MOLECULAR MODELING BASED DESIGN OF MINERAL PROCESSING REAGENTS –A FEW ILLUSTRATIVE CASE STUDIES FROM OUR WORK

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SUMMARY

With recent advances in the understanding of molecular level phenomena governing adsorption and self-assembly of surfactants at interfaces, accessibility of application oriented molecular modelling tools and availability of relatively inexpensive computing power; it is possible to rigorously model the underlying surface phenomena using first principles ab initio as well as classical simulations tools such as molecular dynamics (MD).

During the past two decades, we have developed appropriate methodologies for the design and selection of surfactants, customized for specific applications. We demonstrate in this position paper, the power and the utility of such theoretical computations with the help of an illustrative example drawn from our work on the adsorption of surfactants on calcium minerals. Adsorption of oleate surfactant at the mineral surface is modelled, wettability of self-assembled mono-layers (SAM) of surfactants adsorbed at the mineral surfaces is studied and corresponding computed contact angles are predicted and correlated with their flotation response. The methodology thus developed is applied for the design of highly selective reagents for the separation of natural fluorapatite minerals from its associated undesirable minerals, dolomite (calcium magnesium carbonate). We have successfully employed this approach in the design and development of several families of reagents for example, flotation collectors, frothers & depressants, selective flocculants and dispersants, filtration aids, crystal growth modifiers, corrosion inhibitors and reagents for controlling rheology.

Keywords
Molecular modelling, surfactant, calcium minerals, oleate, apatite, dolomite
1 | INTRODUCTION

We present one case study on flotation separation amongst calcium minerals using a set of different families of flotation collectors for illustration in the following sections.

1.1 | Methods and Materials

Mineral Surfaces

The atom positions in the unit cell of the minerals have been taken from the experimental structural reports based on X-ray studies (Dana and Ford, 1949). A periodic surface cell has been created from the unit cell of the mineral crystal at its cleavage plane and optimized. The surface cell thus created has been extended in x and y directions to create a larger surface slab. While relaxing the surface slab, top few atomic layers were allowed to move and rest of the bulk atomic layers were constrained.

Reagent Molecules

The molecules were optimized using universal force field. Parameters for the force field were also obtained from ab initio methods. Experimental data on the bond lengths, bond angles and other properties is utilized to validate the optimized structure.

Water Droplet and Computation of Contact Angles

Water molecules have been modelled using SPC/E potential – a rigid three point model with fixed charges assigned to hydrogen and oxygen (Berendsen Grigera and Straatsma, 1987). Partial charges on oxygen and hydrogen atoms of water molecules have been taken from SPC/E model (qO = -0.8476e and qH = -qO/2). A 3D periodic cubic cell (a= 31.29 Å, 1024
water molecules) has been generated using amorphous builder module of Material Studio (V. 4.1, Accelrys Ltd., San Diego, USA). The cell has been optimized and equilibrated using MD simulation. A spherical droplet of water (419 molecules) has been cut from this equilibrated 3D periodic box of water molecules and placed on the mineral surfaces for wetting studies. The methodology proposed by Fan and Cagin (1995) has been utilized to extract the microscopic parameters namely, the drop volume (V) and the interfacial area (S) of water droplet from the MD simulations which are utilized for computing the contact angle.

Simulation Details

Molecular simulations have been carried out using Materials Studio (V. 4.1, Accelrys Ltd., San Diego, USA). Universal force field (Rappe’ et al, 1992; Rappe’, Colwell and Casewit, 1993) as implemented in Materials Studio has been used to model the mineral – water interactions. Universal force field (UFF) has been used in the past to model the mineral-reagent systems with reasonable accuracy (Pradip et al, 2002a; Pradip et al, 2002b; Rai and Pradip, 2003, Pradip and Rai, 2003; Rai and Pradip, 2008). The geometry of reagent molecule is optimized and the optimized molecule is docked on the mineral surface. The initial geometry of surface-reagent complex is created physically on the screen with the help of molecular graphics tools, taking into consideration the possible interactions of reagent functional groups with surface atoms. The reagent molecule is then allowed to relax completely on the surface using geometry optimization. Several initial conformations (~20) are assessed so as to locate the minimum energy conformation of the inorganic surface-reagent complex. Partial charges on the atoms have been calculated using QEq method, the basis of which is the equilibration of atomic electrostatic potentials with respect to a local charge distribution (Rappe and Goddard, 1991). The intra-molecular van der Waal interactions are calculated only between atoms which are located at distances greater than fourth nearest neighbors. Smart minimizer as
implemented in Forcite module of MS is used for geometry optimization. Non-bond interactions (van der Waals and columbic) have been modelled using a modified Ewald summation method (Karasawa and Goddard, 1989). The optimization is considered to be converged when a gradient of 0.0001 Kcal/mole is reached. The interaction energy is calculated for the most likely/favorable conformation using the following equation:

\[
\text{Interaction energy (}\Delta E\text{)} = E_{\text{complex}} - [E_{\text{reagent}} + E_{\text{surface}}]
\]

Molecular dynamics (MD) simulations have been run using microcanonical NVT (constant number of particles, volume, and temperature) and canonical NVE (constant number of particles, volume, and energy) ensemble (Allen and Tildesley, 1987) at 298K. The equations of motions have been solved using Verlet algorithm (Allen and Tindsley, 1987). The bond lengths and angles have been constrained using RATTLE algorithm (Ryckaert, Ciccoti and Berendsen, 1997) as implemented in Materials Studio. A time step of 1 fs has been used. During NVT run, the temperature has been controlled using a thermostat (Brendsen, 1984). A vacuum of 100 Å above the top atomic layer of the surface cell has been used (in the z direction) to screen the interactions of water droplet/adsorbed reagent from the bottom layers of the surface slab. The surface atoms have been kept fixed during interactions with water droplet/reagent molecule. The system has been equilibrated for 200 ps with NVT ensemble followed by a production run of 500 ps with NVE ensemble.

For modeling self-assembled monolayers (SAMs), a monolayer of reagent molecules is placed on the inorganic surface. The reagent molecules are placed as per the most stable conformation obtained through optimized single molecule-surface complex. In order to find the equilibrium structures of the adsorbed monolayers, the clusters thus created are subjected to geometry optimization followed by molecular dynamics (MD) simulations at 298K. The surface atoms are
kept fixed during the entire simulation run and only adsorbed reagent molecules are allowed to relax.

Design of Reagents

All surfactants essentially consist of one or more functional groups and a backbone (polymeric or organic). Our molecular modeling computations take into account the whole molecule, that is, we can study the effect of the nature of the functional groups as well as investigate the influence of the molecular architecture of the reagent. The computations can be carried out both for bulk complexation (for example with density functional computations) and/or surface interactions.

We have now been able to successfully predict the interfacial and surface tensions of the reagents, the adsorption and self assembly of surfactants (including a mixture of surfactants) at the interface and compute the contact angle and study the wettability of the interfaces with and without self-assembled monolayers (SAM).

We shall illustrate our approach with several examples taken from our own work on this topic. Only one example is included in this brief write up. Certain results are presented for illustration. We have included a few key references in the end to our published work for those interested in details.

We would like to suggest that the molecular modeling has certainly matured to a level that it can be used as an extremely valuable tool to design and develop engineered molecules with customized molecular architecture and consisting of one or more desirable functional groups compatible with the surface under investigation. This approach is useful both for the design of novel reagents as well as for the selection of reagents for a specific problem, for example, beneficiation of a complex ore.
2 | KEY RESULTS AND ILLUSTRATIONS

Virgin Surface – Wetting characteristics simulated by MD

MD Simulation of Spreading of water droplet on the fluorite {111} surface - at time t=0 (left) and t= 300 ps (right)

Contact angle for water for fluorite {111} surface was computed by MD Simulation to be 48 degrees as compared to the values measure experimentally (10 to 55 degrees).
Comparison of experimental flotation results for the most selective phosphonic acid reagent, IMPA-8: octyliminobismethylene phosphonic acid with its computed interaction energies at different mineral surfaces.
Snapshots of a water droplet on adsorbed SAMs on fluorite, fluorapatite and calcite surfaces (a) before equilibration (b) after 300 ps of MD run.
<table>
<thead>
<tr>
<th>Depressant ((x))</th>
<th>Interaction energy (kcal/mole)</th>
<th>Energy Difference (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Apatite ((100))</td>
<td>Dolomite ((104))</td>
</tr>
<tr>
<td>2</td>
<td>-230</td>
<td>-100</td>
</tr>
<tr>
<td>3</td>
<td>-236</td>
<td>-103</td>
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<tr>
<td>4</td>
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<tr>
<td>10</td>
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<td>-116</td>
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<tr>
<td>12</td>
<td>-246</td>
<td>-131</td>
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</tbody>
</table>
• Jhamarkotra Rockphosphate Ore (India): 23.8% P2O5 (10.4% P), 7.2% insolubles (SiO2), 13.3% MgO

• C2P4 (Aquacid 109EX) and C6P4 (Aquacid 1076EX), Aquapharm, Pune, India

• C8P4 and C12P4 synthesized at our laboratories

• Phosphonic Acids used as depressants for fluorapatite
Where $x = 2 - 12$
KEY REFERENCES (OUR GROUP)

Vinay Jain, Beena Rai, Umesh V. Waghmare, Venugopal Tammisetti and Pradip, Processing of Alumina Rich Iron Ore Slimes - Is the selective dispersion – flocculation – flotation the solution we are looking for the challenging problem facing the Indian iron and steel industry?, *Transactions Indian Institute of Metals*, 66 (5-6), 2013, pp 447-56


