Multiscale molecular simulations applied to enhanced oil recovery: low salinity in carbonates

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Nowadays, one of the most promising and cost-effective enhanced oil recovery (EOR) processes is the so-called low-salinity water injection (LSWI). However, the underlying molecular mechanisms involved in LSWI for EOR are underexploited and poorly understood. Several physical and chemical processes occurring concomitantly at the complex interface formed among brine, oil, and rock can influence the EOR efficiency.

Here, a combination of first principles calculations and atomistic simulations was used and coupled with reservoir simulators. In this context, molecular simulations provide a much-needed characterization of the geochemical reactions, as well as the thermodynamic and kinetic properties involved in the intra-aqueous reactions. It has been shown to be a suitable alternative for the study of reaction mechanisms, since it allows the separation of the variables and observing the system's properties of interest.

In this work, we study i) the ionic exchange reactions energy of several minerals ($CaSO_4$, $MgSO_4$, $BaSO_4$, Na_2CO_3 and calcite itself $CaCO_3$) ii) the adsorption brine ions (Ca^{2+}, CO_3^{2-}, Cl^- and Na^+) energy iii) organic molecules with different functional groups, and in different protonation states adsorbed on calcite and iv) the incorporation of divalent ions (SO_4^{2-}, Ba^{2+}, and Mg^{2+}) in carbonate matrix. The calculations were carried out using LAMMPS and QUANTUM ESPRESSO codes, respectively,

Our results suggest the equilibrium system to the ions Ca_2^+ and CO_3^{2-} being on brine and calcite mineral, the adsorption of other ions (Na^+ and Cl^-) is not a spontaneous path and requires high energies estimated as 10 and 50 kcal.mol^{-1}, respectively. The adsorption energies were higher for aniline at higher pHs and smaller for the deprotonated cases, the desorption processes would be favored. Also, it was observed that the pH affects the calcite dissolution since the free energy variation (ΔG) of the dissolution process mediated by H_3O^+ is lower than the ΔG for the neutral pH process. The energetics of the ionic incorporations, in both calcite and aragonite, is most favorable for the SO_4^{2-} than for the Mg^{2+}. The Ba^{2+} showed unfavorable incorporation energy. From the molecular modeling, we could provide accurate input parameters for the large-scale reservoir simulators, thus, improving their accuracy. Therefore, the molecular modelling approaches can be an efficient tool to optimize the EOR via LSWI.