2.6 First-principles calculations

This study utilized first-principles calculations to investigate the adsorption configurations of α-SMA on the surfaces of fluorite and calcite, as well as the structures of various monovalent α-sulfonate group stearic acid (α-SSA$^-$) anions and divalent α-SSA^{2-} anion. The adsorption energies of α-SMA on fluorite and calcite surfaces, along with the energies of various α-SSA$^-$ anions and α-SSA^{2-} anion, were computed. Based on these results, the difference in adsorption affinities of α−SMA on fluorite and calcite are examined, and an explanation is provided for the significantly weaker collecting ability of α-SMA in calcite flotation.

These calculations were carried out using Vienna Ab-initio Simulation Package (VASP). Generalized Gradient Approximation (GGA) was employed for exchange-correlation functional, utilizing Perdew-Burke-Ernzerhof (PBE) formulation with projector augmented wave (PAW) potentials. A plane-wave cut-off energy of 400 eV was used for the adsorption configuration optimization of α-SMA on mineral surfaces. The Gaussian smearing method with a width of 0.05 eV was applied. Reciprocal space sampling was performed using a gamma-centered (2×2×1) Monkhorst-Pack k-point grid. The convergence criteria for electronic and geometric steps were set to 10^{-4} eV and 0.05 eV·Å^{-1}, respectively. For the adsorption energy calculations of α-SMA on mineral surfaces, a higher plane-wave cut-off energy of 500 eV was used, and tetrahedron method with Blöchl corrections was applied. Energy convergence was achieved to below 10^{-5} eV. Based on previous studies [1-3], the (111) surface of fluorite and the (104) surface of calcite are the most commonly exposed surfaces of these minerals and were therefore selected for this study. The fluorite surface model was generated by cleaving the optimized crystal cell along (111) direction. The (111) surface model of fluorite has dimensions of 15.58 Å × 15.58 Å × 4.77 Å, consisting of 32 Ca^{2+} ions and 64 F^- ions. Similarly, the calcite surface model was generated by cleaving the optimized crystal cell along (104) direction. The (104) surface model of calcite has dimensions of 17.21 Å × 14.95 Å × 4.86 Å, including 24 Ca^{2+} ions and 24 CO_3^{2-} groups. To prevent interactions between the top and bottom layers of atoms in the mineral surface models during the optimization of α-SMA adsorption configurations, a vacuum layer with a thickness of 30 Å or 15 Å was introduced.

In the aqueous solution of α-SMA, two types of monovalent anions can be formed. First, the carboxyl group can dissociate a proton (H+) to form a monovalent α-SMA anion. Second, the sulfonate group can also dissociate a proton (H^+) to form a negatively charged α-SMA anion. To determine which type of anion is more stable and present in higher concentration, first-principles calculations were performed on the two types of monovalent α-sulfonic acid-stearic acid (α-SSA−) anions to compute their energies. The anion with the lower energy and more stable structure was identified. The calculation were carried out using Gaussian software, with PBE0 functional, def2tzvp basis set, and Grimme D3 dispersion correction with Becke-Johnson damping to account for long-range van der Waals interactions.

References

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