



## Ab initio based model for subsurface flow and wettability alterations at reservoir condition for variation in ionic composition for carbonates

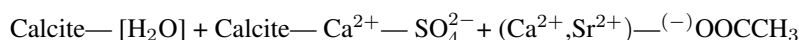
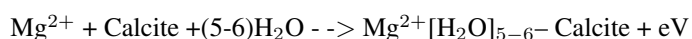
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Through both field and laboratory studies it has been well established that wettability and flow rate in carbonate and sandstone reservoirs during water flooding is dictated by the sub-surface chemistry connected to stability of the water film amidst the oil phase and the rock surface, but there is no mathematical model to explain the flow rate and wettability mechanism on insertion of a low saline water in the rock system and its interaction with the hydrocarbons.

Here, a model for calculating the feasible surface reactions has been developed based on free energy profiles of the different combinations of water, metal (Calcium, strontium and Magnesium) ions and hydrocarbons over a temperature regime of 273 K to 373 K. The approach uses Density Functional Theory based Local Density Approximation on molecular dynamic simulation using standard plane wave pseudopotential scheme. Herein we observe a two shell model during the interaction of water molecule with free energy of -2.8 and -2.5 kJ/mol at 2.4 and 4.2 Å heights from the calcite surface.  $Mg^{2+}$ -water complex also retains a two layer model, while  $Ca^{2+}$  and  $Sr^{2+}$  metal ion-water complex show one major layer model of the free energy profile. The metal ion-water cluster adsorbs as an inner sphere complex directly above a surface carbonate group at a height of 3.9, 4.1, and 4.2 Å for calcium, strontium and magnesium respectively at a temperature of 273 K, which is almost at the same height of the outer shell (4.2 Å) of bulk water profile and thus provides a local energy well for interaction among the complexes. Moreover at this height  $Mg^{2+}$  shows significantly more stability than water or other metal ion complex and it retains a similar pattern of energy profile at temperatures upto 373 K while outer shells lose their structure at higher temperatures in other metal ion complexes.

A series of calculations were conducted to achieve the most stable polar hydrocarbon-metal ion-water complex for each metal individually. A free energy profile was also developed for polar hydrocarbon-Metal ion-water complex ( $CH_3COO^{(-)}-M^{2+}-[H_2O]_n$ ). Herein the two layer model was observed with  $Ca^{2+}$  and  $Sr^{2+}$  while the inner shell was still inconsistent with the 4.2 (i.e. 3.9 to 4.4) Å local energy well model, the outer shell was observed near 6 Å. While with  $Mg^{2+}$  one major shell free energy model was obtained with several minor variations with changing temperature. Here the  $Ca^{2+}$  complex was significantly more stable being the only complex with a negative energy profile around 4.2 Å. Further these observations were together investigated to propose a wettability and flow rate model at on the surface described as:



A large part of the work also includes the categorical rejection of many other possible structures, complexes and clusters formations. The model abides to all the experimentally observed points both in field and lab in wettability alteration, and enhanced oil recovery, and through these energy variations the model categorically explains the effect of temperature on the flow behavior. This model provides a new view to the activity of  $Mg^{2+}$  in surface chemistry for carbonate rock structures in general and can have application in study of erosion, corrosion and other fields as well. This is the first comprehensive mathematical model to extensively explain the low salinity behaviors observed in enhanced oil recovery from a microscopic level to the best of our knowledge.