Characterisation of Surface Electrical Charge and Wettability in Carbonates with Application to Controlled Salinity Waterflooding*

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Abstract

It is well known that the wetting behavior of carbonate mineral surfaces is affected by their surface electrical charge (Strand et. al., 2006; Hiorth et. al., 2010) and that the surface charge in saturated porous media can be characterized using measurements of streaming potential (Jouniaux and Pozzi (1995); Delgado et. al., 2007). Streaming potentials in porous media arise from the charge separation that occurs in the electrical double layer at mineral-fluid interfaces (Hunter, 1981). If the fluid is induced to flow by an external potential (pressure) gradient, then some of the excess charge within the double layer is transported with the flow, giving rise to a streaming current. Divergence of the streaming current density establishes an electrical potential, termed the streaming potential. The closest plane to the mineral surface at which flow occurs in the double layer is termed the shear plane; the electrical potential at this plane is termed the zeta potential.

The relationships between streaming potential and surface electrical charge, and between surface electrical charge and wettability, suggest that measurements of streaming potential may be used to probe the wetting state of mineral surfaces in intact core samples. Previous studies have measured streaming potential in core samples saturated with oil, and with oil and brine, but the samples had not been aged to alter their wetting behavior (Alkafeef et. al., (2001); Alkafeef and Alajmi (2006); Vinogradov and Jackson (2001). Consequently, the relationship between streaming potential and wettability has not been investigated. Yet if streaming potential measurements, and the electrical properties interpreted from these measurements such as zeta potential and surface electrical charge, are affected by wettability in a direct and quantifiable manner, then streaming potential measurements may be of great utility in characterizing wettability and processes that affect wettability. The aim of this paper is to determine whether wettability alteration in carbonate core samples leads to measurable changes in streaming potential.

Method

We used two carbonate samples with very similar transport properties, and began by confirming that the streaming potential coupling coefficient, zeta potential and excess charge transported by the flow in clean, brine saturated samples were identical within experimental error. The properties of the samples and brine are given in Table 1 and Table 2. We then drained both samples to the irreducible saturation

by injecting crude oil. Sample 1 was then aged at 93°C and 6.9MPa confining pressure for 8 weeks, to alter its wettability; sample 2 was not aged. Brine was then injected into both samples until the residual oil saturation was reached. The streaming potential coupling coefficient, zeta potential and excess charge transported by the flow were measured again and compared. The crude oil used in the experiments has been observed to alter wettability in these carbonate samples in previous studies, but its composition cannot be reported for commercial reasons.

Results

The values of streaming potential coupling coefficient obtained from the experimental results, along with interpreted values of zeta potential and excess charge transported by the flow, are summarized in Figure 1. The streaming potential coupling coefficient, zeta potential and excess charge transported by the flow of both the clean, brine saturated samples are identical within experimental error, which is consistent with the similarity of the porosity, permeability and electrical conductivity (Table 1). The streaming potential coupling coefficient and zeta potential of the non-aged sample 2 at the residual oil saturation, are also identical to the values obtained from the clean, brine saturated samples within experimental error, although the excess charge transported by the flow is significantly larger in magnitude. This is consistent with the results of Vinogradov and Jackson (2011), who obtained values of the streaming potential coupling coefficient in water-wet sandstone samples at the residual oil (undecane) saturation, which were identical within experimental error to values obtained from the same samples saturated with brine. The streaming potential coupling coefficient and zeta potential of sample 1 at the residual oil saturation are both interpreted to be zero, which is clearly different from the positive values obtained in the other three experiments. However, the large experimental error bars association with the coupling coefficient and zeta potential of sample 1 at the residual oil saturation encompasses the values obtained in the other experiments. Regardless of this, the excess charge transported by the flow in sample 1 at the residual oil saturation is clearly different, both from the clean, brine-saturated samples, and from sample 2 at the residual saturation.

Discussion

The positive values of zeta potential we observe for both samples when saturated with brine, and sample 2 when saturated with brine and residual oil, are consistent with the positive values measured previously on natural and artificial calcite samples in equilibrium with brine of similar pH with added Ca ions. They are also consistent with the predicted values of zeta potential obtained from the model of Guichet et. al. (2006) at pH 6.3, obtained for Ca ion concentrations in the range 0.5-1.3x10-3M. In the experiments reported here, the presence of Mg and SO_4 ions in the brine is likely to have further affected the surface charge. Zhang and Austad (2006) measured the zeta potential of chalk in equilibrium with 0.573M NaCl brine containing various concentrations of Mg (as $MgCl_2$) and SO_4 (as Na_2SO_4), and observed that the zeta potential was negative in the pure NaCl solution, but became increasingly positive with increasing Ca or Mg concentration, and increasingly negative with increasing SO_4 concentration. The pH was held constant at 8.4. Strand et al. (2006) observed similar behavior. The positive values of potential observed in this study reflect the brine pH and the relative concentrations of Ca, Mg and SO_4 ions (Table 2).

Classically, the pH at which zero zeta potential is observed in sample 1 at the residual oil saturation would be interpreted to represent the iso-electric point, at which the net charge at the shear plane is zero (e.g. Delgado et. al., 2007). However, that is not the interpretation we adopt here. Instead, we suggest that some areas of the mineral surfaces in sample 1 became oil-wet after aging, and some remained water-wet (Figure 2). In water-wet areas, the mineral surfaces were never in contact with oil, so the original mineral-brine interfaces and associated

double layers are preserved. The positive values of zeta potential we observe for both samples when saturated with brine, and sample 2 when saturated with brine and residual oil, suggest that the original (water-wet) mineral-brine interfaces are positively charged. However, in oil-wet areas, the mineral surfaces are in direct contact with the oil, and electrical double layers form at the oil-brine interface. Consequently, the electrical double layers at the mineral-brine interface are no longer continuous throughout the pore-space, which significantly reduces the excess electrical charge transported by the flow of brine. Moreover, although we cannot directly interpret the charge on the oil-brine interface from the results we present here, previous studies have found that it is typically negatively charged (Beattie and Djerdjev, 2004). Hence, it is likely that the zeta potential at water-wet pore surfaces is positive; yielding an excess negative charge in the adjacent brine, but the zeta potential at oil-wet pore surfaces is negative, yielding an excess positive charge in the adjacent brine (Figure 2). Thus in sample 1, saturated with brine and residual oil after aging, different regions of the pore-space have excess charge of different sign (and concentration) transported by the flow.

The excess charge density transported by the flow of brine in both samples at the residual oil saturation is clearly different, and is different from the value observed in the clean samples saturated with brine (Figure 1). Previous models have suggested that the excess charge density transported by flow in water-wet porous media increases as the brine saturation decreases, consistent with our results (e.g. Jackson, 2010; Revil et. al., 2007). However, these models were developed to describe primary drainage (brine saturation decreasing from the fully saturated initial state); as yet, no model has been presented to predict the variation in excess charge density with brine saturation during imbibition in oil-brine displacements (brine saturation increasing). Moreover, comparable experimental data are rare; most previous studies report streaming potential measurements during primary drainage of brine under air from unconsolidated sand packs (e.g. Revil et. al., 2007; Allègre et. al., 2010). Only Vinogradov and Jackson (2011) have measured streaming potential during primary drainage of brine by oil to the irreducible brine saturation, followed by brine injection to the residual oil saturation, and they investigated water-wet sandstone samples with rather different transport properties to the carbonate samples we consider here. Nevertheless, they also found that the excess charge density transported by the flow of brine was larger in magnitude at the residual oil saturation than at full brine saturation, consistent with our results. Jackson (2010) argued that the excess charge density transported by the flow of brine increases with decreasing brine saturation in water-wet porous media, because wetting brine layers are present even in pores occupied by oil. These wetting layers host the electrical double layer within which the excess charge resides. Consequently, the total excess charge within the pore-space remains approximately constant regardless of brine saturation, so the excess charge density transported by the flow of brine increases as the brine saturation decreases.

In contrast to sample 2, the excess charge transported by the flow in sample 1, which was aged prior to brine injection, is significantly smaller in magnitude at the residual oil saturation. As discussed above, we interpret this to reflect the variation in sign and concentration of excess charge in water- and oil-wet regions of the pore-space. Jackson (2010) suggested that the density of excess charge decreases in magnitude with decreasing brine saturation in oil-wet porous media, but used a model in which the pore-surfaces are uniformly oil-wet, for which the magnitude of the predicted change in excess charge with brine saturation is much lower than observed here. Further work is required to understand the variation in excess charge with brine saturation during imbibition, and at oil- or mixed-wetting conditions. Nevertheless, our results demonstrate that aging carbonate samples with crude oil leads to measurable changes in the streaming potential coupling coefficient, zeta potential and, in particular, excess charge transported by the flow of brine. This latter parameter has not been calculated in most previous studies, which focused instead on interpreting streaming potential measurements to yield estimates of the zeta potential [see Delgado et. al., (2007) for a review]. However, here we find the most clearly expressed contrast between the clean, brine-

saturated samples, the aged sample 1 at residual oil saturation, and the non-aged sample 2 at residual saturation, is exhibited by the excess charge transported by the flow of brine. This is interpreted from measurements of the streaming potential coupling coefficient, brine permeability, and the electrical resistivity of the saturated sample. Each of these parameters is sensitive to wettability.

Measurements of streaming potential, supported by measurements of permeability and electrical conductivity, could therefore be used to probe the surface electrical charge properties of carbonate (and sandstone) core samples saturated with brine and crude oil. The results could be used to quantify the wetting state, and to determine if and how changes in surface charge and wetting state are responsible for improved oil recovery during controlled salinity waterflooding. Previous studies have measured zeta potential on powdered carbonate samples in aqueous solutions without crude oil present and at laboratory conditions (e.g. Strand et. al., 2006; Hiorth et. al., 2010; Vdovic 2001; Thompson and Pownall, 1989; Cicerone et. al., 1992; Zhang and Austad, 2006), or oil recovery from intact core samples at reservoir conditions by imbibition or waterflooding with brine of varying composition, without measuring the streaming potential (e.g. Strand et. al., 2006; Hiorth et. al., 2010; Zhang et. al., 2007). Consequently, the relationship between surface charge/zeta potential, wettability and oil recovery has not been investigated using an integrated experimental approach. Streaming potential measurements are useful, because they yield key surface electrical properties such as specific charge and zeta potential, and can be obtained whilst measuring recovery and other multiphase flow properties during oil-brine displacements in intact core samples at reservoir conditions.

Conclusions

Our results suggest that aging carbonate samples in crude oil leads to measurable changes in the streaming potential coupling coefficient, zeta potential and excess charge transported by the flow of brine. Consequently, measurements of streaming potential could be used to probe the surface electrical charge properties of carbonate (and sandstone) samples saturated with brine and crude oil. The results may be used to quantify the wetting state; they may also to determine if and how changes in surface charge and wetting state are responsible for improved oil recovery during controlled salinity waterflooding. In the experiments reported here, aging of sample 1 caused some areas of the mineral surfaces to become oil-wet. This disrupted the continuity of the double layers at the mineral-brine interface, thus significantly reducing the excess electrical charge transported by the flow of brine, yielding zero streaming potential coupling coefficient, zeta potential and excess charge transported by the flow, within experimental error.

Acknowledgements

References

Alkafeef, S., R.J. Gochin, and A.L. Smith, 2001, The effect of double layer overlap on measured streaming currents for toluene flowing through sandstone cores, Colloids and Surfaces A: Physiochemical and Engineering Aspects, v. 195, p. 77-80.

Alkafeef, S.F., and A.F. Alajmi, 2006, Streaming potentials and conductivities of reservoir rock cores in aqueous and non-aqueous liquids, Colloids and Surfaces A: Physiochemical and Engineering Aspects, v. 289, p. 141-148.

Allègre V., L. Jouniaux, F. Lehmann, and P. Sailhac, 2010, Streaming potential dependence on water-content in Fontainebleau sand: Geophysical Journal International, v. 182, p. 1248-1266.

Beattie, J.K., and A.M. Djerdjev, 2004, The Pristine Oil/Water Interface: Surfactant-Free Hydroxide-Charged Emulsions: Angewandte Chemie, v. 116, p. 3652-3655.

Cicerone, D.S., A.E. Regazzoni, and M.A. Blesa, 1992, Electrokinetic Properties of the Calcite/Water Interface in the presence of magnesium and organic matter: Journal of Colloid and Interface Science, v. 154, p. 423-433.

Delgado, A.V., F. Gonzalez-Caballero, R.J. Hunter, L.K. Koopal, and J. Lyklema, 2007, Measurement and interpretation of electrokinetic phenomena: Journal of Colloid and Interface Science, v. 209, p. 194-224.

Guichet, X., L. Jouniaux, and N. Catel, 2006, Modification of streaming potential by precipitation of calcite in a sand-water system: laboratory measurements in the pH range from 4 to 12: Geophysical Journal International, v. 166, p. 445-460.

Hiorth, A., L.M. Cathles, and M.V. Madland, 2010, The Impact of Pore Water Chemistry on Carbonate Surface Charge and Oil Wettability: Transport in Porous Media, v. 85/1, p. 1-21.

Hunter, R. J., 1981, Zeta Potential in Colloid Science: Academic Press, New York, 386 p.

Jackson, M.D., 2010, Multiphase electrokinetic coupling: Insights into the impact of fluid and charge distribution at the pore-scale from a bundle of capillary tubes model: Journal of Geophysical Research, v. 115/B07206, 17 p.

Jouniaux, L., and J.P. Pozzi, 1995, Streaming potential and permeability of saturated sandstones under triaxial stress: consequences for electrotelluric anomalies prior to earthquakes: Journal of Geophysicl Research, v. 100, p. 10197-10209.

Revil, A., N. Linde, A. Cerepi, D. Jougnot, S.K. Matthai, and S. Finsterle, 2007, Electrokinetic coupling in unsaturated porous media: Journal of Colloid and Interface Science, v. 313, p. 315-327.

Strand, S., E.J. Høgnesen, and T. Austad, 2006, Wettability alteration of carbonates-Effects of potential determining ions (Ca and SO4) and temperature: Colloids and Surfaces A: Physiochemical and Engineering Aspects, v. 275, p. 1-10.

Thompson, D.W., and P.G. Pownall, 1989, Surface electrical properties of calcite: Journal of Colloid and Interface Science, v. 131, p. 74-82.

Vdovic, N., 2001, Electrokinetic behaviour of calcite - the relationship with other calcite properties:Chemical Geology, v. 177, p. 241-248.

Vinogradov, J., and M.D. Jackson, 2011, Multiphase streaming potential in sandstones saturated with gas/brine and oil/brine during drainage and imbibition: Geophysical Research Letters, v. 38/L01301, 7 p.

Zhang, P., and T. Austad, Wettability and oil recovery from carbonates: Effects of temperature and potential determining ions, Colloids and Surfaces A: Physiochemical and Engineering Aspects, v. 279, p. 179-187.

Zhang, P., M.T. Tweheyo, and T. Austad, Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of potential determining ions Ca, Mg and SO4, Colloids and Surfaces A: Physiochemical and Engineering Aspects, v. 301, p. 199-208.
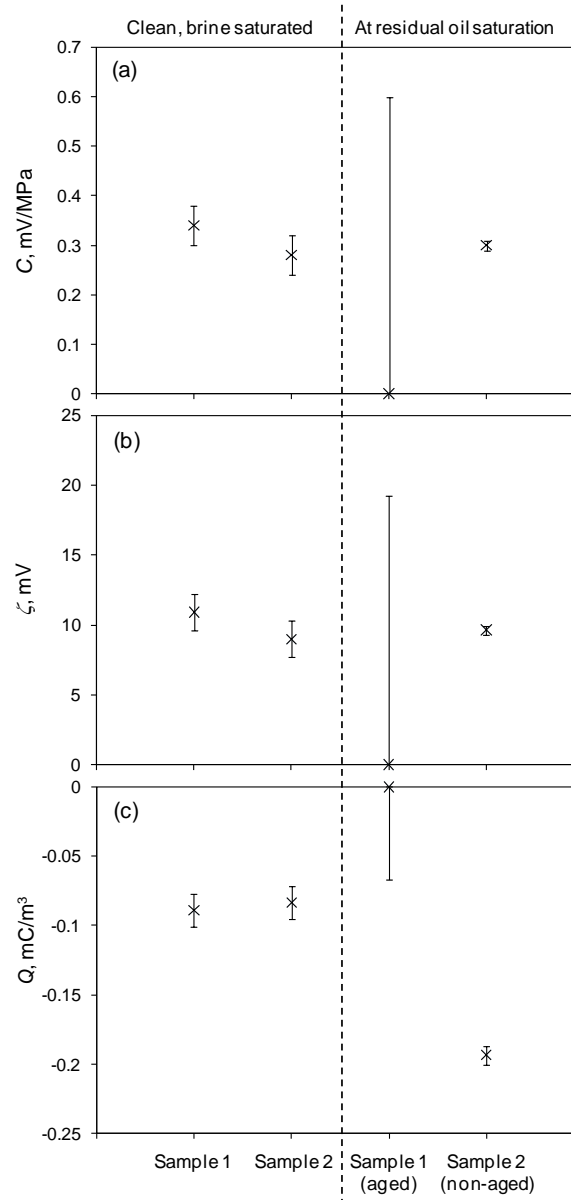
Figure 1. Summary of the (a) streaming potential coupling coefficient, (b) zeta potential and (c) excess charge transported by the flow, obtained for each sample, saturated with brine, and saturated with brine and residual oil.
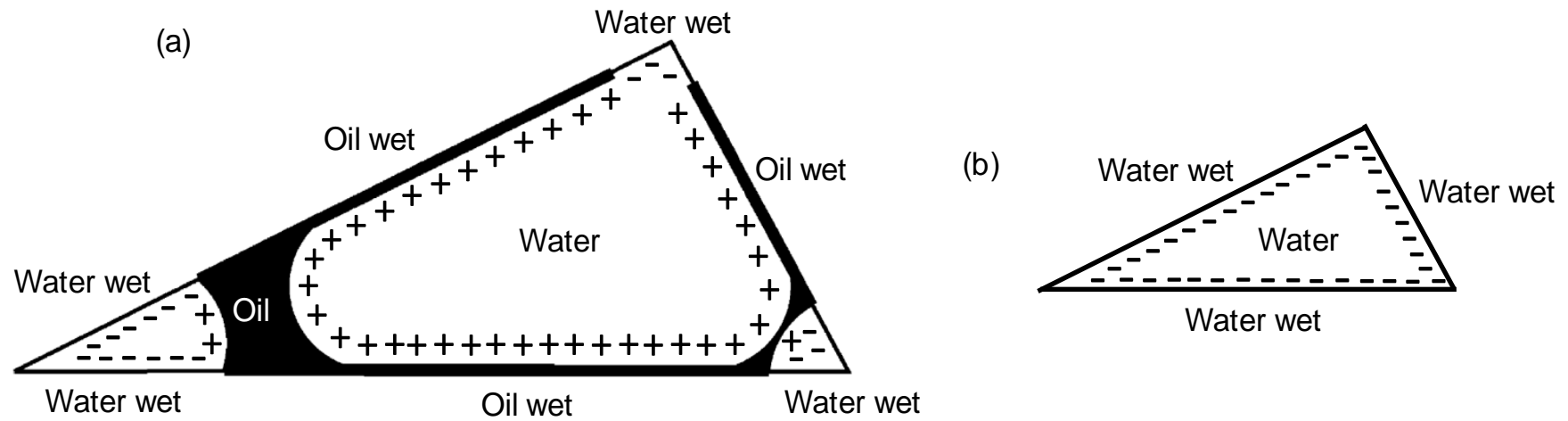
Figure 2. Schematic showing postulated wettability alteration in sample 1 after aging and brine injection to the residual oil saturation. Pores are shown as simple triangles. Mineral-brine interfaces are positively charged, yielding an excess of negative charge in the adjacent brine; oil-brine interfaces are likely to be negatively charged, yielding an excess of positive charge in the adjacent brine. (a) Large pores are occupied by oil after primary drainage. The mineral surfaces become oil-wet after aging, except for corners and crevices where oil does not penetrate, due to the curved nature of the oil-water interface. Injected brine then occupies the centre of the pores. (b) Small pores are not invaded by oil during primary drainage, due to the high capillary entry pressure. The mineral surfaces remain water-wet.

	Sample 1	Sample 2
Porosity (%)	20.2 (±0.7)	19.9 (±0.7)
Permeability (mD)	2.91 (±0.08)	2.46 (±0.08)
Conductivity (S/m)	0.63 (±0.01)	0.61 (±0.01)
Irreducible water saturation (S_{wi})	0.35 (±0.05)	0.38 (±0.05)
Residual oil saturation (S_{orw})	0.32 (±0.05)	0.31 (±0.05)
Permeability at 1-S_{orw} (mD)	0.80 (±0.08)	0.53 (±0.08)
Conductivity at 1-S_{orw} (S/m)	0.07 (±0.01)	0.28(±0.01)

Table 1. Properties of the carbonate plug samples, saturated with the brine described in Table 2, including experimental error (in brackets).

Compound	Amount (g)	Concentration (M)
NaCl	116.025	2.02
$CaCl_2.2H_2O$	51.944	0.35
$MgCl_2.6H_2O$	9.496	0.0467
$NaHCO_3$	0.477	5.68×10^{-3}
Na_2SO_4	0.356	2.51×10^{-3}
Water	821.703	
Total	1000	2.18

Table 2. Brine composition used in the experimental study. The brine remained at pH 6.3 in all experiments.