



Behaviour of complexes of *f*-elements in the environment – An experimental and theoretical analysis



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ABSTRACT

The paper provides a comprehensive study of lanthanide and actinide complexes to a matter of key area in the field of the chemistry, *i.e.* environmental analytical chemistry. The content has involved: (i) solution and sorption behaviour of lanthanides (Ln^{n+} , $\text{Ln} = \text{Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb}$ and Lu) onto $\text{Y}(\text{O})\text{O}(\text{H})$ minerals ($\text{Y} = \text{Fe, Mn}$ or Si); (ii) ligand exchange processes with participation of inorganic OH^- , F^- , Cl^- , Br^- , SO_4^{2-} , SO_3^{2-} , IO_3^- , NO_3^- , CO_3^{2-} and/or HCO_3^- ligands as well as mixed ligand complexes, including solvent molecules such as $\{[\text{LnOR}]^{2+}\}$, $\{[\text{Ln}(\text{OR})_2]^{+}\}$ ($\text{R} = \text{CH}_3\text{OH, CH}_3\text{CH}_2\text{CH}_2\text{OH}$) and $\{[\text{Ln}(\text{CH}_3\text{CN})_x(\text{H}_2\text{O})_z]^{3+}\}$ ($x = 6-8, z = 0-4$); (iii) the actinide speciation has involved different oxidation states (+4)–(+6) and ions $\{[\text{UOH}]^{3+}\}$, $\{[\text{UX}]^{3+}\}$ ($\text{X} = \text{F}$ or Cl), $\{[\text{UF}_x]^{y+/}\}$ ($x = 2-6, y = 0-2$), $\{[\text{U}(\text{CO}_3)_x]^{y-}\}$ ($x = 4$ or $5, y = 4$ or 6), $\{[\text{U}(\text{SO}_4)]^{2+}\}$, $\{[\text{U}(\text{NO}_3)]^{3+}\}$, $\{[\text{U}(\text{NO}_3)_2]^{2+}\}$, $\{[\text{UO}_2(\text{CO}_3)_3]^{5-}\}$, $\{[\text{UO}_2]_x(\text{OH})_z]^{y+/}\}$ ($x = 1-4, y = 1$ or $2, z = 1-7$), $\{[\text{UO}_2\text{F}_x]^{y+/}\}$ ($x = 1-4, y = 1$ or 2), $\{[\text{UO}_2(\text{CO}_3)_x]^{y-}\}$ ($x = 2, \text{ or } 3, y = 2, \text{ or } 4$), $\{[\text{UO}_2]_2(\text{CO}_3)(\text{OH})_3]^{+}\}$, $\{[\text{UO}_2]_3\text{O}(\text{OH})_2(\text{HCO}_3)]^{+}\}$, $\{[\text{UO}_2]_{11}(\text{CO}_3)_6(\text{OH})_{12}]^{2-}\}$, $\{[\text{UO}_2(\text{SO}_4)_x]^{y-}\}$, ($x = 2$ or $3, y = 2$ or 4), $\{[\text{UO}_2\text{SiO}(\text{OH})_3]^{+}\}$, $\{[\text{AnC}_x]^{y+/}\}$ ($x, y = 1$ and 2), $\{[\text{CANH}]^{+/-}\}$, $\{[\text{C}_x\text{An}_y]^{0}\}$ ($x, y = 2$ and 3), $\{[\text{AnH}_x]^{y+/}\}$ ($x = 1-3, y = 0-5$), $\{[\text{AnX}_n]^{m+/}\}$ ($n = 1-6, m = 1-4, \text{X} = \text{F}^-, \text{Br}^-, \text{I}^-$), $\{[\text{AnO}_x\text{F}_z]^{y+/}\}$ ($x, z = 1$ or $2, y = 0, 1$ and 2), $\{[\text{AnN}_x]^{y+/}\}$ ($x = 1$ and 2), $\{[\text{An}_x\text{O}_z(\text{OH})_n]^{y+/}\}$ ($x = 1-3, z = 1-4, y = 0, 1$ or $2, n = 0$ or 1) and An^{n+} ($n = 0-6$) at $\text{An} = \text{Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No}$ and Lr , respectively. Correlation analysis between thermodynamic parameters, accounting for different surface interactions of adsorbed species and experimental mass spectrometric data, including liquid, semi-liquid and solid-state measurements in a large set of experimental conditions such as $\text{pH} = 2-13$, low and intermediate ionic strength, solvent type, $\epsilon = 0-78.0$, variety of solvent proton accepting and donating numbers and $T = 25-400$ °C has carried out.

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1. Introduction

Environmental analysis of actinides and lanthanides has been described as the most important task in programmes for assessment of the risk for the human and the nature from exposure of fission products, due to their both radiological and chemical toxicity [1]. The origin of such as wastes has been addressed to nuclear processing plants, and various processes involved in the nuclear fuel cycle; weapons' conversion; laboratory experiments; as well as medicinal wastes. There have random sources of contamination, related the nuclear reactor accidents; uncontrollable use of radionuclides for terrorism and; illicit traffic as well [1p]. Towards Lns, their accumulation in the human skeleton has been reported, but the potential human health risk is still not well understood [1i]. The distribution and deposition of Lns and Ans species have been termed as migration processes, which is mainly

Acronyms and abbreviations: Ans, actinides; APCL, atmospheric pressure chemical ionization (mass spectrometric method); BLYP, Becke–Lee–Yang–Parr (functional); B3LYP, Becke, three-parameter, Lee–Yang–Parr (functional); CAS, complete active space; DFT, density functional theory; DHB, 2,5-dihydroxybenzoic acid; ESI, electrospray ionization (mass spectrometry); FAB, fast atom bombardment (mass spectrometry); GP, gas-phase; HF, Hartree–Fock; HPLC, high performance liquid chromatography; JT, Jahn–Teller (effect); Lns, lanthanides; MALDI, matrix assisted laser desorption/ionization (mass spectrometry); MP2, Møller–Plesset perturbation theory; MS, mass spectrometry; M06–2X, meta-hybrid functional; NEA–TDB, Nuclear Energy Agency Thermochemical Database; NECs, Natural electron configurations; NBO, natural bond orbital; PCM, polarizable continuum model; PW91, Perdew–Wang generalized-gradient (quantum chemical method); RI, Relative intensity; SDD, Stuttgart–Dresden pseudopotential; TDDFT, time-dependent density functional theory; UV, Ultraviolet (region of the electromagnetic spectrum).

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associated by sorption process *onto* minerals [1]. Accounting for the fact however that a major competitive coordination reactions with humics occur as well. In aquatic geochemical systems, these processes are conducted *onto* colloids, thus defining the chemical behaviour of complexes of *f*-elements in the boundaries of liquid/solid (water/rock (soil)) heterogeneous phase [1w]. In general, sorption/desorption reactions are those governing the diffusion, bioavailability, migration, and the mobility of the radionuclides in the nature. As far as the surface interactions of chemical forms of *f*-elements have concerned both migration of radioactive pollutants and storage disposal strategies of nuclear waste, the understanding of mechanistic aspects of surface interactions *onto* minerals and mechanisms governing ligand exchange reactions have great importance. The accurate prediction of physical properties and thermodynamic of such as complex heterogeneous systems, depends on an accurate modelling and description of surface interaction modes and structures of corresponding Lns and Ans species [2]. Despite decades research efforts in understanding of environmental behaviour of radionuclides, and in general the migration of heavy metal ions, the mechanistic aspects of sorption/desorption processes *onto* minerals are still not well understood. The main reason for this, rather lack of comprehensive knowledge, has been associated with the complex nature of the *f*-elements, causing for a diversity of chemical forms and oxidation states which can be stabilized under environmental conditions. The determination of an accurate model of complex environmental heterogeneous colloids of Lns and Ans complexes under different environmental physical; chemical and biological factors still represents a significant challenge in front environmental chemical and geochemical researches. Moreover, many crucial methodological developments of the quantum chemistry enabling an accurate prediction of thermodynamic parameters of complex systems of *f*-elements in condense phase have been more recently reported [1p,2,3]. Talking about experimental methods allowing to study the coordination ability of *f*-elements, the methods of mass spectrometry, particularly highlighting the soft-ionization conditions enable to describe highly accurate the coordination behaviour of organic and inorganic ligands. The structural models of Ans in solution are mainly associated with mono-, bi- and/or polydentate coordination of $\{[OXO]^{y+}\}$ groups, forming chelate rings at the equatorial plane of $O^{2-} \equiv U^{VI} \equiv O^{2-}$ ion. Such as type ions have been regarded as among the most stable formulations of Ans, which are significantly demarcated comparing with the most stable chemical structure of Lns complexes. The *trans-oxo* (or so-called "yl") O-centre in uranyl type ions has highly inert character and is difficult of involvement in ligand exchange reactions in solution. As can be expected from this, studies devoted to coordination chemistry of Ans in solutions are associated with thermodynamics and ligand-exchange processes of the inner coordination sphere disposed within the framework of the equatorial plane of the actinyl ion. The corresponding correlation analysis between theoretical models and experimental mass spectrometric data in solution can provide meaningful information about the chemistry of the *f*-elements and those molecular factors, contributing strongly to their stability. It should, of course be mentioned here that the uranium in $\{[UO_2]^{2+}\}$ ion is in its oxidation state +6, which is regarded as most broadly distributed oxidation state. In fact the behaviour of U^V in $\{[UO_2]^+\}$ can be studied in gas-phase, employing MS methods, however. Despite that for Np and Pu the oxidation state +5 in solution has been denoted as the chief soluble form of these actinides [2]. In addition, to the fact that trivalent Lns and Ans like $^{152+154}Eu^{III}$, $^{243}Am^{III}$ and $^{244}Cm^{III}$ is a form of these *f*-elements stable in the nature [1w,x]. So that there have been devoted numerous studies dealing with their sorption/resorption reactions with humics and minerals [1w]. By contrast to condense,

where, +5 oxidation state is determined as highly unstable, and the corresponding complexes can participate in disproportional reactions (stabilization of An^{IV} and $\{[AnO_2]^{2+}\}$ ions), largest number $\{[AnO_2]^{2+}\}$ ions are of great interest for quality control and assessment of the risk for the human health associated with disposal of radioactive wastes [1–3]. Because of they are characterized with a high solubility in water, mobility under environmental conditions and biological availability. By contrast to gas-phase, where depending on experimental conditions; ionization methods; temperature and more, there is enable to observe experimental variety of competitive reactions, and fragmentation products, encompassing different oxidation states. Given that, the correlation between experimental mass spectrometric data and theoretical quantum chemical modelling provides direct relationship between the thermodynamic and kinetic parameters as function of corresponding molecular structural and environmental factors, determining the chemical stability of the corresponding coordination compounds [4]. In light of these considerations, we should point out that objects studied in this paper are restricted to those complexes of Ans and Lns involved in the technology of the nuclear energy as well as forms having significant stability under environmental conditions. So, our study aims to provide a comprehensive analysis of molecular factors governing the stability of Lns and Ans complexes in the environment. It also aims to illustrate the great applicability of the theoretical quantum chemical and experimental MS methods, in context of a wide interdisciplinary having both fundamental and applied scientific impacts. Thus, these results reported would be of interest for the fields of: (i) analytical radiochemistry and assessment of the risk for the human health from radionuclide contamination; (ii) coordination chemistry of An *f*-elements, because of, we present a study on the effect of intra-molecular and environmental factors on electronic *f*-states in complexes of Ans within the frame of the whole series of elements; (iii) nuclear forensic analysis, since soft-ionization MS methods which primarily provided significantly important qualitative, quantitative and structural information for the diversity of analytical formulations of Ans is described; and (iv) nuclear technologies and related branches of nuclear industry and energy utilizing developments and improvements of the processes, which generally aimed to increase their effectiveness and capacity. In this respect, many other examples of chemical forms of Ans and Lns can be chosen for theoretical modelling of aquatic and sorbed systems, but these ones have provided a representativeness towards real environmental problems for the radionuclide speciation. The common theoretical modelling and parallel analysis of actinide and lanthanide complexes discussed, but involving all Lns and Ans elements aim to illustrate the great sensitivity of the theoretical quantum chemical methods, predicting thermodynamic parameters of interacting species strongly demarcating both the structural factors such as, for example, geometry of the chromophore, and the coordination mode as well as the oxidation state of the corresponding *f*-element. In this study we have described sorption phenomena of mentioned above species *onto* minerals and as far as these processes are governed by electrostatic forces and specific surface interactions the experimental factors such as pH, T, solvent polarity, solvent donor, ionic strength and acceptor ability have main contribution to the behaviour of the complexes of *f*-elements in solution and *onto* solid mineral surfaces. As natural inorganic adsorbents there are regarded clay (silicates), carbonates and hydroxides of Al, Fe, Mn and Si, respectively [1]. Like Fe-containing mineral goethite (α -Fe(O)OH), Mn-oxyhydroxides (groutite, Mn(O)OH) are common ubiquitous surfaces in nature with strong affinity to adsorb both Lns and Ans. Particularly, the naturally occurring MnO₂ has been described as a controlling fractionation of the rare earth elements and their modifiability in water [1j]. Similar

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