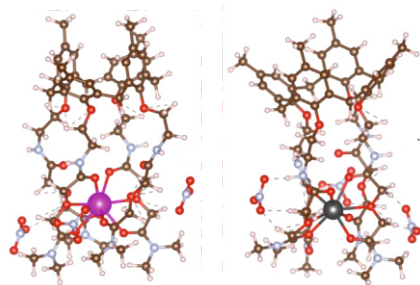# Density Functional Theory

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Atomistic Modeling (Odourless, Fumeless and Zero Toxicity) Driven Laboratory Experiments

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Eu(NO$_3$)$_3$(C4DGA) and Am(NO$_3$)$_3$(C4DGA)

ABSTRACT

Atom by atom design and engineering of a molecular assembly using the tools of atomistic modeling nowadays has become very useful and popular for application in the various fields of science and engineering. This computational atomistic modeling has become very demanding due to its ability to predict quantitatively the structural, mechanical, thermo-physical and dynamical properties which are useful in interpreting the experimental findings and planning the new experiments. The present article focuses on the demonstration of atomistic modeling consisting of Quantum electronic structure calculations, classical and ab-initio molecular dynamics simulations and statistical mechanics carried out in Atomistic Modeling and Chemical Analysis Section, Chemical Engineering Group of BARC pertinent to DAE application.

KEYWORDS: *Atomistic modeling, DFT, Molecular dynamics, SX and IX, Multi-component glass, Barrier materials*

Introduction

Atomistic modeling consisting of electronic structure calculations, classical molecular dynamics simulations, on the fly force based molecular dynamics simulations has become very powerful tool to design and develop the tailor made molecular architecture for varieties of application. The use of atomistic modeling driven molecular engineering is growing exponentially with continuing advance of CPU-GPU accelerated parallel computing, innovative and robust algorithms and accessibility of parallelized software [1]. Atomistic modeling (AM) predicts the properties of materials before their manufacture and determines the parameters and behavior needed to develop the advanced chemical process [2]. Tri-n-butyl phosphate (TBP) is extensively used in the PUREX process. In spite of great success, there is a demand and continuing search for an alternative of TBP. Due to inherent chemical similarities of Ln and An, identification of a suitable extractant for separation of the minor actinides (MA) from Ln is a major challenge in reprocessing of spent fuel. Similarly, separation of Zr and Hf is very difficult due to similar chemical properties and thus poses a challenge. Currently TBP is used on a commercial scale to separate Hf from Zr ions though it has low separation factor. There is a continuing search for finding an alternative of TBP. The finding of a right ligand-solvent system for selective metal ion extraction and enrichment is quite time consuming and a tiresome which can be cost-effective if the screening is done beforehand of the experiment. Since, the fabrication methodologies of nano membrane using graphene are yet to be simplified, computational investigations are the only means for advancing the progress. The screening of cost effective titanium alloy as neutron targets keeping its high absorption of hydrogen can be

conducted by AM. Selection of suitable glass composition for vitrification of HLLW can be predicted with the guide of AM. Therefore, to achieve this goal, a strategy has been conceived employing the concepts of AM for solvent extraction, isotope separations, desalination, hydrogen storage materials and multi-component glass. First, a computational modeling strategy has been envisaged to design the molecular system followed by synthesis and characterization and finally, testing of the synthesized materials for targeted applications.

Computational Methods

Density functional theory (DFT) with generalized gradient approximation and appropriate basis set (SVP, TZVP etc.) were used for structural relaxation, energy and hessian calculations for isolated molecules. COSMO solvation modeling was used to account for the solvent effect in the energetics and thus in thermodynamics. Classical and ab-initio molecular dynamics simulations using the appropriate ensembles (NVT, NPT etc) and boundary condition were used for evaluating the structural, thermophysical, mechanical and dynamical properties of molecules and materials in different state of matters. For periodic system, PBE functional including projector augmented wave potentials with an energy cut-off of 350 eV were employed. Monkhorst–Pack k-points were used for the Brillouin zone integration. The forces on all the atoms are kept less than 0.01 eVÅ^{-1}.

Results and Discussion

Density functional theory at the B3LYP level [3] was used to establish that ditertiary butyl dicyclohexano 18-crown 6 (DTBDCH) was the right extractant for removal of Sr^{2+} ion. The preferential extraction of Zr over Hf towards organophosphorus extractant has been established using DFT and experimental results [4]. The optimized complexes of Zr and Hf ions with b is

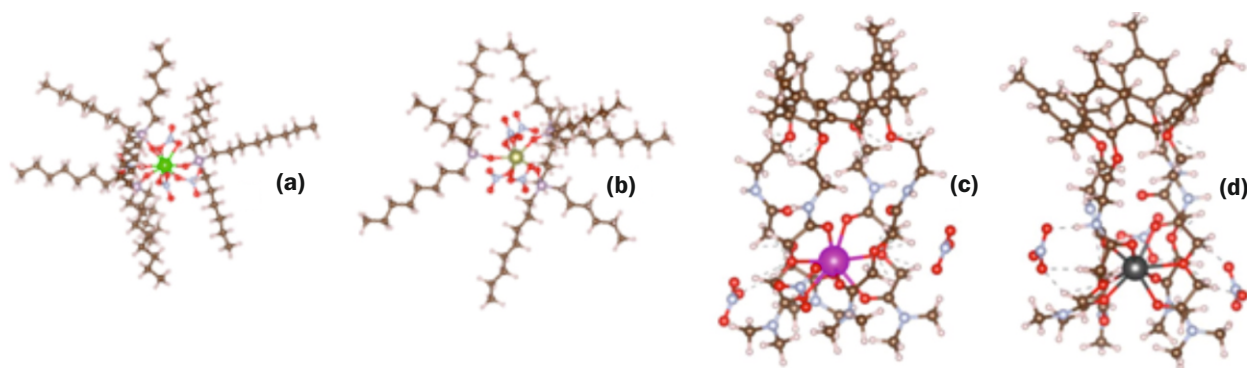*Author for Correspondence: Sk. Musharaf Ali
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Fig.1: Structures of (a) Zr(NO₃)₄ (Cyanex923)₃ (b) Hf(NO₃)₄ (Cyanex923)₃, (c) Eu(NO₃)₃(C4DGA) and (d) Am(NO₃)₃ (C4DGA).

(hexyl)-octyl phosphine oxide (Cyanex923) are displayed in Fig.1 (a,b). DFT successfully captures the complexation stability order as Cyanex923>Cyanex925 for both Zr and Hf ions. Cyanex923 is the best extractant in terms of high distribution constant and displays higher selectivity over Cyanex925 for Zr which is in excellent agreement with the experimental results. As per recent experimental results, TODGA (*N,N,N',N'*-tetra-*n*-octyldiglycolamide) is shown to be promising for actinides extraction. Computational studies of An/Ln complexes are rather limited [5].The optimized complexes of Eu^{3+}/Am^{3+} ions with TODGA are depicted in Fig.1 (c,d). The ΔG_{ext}[5] was higher for Eu ion than Am ion. The structures, energy and thermodynamics were calculated to investigate coordination mode, reaction energy and extraction ability of DGA appended calix[4]arene (C4DGA) [5]. The ΔG_{ext} for Eu ion was higher over Am ion which corroborates the experiments. The entropy of complexation, S was seen to be reduced for DGA to large extent compared to C4DGA. The ΔG was found to be negative and higher for Eu ion in absence of nitrate ion. The S was found to be negative in the presence of nitrate ion for 1:4 stoichiometry whereas slightly positive for 1:3. The role of nitrate was shown to be indispensable.

MD simulations were conducted to assess the uranyl extraction using LAMMPS package [6]. The extent of ion transfer from aqueous to organic phase is defined in terms of distribution constant, K_d which is an important process parameter for plant design. Therefore, K_d of UO_2^{+2} ion by varying uranyl and acid concentration were estimated. The results in Fig.2 (a) show the non-linear increase in K_d with increase in UO_2^{+2} ion. There is a rise in K_d with increase in acid up to 6M, thereafter a fall in K_d with further increase in acid (Fig.2 (b)) as observed in the experiments. It is expected that the initial increase in HNO_3 concentration facilitates UO_2^{+2} migration from

interface to the organic phase by increasing the interfacial roughness, and so creating pathways for UO_2^{+2} ion migration from interface to the organic phase. However, at very high acid concentration (>6M), the decrease in K_d might be possible from two reasons: first, the competition between UO_2^{+2} ions and HNO_3 molecules to be picked by TBP and second, the increased accumulation of HNO_3 molecules near the interface, which actually blocks the pathways for UO_2^{+2} ion migration from aqueous to the organic phase.

DFT calculations were conducted to design functionalized resins for isotopic enrichment of Gd [7] using vibrational frequency of hydrated Gd^{3+} ion and Gd^{3+}-crown ether complex ion by evaluating separation factor (α) (Fig.3). The results show that the separation factor with DB18C6 is higher than B18C6 and DCH. Because of comparatively high , DB18C6 is considered to be promising for isotopic enrichment of Gd, and hence DB18C6 was functionalized with chloromethylated polystyrene (CMPS) resin. Experiments were conducted by column chromatography and the separation factor was found to be in good agreement with the calculated results and thus hold promise for the future isotopic enrichment technology.

Using MD and DFT calculations, the binding affinities of graphene-embedded 18-crown-6, 16-crown-5 and 14-crown-4 for Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+} metal ions were investigated [8]. The binding preference of these membranes depends on the crown ether cavity and the stability of hydration shell of the binding ion. The adsorption capacity of simulated crown ether graphene membranes for different cations is shown in Fig.4. 18C6 was found to be highly selective for K^+ ions. The order of selectivity was : $K^+>Na^+>Li^+$ for graphene embedded 18C6 with a strong competition between Na^+ and K^+ whereas for 14C4
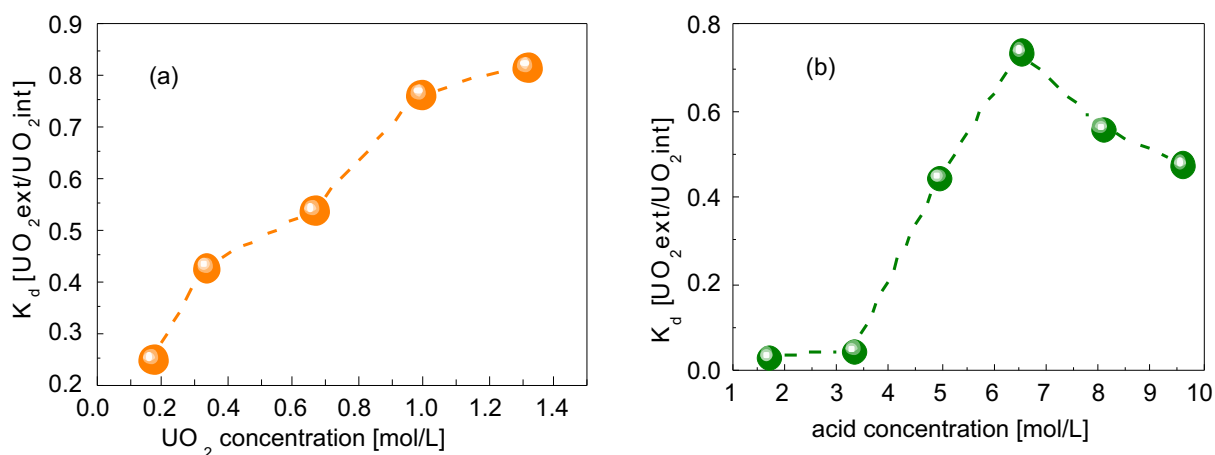

Fig.2: Calculated values of K_d for uranyl as a function of (a) uranyl concentration and (b) acid concentration in the system.
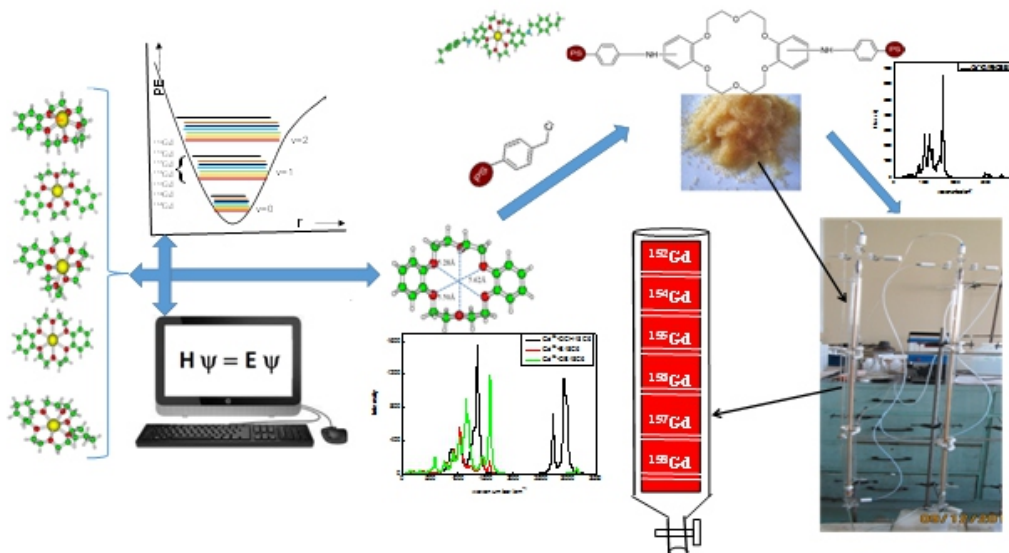
Fig.3: Computer aided molecular engineering for isotope separation of gadolinium using column chromatography.

and 16C5, the order of selectivity was: Na^+>K^+>Li^+.In spite of strong interaction of Na^+ and K^+ with 16C5-graphene and 14C4-graphene, no permanent trapping of ions was noted for K^+ with graphene-18C6. The results show Langmuir type adsorption profile, where one site can be occupied only by single cation. The adsorption capacity of ions/pore was always smaller than 1.0, which indicates that only one ion can be adsorbed by single crown ether pore, corresponding to 1:1 crown ether pore: cation ratio. Fig.4 (a,b) shows hydration number of cation as a function of distance from membrane surface. Fig.4 (c) shows the ions hydration w.r.t. distance from graphene-16C5. Results show reducing hydration number of ions while their transfer from bulk solution to crown ether. The maximum hydration number of metal ions was noted not in bulk but at few distance away from graphene membrane.

Titanium is preferred as neutron targets due to high hydrogen storage capacity and is of importance to understand the interaction of hydrogen with Ti. The calculations are conducted using PBE with GGA using linear combination of atomic orbitals (LCAO) and projector augmented wave (PAW) potential as implemented in the Atomistic Toolkits (ATK). The climbing image nudged elastic band technique was employed to find the minimum energy paths for H atom migration. The activation energy barrier from top to bridge and top to hollow sites was negative for H atom indicating barrier less diffusion. The calculated barrier height for dissociation was 0.4eV at surface coverage of θ_H> 0.5ML whereas the barrier height for recombination was found to be much higher than that of dissociation (Fig.5). In case of recombination the H atom has to be detached from the binding of Ti atom and it recombines with another H atom to form H_2 molecule and this requires higher activation energy which is generally provided by applying external temperature.

Combined experiments and MD simulations were performed to understand the improved durability of borosilicate glass with addition of ZnO [10-13]. The MD results were found to be in good agreement with the experimental data for Young's Modulus, glass transition temperature and leaching. Both experiments and MD simulations report the enhanced chemical durability of glass with addition ZnO. Low R (Na_2O/B_2O_3) and high K (SiO_2/B_2O_3) of ZnO doped sodium borosilicate (Zn-NBS) glass surface compared to bare NBS represents the more stable structure of glass surface for Zn-NBS than NBS. During simulation, Na^+ ions were found to diffuse from bulk glass region to the interface and some of them were even migrated to the bulk side of the aqueous phase. The results in Fig.6 show that the leaching of Na+ ions can be reduced with ZnO doping and similar trend was noticed
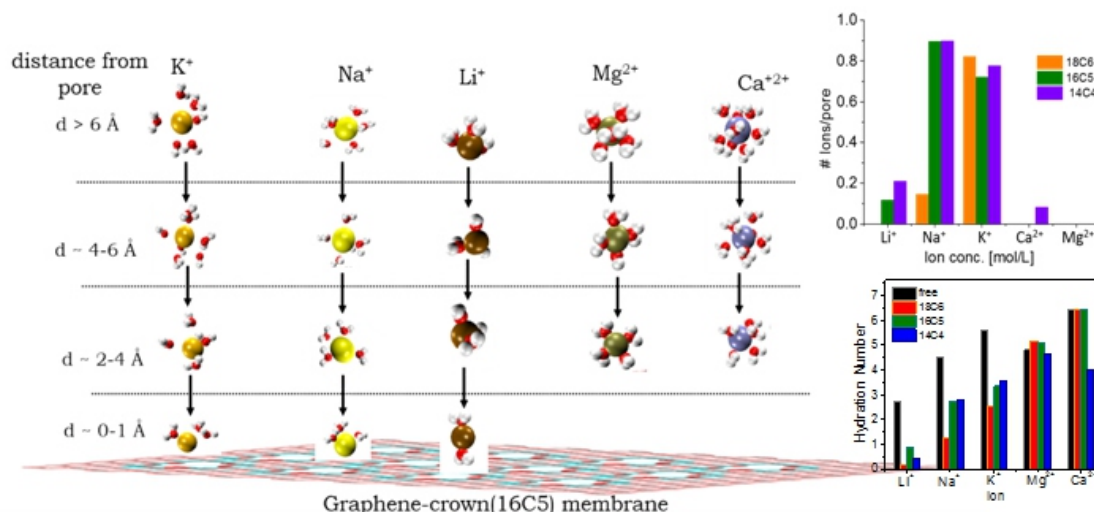

Fig.4: Dehydration of metal ions on graphene-16C5 membrane. Hydration number of metal ions as a function of ion distance.
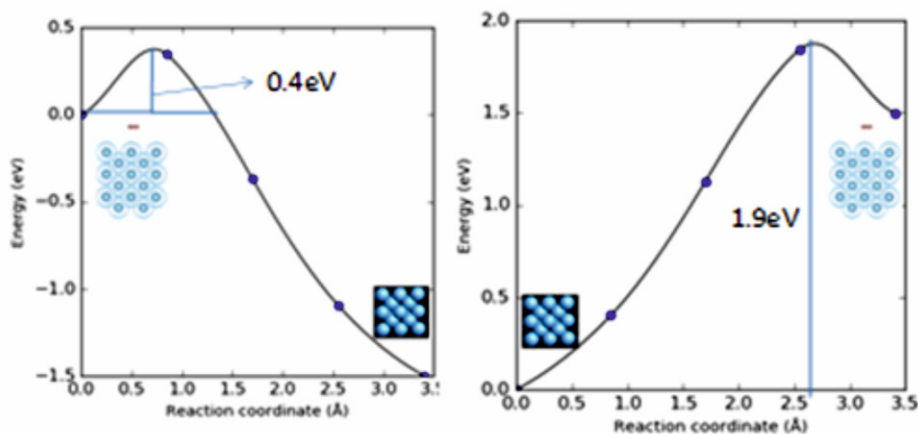
Fig.5: (a)barrier for dissociation and recombination of H_2 molecule on the Ti (100) surface using LCAO basis set.
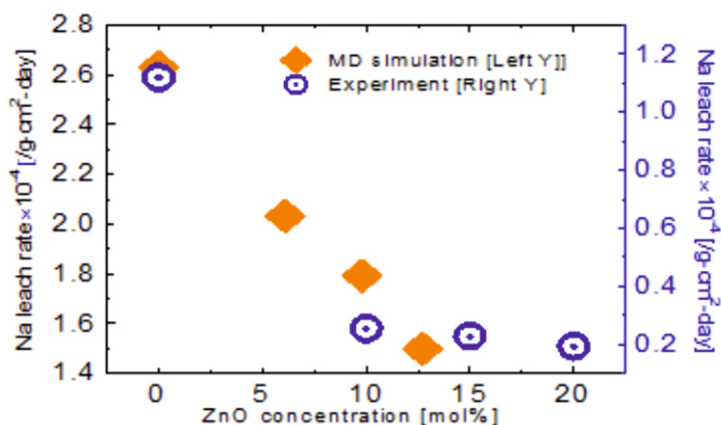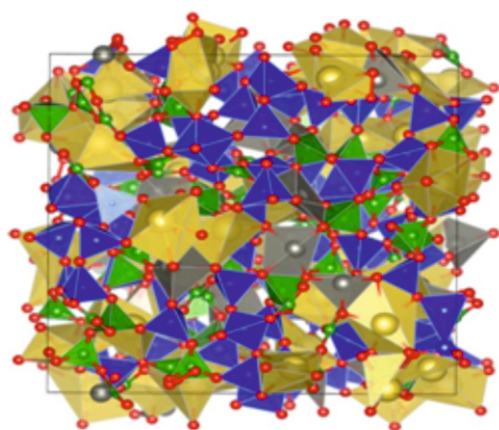

Fig.6: ZnO-NBS (9.8% ZnO) glass andNa leaching rate from MD simulation (left Y) and experimental (right Y) studies.

in experimental studies. MD simulations as well as experimental observations support the fact that ZnO would increase the chemical durability of glass. Low R and high K of ZnO doped NBS glass surface compared to bare NBS represents the more stable structure of glass surface with Zn doping, in which atoms will remain intact with the bulk structure of glass and would be less prone to leaching. The water adsorption in glass was found to affect the glass structure significantly at surface region while marginally in bulk region. The enhanced chemical resistivity of Zn-NBS was also established from the reduced diffusivity and higher activation energy for diffusion of Na+ ions while Zn doping or increasing ZnO concentration in NBS glass.

Conclusion

DFT in combination with COSMO solvation model can be used as a pre screening tool for the selection of ligand-solvent systems. It can be stated that DFT-based computational methods have played and are still playing a key role in understanding the separation mechanism of various metal ions and isotope separation. High-fidelity MD simulations were shown to capture the experimentally observed migration of uranyl nitrate from the aqueous to the organic phase andultrafast water transport in graphene based membranes and thus are useful in planning the experiments. The identification of neutron generator and glass composition for waste immobilization can be predicted by atomistic calculations. To conclude, presently atomistic modeling is indispensable in the development of molecular engineering based nuclear technology.

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