.; Lirio, J. A. Binding of divalent metal ions by cross-linked polyacrylic acid. *J. Phys. Chem.* **1968**, *72* (5), 1502–1505.
(9) Yamashita, F.; Komatsu, T.; Nakagawa, T. Study of metal-polycarboxylate complexes employing ion-selective electrodes. Cu(II) and

Cd(II) complexes with poly(acrylic acid) and poly(itaconic acid). *Bull. Chem. Soc. Jpn.* **1976**, *49* (8), 2073–2076.

(10) Yamashita, F.; Komatsu, T.; Nakagawa, T. Study of metal-polycarboxylate complexes employing ion-selective electrodes. II. Stability constants of copper(II) complexes with poly(acrylic acid) and poly(methacrylic acid). *Bull. Chem. Soc. Jpn.* **1979**, *52* (1), 30–33.

(11) Marinsky, J. A. Complexation of copper(II) by poly(methacrylic acid) gel. *J. Phys. Chem.* **1982**, *86*, 3318–3321.

(12) Miyajima, T.; Mori, M.; Ishiguro, S.; Chung, K. H.; Moon, C. H. On the complexation of Cd(II) ions with polyacrylic acid. *J. Colloid Interface Sci.* **1996**, *184*, 279–288.

(13) Miyajima, T.; Mori, M.; Ishiguro, S. Analysis of complexation equilibria of polyacrylic acid by a Donnan-based concept. *J. Colloid Interface Sci.* **1997**, *187*, 259–266.

(14) Luciow, R. R.; Sarraf, L.; Morcellet, M. Complexes of poly(acrylic acid) with some divalent, trivalent and tetravalent metal ions. *Eur. Polym. J.* **2001**, *37*, 1741–1745.

(15) Morlay, C.; Cromer, M.; Mouginot, Y.; Vittori, O. Determination of the complexation properties of a crosslinked poly(acrylic acid) gel with copper(II), nickel(II), and lead(II) in dilute aqueous solution. *Can. J. Chem.* **2001**, *79*, 370–376.

(16) Morlay, C.; Mouginot, Y.; Cromer, M.; Vittori, O. The removal of Cu(II), Cd(II), Ni(II) and Pb(II) from dilute aqueous solution by a poly(acrylic acid) flocculant and its cross-linked analogue. *Water Sci. Technol.* **2002**, *2* (2), 27–34.

(17) Morlay, C.; Cromer, M.; Mouginot, Y.; Vittori, O. Potentiometric study of Cu(II) and Ni(II) complexation with two high molecular weight poly(acrylic acids). *Talanta* **1998**, *45*, 1177–1188.

(18) Morlay, C.; Cromer, M.; Mouginot, Y.; Vittori, O. Potentiometric study of Cd(II) and Pb(II) complexation with two high molecular weight poly(acrylic acids); comparison with Cu(II) and Ni(II). *Talanta* **1999**, *48*, 1159–1166.

(19) Mouginot, Y.; Morlay, C.; Cromer, M.; Vittori, O. Potentiometric study of copper(II) and nickel(II) complexation by a cross-linked poly(acrylic acid) gel. *Anal. Chim. Acta* **2000**, *407*, 337–345.

(20) Morlay, C.; Mouginot, Y.; Cromer, M.; Chatelut, M.; Vittori, O. Potentiometric study of cadmium(II) and lead(II) complexation by a cross-linked poly(acrylic acid). Comparison with the linear analogue. *Can. J. Chem.* **2000**, *78*, 1637–1641.

(21) Benegas, J. C.; Cleven, R. F. M. J.; van den Hoop, M. A. G. T. Potentiometric titration of poly(acrylic acid) in mixed counterion systems: Chemical binding of Cd ions. *Anal. Chim. Acta* **1998**, *369*, 109–114.

(22) Porasso, R. D.; Benegas, J. C.; van den Hoop, M. A. G. T. Chemical and electrostatic association of various metal ions by poly(acrylic acid) and poly(methacrylic acid) as studied by potentiometry. *J. Phys. Chem. B* **1999**, *103*, 2361–2365.

(23) Kirishima, A.; Tanaka, K.; Niibori, Y.; Tochiyama, O. Complex formation of calcium with humic and polyacrylic acid. *Radiochim. Acta* **2002**, *90*, 555–561.

(24) Francois, J.; Heitz, C.; Mestdagh, M. M. Spectroscopic study (u.v.-visible and electron paramagnetic resonance) of the interactions between synthetic polycarboxylates and copper ions. *Polymer* **1997**, *3821*, 5321–5332.

(25) Esteban, M.; Casassas, E. Direct-current, normal-pulse and reverse-pulse polarography of some heavy metal-polycarboxylate complexes. *Anal. Chim. Acta* **1990**, *229*, 93–100.

(26) Diaz-Cruz, J. M.; Ariño, C.; Esteban, M.; Casassas, E. Polarography and stripping voltammetry of metal-polycarboxylate complexes: complexes of cadmium and zinc with polyacrylic and polymethacrylic acids. *Electroanalysis* **1991**, *3* (4−5), 299–307.

(27) Diaz-Cruz, J. M.; Ariño, C.; Esteban, M.; Casassas, E. Voltammetry of Cu(II) in the presence of polymethacrylate. *Anal. Chim. Acta* **1993**, *273* (1−2), 289–296.

(28) Diaz-Cruz, J. M.; Ariño, C.; Esteban, M.; Casassas, E. Polarography and strypping voltammetry of metal-polycarboxylate complexes: the Cu(II)-polyacrylate system. *Electroanalysis* **1993**, *5*, 677–684.

(29) Morlay, C.; Cromer, M.; Vittori, O. The removal of copper (II) and nickel (II) from dilute aqueous solution by a synthetic flocculant: a polarographic study of the complexation with a high molecular weight poly(acrylic acid) for different pH values. *Water Res.* **2000**, *34* (2), 455–462.

(30) Perret, S.; Morlay, C.; Cromer, M.; Vittori, O. Polarographic study of the removal of cadmium(II) and lead(II) from dilute aqueous solution by a synthetic flocculant. Comparison with copper(II) and nickel(II). *Water Res.* **2000**, *34* (14), 3614–3620.

(31) Garrigosa, A. M.; Gusmão, R.; Ariño, C.; Diaz-Cruz, J. M.; Esteban, M. Determination of complex formation constants by phase sensitive alternating current polarography: cadmium-polymethacrylic acid and cadmium-polygalacturonic acid. *Talanta* **2007**, *73*, 776–782.

(32) van den Hoop, M. A. G. T.; van Leeuwen, H. P. Stripping voltammetry of heavy-metal−(bio) polyelectrolyte complexes Part 1. Influence of supporting electrolyte. *Anal. Chim. Acta* **1993**, *273* (1−2), 275–287.

(33) Van den Hoop, M. A. G. T.; Benegas, J. C.; van Leeuwen, H. P. Stripping voltammetry of heavy metal/polyelectrolyte complexes Part 2. Analysis in terms of polylectrolyte theory. *Anal. Chim. Acta* **1995**, *317*, 327–334.

(34) Cleven, R. F. M. J.; Van Leeuwen, H. P. Electrochemical analysis of the heavy metal/humic acid interaction. *Intern. J. Environ. Anal. Chem.* **1986**, *27*, 11–28.

(35) Luciow, R. R.; Sarraf, L.; Morcellet, M. Concentration effects during the formation of poly(acrylic)-metal complexes in aqueous solutions. *Polym. Bull.* **2000**, *45*, 411–418.

(36) Crea, F.; De Stefano, C.; Gianguzza, A.; Pettignano, A.; Piazzese, D.; Sammartano, S. Acid - base properties of synthetic and natural polyelectrolytes: experimental results and models for the dependence on different aqueous media. *J. Chem. Eng. Data* **2009**, *54*, 589–605.

(37) De Stefano, C.; Gianguzza, A.; Piazzese, D.; Sammartano, S. Speciation of Organic Matter in Natural Waters-interaction of polyacrylates and polymethacrylates with major cation components of seawater. *Mar. Chem.* **2004**, *86*, 33–44.

(38) De Stefano, C.; Sammartano, S.; Gianguzza, A.; Piazzese, D. Speciation of polyelectrolytes in natural fluids. Protonation and interaction of polymetacrylates with major components of seawater. *Talanta* **2002**, *58* (2), 405–417.

(39) Diaz-Cruz, J. M.; Arino, C.; Esteban, M.; Casassas, E. Influence of the counterion concentration on the formation constants of some metal/polycarboxylate complexes: study by differential pulse anodic stripping voltammetry. *Biophys. Chem.* **1992**, *45*, 109–117.

(40) Siegel, K.; Mauer, Ü.; Keis, H. Polarography and stripping voltammetry of some metal-carboxylate complexes on mercury drop and rotating disc electrodes. *Electrochim. Acta* **1997**, *42*, 2955–2960.

(41) De Stefano, C.; Mineo, P.; Rigano, C.; Sammartano, S. Computer tools for the speciation of natural fluids. In *Marine Chemistry-An environmental Analytical Chemistry Approach*; Gianguzza, A., Pelizzetti, E., Sammartano, S.,Eds.; Kluwer: Amsterdam, 1997.

(42) Crea, F.; Giacalone, A.; Gianguzza, A.; Piazzese, D.; Sammartano, S. Modelling of natural and synthetic polyelectrolyte interactions in natural waters by using SIT, Pitzer and Ion Pairing approaches. *Mar. Chem.* **2006**, *99*, 93–105.

(43) Hogfeldt, E.; Miyajima, T.; Marinsky, J. A.; Muhammed, M. Application of a simple three parameter mode to titration data for some polyelectrolytes. *Acta Chem. Scand.* **1989**, *43*, 496–499.

(44) Katchalsky, A.; Spitnik, P. Potentiometric titrations of polymethacrylic acid. *J. Polym. Sci.* **1947**, *2*, 432–446.

(45) Katchalsky, A. Problems in the physical chemistry of polyelectrolytes. *J. Polym. Sci.* **1954**, *2*, 159–184.

(46) Baes, C. F.; Mesmer, R. E. *The hydrolysis of cations*; J. Wiley & sons: New York, 1976.

(47) De Robertis, A.; De Stefano, C.; Foti, C.; Signorino, G. Thermodynamic parameters for the formation of dimeric hydrolytic species of copper(II) in aqueous $NaClO_4$ solution at different ionic strengths. *Talanta* **1997**, *44*, 1839–1846.

(48) Martell, A. E.; Smith, R. M.; Motekaitis, R. J. *NIST Standard Reference Database 46*,vers. 8, Gaithersburg, 2004.

(49) Ciavatta, L. The specific interaction theory in evaluating ionic equilibria. *Ann. Chim. (Rome)* **1980**, *70*, 551–567.

(50) De Stefano, C.; Milea, D.; Porcino, N.; Sammartano, S. Speciation of phytate ion in aqueous solution. Sequestering ability towards mercury(II) cation in $NaCl_{aq}$ at different ionic strengths. *J. Agric. Food Chem.* **2006**, *54* (4), 1459-–1466.

(51) De Stefano, C.; Gianguzza, A.; Milea, D.; Pettignano, A.; Sammartano, S. Sequestering ability of polyaminopolycarboxylic ligands towards dioxouranium(VI) cation. *J. Alloys Compd.* **2006**, *424* (1−2), 93–104.

(52) Giacalone, A.; Gianguzza, A.; Pettignano, A.; Sammartano, S. Sequestration of organometallic compounds by natural organic matter. Binding of trimethyltin(IV) by fulvic and alginic acids. *Appl. Organomet. Chem.* **2006**, *20*, 706–717.

(53) De Stefano, C.; Gianguzza, A.; Pettignano, A.; Sammartano, S.; Sciarrino, S. Sequestration of organometallic compounds by synthetic and naturally occurring polycarboxylate ligands. Binding of monomethylmercury(II) by polyacrylic and alginic acids. *Chem. Spec. Bioavail.* **2007**, *19* (3), 131–142.

(54) Crea, F.; Foti, C.; Sammartano, S. Sequestering ability of polycarboxylic ligands towards dioxouranium(VI). *Talanta* **2008**, *75*, 775–785.

Received for review May 14, 2009. Accepted August 1, 2009. The authors thank the Universities of Palermo and Messina for their financial support.

JE9004245