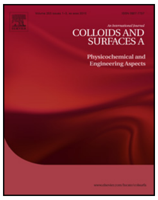
Colloids and Surfaces A: Physicochem. Eng. Aspects 482 (2015) 290–299

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



Effect of Ca^{2+}, Mg^{2+} and $SO_4{}^{2-}$ ions on the zeta potential of calcite and dolomite particles aged with stearic acid

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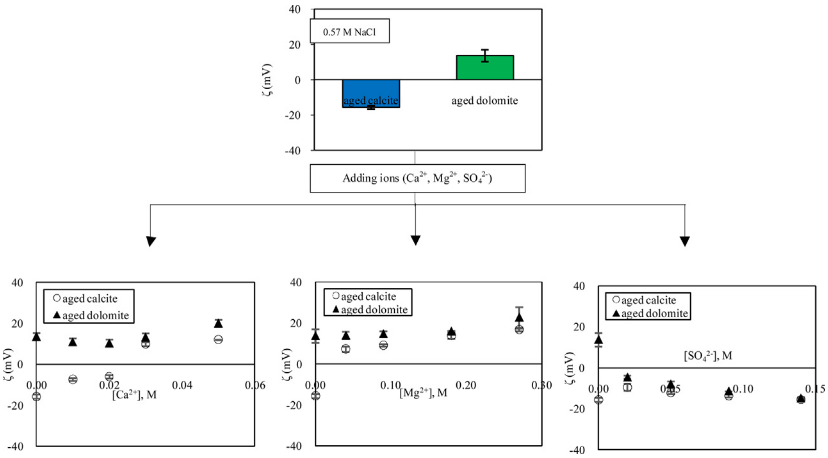
HIGHLIGHTS

- Zeta potential of two carbonate crystals aged with stearic acid was studied.
- Zeta potential was evaluated in deionized water and in saline brines.
- Mg^{2+} and $SO_4{}^{2-}$ ions have stronger effect on the zeta potential of both samples.
- Surface dissolution has a significant effect on the zeta potential of aged calcite.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 December 2014
Received in revised form 12 May 2015
Accepted 15 May 2015
Available online 17 June 2015

Keywords:
Zeta potential
Carbonate rocks
Wettability
Potential determining ions
Carboxylic materials
Dissolution

ABSTRACT

We report a detailed investigation of the effects of Ca^{2+}, Mg^{2+} and $SO_4{}^{2-}$ ions on the zeta potential of calcite and dolomite particles aged with stearic acid. Suspended in deionized water, the native and aged calcite particles have negative zeta potentials while the dolomite particles have positive zeta potentials. Our studies using optical and atomic force microscopy clearly show rhombohedral shapes on cleaved calcite chips when contacted by deionized water. On dolomite chips, however, no clear rhombohedral shapes are found. Increasingly higher concentration of divalent Ca^{2+} and Mg^{2+} ions increased the original positive zeta potential of the aged dolomite particles and altered the zeta potential of the aged calcite from negative to positive. The $SO_4{}^{2-}$ ions caused the original negative zeta potential of the aged calcite to be more negative and altered the zeta potential of the aged dolomite from positive to negative. Zeta potential measurements showed the affinity of Ca^{2+}, Mg^{2+} and $SO_4{}^{2-}$ ions is affected by the presence of other potential determining ions. The presence of Mg^{2+} ions significantly affects the ability of $SO_4{}^{2-}$ ions to modify the original surface charges of aged calcite and aged dolomite while the presence of Ca^{2+} ions has less significant effect on the negative surface charges developed by $SO_4{}^{2-}$ ions.

Abbreviations: ζ, zeta potential; AFM, atomic force microscopy; ASTM, American society for testing and materials; EDS, energy dispersive spectroscopy; IEP, isoelectric point; PDI, potential determining ion; PZC, point of zero charges; SEM, scanning electron microscopy; TAN, total acid number (mg KOH/g); TDS, total dissolved solids (g/l); XRD, X-ray diffraction.

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http://dx.doi.org/10.1016/j.colsurfa.2015.05.043
0927-7757/

1. Introduction

During the last two decades, increasing number of research and several pilot field trials proved that substantial amount of oil could be recovered from sandstone and carbonate oil reservoirs by injecting optimized water. The water is optimized only in terms of salinity and ionic composition. Researchers developed a variety of water flooding techniques, such as low salinity water flooding (LoSal), Water-Based Enhanced Oil Recovery (WEOR), Smart Water flooding, Advanced Ion Management (AIM) and Dynamic Water flooding. In carbonate reservoirs, improving the water wetness of the rock surfaces is believed to be one of the responsible mechanisms for the observed incremental oil recovery [1–5].

Carbonate mineral surfaces are believed to be positively charged due to high concentration of cations in the formation brine. This will form a positively charged interface attracting excess negative charges at the adjacent brine. In parallel, when the crude oil comes in contact with the formation brine, dissociation of the organic polar compounds will create negatively charged interfaces which attract an excess of positive charges at the adjacent brine [6,7]. Electrostatic attractions between the positively charged mineral/brine interfaces and the negatively charged crude oil/brine interfaces will create an unstable water films which eventually collapse and allow negatively charged polar compounds to come into contact with the active adsorption sites on the mineral face [8]. Carboxylic acids (with straight and cyclic chains) are strongly bound to the cations on the carbonate surfaces and create a preferential oil-wet condition at the pore surfaces together with the other polar organic compounds present in the crude oil such as asphaltenes [9–13].

The wettability of a reservoir is directly related to the surface electrical properties of the rock/water/oil interfaces [14–16]. Strand et al. [17] used zeta potential measurements to investigate the relative affinity of Ca^{2+} and SO_4^{2-} ions towards a chalk surface in order to support their findings from spontaneous imbibition and chromatographic adsorption experiments. They observed that desorption of negatively charged carboxylic materials is triggered by the co-adsorption of SO_4^{2-} and Ca^{2+} ions. They also recognized that the relative concentration of Ca^{2+} and SO_4^{2-} ions and temperature affect the overall mechanism. In a similar context, Zhang et al. [18–20] studied the interplay between Ca^{2+}, Mg^{2+} and SO_4^{2-} ions towards chalk samples using spontaneous imbibition, zeta potential and chromatographic adsorption tests. They concluded that co-adsorption of the three potential determining ions (PDIs) increases the water wetness of the chalk surface by displacing adsorbed carboxylic material. CO_3^{2-}, H^+ and OH^- are also reported as potential determining ions toward carbonate surfaces [21,22]. Hiorth et al. [15] developed a chemical model that couples aqueous and surface chemistry and used it to predict some of the reported zeta potential and adsorption experiments by Strand et al. [17] and Zhang et al. [18–20]. They concluded that dissolution of the chalk minerals better explains the reported incremental recoveries by spontaneous imbibition compared to the changes in the surface charges. Gomari et al. [23] investigated the effect of adsorbed stearic acid on the contact angle and the zeta potential of calcium carbonate. They found that adsorbed carboxylic acid shifted the original surface charges from positive to negative; and that Mg^{2+} and SO_4^{2-} ions are able to displace the adsorbed stearic acid as evidenced from measured changes in the zeta potential. Jackson and Vinogradov [7] measured the streaming potential of carbonate core samples saturated with high salinity formation brine and natural crude oil. They showed that changes in wettability led to a measurable changes in the zeta potential; and that the wetting state of the carbonate during low salinity water flooding could be quantified by streaming potential measurements. Alotaibi et al. [24,25] assessed the zeta potential of limestone, dolomite and crude oil particles in different aqueous brines with varied salinity and ionic content. They showed that changing the rock surface charges from positive to negative would increase the water wetness of the carbonate surface; and that the increased magnitude of the zeta potential in the low salinity brines is due to the expansion of the electrical double layers. Yousef et al. [26,27] studied the effect of using diluted seawater on the oil recovery from carbonate, and found that diluted seawater increased the magnitude of the negative surface charges of carbonate rock particles. Very recently, Mahani et al. [28] investigated the underlying mechanism for improved oil recovery from carbonates during low salinity water flooding using contact angle measurements, geochemical modeling and zeta potential measurements. They showed that changes in the carbonates surface charges are responsible for altering the wettability towards less water wet which enhances the recovery of oil.

From the aforementioned studies, it is clear that assessing the electrokinetic (zeta; ζ) potential of the carbonate rocks is a useful tool in explaining the interactions between the reservoir's pore surface, the adsorbed organic compounds and the potential determining ions present in the injected water. The current study reports the results of a zeta potential investigation on two common carbonate crystals (calcite and dolomite) aged in stearic acid and conditioned in a wide range of aqueous brines with varied concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-} ions. The ultimate objective of this paper is to understand the effect of Ca^{2+}, Mg^{2+}, and SO_4^{2-} ions and their ratios on the surface charges of the aged carbonates at atmospheric conditions to identify the main PDIs.

2. Experimental

2.1. Materials

2.1.1. Calcite and dolomite crystals

Iceland spar calcite crystals from Creel, Chihuahua, Mexico and dolomite crystals from Butte, Montana (both purchased from Ward's Natural Science) were used. Mineralogical purity of both crystals was confirmed by X-ray diffraction (XRD) analysis on fine powders and by scanning electron microscopy (SEM), coupled with energy dispersive spectroscopy (EDS), on cleaved chips. The calcite sample showed very high purity (~100% $CaCO_3$) while small percentages of quartz and ankerite (<3 wt%) were detected in the dolomite sample.

2.1.2. Model oil

Model oil was used to represent the oil phase in all experiments in the current study. 5 g of stearic acid ($CH_3(CH_2)_{16}COOH$) were dissolved in ~493 g of toluene (which served as non-polar organic solvent) to develop a stock of model oil with a calculated total acid number (TAN) of 2 mg KOH/g. The mixture was stirred for 24 h to make sure the stearic acid has dissolved in the toluene. To verify the calculated TAN, a color-indicator titration test was conducted on the prepared model oil according to the ASTM Standard D974-12 [29]. A value of TAN = 1.95 mg KOH/g was measured, which is in good agreement with the calculated TAN. The model oil was made from high purity materials purchased from Sigma-Aldrich (>98.5% and ~99.8% purity for stearic acid and toluene, respectively).

2.1.3. Brines

Synthetic brines were prepared based on the ionic composition of the Arabian Gulf water using chemical reagents (NaCl, $CaCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$, Na_2SO_4, $NaHCO_3$) purchased from Pan-Reac, and deionized water produced by a Barnstead Ultrapure Water System which has a resistivity of 18.6 MΩ cm at 23 °C. Table 1 summarizes the ionic composition of the Arabian Gulf water [30]. The concentration of each ion was increased alone and in the presence of another PDI to enable assessing the individual and the