Cation specific bridging of acid oil on muscovite surface: Improved description of low-salinity EOR

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Origin of enhanced oil recovery by low-salinity water flooding (LSWF) is still controversial. It is because crude oil/brine/mineral interactions are sensitive to ionic composition and concentration of injection and formation water [1]. Cation bridging is crucial to explain the ionic composition dependence. Atomic force microscopy experiments measuring adhesion force between sandstone and -COOH/-COO^- covered tip imply that the cation bridging (e.g. COO^-–Ca^{2+}–Clay) is responsible for the decrease in the adhesion force under low-salinity conditions [2]. It agrees with the results of core flooding and wettability experiments [3,4]. That is, Ca^{2+} and Mg^{2+} in formation water are essential for wettability alteration and additional oil recovery by LSWF, whereas Na^+ is not. In short, cation bridging is cation specific and it affects efficiency of LSWF. These observations have not been well explained by structures of cation bridging in molecular scale and by stability of the structures depending on cations. In this paper, we implemented molecular dynamics simulations in order to reveal structures and stability of the oil molecules ($C_9H_{19}COOH$ or $C_9H_{19}COO^-$) adsorbed on muscovite surfaces in aqueous solution. The muscovite surfaces are covered by different cations (Na^+, K^+, Mg^{2+}, Ca^{2+}). Structural analysis of the adsorbed oil molecules and evaluation of the adsorption free energy revealed that; (i) Presence of Ca^{2+} on muscovite surface significantly enhances the adsorption of $C_9H_{19}COO^-$, (ii) Ion specific effect is hardly observed when carboxyl group is protonated (i.e. $C_9H_{19}COOH$), (iii) Ca^{2+} and K^+ cause cation bridging, whereas Mg^{2+} and Na^+ cause water bridging. These findings well explain the results of the core flooding and wettability experiments [3,4]. Our study provide molecular basis of crude oil/brine/mineral interactions in reservoirs.

[1] RezaeiDoust *et al.* (2009) *Energy and Fuels* **23**, 4479-4485. [2] Hassenkam *et al.* (2011) *Colloids Surf., A* **390**, 179-188. [3] Lager *et al.* (2008) *Petrophysics* **49**, 28-35. [4] Mugele *et al.* (2015) *Sci. Rep.* **5**, 10519.