The effects of Concentration and Salinity on Polymer Adsorption Isotherm at Sandstone Rock Surface

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The effects of Concentration and Salinity on Polymer Adsorption Isotherm at Sandstone Rock Surface

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Abstract. Adsorption of hydrolyzed polyacrylamide (HPAM) polymers on sandstone rock surface was studied by static adsorption experiments. Total of 10 Runs of static experiments were conducted in test tubes by mixing the desired solution with crushed rock sample, at temperature of 25 °C, and salinity range from 0-4 wt%. The results are in conformity with Langmuir's isotherm. Ten different isotherms were generated at each Run. The initial polymer concentration was varied from 0.3-2.1 g/l. The effects of salinity have been studied by observation on Langmuir adsorption coefficients (Y and K). The results show that the adsorption coefficient (Y) was found to have linear relationship with salinity. The adsorption coefficient (K) was found to be related to salinity by a quadratic relationship.

1. Introduction

The polymer used in the flood application in its hydrolyzed form [1]. Hydrolyzed polyarylamide (HPAM) was used in this study, which is a straight-chain polymer that has the acrylamide molecule as the monomer. This partial hydrolysis can occur in some of these monomers [2]. One of the most important properties which made polymer interested for EOR processes as mentioned earlier was the viscosyfing property. Another important parameter which may affect the feasibility study plan of a polymer flooding project is the adsorption of polymer in porous medium [3]. Adsorption may be defined as the interaction between the polymer molecules and the porous medium which leads polymer to be adsorbed. The adsorption of polymer will affect both, polymer and porous medium properties [4]. For example the viscosity of adsorbed polymer will be lower than the viscosity of the injected polymer.

Polymer adsorption is mainly physical interaction, electrostatic attraction due to the charges differences between the solid surface and the polymer molecules [5]. The difference in concentration of a chemical agent in the solution and rock surface is the main driving force for the adsorption [6]. Normally, adsorption is measured by what called isotherms. Isotherms are simply plots of the amount of adsorbed chemical per gram of solid or per surface area of solid vs. the equilibrium concentration at a constant temperature. Adsorption isotherm of polymer is influenced by many parameters; in this work only concentration and salinity are considered for investigation.

Among many adsorption isotherms, HPAM polymer was found to follow Langmuir isotherm [6]. The Langmuir adsorption isotherm equation was developed to describe the adsorption of gases onto clean solids and implies uniform adsorption sites and absence of lateral interactions. The Langmuir isotherm is expressed as follow:

$$Ad = \frac{YKC}{(1+KC)} \tag{1}$$

where *Ad* is the amount adsorbed per unit mass; C is the equilibrium solution concentration; and Y and K are empirical coefficients [7]. However, the use of this model to predict adsorption in presence of salinity effects is not possible since it relates adsorption amounts to only equilibrium concentration. Static adsorption experiments in test tubes were conducted at 25 °C and different salinities. Adsorption isotherm was generated at each experiment (Run). The effect of salinity on the polymer adsorption has been studies by observing the values of adsorption coefficients (K and Y).

2. Materials and Methods

2.1. Materials
The polymer used in this study is the well-known partially hydrolyzed polyarylamide (HPAM). Polyarylamides are water soluble polymers which are produced by many manufactures in many ways for different purposes. For instance as enhanced oil recovery (EOR) agent. The monomer acrylamide is a compound derived from acrylic acid. The molecular weight of polycryamides is $14*106$ Daltons. The size of the molecules is about 0.2 μm. By hydrolysis in a caustic water solution some of the $CONH_2$ groups react to form carboxyl groups (COOH). The degree of hydrolysis is an important parameter which determines the properties of polyacrylamide in aqueous solutions as used in EOR [8]. The polymer used here has hydrolysis degree about 25 % as provided by SNF group.

Rock samples used in this study are sandstone type which is a clastic sedimentary rock composed mainly of sand-sized minerals or rock grains. Most sandstone is composed of quartz and/or feldspar because these are the most common minerals in the Earth's crust. Like sand, sandstone may be any color, but the most common colors are tan, brown, yellow, red, gray, pink, white and black [9].

2.2. Static Adsorption Tests
It is simply, measuring the adsorption of solution on rock by mixing both in test tubes under static condition of flow. Samples of reservoir rock should be grounded for static measurements of adsorption so that the adsorptive has good access to the solid surface. As adsorption of EOR-agents is measured from a liquid phase, it may be difficult to measure directly (in the solid) the increase in weight, but it should be possible to measure this weight increase after the sample is dried. Total of 10 Runs of static adsorption tests were performed at different conditions of concentration and salinity. Each Run consists of ten solutions with different initial concentrations.

The adsorbed substance was determined from the decrease in concentration of the chemical solution after it has been brought into contact with the adsorbent and equilibrium has been reached, as in equation (2). The experiment was designed in such a way that the decrease in concentration is significant and can be easily measured; the mass of the adsorbent should not be too small and the volume of the solution not too big. For this purpose the solid to liquid (S/L) ratio of all static experiments was fixed at 0.1, which was found to be representative for the rock type we used (sandstone).

$$Ad = \frac{V}{M}(C_o - C_e) \tag{2}$$

where V is the volume (litre) of solution used, M is the weight of the solid sample (g), and C_0 and C_e are the initial and equilibrium concentrations (g/l), respectively of polymer solutions.

2.3. Concentration Measurements
To measure the concentration of polymer after adsorption a starch-triiodide method was used. This method gives a linear response in a concentration range of 0-3 g/l [10]. The samples had a higher

concentration than this, so they were diluted first. Around 30 ml of the diluted sample was used. First of all 5 ml of a buffer solution (pH=3.5) is added. Secondly 1ml of saturated bromine water is added to the sample. After 15 minutes 5 ml of 1 wt. % sodium formate solution is added. At the end after 5 minutes 5 ml of a solution containing starch is added. The iodide is then reduced to iodine by a reaction product of bromine and the polymer. Starch forms a blue color with iodine and the adsorbance of the sample was measured using a UV-VIS spectrometer.

The adsorbance at peak wavelength, at around 568 nm, is used. It is necessary to have standard curve to measure the polymer concentration. The standard curve was generated using the same method as described above for known concentrations of polymer solution. The standard curve gives a linear relationship between the polymer concentration and absorbance of the solution.

3. Results and Discussions

3.1. Polymer Adsorption Isothermal

Ten solutions of polymer were used and were named P1 to P10, where the range of concentrations was between 0.3-2.1 g/l. The polymer is normally injected into reservoir with a concentration between (0.5-2 g/l) [21]. The adsorption isotherm of polymer is shown in Figure 1. Equation (3) was used to estimate adsorption coefficients for Langmuir isotherm.

$$\frac{1}{Ad} = \frac{1}{YKC} + \frac{1}{Y} \qquad (3)$$

Figure 1 shows the adsorption of polymer as a function of equilibrium concentration for the solutions with no salinity. As it can be seen from Figure 1, at low polymer concentrations (below 1 g/l), polymer adsorption is directly proportional to the polymer concentration. Increasing concentration of polymer solution increases the numbers of polymer molecules per unit volume. Thus, it increases the probability of polymer adsorption on available adsorption sites in the rock surfaces. After concentration of the polymer solution reaches 1.5 g/l, polymer adsorption is basically concentration-independent (see Figure 1). The corresponding value of polymer adsorption at concentrations higher than 1.5 g/l was 1.87 mg/g. Based on the previous discussion, the maximum adsorption level of HPAM polymer solution (salinity = 0) on sandstone rock surface at 25 °C, and S/L ratio of 0.1 is 1.87 mg/g. From Figure 1, it can also be observed that the Langmuir model agrees better with the experimental data in the whole range of test concentration for polymer solution

3.2. Effect of Salinity

Many reservoirs suitable for chemical EOR have high salinities, i.e., brines with substantial hardness and having total dissolved solids (TDS) contents up to about 200 g/L [11]. Many physical and chemical properties of the injected chemical agents are affected by salinity, like viscosity, chemical activity, stability, and adsorption [12].

Adsorption, mainly physisorption of chemical molecule on the rock surface is exaggerated by changes in the ionic strength (salinity). Charge type (positive, negative, or neutral) of rock surface is disturbed in the presence of salinity, which leads to different behavior of the rock surface [12]. While the salinity (ionic strength) is an important factor that influences the adsorption of polymer to the rock surfaces. Salinity in this study reflects the concentration of Sodium Chloride (NaCl) in the system. Irrespective of the process and the nature of the polymer, the quantity of adsorbed polymer is increased by a factor of 2 to 5 in the presence of NaCl (100 g/l).

On the other hand, the maximum adsorption limit increases with the degree of polymer hydrolysis, with or without the presence of salt [13]. Some explanations of the general increase in the quantity of the polymer adsorbed in the presence of sodium chloride may be considered. First, a polyelectrolyte may have a coagulation effect on dispersed solids, due to a decrease in the electric double layer at the interface solution-dispersed solid particle [14], and a flocculation effect, resulting from polymer

bridges between the mineral particles in suspension [15]. In addition, the decrease in thickness of the double layer of the dispersed particles and the surface potential due to polyelectrolyte results generally in polymer adsorption [16].
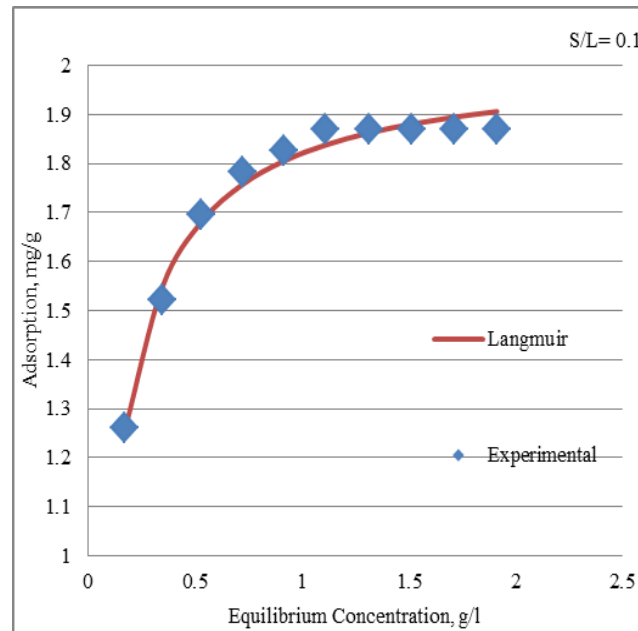

Figure 1: Polymer Adsorption Isotherm

The adsorption increase in the presence of NaCI may also be explained by a decrease in macromolecular bridges between the clay particles (viscosity decrease); the mineral particles are no longer connected, allowing a fixation of larger quantities of polymer (greater occupation of the adsorption sites) [18]. Different polymer adsorption isotherms were developed at different salinities (0-4 wt %) and are shown in Figure 2.

From Figure 2, it is clear that the adsorption of polymer was increased by adding (NaCl) to the polymer solution during the static adsorption test. The amount of absorbed polymer increased from 1.87 to 2.48 mg/g by adding 4 wt% salinity. This effect can be explained by the bridging of negatively charged polymer molecules to the negatively charged grain surface, and by coordination of negatively charged groups on the polymer molecule [17]. Moreover, at high salinity values, polymer molecules are more compact; this is due to electrolyte that leads to the reduction in the extension of the polymer molecule.

More compacted polymer molecules require smaller surface area than normal molecules to be absorbed on the rock surface, then the additional available area for adsorption (in case of compacted molecules) will attract more polymer molecules. As a result, adsorption of polymer increases with increasing salt concentration (salinity). The results shown in Figure 2 are in agreement with the results of the other researchers [17], [18].

To study the effect of salinity on adsorption of polymer on sandstone surfaces, four different sets of the polymer solutions with different levels of salinity ranging from 0 to 4 wt % were prepared. Adding salinity will change the values of Langmuir adsorption parameters Y and K. The parameter values were estimated by plotting $(1/A_d)$ vs. $(1/C)$ and then using the straight line analysis procedure based on equation (3). The estimated values of the parameters are given in Table 1.

From Table 1, it can be noted that when salinity is increased from 0 to 4 wt %, K increases from 9.648 to 29.673 l/mg, while Y_m values increases from 2.009 to 2.497 mg/g. To establish a

mathematical relationship between the salinity and each of the parameters *Y* and *K*, *Y* vs. salinity and *K* vs. salinity were plotted in Figure 3 and Figure 4, respectively.
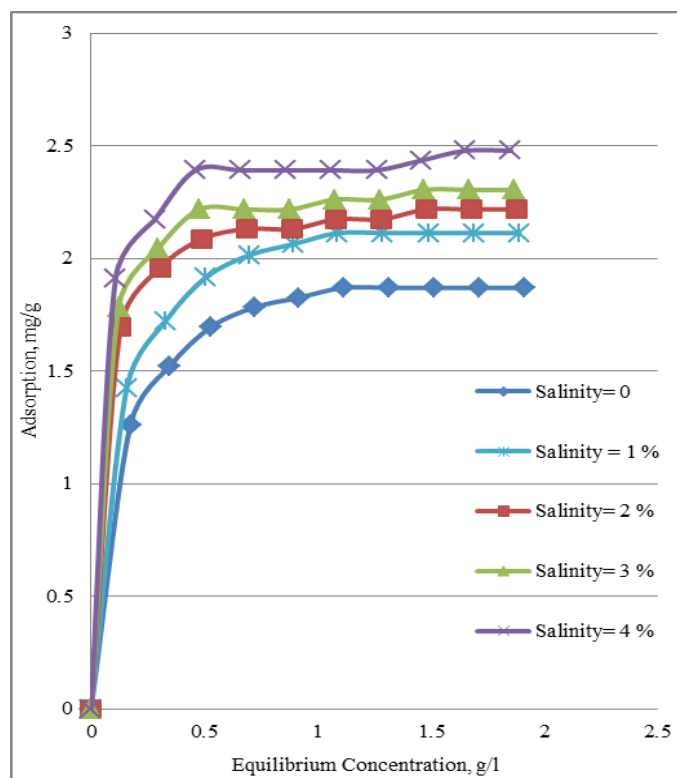

**Figure 2**: Effect of Salinity on Polymer Adsorption Isotherm

Table 1: Langmuir adsorption parameters for polymer with different salinities

Salinity, wt %	Y, mg/g	K, l/g
0	2.0094	9.6481
1	2.2533	10.7981
2	2.2626	22.6646
3	2.3468	25.7158
4	2.4964	29.6726

Figure 3 shows that Y changes with salinity in a linear manner. These findings are in agreement with the modified Langmuir model that have been used in some simulators to find the adsorption amount of chemicals species in presence of salinity effects [19], [20]. Whereas Figure 4 shows that the relationship between salinity and the adsorption coefficient K is of quadratic (see the equation given in the inset of Figure 4) in nature. The coefficient of determination for the fit of observed data of K with the quadratic model is very close to unity (0.996) which further improves the validity of the predicted quadratic relationship.
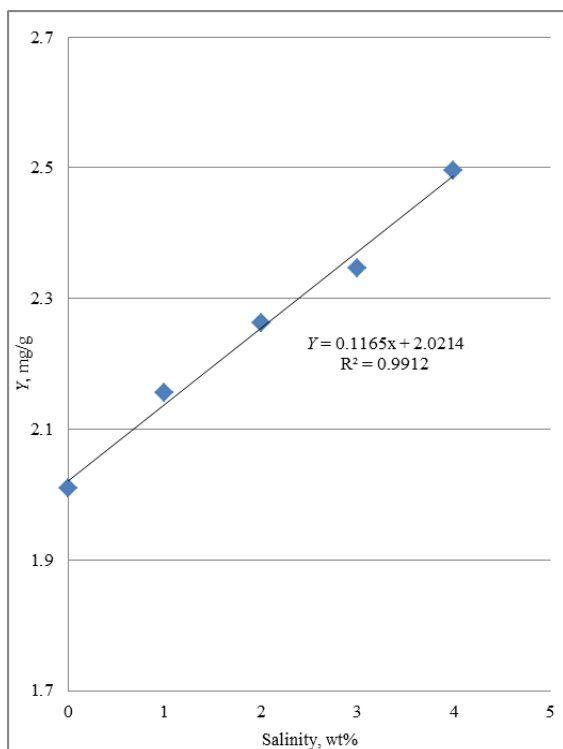
Figure 3. Relationship between salinity and *Y* for polymer
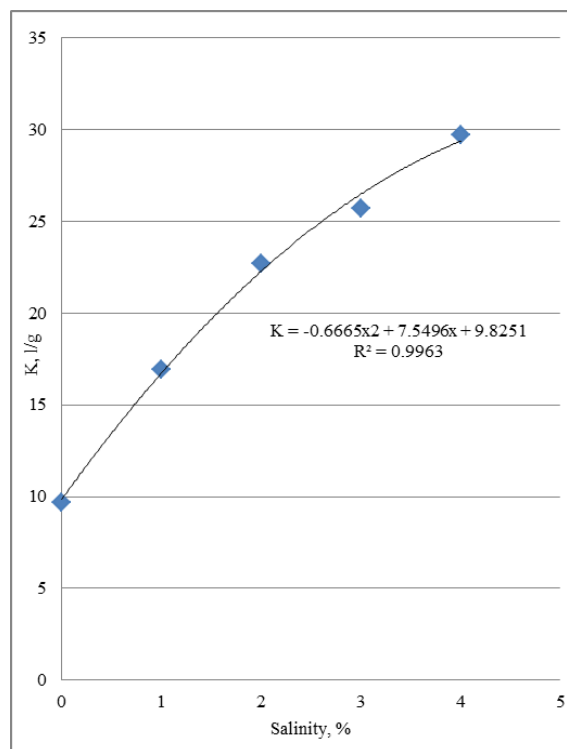
Figure 4. Relationship between salinity and *K* for polymer

4. Conclusions

- It was found that the adsorption data from the static experiments are best represented by the Langmuir model when compared to the Freundlich model.
- It was found that, adsorptions HPAM polymer increases when the salinity increases.
- It was found that for the HPAM polymer, adsorption coefficient *K* was bonded by a quadratic relation with salinity. While adsorption coefficient *Y* was found to be related by linear relation to the salinity.

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