Chemosphere 186 (2017) 535–545

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Sequestration of Aluminium(III) by different natural and synthetic organic and inorganic ligands in aqueous solution

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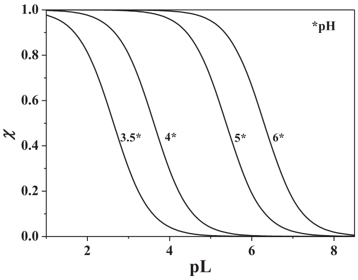
HIGHLIGHTS

- Higher sequestering ability towards Al^{3+} of the organic ligands with respect to the inorganic ones.
- Higher sequestering ability ($pL_{0.5}$) of citrate towards Al^{3+} with respect to the other investigated ligands.
- Quite different speciation models were obtained for the Al^{3+}/Ligand systems.
- The mean contribution of each carboxylic group to the stability of the was estimated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 May 2017
Received in revised form
11 July 2017
Accepted 4 August 2017
Available online 7 August 2017

Handling Editor: Patryk Oleszczuk

Keywords:
Aluminium(III)
Speciation
Inorganic ligands
Low and high molecular weight carboxylic ligands
Sequestration

ABSTRACT

The speciation of Al^{3+} in aqueous solutions containing organic and inorganic ligands important from a biological (citrate (Cit^{3-}), gluconate ($Gluc^{-}$), lactate (Lac^{-}), silicate ($H_2SiO_4^{2-}$), carbonate (CO_3^{2-}), fluoride (F^-)) and industrial (Gantrez®; polymethyl-vinyl-ether-*co*-maleic acids; *GTZ S*95 and *GTZ AN*169) point of view is reported. The stability constants of Al^{3+}/L^{z-} complexes (L^{z-} = ligand with z^- charge) were determined by potentiometry at $T = 298.15$ K and $0.10 \leq I/M \leq 1.00$ in $NaCl_{(aq)}$ (in $NaNO_{3(aq)}$ only for $Al^{3+}/GTZ\ S95$ and $Al^{3+}/Gluc^{-}$ acid systems). For Al^{3+}/Cit^{3-}, Al^{3+}/Lac^{-} and $Al^{3+}/GTZ\ AN169^{4-}$ systems, the investigations were also carried out at $283.15 \leq T/K \leq 318.15$. The dependence of the thermodynamic parameters on ionic strength and temperature was modelled with a Debye-Hückel type equation. Different speciation schemes of Al^{3+}/L^{z-} systems were obtained, including protonated, simple metal-ligand, polynuclear and hydrolytic mixed species. At $I \rightarrow 0$ M and $T = 298.15$ K the stability trend for the $AlL^{(3-z)}$ species is: 14.28 ± 0.02, 13.99 ± 0.03, 10.16 ± 0.03, 3.16 ± 0.08, 2.84 ± 0.10 for *GTZ S*95, *GTZ AN*169, Cit^{3-}, $Gluc^{-}$ and Lac^{-}, respectively. From the investigations at different temperatures, it results that the entropic contribution is the driving force of the reactions. The sequestering ability of the ligands towards Al^{3+} was investigated determining the $pL_{0.5}$ parameter at different experimental conditions, finding the following trend: $Cit^{3-} \gg Gluc^{-} > GTZ\ S95^{4-} > GTZ\ AN169^{4-} > Lac^{-}$ for the organic ligands, and $pL_{0.5}$: $F^- \gg CO_3^{2-} > H_2SiO_4^{2-}$ for the inorganic ones.

1. Introduction

Aluminium is present in the earth's crust for 7.8% of the total mass of the earth and it is a reactive metal difficult to extract from

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http://dx.doi.org/10.1016/j.chemosphere.2017.08.015
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its ore (Al_2O_3) and to refine since it oxidizes very quickly.

From a toxicological point of view, although aluminium is considered a safe element, exposition to high levels can cause severe health problems (Rosseland et al., 1990; Namiesnik and Rabajczyk, 2010).

In the environment, aluminium is susceptible to external agents and undergoes numerous chemical reactions governing its bioavailability and mobility in the ecosystems. As heavy metals, aluminium occurs in the form of free hydrated ions to only a small degree, and a considerable portion is bound to organic substances (acids, amines, sugars, organic acids, humic and fulvic acids, and many others nitrogen or sulfur containing compounds) (Rosseland et al., 1990; Namiesnik and Rabajczyk, 2010). The chemistry of aluminium was widely studied in the past, many papers and book chapters deal with its properties, toxicity and applications (Lewis, 1989; Nicolini et al., 1991; Taylor et al., 1992; Berthon, 1996; Corain et al., 1996; Harris et al., 1997; Williams, 1999; Berthon, 2002; Ščančar and Milačič, 2006; Chadwick and Whelan, 2007; ProjectCureFoundation, 2009). In the last decades, the interest of research towards the effect of aluminium in the presence of organic and inorganic ligands of biological and environmental interest has greatly increased (Cigala et al., 2011, 2013; Bretti et al., 2012; Cardiano et al., 2016, 2017).

The aim of this work is to investigate the speciation and sequestration of aluminium in the presence of some inorganic (carbonate, fluoride, silicate) and organic ligands (citrate, gluconate, lactate). In addition, particular attention was paid to the interaction of aluminium with the two high molecular weight synthetic copolymers of methyl-vinyl-ether and maleic anhydride (Gantrez®, *GTZ*), for their applications in the textiles, paper, adhesive, cosmetic industry (Glicksman, 1963).

Al^{3+}/GTZ systems were investigated in NaCl (*GTZ AN*169) and $NaNO_3$ (*GTZ S*95) aqueous solutions.

Other Al^{3+}/L^{z-} (L^{z-} = citrate, lactate, gluconate, silicate, carbonate) systems were also studied in NaCl or $NaNO_3$ aqueous solutions. Al^{3+}/Cit^{3-}, Al^{3+}/Lac^{-} and $Al^{3+}/GTZ\ AN169$ investigations were also carried out at different temperatures: $283.15 \le T/K \le 318.15$.

The dependence of the formation constants on ionic strength and temperature was modelled using of a modified Debye-Hückel equation, and the sequestering ability of the ligands towards Al^{3+} was quantified by means of the $pL_{0.5}$ parameter (Berto et al., 2012b; Crea et al., 2014).

The results here obtained were compared with the literature (Sawyer, 1964; Wiese and Vieth, 1975; Öhman and Forsling, 1981; Öhman, 1983; Öhman and Sjoberg, 1983; Gregor and Powell, 1986; Hedlund et al., 1987; Marklund and Ohman, 1990; Kiss et al., 1994; Lakatos et al., 2001; Rubini et al., 2002; Martell et al., 2004; Lakatos et al., 2008).

2. Experimental section

2.1. Chemicals

Citric acid, D-gluconic acid sodium salt, (+)-lactic acid (Fluka products) were used without further purification and their purity, checked alkalimetrically, was found to be >99%. As concerns Gantrez® ligands (purchased from Ashland), two polymers with different molecular weights (MW) were studied, namely *GTZ AN*169 and *GTZ S*95, with MW = 2000 and 220 kDa, respectively. Gantrez® *AN* has an anhydride group that hydrolyzes forming Gantrez® *S* with two free carboxylic groups (Vandamme et al., 2011), according to the reaction reported in Fig. 1.

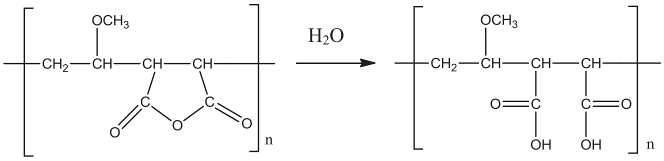

Fig. 1. Hydrolysis reaction of Gantrez® *AN* (anhydride form) to Gantrez® *S* (carboxylic acid form).

A standard solution of silicon (TraceSELECT®, Fluka) in 2% NaOH was used as source of silicate. Carbonate solutions were prepared by weighing the sodium salt previously dried in an oven at $T = 383.15$ K for at least 2 h. Hydrochloric acid and sodium hydroxide solutions were prepared by diluting concentrated ampoules (Riedel-deHäen) 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. Aluminium solutions were prepared by weighing the nitrate nonahydrate salt (Fluka), without further purification. Its purity was checked by titrations with EDTA standard solutions and was always ≥98%. NaCl and $NaNO_3$ aqueous solutions were prepared by weighing the pure salt (Fluka), previously dried in an oven at $T = 383.15$ K for at least 2 h. All the solutions were prepared with analytical grade water (R = 18 MΩ cm) using grade A glassware.

For measurements of the Al^{3+}/CO_3^{2-} system, analytical grade water was previously boiled to remove dissolved CO_2.

2.2. Potentiometric apparatus and procedure

Potentiometric measurements were carried out using a Metrohm model 809 Titrando, a potentiometer connected to an automatic burette, and equipped with a combined glass electrode (Ross type 8102, from Thermo-Orion). The apparatus was linked to a PC and automatic titrations were performed using the Metrohm TiAMO 2.5 software to control titrant delivery, data acquisition and to check for e.m.f. stability. Estimated accuracy was ±0.15 mV and ±0.003 mL for e.m.f. and titrant volume readings, respectively.

Potentiometric titrations were carried out at different temperatures ($283.15 \le T/K \le 318.15$) and ionic strengths ($0.10 \le I/M \le 1.0$) in NaCl or $NaNO_3$ ionic medium, in thermostatted cells under magnetic stirring and bubbling purified presaturated N_2 through the solution to exclude O_2 and CO_2 inside. Independent titrations of strong acid with standard base solutions were performed, at the same experimental conditions (ionic medium, ionic strength (I) and temperature (T)) of the investigated systems, to determine the value of standard electrode potential (E^0), the acidic junction potential ($E_j = j_a[H^+]$), and the ionic product of water (K_w). The pH scale used was the free scale ($pH \equiv -\log[H^+]$), where $[H^+]$ is the free proton concentration. For each titration, 80–100 data points were collected, and the equilibrium state during titrations was checked by adopting the usual precautions (Braibanti et al., 1987), such as to check the time necessary to reach equilibrium and performing back titrations.

2.3. Calculations

The non-linear least squares computer program ESAB2M (De Stefano et al., 1987) was used for the refinement of all the parameters of the acid–base titration such as E^0, pK_w, liquid junction potential coefficient j_a and analytical concentration of reagents. The BSTAC, STACO (De Stefano et al., 1996) and HYPERQUAD 2008 (Gans et al., 1996) were used for the elaboration of the experimental data. The protonation constants of the ligands were calculated by using all these software, whilst complex formation constants by means of BSTAC or STACO. The LIANA (De Stefano et al., 1997) computer