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Sequestration of *HEDPA*, *NTA* and phosphonic *NTA* derivatives towards Al^{3+} in aqueous solution

Paola Cardiano, Concetta De Stefano, Claudia Foti, Fausta Giacobello, Ottavia Giuffrè *, Silvio Sammartano

Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy

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The sequestration of Al^{3+} by etidronic acid (1 Hydroxyethane 1,1 diyil)bis(phosphonic acid) (*HEDPA*), nitrilotriacetic acid and its phosphonic derivatives, namely *N* (phosphonomethyl)iminodiacetic acid (PMIDA, *NTAP*), *N,N* bis (phosphonomethyl)glycine (*NTA2P*) and [bis(phosphonomethyl)amino]methylphosphonic acid (*NTA3P*) was studied in aqueous solution at $T = 298.15$ K and $I = 0.15$ mol L^{-1} in NaCl. Formation constants and speciation models are discussed on the basis of potentiometric results. The speciation models found for all the systems include MLH, ML and MLOH species, in addition for Al^{3+}-*NTA* system $ML(OH)_2$ and $M_2L_2(OH)_2$, for *NTAP* system ML_2, for *NTA2P* and *NTA3P* systems MLH_2 species, for *HEDPA* system ML_2 and ML_2OH species were detected as well. The formation constant values for ML species show the trend *NTA* < *NTAP* < *HEDP* < *NTA2P* < *NTA3P*. Investigations using ^1H NMR spectroscopy were also performed for the study of Al^{3+}-*NTAP* system. The ^1H NMR findings are in agreement with the speciation model obtained by potentiometry, confirming the stabilities of the main species. The dependence of formation constants on ionic strength over the range $I = 0.15$ to 1 mol L^{-1} in NaCl is also reported for *NTA*, *NTAP*, *NTA2P* systems. Enthalpy change values obtained by titration calorimetry at $T = 298.15$ K and $I = 0.15$ mol L^{-1} in NaCl, for the main Al^{3+}-*NTA, -NTAP, -NTA2P* and *NTA3P* species, are mainly endothermic, as typical for hard-hard interactions. The sequestering ability of the ligands under study towards Al^{3+} was also evaluated, under different pH conditions by the empirical parameter $pL_{0.5}$.

1. Introduction

Aluminium is the third constituent of the earth's crust and the most abundant metallic element. It has a wide variety of uses, such as medicines, surgery materials, cosmetics, as well as in water purification, building, food packaging, beverage cans, food additives, cooking tools, etc. [1]. It occurs ubiquitously in the environment, but since it is not an essential element in bioprocesses, it results toxic for animals, plants and humans [1–3]. The aluminium hydrolysis significantly affects its solubility and its bioavailability [1]. Because of its hard nature, it preferentially interacts with various ligands having the same character, such as phosphate, carboxylate, phenolate and catecholate [4–7].

Among chelating agents, polyphosphonates are of great interest, since these ligands are used in medicine, biology, environmental field and in several industrial and technological applications as scale inhibitors [8–12]. Phosphonates are characterized by a low toxicity, by high chemical stability and resistance against enzymatic hydrolysis [9]. Diphosphonic acids, containing the P-C-P backbone, are commonly named bisphosphonates and are employed for the treatment of several diseases related to the excessive bone resorption, such as osteoporosis, myeloma and bone metastases [9,13]. Polyphosphonate derivatives were also studied for applications as therapeutic radiopharmaceuticals. They are also present in several detergent formulations, since they bind Ca(II) ions, improving the cleaning action [10,14,15]. As a result these ligands enter the aquatic ecosystem being released with domestic waste waters [14,15]. Flowing through plants of water potabilization, they undergo a process of coagulation/flocculation with aluminium or ferric hydroxides [15]. Other applications of *HEDPA* include those for scale inhibition in water treatment, as dye-fixing agent, in therapeutic treatments [10,16]. Several biological uses of phosphonates are based on their ability to give electrostatic interactions, to form hydrogen-bonds and to interact with various metal ions. Di- and tri-phosphonates can give rise to a multi oxygen coordination to metal ions forming oligomeric or polymeric structures [9,13]. The most common phosphonates are structural analogues of aminopolycarboxylates, such as ethylenediaminetetraacetate (*EDTA*) and nitrilotriacetate (*NTA*) [11]. Aminopolycarboxylates present a tertiary nitrogen atom in the centre of the molecule and acidic groups linked to alkyl residues. Accordingly, at least four donor groups, can potentially form 1:1 species with metal cations [17]. Phosphonates are effective in the complexation of strongly hydrolyzed cations, such as Al^{3+} [12]. As

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* Corresponding author.
E-mail address: ogiuffre@unime.it. (O. Giuffrè).

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underlined by Galezowska et al. and Popov et al. reliable data on the stability constants of the metal cation-phosphonate complexes are necessary for modeling and prediction of technological and environmental applications [9,12].

The ligands understudy are the non-amino-bisphosphonate *HEDPA*, *NTA* and the aminopolyphosphonates *NTAP*, *NTA2P* and *NTA3P* (see Fig. 1), that can be considered as derivatives of *NTA,* where the three acetate groups are replaced by one or more phosphonates. This paper is part of a larger study on the complexation of Al^{3+} with different classes of ligands in aqueous solution, such as amino acids, polycarboxylates [18], thiocarboxylates [19], citrate, gluconate, lactate, silicate, carbonate, fluoride and two synthetic copolymers (Gantrez®) [20], oligophosphates [21], nucleotides [22].

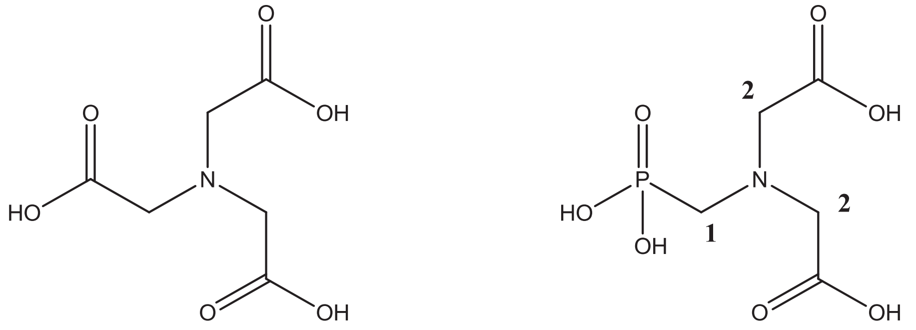
One of the aims of this study is to assess the effect of the replacement of the carboxylic groups with phosphonic functions on *NTA* molecule on the speciation and on the binding ability of the ligands towards Al^{3+}. Some selected systems (*NTAP*, *NTA2P* and *NTA3P*) have also been investigated under different ionic strength conditions for better modeling their speciation in real conditions. Enthalpy change values for all the systems under study were determined by direct calorimetric titrations. The sequestering ability of all the ligands towards Al^{3+} was evaluated by the calculation of $pL_{0.5}$ values, under different pH and ionic strength conditions.

2. Experimental section

2.1. Materials and methods

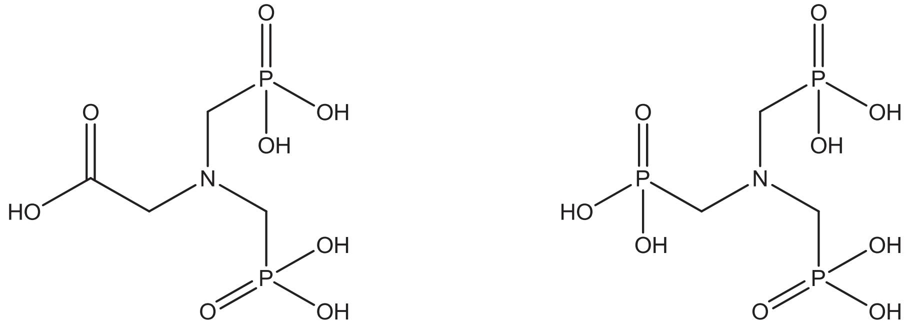
Solutions of $AlCl_3 \cdot H_2O$ were prepared by weighing the Sigma-Aldrich salt, (purity ≥ 99%). The concentration of these solutions was determined by a back-titration with *EDTA*, using copper sulfate as titrant. The ligand solutions were also obtained by weighing the Fluka and Sigma/Aldrich products and were used without further purification (*HEDPA* and *NTA* are Fluka product, *NTAP, NTA2P* and *NTA3P* are Sigma/Aldrich products), whose purity was checked potentiometrically by alkalimetric titrations, resulting always >99%.

Hydrochloric acid and sodium hydroxide solutions were prepared using Fluka ampoules and were standardized with sodium carbonate



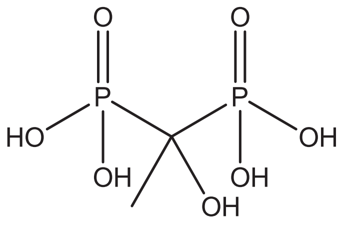
Nitrilotriacetic acid (*NTA*)

N-(phosphonomethyl)iminodiacetic acid (PMIDA, *NTAP*)



N,N-bis-(phosphonomethyl)glycine (*NTA2P*)

[bis(phosphonomethyl)amino]methylphosphonic acid (*NTA3P*)



Etidronic acid or (1-Hydroxyethane-1,1-diyil)bis(phosphonic acid) (*HEDPA*)

Fig. 1. Ligands under study.