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Role of Rock Surface Charge in the Carbonated Water Flooding Process

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SUMMARY

Carbonated Water Flooding (CWF) is an alternative EOR method where an oil reservoir is flooded with carbonated (CO2-enriched) water. It is a promising solution for improving oil recovery that benefits from oil viscosity reduction, an increase in oil relative permeability and enhancement of oil mobility. At the same time CWF is a possible mitigation option for the increasing carbon dioxide concentration in the atmosphere and a chance for safe disposal of CO2 underground. We present Bentheimer sandstone surface charge behavior, mainly as a function of the CO2 concentration, in an aqueous solution. To investigate the electrokinetic properties of Bentheimer surface, the coupling coefficient and zeta potential are measured in a streaming potential experiment. The results show that the zeta potential can vary over at least one order of magnitude with different salinities and different CO2 concentrations. It strongly depend on both pore fluid concentration and pH, as well as a set of mineral and temperature specific electrochemical parameters.

The results are base case results for the determination of surface behavior of Bentheimer sandstone with presence of oil. The results of the conducted experiment have an application in planning CWF processes, monitoring CO2 sequestration and streaming potential measurements in reservoirs.
Introduction

Carbonated Water Flooding (CWF) is an alternative EOR method where an oil reservoir is flooded with carbonated (CO$_2$-enriched) water. It is a promising solution for improving oil recovery that benefits from oil viscosity reduction, an increase in oil relative permeability and enhancement of oil mobility. At the same time CWF is a possible mitigation option for the increasing carbon dioxide (CO$_2$) concentration in the atmosphere and a chance for permanent and safe disposal of CO$_2$ underground. We present Bentheimer sandstone surface charge behaviour in an aqueous solution (water and brine) with and without CO$_2$. Literature data regarding reservoir surface charge measurements of Bentheimer, especially in aqueous electrolyte containing significant amounts of carbon dioxide, are limited. To investigate the electrokinetic properties of Bentheimer surface, the coupling coefficient and zeta potential are measured in a streaming potential experiment.

Theory

The efficiency of CWF (both oil recovery and CO$_2$ trapping) is related to the sensitivity of the reservoir minerals to any changes in the solution properties. This phenomenon is indirectly dependent on the rock surface charge (Schramm et al., 1990). Variations in the surface charge and wettability may lead to inter alia adsorption or/and chemical mobilization (Linghtelm et al., 2009). The rock wettability depends on the stability of an aqueous film between rock surface and oil (Hirasaki, 1997). Furthermore, stability of aqueous films is a function of the electrical double layer (EDL) repulsion. EDL repulsion is created as a result from surface charge of solid/water and water/oil interfaces. If a mineral surface is in contact with a solution of an electrolyte, it gives rise to an electric potential, $\psi_0$, at the surface, and a decreasing potential, $\psi$, as we move through the bulk solution away from the surface. With respect to that two regions are of primary importance: the Stern layer and a diffuse layer (outside the Stern region). In the case of liquid, which flows along charged solids due to the applied external force (pressure gradient), movement of the diffuse layer relative to the solid surface occurs. The relative movement of molecules takes place at a surface of shear (or shear plane or slipping plane). It is an imaginary surface that is located not directly at the interface but outside the Stern layer on a distance $\delta$ away from the surface. For practical reasons, it is assumed to be identical to the Stern surface. With regard to this fact the potential at the Stern layer is defined as the actual potential influencing the behaviour of the charged species. However, as this potential cannot be measured directly, the zeta ($\zeta$) potential is often considered as an adequate substitute. Therefore, the zeta potential and surface charge are the value that are typically used to characterize the electrical properties of the surface. Zeta potential measurements may characterize the effective surface charges due to the fact that it is derived from the actual surface charges modified by the molecules and ions which are dragged along with a particle as it moves in a solution.

Experimental determination of $\zeta$ potential and surface charge

The electrokinetic properties of Bentheimer: surface charge and zeta potential were determined in a streaming potential and potentiometric titration experiment. The measurements were conducted with a use of laboratory sets ups that are shown in Figure 1(a-b).

Streaming potential experiment

A measurement sequence of streaming potential consisted of applying different flow rates of an aqueous solution through a sample. Simultaneously, streaming potential and differential pressure were continuously recorded. Additionally the conductivity of electrolyte (before and after the sample) was measured when the flow had been terminated. This procedure was repeated for various Bentheimer samples, electrolytes and pH values.
Figure 1 The coupled experimental set up for study on surface charge and surface potential (a) streaming potential setup; (b) potentiometric titration setup.

The potentiometric titration experiment
The potentiometric titration is conducted for ascertaining the exact volume of titrant (0.1M HCl or 0.1M NaOH). It is chemically equivalent to a given amount of another substance, either blank electrolyte (H₂O or brine) or a given amount of Bentheimer sandstone dissolved in a electrolyte. The solution of a given mass of Bentheimer dissolved in electrolyte was stirred with a teflon magnetic stirrer for 24h before the experiment was started. The acid/base properties of mixtures were investigated before starting the main experiment. The pH values of different rock fractions showed that the Bentheimer sandstone increased the pH of the mixture (see Table 1). The potentiometric titrations were performed in a nitrogen atmosphere (constantly stirred) by adding small equal amounts of HCl or NaOH to the solution cell. The pH data were recorded at certain time lapses (5min) after switching off the stirrer. During that time, the mixtures were continuously stirred, which allowed achieving the equilibration of the solution at any stage of the experiment.

Table 1. The pH values of different rock fractions dissolved in the electrolyte (after 24h of stirring).

<table>
<thead>
<tr>
<th>solid</th>
<th>pH (electrolyte: 100 ml of H₂O)</th>
<th>pH (electrolyte: 100 ml of 2.2 mol/dm³ NaCl solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No solid</td>
<td>5.6</td>
<td>6.2</td>
</tr>
<tr>
<td>0.5 g Bentheimer</td>
<td>6.67</td>
<td>7.08</td>
</tr>
<tr>
<td>5g Bentheimer</td>
<td>8.62</td>
<td>8.87</td>
</tr>
<tr>
<td>10 g Bentheimer</td>
<td>9.10</td>
<td>9.35</td>
</tr>
</tbody>
</table>

Examples of results
Figures 2 and 3 show a typical example obtained from the streaming potential experiments data. They represent a plot of streaming potential measurements against the corresponding pressure difference for Bentheimer sandstone. A linear regression applied to those data creates a value of the streaming potential coupling coefficient. Figure 3a shows the calculated from measured data zeta potential against corresponding flow rate. The zeta potential values are in the same range as the values reported for Bentheimer in literature. Stoll (2005) presented the value of zeta potential between 20-40 mV. Values obtained in our experiment have a negative sign, because the potential difference measurement goes downstream with the flow.
Figure 2 Streaming potentials generated by pressure drop for the core test (a) SAMPLE 1: deionized water, $T=20^\circ C$, pH=7.62; (b) SAMPLE 2: deionized water, $T=20^\circ C$, pH=4.70.

Figure 3 Streaming potentials generated by pressure drops for the core test (a) SAMPLE 3: deionized water, $T=18^\circ C$, pH=6.88 (b) Calculated zeta potential vs. pH for presented sample.

Figure 4 (a) Potentiometric titration of Bentheimer sandstone dissolved in deionized water (Experimental conditions $T = 22 \, ^\circ C$) (b) Surface charge density $\sigma_0$ and sample dissolution effect $\Delta n_{H^+}$ for Bentheimer in deionized water.
Figure 4a represents the raw results obtained from potentiometric titration. The experimental data represent the consumption curves. They indicate that the acid consumption occurs as a result of creation of surface electric charge (adsorption of ions, dissociation of surface groups) and dissolution and/precipitation (Janusz, 1999). The assumption was made that the electrolyte solution is saturated with dissolved sample. Based on the raw results, the point of zero charge and the differences in acid/base consumption balance were obtained (pHzpc=8.5). As the common intersection point (CIP) of the consumption curves lies very close to electrolyte titration curve, but not on it (figure 4a) it indicates that additional aspects like: solid dissolution or occurrence of impurities need to be considered in this pH range when surface charge was computed. Subsequently, data were used to calculate surface charge and acid/base consumption for sample dissolution (figure 4b).

Conclusions

The results show that the zeta potential can vary over at least one order of magnitude with different initial concentrations of electrolyte. It mainly depends on pore fluid concentration and pH, and as well on a set of electrochemical constants that are constant for a given mineral and a given temperature. The potentiometric titration experiment showed that the surface becomes negatively charge at pH values higher than 8.5. Then the repulsion of clays should occur. The obtained results shows that there is a difference between point the pHpc obtained by potentiometric titration and isoelectric point (iep) obtained by streaming potential measurements. This can be the result of the heterogeneity of Bentheimer sandstone (Quast, 2012). The presence of silica cementation in the Bentheimer sandstone may influence the surface properties measured by streaming potential. The iep value lies between the iep values of mineral components (minerals that compose Bentheimer and possess extreme values are quartz <3, hematite (8.5 – 10), calcite (9.5- 10) (Kosmulski, 2002).

The obtained results are base case results for the determination of surface behaviour of Bentheimer sandstone with presence of oil. The data from the conducted experiments have an application in planning CWF processes, monitoring CO2 sequestration and streaming potential measurements in reservoirs.

References


