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Exploring various ligand classes for the efficient sequestration of stannous cations in the environment

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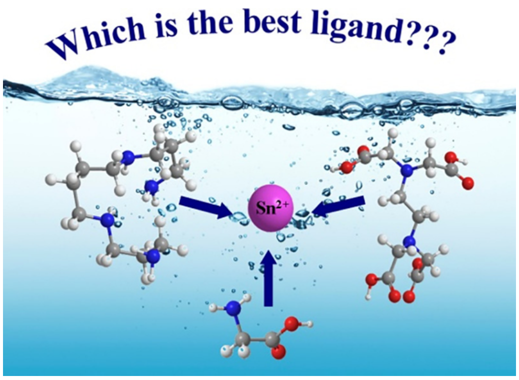
HIGHLIGHTS

- The data published for the interaction of Sn^{2+} with 38 molecules are surveyed.
- A chemometric approach for the estimation of unknown thermodynamic data is given.
- Amino groups and thiols are important for the efficient sequestration of Sn^{2+}.
- The work is useful for applications in biosphere, hydrosphere and lithosphere.
- PLS coefficients help in design new ligands for the efficient sequestration of Sn^{2+}.

GRAPHICAL ABSTRACT



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ABSTRACT

Metal pollution, coming from both natural and anthropogenic sources, has become one of the most serious environmental problems. Various strategies have been tested with the aim of removing heavy metals from environment. In this contribution, containing a robust experimental work together with a critical literature analysis, the sequestering ability of a variety of ligands towards Sn^{2+} cation will be evaluated in the conditions of several natural fluids, i.e. sea water, fresh water, human blood plasma, urine and saliva. 13 structural and 11 thermodynamic descriptors will be selected for a total of thirty-eight molecules belonging to different classes (carboxylic acids, amines, amino acids, phosphonates, polyelectrolytes etc. …). For the filling of those missing data relative to the 11 thermodynamic descriptors, different strategies will be adopted, including simple correlations and Nipals algorithm.

The evaluation of the sequestering ability of the ligands is assessed in terms of estimation of $pL_{0.5}$ (total concentration of ligand required to bind the 50% of metal in solution), an empirical parameter that takes into account all the side reactions in solutions and does not depend on the speciation scheme.

Partial least square calculations were performed to model the $pL_{0.5}$ and to determine its correlation with the abovementioned descriptors.

The possibility to design and build up new tailor-made molecules capable of effectively sequester Sn^{2+} in various conditions is crucial for practical applications in biosphere, hydrosphere and lithosphere.

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1. Introduction

During the EuCheMS congress held in Brussels in 2015, Nicola Armaroli has masterfully brought the attention to the problem of hunting the elements of the periodic table (EuCheMS, 2015) for the needs of the modern society. This fact, which mostly regards metals, is due to several bad habits, for example uncontrolled wasting of objects and average poor ability to recover raw materials.

Moreover, the problem of pollution of natural waters and soils is crucial for the future of the Earth.

As a result, the interest in molecules that may sequester metal cations is growing accordingly, moving from the classical aminopolycarboxylates (APCs) such as EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid), to new biodegradable ligands, biopolymers, sorbents etc. [see, e.g., refs (Wei et al., 2003; Tandy et al., 2004; Tandy et al., 2006; Cao et al., 2007; Tsang et al., 2009; Yip et al., 2009; Kołodyńska, 2011; Kołodyńska, 2013; Gautam et al., 2014; Samiey et al., 2014; Turhanen et al., 2015; Bretti et al., 2016b; Bretti et al., 2017b; Bretti et al., 2017c; Burakov et al., 2018; Kobielska et al., 2018; Lu and Astruc, 2018)]. However, any molecule may display also side effects, such as the mobilization of pollutants to groundwaters, the persistency in the environment or the poor selectivity causing the lowering of Ca^{2+} and Mg^{2+} levels.

Tin is not generally considered to be among the most important “pollutants”, although some of its compounds are of great importance from an environmental point of view. Beside the reputation of organotin(IV) compounds, inorganic tin species are important from a geochemical and hydrological perspective. In fact, tin is the 24th most abundant element in the Earth's crust, having ten isotopes, the largest number in the periodic table. Among them, ^{126}Sn is a radionuclide produced by nuclear fission, and it is often present in radioactive wastes, with a half-life of 10^5 years (Zang et al., 1996; Schapira, 1997; Peterson et al., 2007). According to the International Tin Association (2017) and United States Geological Survey (2018), the amount of tin refined each year is approaching 360,000 t, 48% in solders, 17% in chemicals, 14% in tinplate, 8% in Pb acid batteries, 5% in copper alloys and 8% in minor activities.

The design of novel strategies able to exert efficient Sn^{2+} removal and recovery from the environment, even in the presence of other contaminants and/or specific conditions, should involve the selection of appropriate ligands on the basis of reliable modeling tools with the aim to predict the optimal conditions for metal sequestration. This approach, meant to avoid “blind” trial and error research, necessarily requires a critical evaluation of the binding ability of several ligands, belonging to different classes, towards the Sn^{2+} cation in different fluids of biological and environmental interest, i.e.: sea water ($I = 0.717$ mol kg^{-1}, pH $= 8.0$), fresh water ($I = 0.0034$ mol kg^{-1}, pH $= 7.0$), human blood plasma ($I = 0.151$ mol kg^{-1}, pH $= 7.4$), urine ($I = 0.304$ mol kg^{-1}, pH $= 6.0$) and saliva (e.g., $I = 0.106$ mol kg^{-1}, pH $= 6.5$).

In order to perform quantitative data analysis, despite the lack of information on the interaction of the Sn^{2+} cation with most of the ligands, the employment of empirical relationships and other chemometric tools, can be a successful method to address this problem.

For this purpose, a total of 38 molecules belonging to different classes, namely aminopolycarboxylates (9 molecules), carboxylates (14), phosphates and phosphonates (5), thiols (2), amines (1), phenols and alcohols (3), amino acids (4) were selected on the basis of their structural and thermodynamic properties and listed in Table 2. A robust experimental work and a critical literature analysis were assessed to produce the initial data matrix, that contains 13 structural and 11 thermodynamic descriptors.

The first issue to deal with is the filling of missing data. As stated above, to model the speciation in natural fluids, the stability constants of Ca^{2+}, Mg^{2+} and Sn^{2+}/L species, together with their parameters for the ionic strength and temperature dependence are required. Unfortunately, many data are unavailable for several ligands, therefore empirical relationships or Nipals algorithm (Forina et al., 2003) were employed to fill these missing information.

The $pL_{0.5}$ parameter is able to take into account all the side reactions competing in a solution, such as the protonation of the ligand, the hydrolysis of the metal cation and the formation of Mg^{2+} or Ca^{2+}/L species, therefore it provides a much more complete picture of the real conditions with respect to the “simple” formation constant. As an example, let us consider a solution containing a certain amount (x1) of Sn^{2+} to be sequestered, a certain amount (x2) of Mg^{2+}, with x2 > x1 and two ligands (L1 and L2), whose stability constants for the SnL1 and SnL2 species are equal. If the stability constant of the MgL1 is higher than that of the MgL2 species, L2 would be more available to form complexes with Sn^{2+} with respect to L1. Thus, $pL_{0.5}$ of L2 towards Sn^{2+} will be higher than L1 one, even if the stability constants of SnL1 and SnL2 are identical. From this simple example it is clear how the use of the $pL_{0.5}$ as indicator for the evaluation of the sequestering ability can really make the difference, since it allows to tune the concentration of a ligand for a specific purpose, reducing drawback effects.

The $pL_{0.5}$ values obtained for the 38 molecules in the different conditions were modeled as a function of the descriptors by means of a PLS (partial least square) analysis, to understand which of them are the most important in each fluid, allowing the possibility to design novel molecules able to show high sequestering ability towards Sn^{2+} in specific conditions.

To graphically describe the paper, a flow-chart is proposed as Supplementary material.

2. Experimental section

2.1. Chemicals

All chemicals were purchased from Sigma Aldrich at the highest purity available and used without further purification. Sodium hydroxide and hydrochloric acid solutions were prepared from concentrated solutions, and standardized against potassium hydrogen phthalate and sodium carbonate, respectively, previously dried in oven at 383.15 K for 2 h. Sodium chloride solutions were prepared weighing the solid previously dried in oven at 383.15 K for 2 h. Calcium and magnesium chlorides solutions were prepared weighing the salts and standardized against EDTA. $SnCl_2$ aqueous solutions were daily prepared weighing the dihydrate salt, adding two equivalents of HCl and bubbling $N_{2(g)}$ into the solution to avoid unwanted acid-base or red-ox processes, respectively; for the same reasons, after having brought to volume, a piece of metallic tin was put into the solution. Sodium poly-α,β-D,L-aspartate (PASP) solutions were prepared diluting a 40% solution purchased from NanoChem Solutions Inc. (A-2C product). The solutions of the ligands (Maltol, Ethylmaltol, Deferiprone, Tranexamic acid, Hexamethaphosphoric acid) were prepared weighing the commercial product from Merck (Italy); their concentration in solutions was determined by alkalimetric measurements.

All solutions were freshly prepared, using grade A glassware and twice-distilled water (ρ ≥ 18 MΩ cm). All chemicals used are listed in Table 1.

2.2. Apparatus and procedure for the potentiometric and voltammetric measurements

The experiments were performed by two operators using two different apparatuses, in order to minimize systematic errors and to check the repeatability of the measurements. For both setups the estimated uncertainty (u) is ± 0.15 mV and ± 0.003 cm^3 for the e.m.f. and titrant volume readings, respectively. The complete description of the apparatuses is reported elsewhere (Cigala et al., 2012b).

All the experimental details are given as Supplementary material. An aliquot of 25 cm^3 was titrated with standard NaOH solutions. The titrand solutions contained the metal cations (Ca^{2+}, Mg^{2+} or Sn^{2+}),