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Effect of polystyrene length for the extraction of Gd^{3+} and UO_2^{2+} ions using dicyclohexano crown ether (DCH18C6) with octanol and nitrobenzene: A molecular dynamics study

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ABSTRACT

The role of polystyrene (PS) grafting to the dicyclohexano crown ether (DCHCE) in extracting the Gd^{3+} and UO_2^{2+} is evaluated for the first time using atomistic molecular dynamics (MD) simulations. The thermodynamic free-energy (ΔG_{Bind}) is calculated to understand the binding of Gadolinium (Gd^{3+}) and Uranyl (UO_2^{2+}) to the DCHCE in nitrobenzene (NB) and octanol (OCT) solvents. The results show that the binding free-energy is favorable for Gd^{3+} and UO_2^{2+} in NB, and unfavorable in OCT. In NB, the ΔG_{Bind} of Gd^{3+} and UO_2^{2+} increases by 2.3% and 3.1% respectively with an increase in the PS length from 0 to 3. On the contrary, in OCT, the ΔG_{Bind} of Gd^{3+} and UO_2^{2+} decreases by 2.4% and 3.4% with an increase in PS length of the grafted DCHCE. The transfer free-energy ($\Delta G_{Transfer}$) for both the ions viz., Gd^{3+} and UO_2^{2+}, from the aqueous phase to an organic phase is also analyzed using NB and OCT as extractants. The $\Delta G_{Transfer}$ for both ions shows encouraging extraction ability in NB while the extraction ability decreases using OCT as an extractant. The partition coefficient (log P) values show an increase with an increase in PS grafting length on the DCHCE using NB as an extractant, while an opposite behavior is observed in OCT. In particular, with increase in the PS length, for Gd^{3+} and UO_2^{2+}, log P values in NB increase by 13% and 9.6% respectively; whereas log P values decrease by 27% and 10% in OCT. In the presence of acidic medium (3 M HNO_3 solution) the $\Delta G_{Transfer}$ values for both Gd^{3+} and UO_2^{2+} show ~6% and 9% increase with NB and OCT, respectively. The structural and thermodynamic solvation properties are in accordance with the observed ΔG_{Bind}, $\Delta G_{Transfer}$, and log P.

1. Introduction

Extraction of lanthanides and actinides from the high-level nuclear waste is a major problem in the nuclear industry due to the difficulty in extracting the toxic gadolinium (Gd^{3+}) and uranyl (UO_2^{2+}) from the high nuclear waste. The macrocyclic polyethers such as crown ethers have been effectively used for the recovery or extraction of lanthanides and actinides in the form of stable metal ion – crown ether complexes [1–7]. The selection of suitable ligand from numerous possibilities for the recovery of specific metal ion depends on the cavity and metal ion diameters have been recognized by various molecular simulation studies and experiments [7–12]. Both experiments and molecular simulations have demonstrated that dibenzo-crown-ether (DB18C6 or DBCE) and dicyclohexano crown ether (DCH18C6 or DCHCE) are suitable ligands for the extraction of Gd^{3+} and UO_2^{2+}. [1,3,13–16].

The organic solvent such as alcohols as an extractant has been shown to play a major role in enhancing the extracting capabilities of ligands through the formation of stable ligand metal-ion complexes [4,6,7,11,14,15,and]. It is shown that the presence of organic solvent in the solution containing crown ether and metal ions further improves the binding of metal ions with the crown ethers [11–15]. The free-metal ions bind on to the oxygen's of crown-ethers via significant electrostatic interaction leading to tight binding with crown ethers [15,16]. For example, the presence of organic solvent like nitromethane and acetonitrile (ACN) enhance the significant extraction of metal ions such as UO_2^{2+}, Pb^{2+}, Ba^{2+} and Cd^{2+} with DCHCE as observed by the conductometric study [7]. A conductometric study by Rounaghi et al. [4] demonstrated that Gd^{3+} show improved complexation with DCHCE as compared to mono-cations such as NH_4^+ and Ag^+ in the mixture of an organic solvent containing tetrahydrofuran (THF) and ACN. The experimental study by Boda. et al. [14,15] have shown that nitrobenzene (NB) and octanol (OCT) act as good extractants for separation of Gd^{3+} and strontium Sr^{2+} from the radioactive waste in the form of stable metal ion crown-ether complexes. Due to the above role of solvent, liquid-liquid extraction is highly accepted method for the separation of heavy metal ions from the high-level radioactive waste.

In a series of recent works, it is revealed that polymer grafted crown ether augments the binding of the metal ion with crown ether [15–18]. An experimental study by Ye et al. [3] has shown that polysiloxane

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based DCHCE exhibited enhanced extraction capacity for Sr^{2+} using OCT. Sinta et al. [17] have developed polystyrene (PS) based ligand for the effective binding of sodium (Na^+) and potassium (K^+). A combined experimental and theoretical study of Boda et al. [15] showed that PS grafted crown ethers such as DB18C6 and DCH18C6 increases the binding of Gd^{3+}. A recent MD simulation study [16] demonstrated that increasing the PS grafting length on the DBCE show significant extractions of Gd^{3+} and UO_2^{2+} from an aqueous solution, and fivefold increase in the partition coefficient values. Furthermore, UV/Vis spectroscopy showed that polymer-supported crown ether exhibits thermodynamically stronger complexation for the metal ion [18].

However, despite the available experimental and simulation results not much is known about the complexation of the metal ions such as Gd^{3+} and UO_2^{2+} with polymer supported DCHCE. There are several questions yet to be answered such as: a) binding affinity of Gd^{3+} and UO_2^{2+} with bare and polymer supported DCHCE; b) the role of polystyrene grafting in extracting these metal ions using liquid-liquid extraction as organic solvents as an extractant; c) the separation efficiency of the polymer grafted DCHCE using NB and OCT as extractants; d) and the thermodynamics of binding and transfer of the Gd^{3+} and UO_2^2 ions from an aqueous phase to an organic phase. In this work, we have used molecular dynamics simulation to address the above questions, which would help in selecting suitable ligands and organic solvents for the effective extraction of heavy metal ions. Thus, the main objective of this study is to understand the effect of polystyrene grafting on DCHCE in enhancing the binding free-energy (ΔG_{Bind}) of Gd^{3+} and UO_2^{2+} in NB and OCT solvents.

2. Methodology and simulation details

We have considered four DCHCE for this study viz., (1) DCHCE-0PS (without polystyrene grafting), (1) DCHCE-1PS (one monomer of polystyrene grafting on the both sides of DCHCE), (3) DCHCE-2PS (two monomers of polystyrene grafting on the both sides of DCHCE) and (4) DCHCE-3PS (three monomers of polystyrene grafting on the both side of DCHCE). The input structures of these crown ethers are prepared in Materials studio [19]. Geometry optimization of these four structures was performed using density functional theory (DFT) using Gaussian09 [20]. All calculations were performed using B3LYP [21] hybrid functional and 6–31 g(d,p) basis set for C, H and O while LANL2DZ effective core potential applied to the heavier atoms. The same level of theory was employed for the charge calculations using ChelpG method [22]. In order to perform MD simulations, Gd^{3+} and UO_2^{2+} ions were placed in the cavity of DCHCE. Fig. 1 presents the DFT optimized structures of Gd^{3+}-DCHCE and UO_2^{2+}-DCHCE at various PS grafting lengths used in the MD simulations. Tables S1–S4 in the supplementary file list all the force-field parameters used in this work. All-atom OPLS force field [23] is used for DCHCE, NB and OCT solvents and Gd^{3+} and UO_2^{2+} ions. In the case of simulation where acidic medium is considered, the acidic

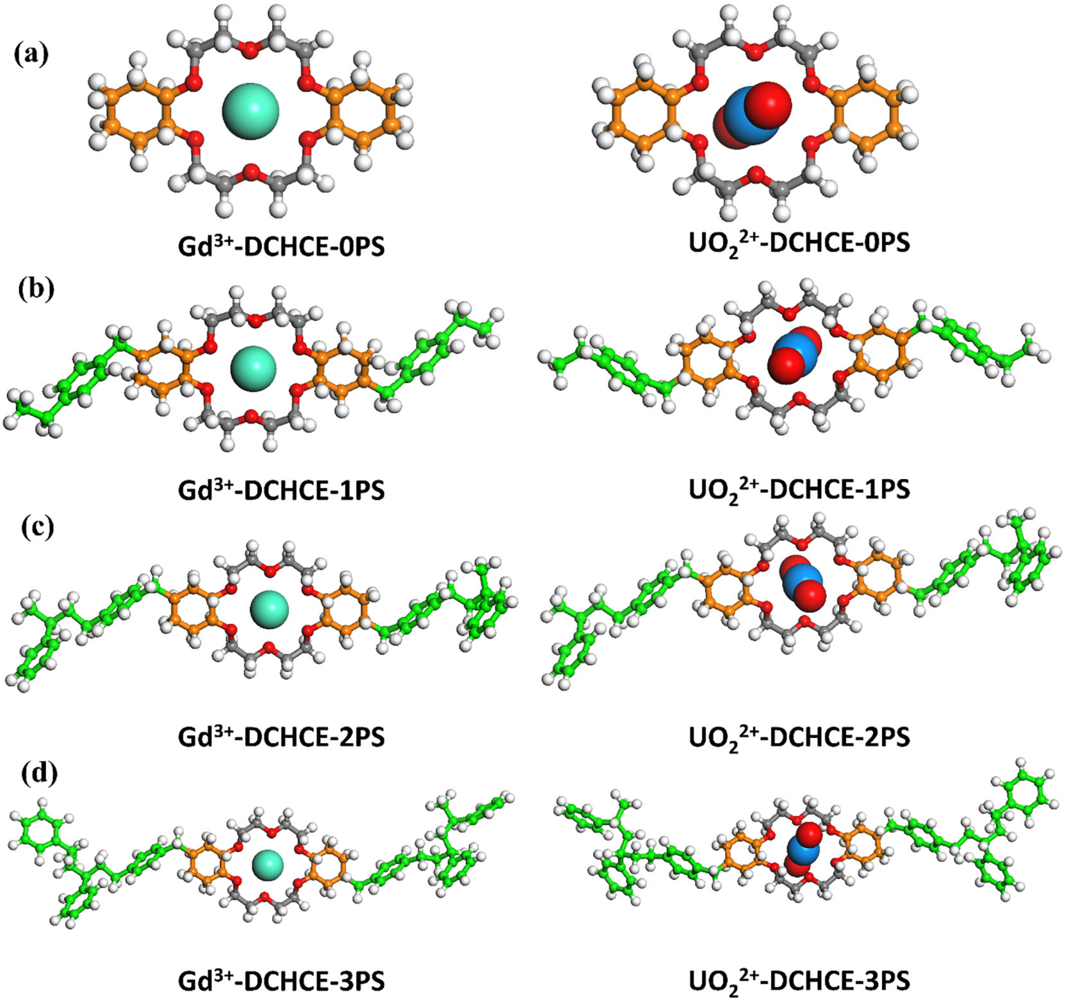

Fig. 1. Schematic representation of ion complexed crown ethers with (a) DCHCE, (b) DCHCE-1PS, (c) DCHCE-2PS and (d) DCHCE-3PS. Color Codes: Gray carbon, white hydrogen, red-oxygen, orange-benzene, green-polystyrene, cyan gadolinium, and blue uranium. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)