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Estimating the stabilities of actinide aqueous species. Influence of sulfoxy-anions on uranium(IV) geochemistry and discussion of Pa(V) first hydrolysis☆

Pierre Vitorge [a,b,]*, Vannapha Phrommavanh [c], Bertrand Siboulet [d], Dominique You [a], Thomas Vercouter [a], Michael Descostes [b,c], Colin J. Marsden [e], Catherine Beaucaire [c], Jean-Paul Gaudet [f]

[a] *Laboratoire de spéciation des radionucléides et des molécules (LSRM), CEA Saclay, DEN/DANS/DPC/SECR, 91191 Gif-sur-Yvette cedex, France*
[b] *UMR 8587, CEA Saclay, DEN/DANS/DPC/SECR, 91191 Gif-sur-Yvette cedex, France*
[c] *Laboratoire de mesures et modélisation de la migration des radionucléides (L3MR), CEA Saclay, DEN/DANS/DPC/SECR, 91191 Gif-sur-Yvette cedex, France*
[d] *CEA Marcoule, DEN/DRCP/SCPS, 30207 Bagnols-sur-Cèze cedex, France*
[e] *Laboratoire de physique quantique, CNRS−UMR 5626, Université Paul-Sabatier, 118, route de Narbonne, 31062 Toulouse cedex 4, France*
[f] *Laboratoire d'étude des transferts en hydrologie et environnement (LTHE), UMR 5564, CNRS/INPG/IRD/UJF, BP 53, 38041 Grenoble cedex 9, France*

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Abstract

Qualitative chemical information is used as a guideline for correlations between equilibrium constants or between equilibrium constants and atomic charges (deduced from quantum mechanics calculations). Pa(V) and Nb(V) hydrolysis constants are also recalculated from experimental data. $\log K_1^\circ(\mathrm{An^{IV}/RO_2^{2-}}) = 6.5_9 \pm 0.5_5$ $(\mathrm{S_2O_3^{2-}})$, $10.0_6 \pm 0.8_8$ $(\mathrm{SO_3^{2-}})$, $11.9_7 \pm 1.0_7$ $(\mathrm{CO_3^{2-}})$, and $10.0_5 \pm 0.8_8$ $(\mathrm{HPO_4^{2-}})$ are estimated based on the trend of affinity for An cations in the series $\mathrm{CO_3^{2-}} > \mathrm{HPO_4^{2-}} \approx \mathrm{SO_3^{2-}} > \mathrm{SO_4^{2-}} \approx \mathrm{S_2O_3^{2-}}$. These ideas and values are used to discuss U(IV) chemistry in S-containing ground-waters. ***To cite this article: P. Vitorge et al., C. R. Chimie 10 (2007).***

Résumé

Des connaissances qualitatives ont été concrétisées sous la forme de corrélations empiriques entre constantes d'équilibres, voire avec les charges atomiques (issues de calculs quantiques) dans la série $\mathrm{CO_3^{2-}} > \mathrm{HPO_4^{2-}} \approx \mathrm{SO_3^{2-}} > \mathrm{SO_4^{2-}} \approx \mathrm{S_2O_3^{2-}}$, pour, par exemple, estimer $\log K_1^\circ(\mathrm{An^{IV}/RO_2^{2-}}) = 6.5_9 \pm 0.5_5$ $(\mathrm{S_2O_3^{2-}})$, $10.0_6 \pm 0.8_8$ $(\mathrm{SO_3^{2-}})$, $11.9_7 \pm 1.0_7$ $(\mathrm{CO_3^{2-}})$, et $10.0_5 \pm 0.8_8$ $(\mathrm{HPO_4^{2-}})$.

☆ Partially presented at the Migration 05 conference [1], and part of the Ph.D. thesis of V. Phrommavanh.

* Corresponding author.
E-mail address: pierre.vitorge@cea.fr (P. Vitorge).

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Ces valeurs sont utilisées pour prévoir l'influence éventuelle d'anions soufrés sur la chimie de U(IV) dans des eaux souterraines. ***Pour citer cet article : P. Vitorge et al., C. R. Chimie 10 (2007).***

Keywords: Actinides; Hydrolysis; Sulphate; Sulfite; Thiosulphate; Carbonate; Groundwaters

Mots-clés : Actinides ; Hydrolyse ; Sulfate ; Sulfite ; Thiosulfate ; Carbonate ; Eaux souterraines

1. Introduction

The geochemical behaviour of actinides have been extensively studied for understanding uranium and thorium ore deposits, and more recently for assessing the environmental impact of the possible disposal of wastes that contain Pa, Np, Pu, Am or Cm. Starting with uranium [1], the Thermochemical Data Base project of the Nuclear Energy Agency (NEA-TDB) organised the reviewing of published experimental data relevant for modelling aqueous chemistries and solubilities of the most important radionuclides. The results of the NEA-TDB project are now well accepted as a reference critical review, essentially for aqueous chemistry and solubility at room temperature, but these reviews proposed data only when convincing experimental validations were published. There is therefore a gap between this restricted set of quantitative validated thermochemical data and qualitative chemical knowledge.

However, besides selected numerical values, the NEA-TDB reviews also provide qualitative information [2,3], which we used together with analogies for estimating the hydrolysis constants and standard potentials [4] needed for drawing Pourbaix' diagrams of actinides [5]. The present paper aims at testing such rough estimates for complexation.

Rules of thumb are currently used by chemists for checking the possible formation of hypothetical chemical species in specific chemical conditions, when these chemical species are not in databases. This might typically be the case for the environmental aqueous chemistry of An(IV), the actinide elements at the +4 oxidation state (An = Th, U, Np and Pu) in the presence of S-containing inorganic ligands; for this reason it is also an aim of the present paper to estimate the stabilities of An(IV) complexes with sulfoxy-anions.

For storing radioactive wastes, several projects are looking for geological sites that are well isolated from surface waters. These often correspond to anoxic conditions, where U, Np and Pu are expected to be stable in the +4 oxidation state [2,4]. Interestingly, chemical analogues are Ce(IV) and Th, and probably Zr and Hf. Selected NEA-TDB equilibrium constants and redox potentials [2] are adequate for reliable modelling of uranium chemistry in most equilibrated groundwaters. Uranium is predicted to be stable in anoxic waters in the form of the $U(OH)_4(aq)$ aqueous species in equilibrium with uraninite, $UO_2(s)$, a compound of low solubility [2,5,6]. Similar behaviour is expected for Np and Pu, even though Pu^{3+} might also be stable [4–7].

In natural under-ground-waters CO_3^{2-}, the carbonate anion is often the dominating ligand among the inorganic ligands (for actinide cations). However, carbonate complexes are predicted to be of little important for An(IV) [2,4,7]. Nevertheless, many $An(CO_3)_i(OH)_j^{4-2i-j}$ complexes have been proposed, but no reliable values could be validated for most of the corresponding formation constants [2,4], for which maximum possible values have been estimated from experimental observations, that also confirmed the similar behaviour of Th, U(IV), Np(IV) and Pu(IV) in carbonate/bicarbonate aqueous solutions [4,5,8]. Values have recently been proposed for the formation constants of several $Th(CO_3)_i(OH)_j^{4-2i-j}$ complexes in an attempt to interpret a solubility study of $ThO_2(s)$ [8,9], but the $Th(CO_3)_4^{4-}$ species were not included in the interpretation, even though we shall see it should not be completely negligible according to the NEA-TDB data [4]. For probing such competition between the HO^- and CO_3^{2-} ligands, the relative stabilities of the corresponding 1:1 complexes of An^{4+} will be compared. In this framework, the stability of $AnCO_3^{2+}$ will be estimated: its existence has never been demonstrated, since it is always hidden by hydrolysed species. This over-stabilisation of hydrolysis is specific to the +4 oxidation state: the 1:1 carbonate complexes are well known, and their stabilities were well established for An(III), An(V) and An(VI) (it is not known for Pa(V), which is known to have a very different aqueous chemical behaviour from the other An(V)).

Several other inorganic hard anions are quite reactive toward actinide cations, specially those of high charge (PO_4^{3-}), of small size (F^-), or polydentade (HPO_4^{2-}): depending on their content in groundwaters they might form complexes with actinide cations. For example, it