Effect of the Polymer Concentration on the Interactions of Water-Soluble Polymers with Metal Ions

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Despite poly(allylamine) forms a complex with Ni^{2+} with three amino groups in the coordination sphere of the metal ion, the corresponding formation constant is of order one considering the polymer concentration. This supports the idea of the existence of polymeric domains with local high and nearly constant ligand concentration. Analogous behavior is found for the system poly(sodium 4-styrenesulfonate) with Pb^{2+}.

Studies on the formation of polymer-metal ion chelates suggest that they are formed in a one-step reaction rather than stepwise[1] when intra-polymer chain chelation occurs. Even at low ligand ratio, only completely coordinated metal ions in equilibrium with uncomplexed ones are found. Physically this fact may be explained considering the metal ions occluded in a cage of contracted polymer chains where the concentration of the ligands is locally higher in the polymer domain. It is, however, admitted to enunciate the chelation reaction as if the ligands where part of low molecular weight molecules, so that

$$M + nL \overset{\beta_n}{\rightleftharpoons} ML_n \tag{1}$$

where M is the metal ion whose charge has been omitted, L is the ligand, β_n is the overall formation constant, and n is a natural number. Does this imply that the dependency of the β_n constant on the overall ligand concentration in the solution is of order n? Upon the consideration that the solution present domains of heterogeneous ligand concentration, this is not evident. We are analyzing in this paper the influence of the polymer concentration on the interactions of water-soluble polymers with metal ions by ultrafiltration.

Ultrafiltration is a technique with potential applications in selective concentration and separation of metal ions from diluted solutions by using high molecular weight water-soluble polymers.[2-5] The metal ion retention profile associated to an ultrafiltration experiment allows obtaining some information about the interactions of the metal ions with the water-soluble polymer. To do this, a model has been enunciated and some semiempirical equations have been obtained.[6] In the analysis of an ultrafiltration profile, it has been considered that the polymer concentration expressed in monomeric units is constant during the whole experiment, since it is in excess, and the relation between the amounts of metal ions bound to the polymer and free in the solution has been obtained (K_Z^{diss}). This ratio is affected by some variables, as the ionic strength or the polymer concentration. It has been found a linear dependency of the logarithm of this magnitude on the logarithm of the ionic strength in a wide range of ionic strength values, and this is related to a linear dependency of the logarithm of K_Z^{diss} on the filtration factor F. In order to compare the retention profiles associated to experiments performed with different values of the polymer concentration, it can be defined a formation constant that includes the concentration of the polymer in monomeric units as:

$$K_Z^f = 1 / (K_Z^{diss} [L]^n) \tag{2}$$

where [L] is the concentration of monomeric units, and n is a factor. From experimental data, we can search the values of n that, for the different experiments, throw a unique value of the formation constant for each polymeric species.

Three experiments have been performed with each of the systems poly(sodium 4-styrenesulfonate) (PSS) / Pb^{2+}, and poly(allylamine) (PALA) / Ni^{2+}, in the presence of an excess of Na^+, and the order of the formation constant related with the concentration of the polymer is quantified. PSS was chosen as a representative of a polyelectrolyte where the sulfonate groups produce typical electrostatic interactions with Pb^{2+}, and PALA was selected as a representative of a coordination-predominant polymer due to the high coordinating ability of the amino groups. The experiments were performed as described elsewhere,[6] and the values of the variables are given in Table

Table 1. Values of the experimental variables and the retention functions obtained

Experiment	Polymer concentration / M	Initial $NaNO_3$ concentration / M	Initial divalent metal ion concentration / M	Retention function
PSS-001	0.02	0.14	$8\ 10^{-5\ a}$	$R = 0.45 + 0.55 \exp(-1.3\ F)$.
PSS-002	0.04	0.14	$8\ 10^{-5\ a}$	$R = 0.62 + 0.38 \exp(-1.3\ F)$
PSS-003	0.08	0.14	$8\ 10^{-5\ a}$	$R = 0.80 + 0.20 \exp(-1.3\ F)$
PALA-001	0.02	0.13	$2\ 10^{-3\ b}$	$R = 0.61 + 0.39 \exp(-0.9\ F)$
PALA-002	0.03	0.13	$2\ 10^{-3\ b}$	$R = 0.72 + 0.28 \exp(-0.9\ F)$
PALA-003	0.07	0.13	$2\ 10^{-3\ b}$	$R = 0.83 + 0.17 \exp(-0.9\ F)$

[a] Pb^{2+}. [b] Ni^{2+}.

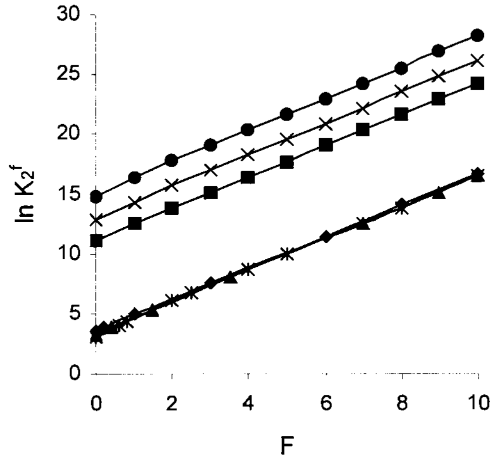

Figure 1. Formation constants for the system PSS / Pb^{2+} as a function of F: (■) 0.08 M, n = 4; (×) 0.04 M, n = 4; (●) 0.02 M, n = 4; (♦) 0.08 M, n = 1; (▲) 0.04 M, n = 1; (✱) 0.02 M, n = 1.

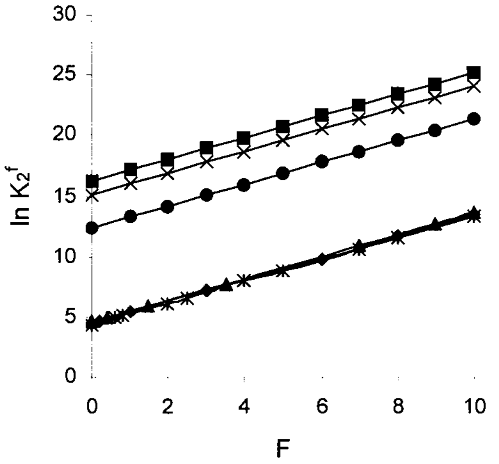

Figure 2. Formation constants for the system PALA / Ni^{2+} as a function of F: (■) 0.02 M, n = 4; (×) 0.03 M, n = 4; (●) 0.07 M, n = 4; (♦) 0.02 M, n = 1; (▲) 0.03 M, n = 1; (✱) 0.07 M, n = 1.

1, as well as the retention functions for each experiment. Figures 1 and 2 show the values of the logarithm of the formation constants as a function of the filtration factor (F) obtained with this procedure, for n = 1 and n = 4. The nature of the interaction of PSS with Pb^{2+} is electrostatic. It is for n = 1 that the values of the formation constants are equivalent, and then, the influence of the concentration of the polymer on the formation constants is of order one. The increase on the polymer concentration is interpreted as the increase on the number of charged polymeric chains. On the other hand, it has been described that PALA forms with Ni^{2+} a complex where three amino groups participate in the coordination sphere of the metal ion.[7] It is also found that the influence of the concentration of the polymer on the formation constants is of order one. This fact is analogously interpreted as the needing of considering the polymer as a whole, despite that at the molecular level, the metal ions may include several monomeric units in their coordination sphere. The increase on the polymer concentration may rather be interpreted as the increase on the number of chains and consequently on the number of polymeric domains with local high and nearly constant ligand concentration.

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