

Molecular Modeling of Interactions of Alkyl Hydroxamates with Calcium Minerals¹

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The results of theoretical computations on the molecular modeling of mineral–reagent interactions in a fluorite–calcite–fluorapatite–alkyl hydroxamate separation system were found to correlate remarkably well with the experimental microflotation test results. The utility of molecular modeling tools in the design/screening of surfactant molecules for flotation separations is discussed. © 2002 Elsevier Science (USA)

Key Words: molecular modeling; interaction energy; quantum chemical methods; force field methods; MNDO; UFF; flotation reagents; fluorite; calcite; hydroxamates.

INTRODUCTION

Recent advances in our understanding of molecular-level phenomena governing surfactant adsorption at interfaces, the accessibility of application-oriented molecular modeling tools, and availability of rather inexpensive computing power have brought the whole field of surfactant design to the threshold of a major breakthrough. Two key features of this emerging paradigm shift from conventional trial and error methodology to rational, scientific approach to arrive at the preferred molecular architecture of the tailor-made surfactant for a specified industrial application are: first, identification of the molecular recognition mechanisms underlying selective surfactant adsorption at the interface (1, 2) and the second, utilizing molecular modeling techniques for quantitatively assessing the relative intensity of surfactant interaction among different surfactant–surface combinations based on completely theoretical computations (3, 4).

We have elucidated the building blocks of the above-mentioned novel paradigm through our recent work in this field (1–4). Design/development and/or selection of surfactants tailor-made for each application is a challenging task. Most of the

industrial surfactants currently being used in the industry are designed by and large, through trial and error methods based on rules of thumb and past experience. With increasing demands of the end users on the efficacy and selectivity of performance chemicals needed for achieving enhanced productivity, quality, and yield in the industry, the biggest challenge facing professionals involved in surfactant design is to reduce the time in developing new products. Currently the search space is also limited since trial and error methodology is indeed expensive both timewise and in terms of resource requirements.

A quantitative methodology for screening out/identifying the appropriate molecular architectures based on determination of the relative efficacy of various structures based on theoretical computations is evidently an economically attractive and elegant option to the conventional approach. Thus, selecting the most promising ones only, for subsequent synthesis, characterization, testing, and pilot plant/plant trials, would certainly save enormous costs in time and efforts to arrive at new formulations. It is in this context that we have been exploring the use of molecular modeling tools for quantifying the interactions of surfactants with mineral surfaces.

Alkyl hydroxamates have been found to be highly selective collectors for a wide variety of flotation separation systems such as those containing iron, rare-earths, tin and tungsten minerals, and kaolin (5–26). Pradip *et al.* (6–8) had reported on the flotation of sparingly soluble calcium minerals with alkyl hydroxamates. The possibility of separation among various calcium minerals, however, using hydroxamate reagents has not yet been explored.

The flotation separation of different calcium minerals from each other is an industrially important area of separation science. Most of calcium minerals such as fluorite (CaF₂), calcite (CaCO₃), fluorapatite [Ca₁₀(PO₄)₆F₂], dolomite [(Ca, Mg)CO₃], and scheelite (CaWO₄) occur in nature in association with each other. Because of their similar surface properties, semisoluble nature, and similar response to conventional fatty acid flotation, the problem of separating one calcium mineral from another still remains unsolved. Any breakthrough in terms of designing a reagent tailor-made for such separation will thus have an obvious industrial impact (2).

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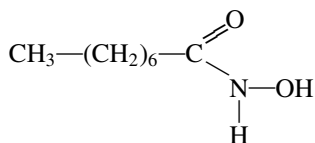
It must be stressed that a number of research investigations in the past have looked at the differences in flotation response (however insignificant those may be) of calcium minerals to selected group of flotation collectors including oleate (27–31). It is, for example, well established that fluorite is the most floatable of all calcium minerals and calcite the least responsive to fatty acid collectors. Fluorite's high affinity for oleate has been attributed to higher density of calcium ions on fluorite surface as compared to calcite (30) and also to fluorite surface being a better template for oleate crosslinking (31). We have attempted to correlate these differences observed during flotation tests in terms of mineral–reagent interactions as quantified through molecular modeling computations.

Several research groups are currently engaged in studying surfactant–surface interactions using molecular modeling tools (3, 4, 31–40). We present in this paper the results of molecular modeling of the interactions of alkyl hydroxamates with three calcium minerals and the correlations of these theoretically computed interaction energies with our own experimental microflotation results on the same system. The excellent correlation observed in our work illustrates the utility of this powerful computational tool in designing highly selective, tailor-made flotation collectors.

MATERIALS AND METHODS

High-purity mineral samples of fluorite, calcite, and fluoroapatite (henceforth referred to as “apatite” in the paper) were procured from Geologist Syndicate (Calcutta, India), Alminrock Indscr (Bangalore, India), and Florida, respectively. The samples were hand crushed and stage ground in a laboratory planetary mill to obtain the desired size fraction, $-48 +65$ mesh for microflotation studies.

Octyl hydroxamic acid (HXMA-8), possessing the following molecular structure, was synthesized and characterized in our laboratory as per the standard method (5).



Microflotation experiments were conducted with 1 g of mineral in a modified Hallimond tube setup (5). The pH of the reagent solutions (solution pH) was adjusted using HNO_3 and NaOH solutions of suitable concentrations. The mineral was conditioned in the reagent solution for 20 min. The equilibrium pH of the solution was measured just before the commencement of the flotation process. Nitrogen gas flow rate was maintained at 40 ml/min. At the end of 1 min of flotation, the concentrate (floated fraction) and tail fractions were collected separately, dried, weighed, and the percentage recovery determined.

MOLECULAR MODELING OF MINERAL–REAGENT INTERACTIONS—THEORETICAL COMPUTATIONS

While all the calcium minerals do form chelate bonds with HXMA-8 on the surface, its interaction with these minerals is remarkably different. We have carried out molecular modeling calculations (quantum chemical and force field) to quantify the relative strength of HXMA-8 interactions with fluorite, calcite, and apatite surfaces.

Quantum Chemical Approach

We have used semiempirical MNDO (MOPAC 6.0) (41) calculations to model the interactions of reagents with mineral surfaces. MNDO (modified neglect of differential overlap) was introduced by Dewar and Thiel (42). It is a self-consistent field (SCF) method that takes into account electrostatic repulsion and exchange stabilization. Due to its semiempirical nature all calculated integrals are evaluated by making approximations such as frozen core approximation or valence electron approximation. These approximations considerably simplify MNDO calculations and it can be used to model much larger molecular systems with reasonable accuracy. It has been parameterized for a range of molecular systems (42–49).

SCF method essentially takes into account the electron–electron repulsion by considering the interaction between an electron in a given orbital and the mean field of the other electrons in the molecule. This involves an iterative process in which each of the electron wave function is optimized with respect to the rest of the electrons from cycle to cycle until the electronic energy reaches a constant minimum value. This situation is described as “self-consistent.” It is also known as Hartree–Fock or single-determinant theory (50).

BFGS technique is a modified Broyden–Fletcher–Goldfarb–Shanno optimization method with minor changes to adapt it for the optimization in chemical systems (51–55).

Octyl hydroxamic acid. The geometry of HXMA-8 was optimized using BFGS method. The optimization criterion for energy was a gradient of 0.1 kcal/mol. The SCF (Self-Consistent Field) convergence criterion was set as 10^{-5} eV.

The optimized structure of HXMA-8 with partial charges on constituent atoms is presented in Fig. 1. The functional group has net negative charge with the electronegative oxygen and nitrogen exposed and the alkyl chain has net positive charge.

Calcium minerals. Cluster models were generated to represent the basal planes, namely, {100}, {110}, and {111}, for all the three minerals. The atom positions were taken from the structural reports of fluorite (56), calcite (57), and apatite (58) based on X-ray studies. The neutral cluster models were two to three layers thick (~ 45 – 50 atoms), possessing the molecular formula $\text{Ca}_{16}\text{F}_{32}$ for fluorite, $\text{Ca}_{10}(\text{CO}_3)_{10}$ for calcite, and $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ for apatite. Semiempirical level calculations using MNDO Hamiltonian (41) were performed to derive the electronic structure. Since the semiempirical parameters for the element Ca are not available in MOPAC 6.0, the Ca was treated as

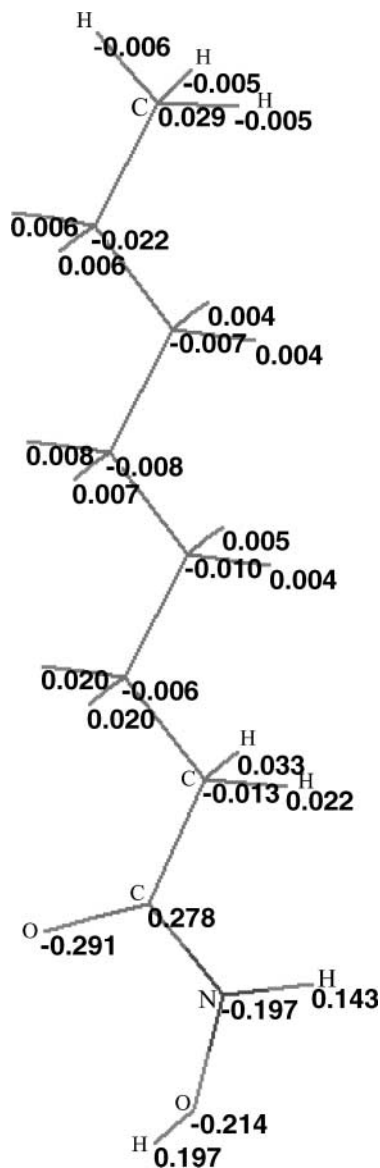


FIG. 1. Optimized structure of HXMA-8 with partial charges on the constituent atoms.

a point charge with two positive charges and as a 100% ionic alkaline earth metal. On the fluorite surface an alternating layer of Ca^{2+} and F^- ions is present. Calcite also has an alternating layer of Ca^{2+} and $(\text{CO}_3)^{2-}$ ions. However, apatite has a complex structure wherein Ca^{2+} and F^- ions are in near planar arrangement, surrounded by $(\text{PO}_4)^{3-}$ tetrahedron.

Mineral-hydroxamate complexes. Initially an adsorption complex was created between HXMA-8 and the mineral surfaces using the molecular graphics method. The criterion was that the interaction between positive centers on the mineral surfaces and negative centers on the molecule should be maximum, while the functional group of the molecule lies over the mineral surface.

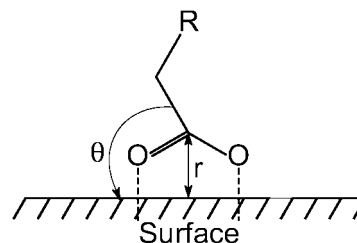


FIG. 2. Schematic representation of the geometry of the adsorption complex.

Since the configuration obtained by molecular fitting is only one of the possible adsorption mode, the configuration was fine tuned and optimized by varying r and θ , as shown in Fig. 2, where r is the shortest distance between mineral surface and the reagent molecule and θ is the angle between the mineral surface plane and the norm of the alkyl chain in the reagent molecule. The optimized conformation thus corresponds to the one with optimum distance r_{opt} and optimum angle θ_{opt} .

However, it should be noted that in order to keep the reference point same, we have defined r as the distance of carbonyl oxygen (O' in $-\text{C}(\text{O}')\text{NHOH}$ functional group) of HXMA-8 molecule from a reference calcium atom at the surface. That is the reason the optimized distance r_{opt} presented in Table 2 appears to be high. The exact distances of the different atoms in the hydroxamate functional group from the surface in the final optimized structure are shown in Fig. 3, wherein $\text{O}-\text{Ca}$ distance between $-\text{NHOH}$ group and surface Ca atoms is within the 1.5- to 3-Å range, that is within the range of chemical bonding (specific interactions).

Force Field Method

Universal force field (UFF 1.02) (59–61), available from molecular modeling program CERIUS-2 (62) from Molecular Simulations, Inc. (USA), was used to model the interaction of HXMA-8 reagent with different calcium mineral surfaces. Though there are many well-parameterized force fields

TABLE 1
Calculated Surface Energies (γ) of Fluorite, Calcite, and Apatite Mineral Surfaces

Mineral	Surface	Surface energy (J/m^2)
Fluorite	{100}	2.9
	{110}	1.4
	{111}	0.8
Calcite	{100}	1.7
	{110}	1.6
	{111}	2.3
	{10 $\bar{1}$ 4}	1.5
Apatite	{100}	1.2
	{110}	1.4
	{111}	3.1

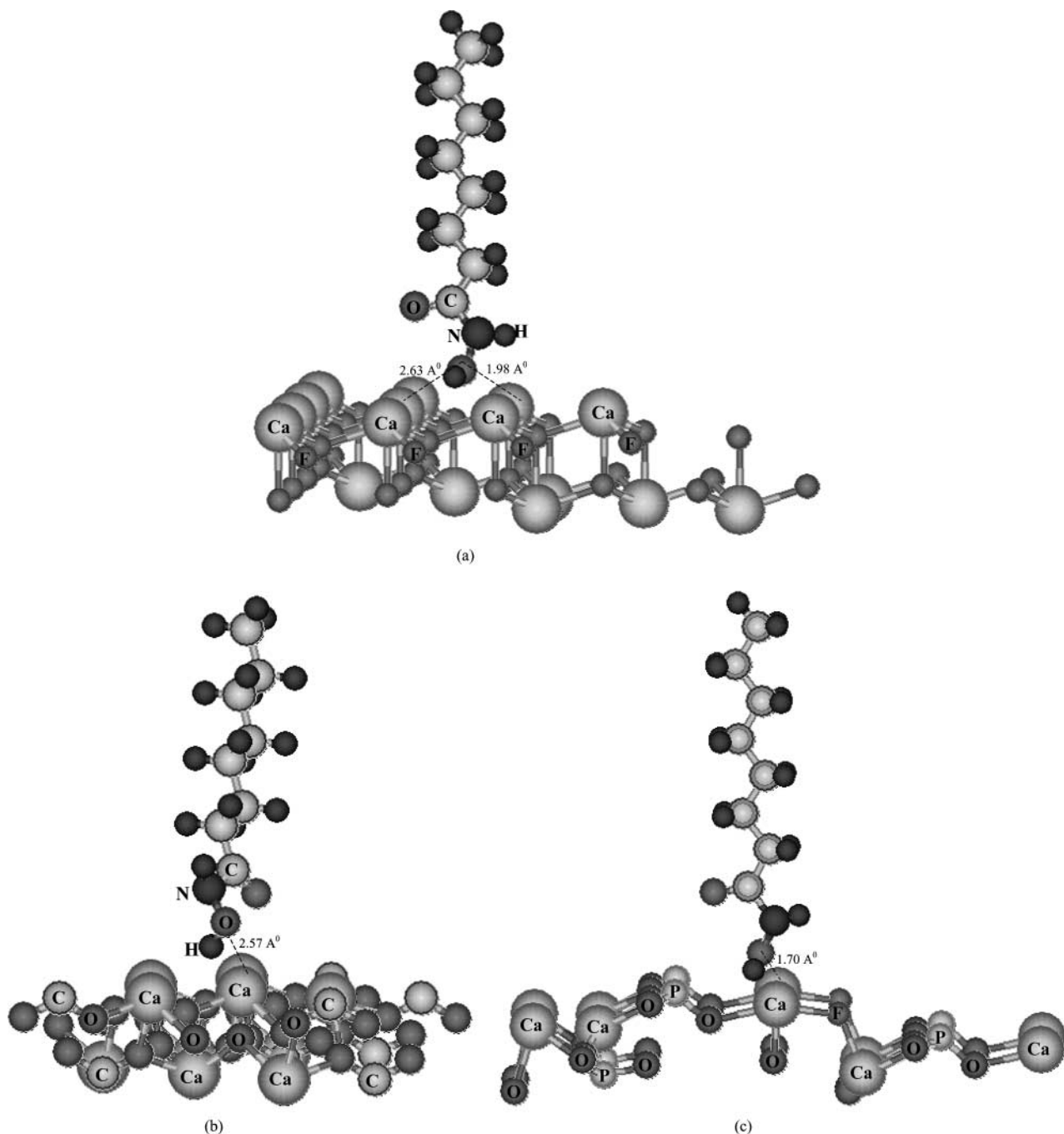


FIG. 3. Optimized complex of HXMA-8 on (a) fluorite {111}, (b) calcite {110}, and (c) apatite {100} surfaces.

(Drieding II, MM2, and CFF) available to model organic and polymer molecules very few can handle inorganic materials such as minerals. We chose to use UFF as it offers a versatile, although approximate, parameterization for a wide range of atoms including calcium, atom of particular interest to this study. Coveney and Humphries (38) have reported their results on UFF computations for the interactions of diphosphonate additives with cement (ettringite) surface. More recently Sieval *et al.* (63) have

used UFF to model the adsorption of alkyl monolayers on silica (111) surface.

Universal force field (UFF) is a purely diagonal and harmonic force field in which bond stretching is described by a harmonic term, angle bending by a three-term Fourier cosine expansion, and torsion and inversion by cosine–Fourier expansion terms. The van der Waals interactions are described by the Lennard–Jones potential and electrostatic interactions

are termed as atomic monopoles and a screened (distance-dependent) coulombic term (59–61).

The molecular modeling methodology followed was similar to that applied by Oliver *et al.* (64). A surface cell was created from the unit cell of mineral at a given Miller plane. Several initial surface cells (pertaining to the cleavage of each Miller plane at different locations) were created. Each of these surface cell was then extended to a periodic super lattice of approximately $25 \times 25 \text{ \AA}$. The cluster obtained from each surface cell was minimized with respect to energy. During optimization the top two layers of the surface cluster were relaxed with respect to energy and the bottom two layers were kept fixed. The stability of the mineral surface was determined by surface energy (γ), which was calculated as per the method described by de Leeuw *et al.* (40). The optimized reagent molecule was docked on this surface cluster and allowed to relax completely. Several initial conformations (~ 20) for the reagent on the surface were considered so as to locate the minimum energy conformation of the complex.

Further, in order to make sure that the surfaces considered for all the calcium containing minerals are morphologically predominant, we used Bravais–Friedel–Donnay–Harker (BFDH) (65) method to calculate the crystal morphology based on a set of geometrical rules. The BFDH-predicted dominant equilibrium faces for fluorite, calcite, and apatite were found to be {111}, $\{10\bar{1}4\}$, and {100}, respectively. These predictions are consistent with experimental finding (66) wherein the cleavage plane for fluorite and apatite is found to be {111} and {100}, respectively. However, for calcite mineral the experimentally observed cleavage plane (66) is {110}, whereas the predicted one is $\{10\bar{1}4\}$. In view of this discrepancy, we modeled the calcite $\{10\bar{1}4\}$ plane as well.

Interaction Energies

The mineral–hydroxamate interaction energy (ΔE), for both MNDO and UFF method, was computed using the following equation:

$$\Delta E = E_{\text{complex}} - (E_{\text{mineral surface}} + E_{\text{reagent}}),$$

where E_{complex} , $E_{\text{mineral surface}}$, and E_{reagent} are the energies of optimized mineral–reagent complex, mineral cluster, and reagent (HXMA-8 or water), respectively. It is worth noting that the more negative magnitude of interaction energy (ΔE) indicates more favorable interactions between mineral surface and the reagent.

RESULTS AND DISCUSSIONS

The surface energies of fluorite, calcite, and fluorapatite mineral surfaces are presented in Table 1. As expected, of the three fluorite surfaces studied, the cleavage plane, that is {111} Miller plane, is also the most stable surface, having the lowest surface energy. For calcite mineral, {110}, the reported cleavage plane (66), and $\{10\bar{1}4\}$, that is, the most stable plane as predicted by

TABLE 2
MNDO Optimized Structures [θ_{opt} (in Degrees) and r_{opt} (in Angstrom)] for HXMA-8 Adsorption on Calcium Mineral Surfaces

Mineral	{100}		{110}		{111}	
	θ_{opt}	r_{opt}	θ_{opt}	r_{opt}	θ_{opt}	r_{opt}
Fluorite	84.0	4.4	105.0	5.5	106.8	3.1
Calcite	104.6	5.3	145.7	5.1	120.0	5.9
Apatite	85.3	4.5	116.1	5.5	103.9	5.1

BFDH method (65), exhibit comparable surface energies. For apatite the cleavage plane {100} was found to have the lowest surface energy.

The MNDO optimized structures of mineral–hydroxamate complexes (only those corresponding to the cleavage plane of the minerals) are shown in Figs. 3a, 3b, and 3c for fluorite, calcite, and apatite, respectively. However, all the three basal crystal planes, namely, {100}, {110}, and {111}, were considered for these computations and r_{opt} and θ_{opt} obtained for the optimized complexes are summarized in Table 2.

The interaction energies for HXMA-8 adsorption on all the three calcium minerals (for three crystal planes) along with corresponding interaction energies for adsorption of water on the same plane are presented in Table 3. It is clear from the magnitude of interaction energies for the reagent as compared to those for water that the HXMA-8 will replace water on all planes of the calcium minerals.

The interaction energies computed by the UFF method were of the same order as MNDO interaction energies and results are summarized in Table 4. Once again, a comparatively lower magnitude of interaction energies for water as compared to that of HXMA-8 indicates that HXMA-8 will replace water from the mineral surface.

Considering that the cleavage planes for fluorite, calcite, and apatite are considered to be {111}, {110}, and {100}, respectively, based on the relative values of corresponding interaction energies (whether using MNDO or UFF) one can predict that the order of flotation response of HXMA-8 toward these minerals should be

$$\text{fluorite} \gg \text{calcite} > \text{apatite.}$$

TABLE 3
MNDO Interaction Energies (kcal mol^{-1}) of HXMA-8 Adsorption onto Calcium Mineral Surfaces as Compared to Water

Mineral	{100}	{110}	{111}
Fluorite	−389.9 (−191.4)	−281.8 (456.6)	−251.2 (286.0)
Calcite	2.5 (20.8)	−121.9 (6.9)	2.1 (90.0)
Apatite	−4.1 (30.0)	−3.2 (20.8)	4.6 (25.4)

Note. The values in brackets are for water.

TABLE 4
UFF Interaction Energies (kcal mol^{-1}) of HXMA-8 Adsorption onto Calcium Mineral Surfaces

Mineral	{100}	{110}	{111}	{10 $\bar{1}$ 4}
Fluorite	-140.4 (-47.6)	-82.6 (-47.2)	-64.6 (-23.6)	
Calcite	-48.7 (-50.0)	-44.0 (-32.2)	-61.3 (-31.0)	-52.4 (-25.6)
Apatite	-43.3 (-42.9)	-43.4 (-44.0)	-29.2 (-26.7)	

Note. The corresponding interaction energies for water are shown in brackets.

Microflotation Tests

Microflotation results on three calcium minerals namely fluorite, calcite, and apatite using HXMA-8 are presented in Fig. 4a. Fluorite responds most favorably and apatite the least. The order of flotation response to HXMA-8 among three minerals was thus observed to be

fluorite \gg calcite $>$ apatite.

A COMPARISON OF THEORETICAL AND EXPERIMENTAL RESULTS

The interaction energies (computed both by MNDO and UFF, respectively) of HXMA-8 on fluorite, calcite, and apatite surfaces (only those corresponding to the cleavage plane of the minerals) are plotted in Figs. 4b and 4c, respectively. The relative order of interaction of HXMA-8 as predicted by molecular modeling is compared with experimental flotation results (Fig. 4a). It is indeed interesting to note that the relative affinity of HXMA-8 with fluorite, calcite, and apatite based on totally theoretical considerations, that is based on quantum-chemical or force-field calculations of mineral–reagent interactions, is the same as observed during flotation of these minerals using HXMA-8.

The excellent correlation between theory and experiment thus indicates that molecular modeling computations can be gainfully employed to assess the relative strengths of interaction of various molecules with mineral surfaces. This remarkable finding also suggests that the interaction of flotation collectors with the mineral surface is the primary discriminatory mechanism controlling selectivity of flotation separation. There are of course a number of other factors such as solvent, pH, solubility, the presence of soluble species in solution, etc., which will influence the selectivity observed in practice. But even in the absence of a suitable methodology to take into account these effects, one is able to predict the order of flotation response. We have observed similar correlations between the theoretical interaction energies computed for surface–reagent complexes with the corresponding macroscopic application related responses for several systems (3, 4). These findings thus increase our confidence in utilizing this approach for the purposes of reagent design.

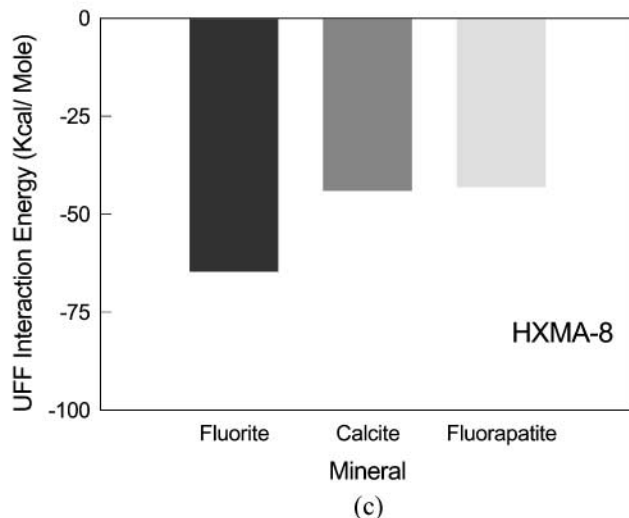
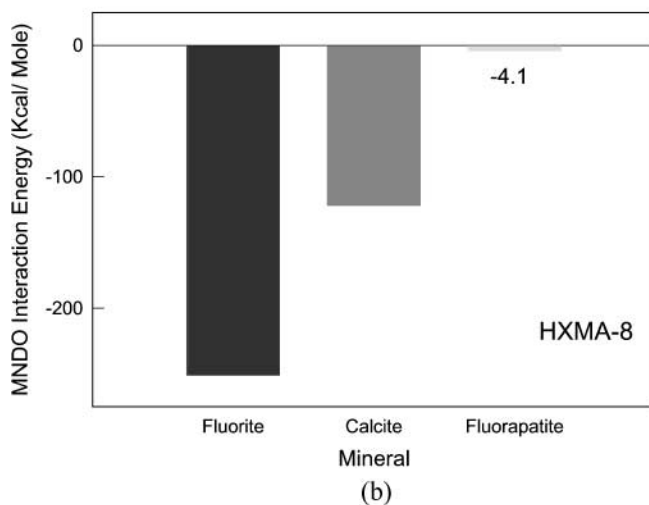
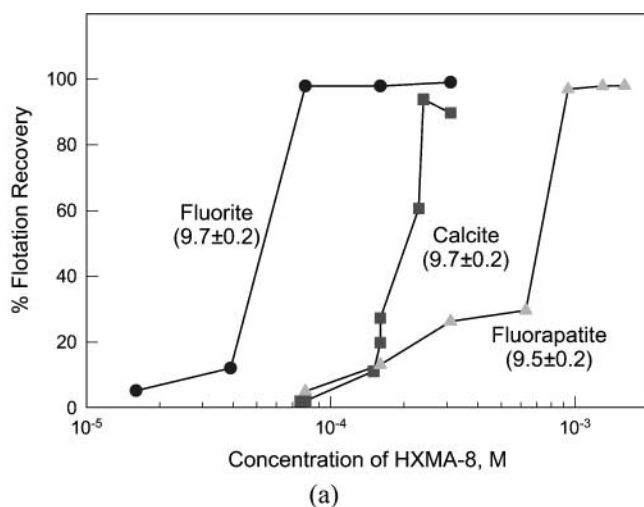


FIG. 4. (a) Recovery of fluorite, calcite, and apatite as function of molar concentration of HXMA-8, (b) MNDO interaction energy, and (c) UFF interaction energy of HXMA-8 on fluorite {111}, calcite {110}, and apatite {100} surfaces.

CONCLUDING REMARKS

The objective of this communication is to illustrate the utility of molecular modeling approach in the design/screening of different molecular architectures for a given separation problem. It is worth noting that the theoretical computations carried out in this work do not require any experimental data. The knowledge of the crystal structure of the surfactant molecule as well as the mineral surface with which it is interacting is sufficient to predict the relative affinity of the particular molecule with different surfaces and/or the relative strength of different surfactant molecules for a given surface. Tremendous implications of this finding in the design/development of surfactant molecules for targeted application are thus obvious. Theoretically computed interaction energies can be used to optimize the molecular architecture of a surfactant molecule for a given application.

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