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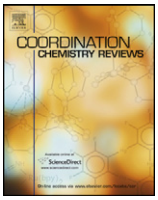

Review

Recent advances in computational modeling and simulations on the An(III)/Ln(III) separation process

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ABSTRACT

The selective extraction of minor actinides(III) from the lanthanides(III) is a key step for spent fuel reprocessing. Theoretical calculations of geometries, electronic structures, coordination complexion, and thermodynamic properties of the actinides are essential for understanding the separation mechanisms and relevant reactions. This article presents a critical review of theoretical studies on actinide systems involved in the An(III)/Ln(III) separation process. We summarize various theoretical methods for electronic and molecular scale modeling and simulations of actinide coordination systems. The complexing mechanisms between metal cations and organic ligands and the strategies for the design of novel ligands for separation are discussed as well.

1. Introduction

With the development of nuclear energy, the processing of spent nuclear fuels has attracted more and more research interest due to the strong radioactive toxicity and extra-long lifetime of minor actinides and some fission products in nuclear wastes. The wet reprocessing technology is dominant among the present reprocessing technologies because of its advantages such as being easy to achieve continuous operation and fast mass transfer. One of the major challenges in the wet processing of spent fuel is the selective extraction of An(III) (e.g. Am(III), Cm(III)) from Ln(III) (e.g. Nd(III), Eu(III)). These actinide and lanthanide elements show similar chemical properties in aqueous solutions, e.g. oxidation state, ionic radii, and forms of hydrated species, leading to the big difficulty in the separation process [1,2]. Therefore, designing efficient extractants at the molecular level is of great importance for the separation of An(III) from Ln(III).

Many soft Lewis bases containing nitrogen and sulfur donor atoms have been developed in experiments to meet the requirements for the An(III)/Ln(III) separation. The representative

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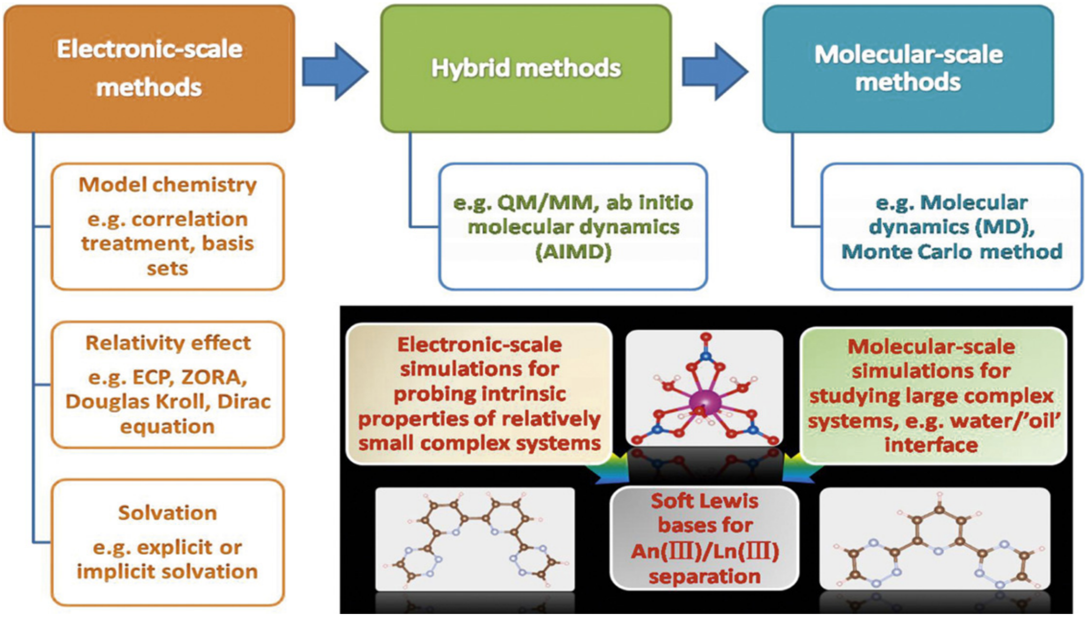
N-donor extractants include 2,6-di(1,2,4-triazin-3-yl)pyridine (BTP) [3–8] and 6,6′-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridines (BTBPs) [9–16] as well as their derivatives. The BTP family has a high Am(III)/Eu(III) separation factor ($SF_{Am/Eu} = 130$) in nitric acid systems [17,18]. One member of the BTBP family, CyMe4-BTBP, possesses not only high separation efficiency for An(III)/Ln(III) ($SF_{Am/Eu} = 140$) but also excellent resistance to hydrolysis and radiolysis in nitric acid systems [19]. As for S-donor extractants, a dialkyldithiophosphinic acid extractant (Cyanex-301) also displays superior performance for Am(III)/Eu(III) separation ($SF_{Am/Eu} > 5000$) [12,20]. Besides, dithiophosphinate ligands with phenyl substituents have also been developed [21]. However, little is known, so far, about the microscopic mechanisms and dynamics of complexation and decomplexation of An(III) and Ln(III) with soft-donor ligands in solutions.

The separation process is generally controlled by the synergetic effect of many factors such as coordination strength, counterions and solvents, ionic strength, pH, kinetics of complexation, equilibration constants, substituent groups, additional reagents, etc. Therefore, to obtain high separation efficiency, it is necessary to explore the interaction mechanisms of those influencing factors. In this review, recent progress of computational actinide and lanthanide chemistry on the An(III)/Ln(III) separation will be illustrated. Firstly, the theoretical methods commonly used for evaluating large complexing systems of An(III) and Ln(III) are introduced. Secondly, recent publications focused on extraction systems for separating An(III) from Ln(III) are reviewed and highlighted. Thirdly, the strategies for the multi-scale design of highly efficient ligands toward An(III) over Ln(III) will be discussed. Finally, we provide some common conclusions and future opportunities and perspectives of the topic. It is difficult, even impossible, to summarize all the latest important results in computational chemistry related to An(III)/Ln(III) separation. We still hope that this review would shed light on the further research directions.

2. Theoretical methods

Recent advances in both theory and computation have made the prediction of physical and chemical properties of organic and inorganic molecules, liquid, and solid materials far more reliable than before. With theoretical modeling and simulations, one can calculate both microscopic electronic structures and measurable molecular properties that can be compared with experimental observations. Furthermore, useful information can be obtained computationally when experimental data are absent. Computational actinide chemistry has been an important frontier of computational chemistry nowadays owing to the difficulties in treating relativistic effects, electron correlation effects, etc. [22–25]. At present, one focus in computational actinide chemistry is to explore the coordination chemistry of An(III) complexes and the complexation mechanisms in the An(III)/Ln(III) extraction process [26–37].

Theoretical investigations of actinide complexes are generally performed at the electronic and molecular (or atom) scales (see Scheme 1). Here, the definitions of "electronic scale" and "molecular scale" are used mainly according to the minimal structural unit treated in the calculation processes. The electronic scale methods principally consist of relativistic ab initio wavefunction theory (WFT) and density functional theory (DFT) methodologies. Using these methods, a wide variety of properties of actinides has been studied, including the geometric and electronic structures, spectra of complexes (e.g. UV–vis, fluorescence, IR, Raman, NMR, photoelectron spectra), complexing reaction pathways, the nature of chemical bonding, thermodynamic stabilities, etc. In contrast, the molecular scale methods mainly concern classical molecular dynamics (MD) [38] and Monte Carlo (MC) [39] simulation techniques. Based on molecular scale simulations, the macroscopic properties of large systems can be predicted, e.g., equilibrium state, coordination spheres of metal ions, diffusion coefficient, viscosity, thermodynamics. However, the molecular scale methods have drawbacks in describing polarization effects and treating chemical events involving bond breaking and forming. In these cases, the so-called ab initio molecular dynamics (AIMD) method is one of the most important developments in this area, which combines finite temperature atomistic molecular dynamics with internuclear forces derived from accurate electronic structure calculations performed "on the fly" as the MD simulation proceeds [40]. For relatively large systems, the hybrid quantum mechanical/molecular mechanical (QM/MM) methods [41,42] have also been developed, guided by the general idea that large chemical systems may be partitioned into an electronically important region that requires a quantum mechanical treatment and a peripheral region that only



Scheme 1. Multiscale theoretical methods used for exploring the complexing mechanisms in the An(III)/Ln(III) separation process.