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Thermodynamic parameters for the protonation and the interaction of arsenate with Mg^{2+}, Ca^{2+} and Sr^{2+}: Application to natural waters

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HIGHLIGHTS

- Thermodynamic parameters for AsO_4^{3-}-H^+, Mg^{2+}, Ca^{2+}, Sr^{2+} interactions are reported.
- For the first time, both ionic strength and temperature are taken into account.
- Speciation profiles of arsenate in some natural waters are simulated.

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ABSTRACT

Thermodynamic parameters for the protonation of AsO_4^{3-} and for the interaction with Mg^{2+}, Ca^{2+} and Sr^{2+} were reported, comprehensive also of their dependence on ionic strength, considering the $0.1 \leq I \leq 1$ M range and using NaCl as background salt. The same speciation models were obtained for Mg^{2+}, Ca^{2+} and Sr^{2+} systems, with the formation of three different species: ML, MLH and MLH_2 ($L = AsO_4^{3-}$). Mono- and di-protonated species were very weak, with formation constant values (log K) ranging from 1.45 to 3.23. In order to have a complete picture of thermodynamic properties of the systems under study and to fill the shortage of thermodynamic data on arsenate complex systems, the ligand protonation and metal complex enthalpies were also determined by calorimetric titrations, at t = 25 °C and in NaCl at $I = 0.7$ M (for H^+-AsO_4^{3-} species also at $I = 0.1$ M). On the light of the proposed speciation models, examples of As(V) distribution in some natural waters are reported.

1. Introduction

Arsenic is an ubiquitous element present in trace amounts in all living organisms and environmental compartments (e.g., groundwaters, surface waters, soils and stream sediments, atmosphere) as a result of both natural processes and anthropogenic pollution (Cullen and Reimer, 1989; Frenkeberg, 2002; Mandal and Suzuki, 2002; Nordstrom, 2002; Bissen and Frimmel, 2003; Merian et al., 2004; Prohask and Stingeder, 2005; Sharma and Sohn, 2009). The natural sources are the volcanic activity and release processes from the minerals. The anthropogenic pollution mainly comes from: (i) the widespread use of As compounds as pesticides in agriculture and for wood preservation, (ii) the disposal of As-bearing wastes from mining and ore processing metallurgy; (iii) other uses such as in electronic or metallurgical industry, but also in medicine (Cullen and Reimer, 1989; Frenkeberg, 2002; Mandal and Suzuki, 2002; Merian et al., 2004). In fact, since the 1900's, As derivatives have been used as therapeutic agents for the treatment of syphilis, psoriasis and rheumatosis. At present, arsenic trioxide is used to treat several tumors (Munshi, 2001; Anderson et al., 2002; Kwong, 2004; Dangleben et al., 2013).

It should be pointed out that the concentration of arsenic present in the earth's crust is extremely variable depending on the type of rocks present, showing values between 0.1 ppm and several hundred ppm making some high-risk areas (Ritchie, 1961; Nordstrom, 2002; Bissen and Frimmel, 2003; Merian et al., 2004; Ng, 2005; Raposo et al., 2006). This, probably, determines the variations of the concentration of arsenic recovered in the various types of water: in sea water, dissolved arsenic, essentially as arsenate, is present in concentrations ranging between 1.5 and 1.7 $\mu g\ L^{-1}$ (Merian et al., 2004; Ng, 2005), in fresh waters (lakes, rivers, creeks, streams, circulating solutions in soils) it has a concentration extremely variable and of less than 1 $mg\ L^{-1}$ (Merian

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et al., 2004); in thermal waters, concentrations up to 8.5 mg L^{-1} were observed (Ritchie, 1961; Merian et al., 2004). Generally, surface waters have lower concentrations of arsenic than the groundwaters, first since the latter interact more with the rocks, but probably also for some other factors such temperature or/and pressure. Strictly related to its concentration are the effects of the arsenic exposure that can be many and with different entities. They range from vomiting and diarrhea to cardiovascular, respiratory, gastrointestinal and neurological problems, as well as cancer.

Arsenic is perhaps the only one, among the metals that form oxyanions, to be movable in the characteristic pH of groundwater ($6.5 \leq pH \leq 8.5$) in both oxidizing and reducing conditions (Smadley and Kinninburgh, 2002). In natural waters arsenic is found mainly in inorganic forms, as As(III) and As(V).

Arsenic contamination is one of the major environmental problems that affects the quality of water and soil. Accordingly, the sorption of As aqueous species by mineral surfaces, such as clays, hydrous oxides and metal oxides of Al, Fe and Mn is the primary topic of the geochemical research (Stumm and Morgan, 1995; Dzomback and Morel, 1990). Conversely, the aqueous complexes between arsenate and arsenite anions and inorganic cations are neglected in the literature (Marini and Accornero, 2007). However, an accurate knowledge of the interactions between dissolved As species and mineral surfaces in aquatic and soil systems cannot be possible without As speciation in the aqueous phase (Sverjensky and Fukushi, 2006).

Unfortunately, not many useful thermodynamic data have been reported on reactions involving As compared to other major solutes and trace elements (May and Murray, 2001; Pettit and Powell, 2001; Martell et al., 2004). In addition, it must be considered that most authors describe the speciation of dissolved As in terms only of acid-base equilibria (i.e. the formation of differently protonated species of arsenate or arsenite, varying pH or the redox conditions) without considering the complexation reactions involving arsenate and arsenite anions and inorganic cations present in natural waters. The knowledge of the thermodynamic parameters of protonation or complex formation in solution is indispensable for a correct and complete speciation study.

The first data on arsenic complexes with cations naturally present in sea water date back to 1956 (May and Murray, 2001; Pettit and Powell, 2001; Martell et al., 2004), but the values of the complex formation constants are often in contradiction with each other. In a recent review, Nordstrom et al. (Nordstrom and Majzlan, 2014). reported a critical examination of As thermodynamic data, in some cases highlighting the discrepancies or the insufficient internal consistency of the data and, mostly, the lack of data.

The aim of this paper is to contribute to the extension of the thermodynamic database on arsenic(V) in order to build a speciation model useful to predict arsenic behavior in real systems, such as natural waters, characterized by very variable composition, temperature, ionic strength and pH (Stumm and Morgan, 1995; Grenthe and Puigdomenech, 1997; Lumsdon and Evans, 2002; VanBriesen et al., 2010).

In this light, a potentiometric and calorimetric study on AsO_4^{3-} -H^+, -Mg^{2+}, -Ca^{2+} and -Sr^{2+} systems is performed in aqueous solution, in NaCl at $0.1 \leq I \leq 1$ M and at t = 25 °C. Examples of applications of thermodynamic speciation models in real systems are reported, taking into account Ca^{2+}, Mg^{2+} and Sr^{2+} real concentrations in two different natural water types.

To our knowledge, it is the first time that both ionic strength and temperature are taken into account for the Ca^{2+}, Mg^{2+} and Sr^{2+} -AsO_4^{3-} interactions, while very interesting studies are reported on arsenate protonation and on Fe(II)-Fe(III)-As(V) systems (Zhu et al., 2016, 2017).

2. Materials and methods

2.1. Reagents

The arsenate solutions were prepared by weighing sodium arsenate dibasic heptahydrate, $Na_2HAsO_4 \cdot 7H_2O$ (Sigma-Aldrich, ≥98%). Magnesium chloride hexahydrate, $MgCl_2 \cdot 6H_2O$ (Fluka, ≥99.0%), calcium chloride dehydrate, $CaCl_2 \cdot 2H_2O$ (Fluka, ≥99%) and strontium chloride hexahydrate, $SrCl_2 \cdot 6H_2O$ (Merck, ≥99.0%) were all prepared by weighing the respective solids and titrating their solutions with a standard EDTA (ethylenediaminotetraacetic acid) solution. Sodium hydroxide solutions and hydrochloric acid, prepared from concentrated Fluka ampoules, were standardised using potassium biphthalate and sodium carbonate, respectively, which had previously been dried in an oven at least for an hour at 110 °C. NaOH was preserved by CO_2 through soda lime traps and stored in dark bottles. Sodium chloride solutions were prepared by weighing the pure salt (Fluka, puriss.), pre-dried in an oven at 110 °C. For the preparation of every solution bidistilled water (conductivity < 0.1 μS cm^{-1}) and grade A glassware were employed.

2.2. Potentiometric equipment and procedure

Potentiometric measurements were performed by an automatic titration system consisting of an automatic dispenser MetrohmDosino 800, a Metrohm model 809 Titrando potentiometer, provided with an Orion-Ross 8102 combined glass electrode. The estimated error of the potentiometric system was ±0.15 mV for e.m.f. and ±0.002 mL for titrant volume readings. This described system was connected to a PC and the titrations were carried out using the Metrohm TiAMO 2.2 software to control e.m.f. stability, titrant delivery and data acquisition. For the protonation constants determination, a volume of 25 mL of the solution containing arsenate ligand ($1 \leq C_L/mM \leq 3$), HCl ($5 \leq C_{HCl}/mM \leq 10$) and NaCl as supporting electrolyte at different ionic strength ($0.1 \leq I/M \leq 1$) was titrated with standard NaOH in the pH = 2–11 range. For the metal-arsenate species determination, a volume of 25 mL of the solution containing arsenate ligand ($1 \leq C_L/mM \leq 10$), HCl ($5 \leq C_{HCl}/mM \leq 10$), and a metal cation such as Ca^{2+} either Mg^{2+} either Sr^{2+} ($1 \leq C_M/mM \leq 5$) together with the supporting electrolyte (NaCl) at different ionic strengths ($0.1 \leq I/M \leq 1$) was titrated with standard NaOH in the pH = 2–10 range. All the measurements were performed into thermostated glass jacket cells at t = 25 ± 0.1 °C, bubbling pure N_2 through the solutions to avoid O_2 and CO_2 inside and under magnetic stirring. For each measurement, independent titrations of HCl with standard NaOH were carried out to determine the standard electrode potential, E^0, and the pK_w values in the same experimental conditions of ionic strength and temperature.

2.3. Calorimetric equipment and procedure

Calorimetric titrations were performed at 25.000 ± 0.001 °C, using a CSC (Calorimetry Science Corporation) 4300 Isoperibol Titration calorimeter. A 2.5 mL capacity Hamilton syringe, model 1002TLL, was used for the titrant delivery. The calorimetric data were acquired by a computer program. The system accuracy was checked titrating a tris-(hydroxymethyl)amino-methane buffer solution with HCl (Sgarlata et al., 2013). The heat of dilution was measured before each experiment. The precision of this calorimetric system was Q±0.015 J and v±0.001 mL.

For the ligand protonation enthalpies determination, 25 mL of the solution containing arsenate sodium salt (Na_2HAsO_4) and NaCl at I = 0.1, 0.7 M was titrated with HCl standard solution (0.5 M). Calorimetric titrations were performed in the range $2.2 \leq pH \leq 11.3$.