Introduction

Recently, many researchers dedicated effort and resources to investigate different methods and additives that could improve the performance of water flooding. Among these methods, modifying the composition of the injection water seems very compelling given its similarity to a normal waterflooding (Yousef et al., 2011), hence a relatively low cost. The success of the modified salinity waterflooding (MSW) is normally evaluated in the laboratory by performing core flooding experiments. However, these tests do not reveal the mechanisms responsible for the additional oil recovery. Complementary experimental procedures (i.e., spontaneous imbibition, chromatographic wettability, adsorption, zeta potential or rock mechanics measurements) are usually carried out to get a deeper insight into this improved oil recovery (IOR) method. These experiments show that the interactions taking place in the crude oil/brine/rock system lead to different mechanisms that are not necessarily exclusive. Identifying and quantifying these physicochemical interactions is especially important for developing mechanistic models, which are necessary for predicting and assessing the performance of MSW at the field scale. Up to now, most published models for MSW in carbonates are built upon a wettability alteration mechanism. The change in the wetting conditions is reflected in the models by a shift in the relative permeability curves between water-wet and oil-wet states by means of an interpolating factor.

The models proposed for MSW can be divided into two main categories. The first category includes the simpler non-compositional models, i.e., models that do not account for the different ions and their interactions in water. In this case, the interpolation usually depends on the salinity of the injected water (Jerauld et al., 2008) or on the adsorption of salt (single component of the water phase) on the rock surface (Yu et al., 2008). However, the total salinity does not dictate the success of the MSW in carbonates (Mahani et al., 2017), thus, it cannot be the cause of wettability alteration nor the additional oil recovery. The models in the second category account for the specific composition of water. These models initially included water-rock interactions, e.g., dissolution and precipitation and relate the shift in the relative permeabilities with the amount of dissolved calcite, adsorbed sulfate, or precipitated anhydrite (Evje and Hiorth, 2010; Andersen and Evje, 2012). Nowadays, the most refined models additionally include an explicit description of the adsorption of ions at the mineral-water and water-oil interfaces.

The development of numerical models that consider mineral-water and water-oil interactions was assisted by the increased number of surface complexation models (SCM) proposed in the context of MSW. These thermodynamic models give a mathematical description of the adsorption at the interfaces between two phases (one aqueous phase) following an equilibrium approach, representing a useful tool in reactive transport modelling. All SCMs rely on some basic common fundamentals, being the electrostatic model the contrasting element. Different electrostatic models have been proposed: constant capacitance (CC), diffuse layer (DL), Basic Stern, triple layer (TL), and charge distribution multisite complexation (CD-MUSIC). A review and a description of their mathematical implementation can be found in (Goldberg, 1992). Many of these models were initially introduced to describe the iron oxides-water interface. These formulations began to be used in the context of MSW in carbonates by adjusting them to the specific case of calcite. One of the first SCM proposed for calcite in the context of MSW for carbonates was a DL model proposed by (Hiorth et al., 2010). (Brady et al., 2012) proposed later two DL for both the calcite-water and water-oil interfaces. This model showed only qualitatively the distribution of species at the calcite surface at different pH and it was not tested against any experimental measurements. Despite that, this model promoted considerably this line of research. Many authors proposed later DL models with different reactions and equilibrium constants (Eftekhari et al., 2017; Mahani et al., 2017; Song et al., 2017) or more novel descriptions of the calcite-water interface (Yutkin et al., 2018). Later, (Eftekhari et al., 2018) compared the zeta potential prediction of a CD-MUSIC (Wolthers et al., 2008), Basic Stern (Heberling et al., 2011), and DL (Song et al., 2017) models for calcite. Even though only the latter model was proposed purposely for MSW applications, the work of Eftekhari et al. concluded that the CD-MUSIC model showed the best match to the zeta potential data reported for chalk (Zhang et al., 2007; Zhang and Austad, 2006). Although fewer than the calcite-water SCMs, models to describe adsorption at the oil surface were also proposed (Bonto et al., 2019b; Brady et al., 2012; Takeya et al.,...
The DL model with the surface reactions proposed by Brady et al. is probably one of the most used thermodynamic model for modeling different experimental data in the context of MSW (Korrani and Jerauld, 2019; Qiao et al., 2016; Sanaei and Sepehrmoori, 2018). Although to a lesser extent, the CD-MUSIC model was also used in the modeling work of (Bonto et al., 2019a; Taheri et al., 2019).

The models that use SCM to describe the interactions at the calcite-brine and brine-oil interfaces provide a broader range of options to describe the wettability alteration. (Brady et al., 2012) proposed a parameter called “bond product sum” (BPS) to interpolate between the relative permeability curves at water-wet and oil-wet conditions. This parameter represents the sum of oppositely charged pair products at the mineral-brine and brine-oil interfaces, depicting in a very elementary way the electrostatic pair abundance. A lower number of bond product pairs reflects a higher separation between the interfaces (more water-wet conditions). Later, this concept gained popularity and was further used in many subsequent publications and showed a correlation with contact angle measurements (Xie et al., 2018). (Qiao et al., 2016) defined a reaction with a corresponding SCM between the protonated calcium sites and the negative polar sites at the oil surface. The wettability interpolant is given by quantifying this interaction as a chemical equilibrium. (Sanaei and Sepehrmoori, 2018) calculated the disjoining pressure from the contribution of electrostatic, attractive, and structural forces. From the disjoining pressure, they inferred a microscopic contact angle that they used for the interpolation of the relative permeability curves. On the other hand, (Korrani and Jerauld, 2019) showed that there is only an insignificant change in the microscopic contact from disjoining pressure calculations; therefore these cannot be used to model the wettability alteration. They suggested a new interpolant, named wetting film “stability number” (SN), to describe mathematically the wettability alteration. This stability condition of the wetting layer represents the ratio of electrostatic forces to van der Waals forces, reflecting the minimum stable electrical potential. (Bonto et al., 2019a) proposed a new wettability interpolator named “available adsorption sites” (AAS) based on the electrical potential at the calcite-brine and brine-oil interfaces and the available sites present at the calcite surface for adsorption of deprotonated organic acids and protonated bases.

Although all these reported approaches for the wettability alteration upon injection of MSW are well documented, there is still a lack of systematic testing of these interpolators against existing experimental data. If a consistent model for wettability alteration is desired, the interpolant used for updating the relative permeability curves should correlate with at least a qualitative wettability indicator. Moreover, most of the models reviewed above fail at explaining the wettability alteration observed in the experiments on chalk. Thus, in this work, we will assess the correlation of some of the proposed wettability interpolants with the remaining oil saturation from spontaneous imbibition tests on chalk.

**Method and Theory**

The wettability of a rock-brine-crude oil system has a great impact on the hydrocarbon production because it dictates the distribution of oil and water within the reservoir. This property is commonly quantified by contact angle measurements, Amott, and USBM tests. The wettability can also be assessed only qualitatively through spontaneous imbibition (SI) tests. A core can be considered more or less water wet depending on the imbibed volume of brine (Anderson, 1986). Many authors performed SI tests with different brine compositions (i.e., Fathi et al., 2010; Zhang et al., 2007; Zhang and Austad, 2006). For the specific case of chalk, these tests are performed on outcrop samples that are brought to desired wettability conditions through an aging procedure. The outcome of the imbibition test will be highly dependent on the aging procedure that sets the initial wettability conditions.

In this work, we assess the correlation of some of the interpolators proposed in the literature and the remaining oil saturation from SI tests (we assume that at the end of these tests the imbibition capillary pressure is zero and oil is no longer produced). The interpolators that we check against different experimental datasets are the BPS (Brady et al., 2012), SN (Korrani and Jerauld, 2019), and AAS (Bonto et al., 2019a). To quantify these parameters we rely on the CD-MUSIC model introduced by (Wolthers et al., 2008) that showed a good prediction of the zeta potential for chalk, and the oil-brine
DL model proposed by (Bonto et al., 2019b). We implement these two models in PHREEQC. For the SI tests, we assume equilibrium conditions for the systems rock/initial brine/oil and rock/imbibing brine/oil. Thus, we compute the values of BPS, SN, and AAS at initial and final equilibrium conditions and we define a ratio between these values. We show their correlation with the remaining oil saturation from the SI tests carried out by (Zhang and Austad, 2006) (Figure 1).

Among the three interpolators, AAS ratio shows the strongest correlation with the residual oil saturation from these SI tests. The SN ratio shows a slightly better performance than the BPS. However, it has the additional drawback that it can take both negative and positive values. In their publication, Korrani and Jerauld imposed an unjustified restriction on the minimum and maximum SN (between 0.1 and 2) allowable in the calculations. They also reported that their approach was not successful at explaining the improved oil recovery observed in chalk by (Zhang and Austad, 2006) or (Fathi et al., 2010).

Conclusions

The success of MSW in carbonates does not rely only on decreasing the salinity of the injection water. Thus, in mathematical models, changing the relative permeability curves as a function of salinity cannot describe the improved oil recovery observed in carbonates, specifically in chalk. Among the different interpolants proposed in the literature, AAS shows the best correlation with the remaining oil saturation from SI tests performed on chalk.

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References