Polymer adsorption at the brine/rock interface: the role of electrostatic interactions and wettability

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Abstract

Injection of polymers that selectively reduce the water permeability can be used to control water production from oil or gas wells. Because this method relies on the adsorption of a polymer layer onto the rock surface, a deeper understanding of the relevant polymer/rock interactions is of primary importance in order to develop reliable chemical selection rules for field applications. In this paper we study the role of electrostatic interactions and wettability in the adsorption of water-soluble polymers bearing differently charged groups onto solid surfaces of siliceous nature. By means of static adsorption tests, we show that the adsorption is dominated by the electrostatic interactions between the polymer molecules and the solid surface. We also show that lithology, brine composition and wettability are critical parameters that can influence the adsorption behavior at a brine/rock interface. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Controlling water production in mature hydrocarbon fields is an increasing concern to oil companies. Typical drawbacks caused by excessive water production include reduced well productivity, costs associated with the disposal of produced water, and premature well abandonment (particularly in gas fields).

Many water shutoff technologies (like cement squeeze and injection of polymer gels) are available to control water production without expensive work-overs, but they require identification and isolation of the water-producing zones in order to eliminate the risk of damaging the hydrocarbon-bearing layers.

Injection of water-soluble polymers into oil or gas producing formations can be an effective way to control water production where conventional water shutoff technologies cannot be applied (Zaitoun and Kohler, 1989; Zaitoun et al., 1990, 1991, 1992). These treatments usually consist in the injection, into all open intervals, of a dilute water-based solution containing a polymer that adsorbs onto the rock surface during shut-in. The adsorbed polymer layer changes the flow properties of the treated rock and determines a selective reduction of the water permeability. Applying these treatments is relatively simple...
and inexpensive, and the risk of impairing the permeability of the hydrocarbon producing layers is small.

However, field tests have generally been carried out in the absence of well-defined rules for candidate and chemical selection (Moffitt, 1993). This trial-and-error approach has hindered the development of this technology, and is responsible for the modest success ratio and the difficulties in interpreting field-test results. In our judgment, a necessary condition for reliable application of this technology in the field is the development of understanding-based candidate selection and chemical selection rules.

Some of the basic issues concerning polymer adsorption in porous media and its effect on fluid flow properties have already been covered, in the framework of polymer flooding technology, by Hirasaki and Pope, 1974. They postulate in their paper that the permeability reduction observed after a polymer treatment is caused by an adsorbed polymer layer that reduces pore throat radii, and derive a dimensionless pore reduction group that correlates the permeability reduction factor with the polymer, brine and rock properties. The potential of watersoluble polymers as water shutoff agents has prompted a renewed interest in the subject in more recent years. Research studies that have helped to define some general issues that are critical at different scales in the reservoir, i.e.:

- a significant polymer adsorption onto the rock surface is a necessary condition for treatment success (Chiappa et al., 1997, 1998; Zaitoun and Chaveteau, 1998);
- the reduction of the dimensions of pore throats and bodies caused by the adsorbed polymer layer plays an important role in reducing the permeability of the porous medium (Hirasaki and Pope, 1974; Zaitoun and Kohler, 1989; Mennella et al., 1998);
- achievement of selective permeability reduction is not sufficient to ensure successful field results, as post-treatment well performance strongly depends on the mechanism by which water is produced (Hwan, 1993).

From the above picture, it can be deduced that controlling polymer adsorption is of primary importance in ensuring a successful and long-lasting treatment. Therefore, a deeper understanding of the basic mechanisms that govern the adsorption/desorption process is a necessary condition for the development of reliable chemical selection rules. In particular, it is essential to define the key interactions that occur between the polymer and the rock surface, and their dependence on reservoir parameters (permeability, lithology, brine salinity, temperature, wettability, etc.)

In a previous study of the adsorption of polyelectrolytes onto sandstone rock, we have highlighted the important role of the electrostatic interactions between charged groups (Chiappa et al., 1997); in particular, the results showed how a correct match of the polymer charge with the surface charge can greatly enhance the polymer tendency to adsorb onto the surface. In this work, we present the results of further investigations aimed at understanding the role of other parameters that can have an impact on polymer adsorption, i.e.: (i) rock lithology, (ii) brine composition and (iii) wettability. Besides confirming the role of electrostatics in the adsorption process, the results obtained highlight the importance of clays and show that matching polymer and rock surface charges is not always necessary to obtain a significant polymer adsorption. Our results also show that wettability has a profound impact on the adsorption process.

2. Experimental

2.1. Fluids / chemicals properties

- Brine was prepared from reagent grade KCl and CaCl$_2$ at concentrations ranging from 1% to 13% in weight.
- The polymers used were all commercially available, completely water soluble and differed mainly in their electrostatic nature (see Table 1). In particular we tested three polymers that were similar in chemical structure (polyacrylamide) and molecular weight (about 4–5 million), but differed in electrostatic charge (anionic, HPAM, weakly anionic, PAM, and cationic, CAT).

Polymer solutions were prepared in brine at concentrations up to 5000 ppm and then filtered through a 2.7 $\mu$m glass-fiber filter before the experiment. Polymer solubility was checked by measuring the
polymer concentration before and after filtration through a 0.2 μm filter.

- Asphaltenes were obtained from a northern Italian light crude oil using a heavy molecular weight fraction collected in the reboiler\(^1\). This fraction was first dissolved in THF and then washed with heptane to separate the asphaltenes from paraffinic compounds.

Asphaltenes solutions were prepared by adding toluene to a given amount of asphaltenes. The solution obtained was stirred over a weekend and then filtered through a filter suitable for use with organic solvents (Millipore FHLP 0.5 μm).

Asphaltenes concentration was determined by UV absorption at 297 nm wavelength, with a calibration curve that was determined for concentrations ranging from 100 to 1074 ppm.

The crude oil from which the asphaltenes were obtained was also used in the dynamic contact angle and Amott-test experiments.

2.2. Rock properties

In our study, we have focused on polymer adsorption onto the following solids of siliceous nature:

- Two different cuts of pure quartzite with average particle diameter of 45 μm (surface area\(^2\) 0.0418 m\(^2\)/g) and 123 μm (surface area 0.0164 m\(^2\)/g), respectively. The sand was previously washed with HCl and rinsed with deionized water (Mennella et al., 1998). The two different cuts will be referred to as sand Q45 and sand Q123, respectively.
- A clay mineral (Wyoming montmorillonite) that was previously cleaned of impurities by suspending in deionized water under stirring, and then centrifuging.
- A mixture of 92% quartzite (Q45) and 8% clay.
- Reservoir sand (referred to as PC16), obtained from a gas field in Southern Italy. It is composed (as reported in Table 2) of quartz, clays, and calcite (about 21% in weight).
- Berea cores, that were used in Amott test experiments for wettability evaluation in porous media.
- Glass plates, that were used in dynamic contact angle measurements.

2.3. Adsorption of asphaltenes on pure quartzite (Q123)

A certain amount of quartzite Q123 was coated with asphaltenes to evaluate the effect of the presence of organic compounds at the brine/solid interface on polymer adsorption. The coated sand (referred to hereafter as oil-wet sand or oil-wet quartzite) was obtained by aging the clean sand under stirring in the asphaltene solution (asphaltene concentration: 1074 ppm) at room temperature. After 24 h aging time the sand was washed four times with clean toluene to remove any organic material that did not adsorb; after each rinsing the amount of removed asphaltenes was determined by UV. At the end of this procedure, the amount of adsorbed asphaltenes (determined by difference) was 0.41 mg/g.

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\(^1\) The reboiler is a heater unit that is positioned after the separator and stabilizes the crude-oil stream coming from the well-head.

\(^2\) Quartzite surface area was determined from optical microscope observations by processing the digitized images with a computer program to calculate the grain size distribution (Mennella et al., 1998).
2.4. Static adsorption test procedure

Static polymer adsorption experiments were performed to evaluate the adsorption of the different polymers. These tests were conducted at room temperature by adding sand to the polymer solution and stirring until adsorption was complete (see below). At the end of the test the supernatant was filtered through a 2.7 μm glass-fiber filter and the amount of polymer remaining in solution was determined by Total Organic Carbon (TOC) analysis. The amount of polymer retained by the sand was then calculated by difference, after correcting for any organic carbon released by the sand itself.

We also estimated the measurement error calculating the propagation of the errors in the individual procedure steps to the final adsorption value.

2.5. Wettability measurements

2.5.1. Contact angle measurements

Polymer adsorption onto oil-wet surfaces was also investigated by means of crude oil/water dynamic contact angle measurements (Wilhelmy plate technique) with glass plates that were previously aged in crude oil (coming from a northern Italian oil reservoir) for 24 h at room temperature. After aging, the plates were rinsed with toluene, air-dried, and then soaked in the polymer solution for 24 h at room temperature. Prior to testing in the dynamic contact angle apparatus, the plates were rinsed with brine.

During the measurement, the plate was cycled through the oil/water interface until an equilibrium force measurement was obtained, from which an equilibrium advancing contact angle was determined. Further details about this experimental technique can be found, for example, in Mennella and Morrow, 1995, and Mennella et al., 1995.

2.5.2. Amott test

Standard Amott–Harvey tests were performed to investigate the effect of the polymer adsorbed in the porous medium on the wettability alteration induced by aging in crude oil. To this end, the Amott–Harvey index of six Berea cores was determined at different aging times (0, 15 and 30 days at 80°C). Three of them were firstly treated with the CAT polymer that was injected into the core at 100% brine saturation and then displaced with brine after a shut-in time of 24 h at room temperature.

3. Results and discussion

3.1. Role of electrostatic interactions on polymer adsorption

Electrostatic interactions play a key role in the adsorption of polymer molecules onto the rock surface. These interactions can be attractive or repulsive depending on: (i) polymer charge, (ii) charges at the rock/brine interface and (iii) brine strength and composition.

In this section, we present experimental results obtained from static adsorption tests to highlight the relationship between these parameters and polymer adsorption. In particular, the following effects have been investigated:

- **Effect of polymer charge.** This was studied by testing polymers of different charge (cationic, anionic and weakly anionic) with quartzite (which is negatively charged at pH close to neutral). Polymer solutions were prepared in 2% KCl brine.
- **Effect of clay content.** This was studied by testing CAT (cationic polymer) on sands with varying clay content. Polymer solutions were prepared in 2% KCl brine.
- **Effect of ionic strength and composition.** This was studied by testing polymers of different charge dissolved in brines of different ionic strength and composition on pure quartzite. Polymer solutions were prepared in KCl and CaCl₂ brines.

3.1.1. Adsorption kinetics and adsorption isotherms

Adsorption time and polymer concentration are two key parameters that need to be fixed in static adsorption tests. This was done by determining the adsorption kinetics and the adsorption isotherm for the three polymers on two different sands, pure quartzite and reservoir sand PC16. Because in all these measurements adsorption of HPAM was always low (very close to zero) in Figs. 1 and 2, we
report results only for PAM and CAT. From these results it is possible to observe that:

- For both sands the adsorption process reaches equilibrium after 18–24 h.
- The adsorption isotherm plateau on Q123 is around 4000 ppm while with sand PC16 the plateau seems to be at somewhat higher concentrations.

In all the subsequent tests we fixed 24 h as the adsorption time, while the polymer concentration was set at 2000 ppm. The choice of 2000 ppm rather that 4000 ppm was dictated by practical constraints; for concentrations over 3000 ppm the solution viscosity is very high and the rheological behavior non-Newtonian. This renders the measurements difficult and time consuming. Moreover, such high concentrations are not used in polymer relative permeability modification treatments, as it is very important to keep the viscosity of the injected solution as low as possible. At 2000 ppm the solution viscosity is close to that of water (about 2 cP, with Newtonian behavior) and the adsorption is not far from the plateau of the adsorption isotherm.

3.1.2. Effect of polymer charge

In Fig. 3, we report a comparison between the adsorption of CAT, PAM and HPAM from a 2% KCl solution onto Q45 quartzite. There is a clear increase in adsorption in passing from the anionic (HPAM) to the weak anionic (PAM) to the cationic polymer (CAT). In light of the negative charge of the quartz surface at pH values greater than 2, the trend
in polymer adsorption is determined by electrostatics.

The adsorption behavior of CAT, PAM and HPAM on a complex reservoir sand (see Table 2 for lithologic composition) reported in Fig. 4 confirms the trend of polymer adsorption vs. the polymer charge observed in Fig. 3. In view of the significant amount of calcite (which has a positively charged surface at pH values less than 9.5) in this sand, the negligible adsorption of the anionic polymer HPAM is puzzling. Some preliminary results obtained from adsorption experiments on pure calcite have shown that trends are not so well defined as those for silicates, reflecting, presumably, a much more complex chemical behavior at the calcite/brine interface.

3.1.3. Effect of clay content

The next step in our study is the investigation of the effect of clay minerals on polymer adsorption. In fact, because clays are characterized by high surface area and predominantly negative charge, we expected a strong impact on polymer adsorption, especially for the cationic polymer CAT. To test this we measured the adsorption of CAT onto a clay mineral (Wyoming montmorillonite) and onto a mixture of pure quartzite (92%) and clay (8%).

The results shown in Fig. 5 (which also report CAT adsorption onto pure quartzite for comparison) confirm the important role of clays in controlling polymer adsorption. These results also indicate that adsorbed polymer will be concentrated on the clay minerals, which may result in non-uniform permeability.

Clay particles are plate-shaped and bear both negative and positive charges. The negative charges are located on plate faces while positive charges are located on plate edges. Positive charges can be considered negligible for montmorillonite but they are more significant for other clays like illite, chlorite and kaolinite.
3.1.4. Effect of ionic strength and composition

The results in Figs. 3 and 4 have shown how electrostatic interactions play a dominant role in the adsorption onto surfaces of siliceous nature. Because these electrostatic interactions depend on the brine characteristics (ionic strength and composition), we carried out a series of adsorption experiments to assess the dependency of polymer adsorption on quartzite Q45 vs. brine composition. In particular we prepared two different brines, one containing a monovalent cation (K\(^+\)) and the second containing a divalent cation (Ca\(^{++}\)).

In Fig. 6, the adsorption of CAT, PAM and HPAM is reported as a function of the concentration of KCl in brine. Although the increase in ionic strength causes a slight decrease in the adsorption of CAT (presumably because of electrostatic screening) the trend in polymer adsorption vs. polymer charge is maintained.

A very different behavior is observed in Fig. 7, which shows the effect caused by the presence of a divalent cation. While the adsorption behavior of CAT is similar to that reported in Fig. 6, the adsorption of PAM and HPAM (which both show very similar trends) is greatly enhanced, attaining values greater than CAT at concentrations of CaCl\(_2\) over 6%. This effect can be explained invoking two different effects that are peculiar to divalent ions (see Fig. 8):

1. bridging of negatively charged polymer molecules to the negatively charged grain surface, that ex-
plains the enhancement in polymer adsorption observed for PAM and HPAM, and
2. coordination of negatively charged groups on the polymer molecule, which tends to reduce the differences in the ionic character between PAM and HPAM.

This result shows that matching the polymer and the surface charges is not strictly necessary to obtain high levels of polymer adsorption, although, from a practical point of view, it is preferable to operate with low-salinity brines containing a monovalent ion. On the other hand, this result also shows that a strong electrostatic attraction between polymer and surface, as between CAT and silicates, is not greatly influenced by the valence and the concentration of the dissolved salt.

3.2. Role of wettability on polymer adsorption

It is widely known that crude oil reservoirs often display mixed wetting conditions (Morrow, 1990). Therefore, during a treatment performed in a mixed-wet reservoir the injected polymer will interact with significant portions of oil-wet rock. In this case it is possible that rock wettability will have a marked effect on polymer adsorption, so that results obtained from clean-sand adsorption tests cannot be extrapolated directly to crude oil bearing formations.

Considering that in field treatments it is necessary that polymer adsorption is maximized and polymer desorption during back production is minimized, it is clear that understanding the effect of the presence of crude-oil components on polymer adsorption/desorption processes can have significant implications from a practical point of view.

To highlight the presence of a wettability effect on these treatments we have conducted some preliminary experimental tests with oil-wet sand, with glass plates and in porous media, with the aim to assess two different aspects of the interaction of polymers with rock formations in petroleum reservoirs, i.e.:

1. the adsorption of polymer molecules onto oil-wet surfaces (studied by means of static adsorption tests and contact angle measurements), and;
2. the effect of the adsorbed polymer on the tendency of crude oil components to alter rock wettability (studied by means of Amott tests conducted in Berea cores).

3.2.1. Polymer adsorption onto oil-wet quartzite

In Fig. 9, we report experimental adsorption isotherms of CAT and PAM measured on clean vs. oil-wet quartzite (Q123).

The figure clearly shows that on the oil-wet sand, polymer adsorption is markedly reduced; however,
while PAM adsorption under these conditions is almost zero, CAT adsorption is still significant. This result indicates that although adsorbed asphaltenes reduce the tendency of polymer molecules to adsorb onto the surface, significant adsorption is still possible for polymers that interact strongly with the surface.

3.2.2. Contact angle measurements

A similar behavior can also be seen in the results reported in Fig. 10, which were obtained from dynamic contact angle measurements with glass plates that were firstly aged in crude oil for 24 h at room temperature and then polymer-treated. Fig. 10 shows that the advancing contact angle was reduced from 120° to 75° after treatment with CAT while it was not reduced after treatment with PAM. This result is in agreement with the behavior of polymer adsorption isotherms shown in Fig. 9 and provides an indirect assessment of the tendency of the two polymers to adsorb onto an asphaltene-covered surface.

3.2.3. Amott test

The aim of this experiment was to assess the effect of an adsorbed polymer layer on the adsorption of crude oil components in porous media.

Fig. 11 reports the $I_w - I_o$ Amott index for Berea cores that were aged in crude oil at 80°C for 0, 15, 30 days respectively. Before establishing initial wa-
ter saturation three cores were polymer-treated by injecting about 10 PV of CAT polymer. The polymer was then displaced by a brine flood after a 24 h shut-in at room temperature.

Both the treated and non-treated cores display a trend towards less water-wetting behavior with increasing aging time. The figure also shows that the presence of the polymer adsorbed within the core reduces the wettability alteration induced by crude oil adsorption, suggesting that there is a competition between adsorption of polymer molecules and polar crude oil components. This result is in good accord with those obtained from the polymer adsorption measurements using oil-wet sands.

4. Conclusions

In this paper we have investigated some mechanisms of polymer adsorption at brine/rock interfaces of siliceous nature. The experimental results obtained support the following conclusions:

- polymer adsorption is dominated by electrostatic interactions between the charged groups that are present at the polymer/brine and rock/brine interfaces. A correct match between the polymer and the surface charges can greatly increase adsorption;
- clays play a dominant role in the adsorption process, presumably because of their high specific surface area and (negative) charge. Even small amounts of clay can cause a significant increase in polymer adsorption;
- brine salinity does not particularly affect the adsorption of a cationic polyacrylamide onto silicates, apart from a small decrease in the adsorption caused by electrostatic screening;
- the presence of a divalent cation (as Ca$^{2+}$) can greatly enhance the adsorption of negatively charged polymers onto quartzite. In fact, Ca$^{2+}$ can bridge the negatively charged polymer molecules to the negatively charged grain surface and coordinate the negative charges on the polymer molecules thus reducing its anionic character.
- Crude oil adsorption reduces the tendency of polymer molecules to interact with the rock surface. If the polymer/rock interactions are strong,
however, it appears that a significant adsorption is still possible. More detailed studies are needed to understand the adsorption mechanisms under these conditions.

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