Molecular Dynamics Study on Wettability Alteration of Minerals for Low Salinity EOR

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Low Salinity Waterflooding (LSWF) is an Enhanced Oil Recovery (EOR) method to recover crude oil by injecting low salinity water (~1500 ppm), which can result in 5 to 20 % additional recovery [1]. The mechanism of LSWF has been widely discussed and it is believed that wettability alteration plays an important role. It was shown that the presence of cations induce partial water wetting, and the resulting wettability is cation specific [2,3]. In this study, we investigated interfacial adsorption structures induced by four different cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) in oil-water-mineral interfacial system by molecular dynamics (MD) simulation.

We employed two approaches: free energy and direct approach caluculations. In free energy calculation, we studied the stability of model acidic oil molecules ($C_9H_{19}COOH$ or $C_9H_{19}COO^-$) adsorbed on muscovite surface in aqueous solution by using potential of mean of force (PMF) calculations. In direct approach calculation, we performed MD simulations for oil/brine/mineral systems, where aqueous solution thin film was sandwiched by oil and muscovite.

Interestingly, it is found that Ca^{2+}-covered muscovite surface significantly enhances the adsorption of $C_9H_{19}COO^-$ in aqueous solution as revealed by the adsorption Gibbs energy [4], which can clearly explain the recent experimental findings [2]. Furthermore, we find clear evidence that Ca^{2+} and K^+ cause cation bridging, whereas Mg^{2+} and Na^+ cause water bridging at muscovite surface from free energy calculation. From direct approach calculation, we find that more cation-carbonxalte pairs are formed within the aqueous solution thin film in the case of Mg^{2+} than any other cations in our work. This result can be related to the unexplained mechanism of wettability alteration by Mg^{2+} [3]. A difference between two approaches is noted by bridging type of oil molecules on Na^+-muscovite. It is shown that Na^+, K^+ and Ca^{2+} cause cation bridging, and Mg^{2+} causes water bridging. Further study is ongoing for direct evaluation of wettability (*i.e.* calculation of the contact angle). The insight obtained in these studies will lead us to optimal design of LSWF for EOR.

[1] RezaeiDoust A. *et al.* (2009) *Energy & Fuels* **23**, 4479.
[2] Mugele F. *et al.* (2015) *Sci. Rep.* **5**, 10519.
[3] Haagh, M. E. J. *et al*. (2017) *Langmuir* **33**, 3349.
[4] Kobayashi K. *et al*. (2017) *J. Phys. Chem. C* **121**, 9273.