Evaluation of the sequestering ability of different complexones towards Ag$^+$ ion

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ABSTRACT

The interaction between Ag$^+$ cation and different ligands was evaluated as a function of temperature and ionic strength by means of potentiometric techniques. Six aminopolycarboxylic (APCs) and aminopolyphosphonic (APPs) ligands were chosen, namely four APCs: nitrilotriacetic acid (NTA), ethylene-glycol-bis(2-aminoethylether)-N,N,N',N'-tetraacetic acid (EGTA), ethylenediamine-N,N,N',N'-tetraacetate (EDTA) and diethylenetriamine-N,N,N',N'',N''-pentaacetic acid (DTPA)] and two APPs: [(1-hydroxyethane-1,1-diyl) bis(phosphonic acid) (HEDP) and [[(Phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]] tetrakis-phosphonic acid (DTPP). Different mononuclear species with general formula AgH$_i$L and different number of protons were found. For example in the case of the DTPP, six species with i = 0 to 5 were determined. The ionic strength dependence of the formation constants was studied for all the six ligands, whereas the temperature dependence only for the EDTA, HEDP and DTPP. Among these ligands, DTPP shows the highest formation constant values for the AgL species. The stability trend is: DTPP > DTPA > EDTA ~ EGTA > HEDP > NTA. It was found that the formation constant values decrease with increasing temperature and ionic strength. All the complex formation reactions are endothermic and enthalpic driven. The sequestering ability was evaluated using a useful tool, named pL$_{0.5}$, which uses a Boltzmann type equation to determine the percentage of metal bound to the ligand as a function of the ligand concentration and other chemico physical parameters (e.g. pH, temperature, ionic strength). Also in this case, the trend traces that of the formation constants, although the difference between DTPP and DTPA is lower.

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1. Introduction

The strong sequestering ability towards metal ions together with the extremely low or non-toxicity towards plants, animals and humans of aminopolycarboxylates (APCs) and aminopolyphosphonates (APPs) make these two classes of chelating agents very useful for many applications. For example, they are used as additives to cleaning agents, as bleach stabilizers and Ca^{2+} and Mg^{2+} binders; in textile and paper industries to bind heavy metal ions that can affect the industrial processes; in agriculture as sources of nitrogen in fertilizers; as chelating therapy agents in biology and medicine; in the remediation processes of polluted soils and sediments as chelators of toxic metal ions, etc [1–9], and for these reasons they are the topic of important reviews (e.g. in refs. [10–12]). Due to their low biodegradability, the wide use of APCs and APPs in these and many other fields can cause their accumulation in the environment with serious consequences. In fact, although they have low toxicity, high concentration of these chelating agents in natural- and waste-waters can produce an increase of

mobilization of the toxic heavy metal ions present in rocks, sediments and industrial sludges.

On the light of these considerations, the knowledge of the binding ability of these molecules towards metal ions is of great importance to study the environmental implications in the use of these molecules in many anthropogenic applications. In the last years, our research group undertook a systematic study on the sequestering ability of several APCs and APPs towards different metal ions of environmental and biological interest [13–16]. As a further contribution, a study on the interaction of Ag$^+$ with four APCs [nitrilotriacetic acid (NTA), ethylene-glycol-bis(2-aminoethylether)-N,N,N',N'-tetraacetic acid (EGTA), ethylenediamine-N,N,N',N'-tetraacetate (EDTA) and diethylenetriamine-N,N,N',N'',N''-pentaacetic acid (DTPA)] and two APPs [(1-hydroxyethane-1,1-diyl)bis(phosphonic acid) (HEDP) and [[(Phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-phosphonic acid (DTPP)] is reported in this paper.

Silver is a rare metal usually present in nature as mineral ore, and the most abundant is argentite. Silver finds application in many fields, and there is a dedicated non-profit international association, "The Silver Institute", which draws its importance from the breadth of the silver industry. According to the last publication of the silver institute [17], the main applications regard photography, electronics, swimming

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pool and drinking water treatment processes, jewellery and drug industry. The increasing worldwide request of silver has brought to an increase in production from $7.4 \cdot 10^6$ kg in 1964 to $20.5 \cdot 10^6$ kg in 2007. The constant release of silver from the different anthropogenic activities has caused in the last decades the increasing of metal concentration in land, water and atmospheric particulate matter. Typical silver concentrations revealed in worldwide water bodies ranged between 0.03 and 500 ng $\cdot$ dm^{-3}. The knowledge of the total silver concentration in the environment is not enough to establish the mobility and the toxicity of the metal towards living organisms. In fact, as for the other heavy metal cations its behavior depends on its speciation, mostly in the presence of molecules, such as APCs and APPs, having high sequestering ability towards metal ions.

Few articles on the complexing ability of APCs and APPs towards Ag$^+$ ion can be found in the literature. They refer only to the complex formation with the most common NTA, EDTA, DTPA and HEDP, and the data are calculated in different ionic media [18–23], while no stability data are reported for the other complexones considered in this work.

The speciation study of APPs and APCs–Ag$^+$ systems was carried out by ISE-H$^+$ potentiometric technique in NaNO$_3$ medium, in a wide range of ionic strength ($0.1 \leq I/\text{mol} \cdot \text{dm}^{-3} \leq 1.0$) that included typical values of natural and waste waters, and at different temperatures ($288.15 \leq T/$K ≤ 318.15). The protonation constants of the ligands were also determined using the same technique. The speciation study gave evidence of the formation of AgL (L = APC or APP) together with different protonated AgH$_i$L species in the pH range investigated, see Table 1.

The dependence of the formation constants on ionic strength and temperature was studied, and some parameters for the modeling have been proposed using the Debye–Hückel type equation and the SIT (Specific ion Interaction Theory) approach. Finally the data have been compared with literature findings. Some empirical relationships were found to model the stability of the Ag$^+$/ligand complexes as a function of the number of the binding sites.

2. Materials and methods

2.1. Chemicals

Analytical grade purity ($\geq 99\%$) silver(I) nitrate (by Sigma-Aldrich) was used without purification, and the solutions, stored in dark flasks, were standardized using the Mohr method. Nitrilotriacetic acid (NTA), ethylene-glycol-bis(2-aminoethylether)-N,N,N',N'-tetraacetic acid (EGTA), ethylenediamine-N,N,N',N'-tetraacetic acid di-sodium salt (EDTA), diethylenetriamine-N,N,N',N'',N''-pentaacetic acid (DTPA), (1-hydroxyethane-1,1-diyl)bis(phosphonic acid) (HEDP) were supplied by Fluka with analytical grade purity. The [[(Phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-phosphonic acid (DTPP) was synthesized and used as reported in Cigala et al. [24]. Sodium nitrate (NaNO$_3$) solutions were prepared by weighing the pure salt (Fluka) after drying in an oven at T = 383.15 K. Nitric acid (HNO$_3$) and sodium hydroxide (NaOH) solutions were prepared by diluting concentrated ampoules (Riedel–deHaën) and were standardized against sodium carbonate and potassium hydrogen phthalate,

respectively. NaOH solutions were preserved from atmospheric CO$_2$ by means of soda lime traps. All solutions were prepared with analytical grade water (R = 18 MΩ) using grade A glassware.

2.2. Apparatus and procedure for potentiometric measurements

Potentiometric titrations were carried out in the temperature range $288.15 \leq T/\text{K} \leq 318.15$ using an apparatus that consisted of a model 809 Metrohm Titrando, equipped with an Orion glass electrode Ross type 8101 coupled with a double junction reference electrode Ross type 900200. A NaNO$_3$ solution of the same concentration of the ionic medium in cell was used for the external junction of the reference electrode. The apparatus was connected to a PC, and automatic titrations were performed using the Metrohm TiAMO 1.2 software to check for e.m.f. stability and to control titrant delivery and data acquisition. The estimated accuracy is $\pm$ 0.15 mV and $\pm$ 0.003 cm^3 for e.m.f. and titrant volume readings, respectively. In each titration 25 cm^3 of titrand solution containing known amounts of silver nitrate, the ligand under study, nitric acid and sodium nitrate, in order to reach the prefixed ionic strength and pH values, was titrated with standard NaOH. All titrations were carried out under magnetic stirring, and presaturated N$_2$ was bubbled through the solution in order to exclude O$_2$ and CO$_2$ inside. Further details of the experimental measurements are reported in Table 1. Eighty to hundred points were collected for each titration, and the equilibrium state during titrations was checked by monitoring the time necessary to reach equilibrium (several titrations were carried out with different equilibration times ranging between 10 and 60 s per data point) and by performing back titrations. For each experiment, independent titrations of strong acidic solution with standard base were carried out under the same temperature and ionic strength conditions as in the systems to be investigated to determine the standard electrode potential (E^0).

2.3. Calculations

The non-linear least squares computer program ESAB2M was used for the refinement of all the parameters of the acid-base titration (E^0, K_w, liquid junction potential coefficient, j_a, analytical concentration of reagents). The BSTAC and STACO computer programs were used in the calculation of formation constants of Ag$^+$–L complex species from potentiometric titrations. The ES4ECI and HySS [25] computer programs were used to draw speciation diagrams and to calculate species formation percentages. The LIANA computer program was used to fit different linear and nonlinear functions. ESAB2M, BSTAC, STACO, ES4ECI and LIANA computer programs were reviewed in De Stefano et al. [26].

Overall and stepwise protonation constants of ligands, hydrolysis constants of Ag$^+$ cation and formation constants of Ag$^+$–L complex species are given according to the Eqs. (1)–(2) (j = 0 for protonation; k = 0 and i < 0 for hydrolysis):

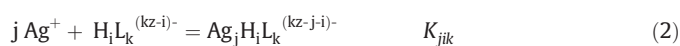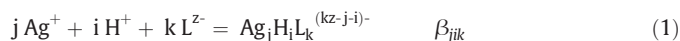$$j \, Ag^+ + i \, H^+ + k \, L^{z-} = Ag_jH_iL_k^{(kz-j-i)-} \qquad \beta_{jik} \qquad (1)$$

$$j \, Ag^+ + H_iL_k^{(kz-i)-} = Ag_jH_iL_k^{(kz-j-i)-} \qquad K_{jik} \qquad (2)$$

Table 1
Experimental conditions of potentiometric titrations in NaNO$_3$ ionic medium.

Ligand	c_{Ag} [a]	c_L [a]	c_H [a]	c_{Ag} : c_L	$I/\text{mol} \cdot \text{dm}^{-3}$	T/K	pH	n. tit
NTA	1.49–3.48	4.65–5.94	13.95–17.81	1:2–1:3	0.147–0.980	298.15	3.0–7.5	16
EDTA	1.00–3.40	1.60–4.00	3.20–8.00	1:1–1:3	0.155–0.996	288.15–318.15	2.0–10.0	20
EGTA	0.41–0.89	0.99–1.22	3.47–4.08	1:1–1:3	0.150–0.972	298.15	3.0–7.5	16
DTPA	0.99–2.69	2.77–4.11	13.84–29.67	1:1–1:3	0.157–0.925	298.15	3.0–8.0	16
HEDP	0.52–2.03	1.00–4.00	4.00–16.00	1:2–1:4.5	0.151–0.962	288.15–318.15	3.0–7.0	26
DTPP	0.99–2.98	1.97–3.48	17.74–31.30	1:1–1:3	0.172–0.931	288.15–318.15	2.0–12.0	35

[a] in mmol $\cdot$ dm^{-3}.