Flow-induced-microgel adsorption of high-molecular weight polyacrylamides

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ABSTRACT

Water soluble polymers are widely used in oil and gas reservoirs and usually injected into the reservoir rocks to alter their flow properties. The rheologies of the polymer solution and their adsorption or interaction with the porous system are crucial for the success of the injection. This work aims to investigate the formation of residual polymer multilayers as a result of the flow of aqueous solutions of high-molecular-weight cationic (CPAM) and non-ionic (PAM) polyacrylamides through single, circular and rectangular capillaries.

Polymer solutions in de-ionized water and weak brine were injected at different flow rates into glass capillaries of circular and rectangular cross sectional area. The adsorption energy and layer thickness on glass surfaces of these polymer solutions have been investigated by Al-Hashmi and Luckham (2010) under static conditions using colloidal force measurements. The apparent viscosity of the polymer in solution on both increasing and decreasing the shear rate are presented to indicate the thixotropic or anti-thixotropic behaviour of the solution. Also, the viscosity-time curves are presented to investigate the rheopectic behaviour of the polymer solutions.

The flow CPAM in water solution through the capillaries resulted in very thick residual polymer layers, around 15 times thicker than those measured under static conditions. This solution shows both anti-thixtropic and rheopectic behaviour, which may be attributed to flow-induced-microgel formations in the bulk of the polymer solution. The same polymer solution has shown almost instantaneous adsorption from the colloidal force measurements due to electrostatic attraction of the cationic groups of the polymer to the negative glass surface. Such thick layers are not formed when CPAM in 0.34 M NaCl is used. Although it has shown strong adsorption on glass, the CPAM in 0.34 M NaCl exhibits neither anti-thixotropic nor rheopectic behaviour. Though it has shown rheopectic behaviour, the non-ionic polyacrylamide in water solution does not result in significantly thick layers, which might be due to its weak adsorption on glass.

In the current study, a new mechanism is proposed to attribute the apparent formation of residual multilayer under the name of flow-induced-microgel adsorption (FIMGA). According to the new mechanism, two criteria have to be satisfied for polymer multilayer formation: the formation of sizable shear-induced-microgel structures in the bulk of the solution, and sufficiently high adsorption energy of the polymer to the solid surface. The new understanding in view of this new mechanism will contribute to more successful applications of polymers in oilfields. It will also allow faster screening of the chemicals for a specific application which may warrant different characteristics of flow and adsorption. For example, polymers used in enhanced oil recovery should have high injectivity and low adsorption. On the other hand, high adsorption and thick residual polymer layers are the key for a successful use of polymers in water shut-off in oil and gas wells.

1. Introduction

The flow of polymer solutions through reservoir rocks is normally used in enhanced oil recovery and in oilfield water shut-off. The rheology of these polymer solutions and the amount of polymer retained are among the essential screening factors carried out to assess the suitability of these polymers in the oil field. Polymer retention is not preferable in enhanced oil recovery due to the associated loss of viscosity with the decrease in polymer solution concentration. On the other hand, polymer systems are injected to be retained for long periods of time around the oil-producing wells, hence inducing preferable selective disproportionate permeability reduction. Irreversible polymer retention is mainly due to the adsorption of polymer on the rock surfaces. Adsorbed polymer layers were found to result in effective hydrodynamic thickness that

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cannot be justified by monolayer adsorption (Szabo, 1972). Apparent multilayer formations were obtained during and after the flow of HMW polymer solutions through simple geometries: Couette and Poiseuille (Thomas, 1976; Grattoni et al., 2004) flow systems. These multilayers have been attributed to mechanisms such as adsorption-entanglement (Hand and Williams, 1973; Zwijnenburg and Pennings, 1975, 1976; Cohen and Metzner (1985); Hikmet et al., 1985) flow-induced adsorption (Zitha et al., 1998; Chauveteau et al., 2002; Asghari, 2004), and the formation of adsorption-gel layers (Kozicki et al., 1967, 1970, 1987, 1988, 1993). Moreover, some studies have attributed the apparent multilayer formation after polymer flow through porous media to mechanical entrapment, hence reducing the accessible pore volume (Szabo, 1975; Thomas, 1976).

In the current study, the flow of aqueous solutions of high molecular weight non-ionic and cationic polyacrylamide through silica capillaries of different cross-sections was conducted to investigate polymer multilayer formations. This was studied more comprehensively by understanding the adsorption kinetics of these systems and their rheological, and in particular their shear thickening behaviour in bulk flow. A relationship has been established between these two effects to promote or demote the multilayer formation of a polymer/solid system. Upon such comprehension, a new understanding on the factors used as screening criteria for each relevant application is established.

2. Experimental section

High molecular weight non-ionic (PAM) and cationic polyacrylamide (CPAM) were used in this study. The PAM is essentially a non-ionic, very high molecular weight, linear polymer made of acrylamide monomers, which has the chemical structure shown in Fig. 1. This polymer was supplied by *Polysciences* as solid granules with a quoted molecular weight of 18 million Daltons. The CPAM is a linear, high molecular weight random copolymer of acrylamide and (N,N,N-trimethyl)-aminoethyl chloride acrylate with a structure shown in Fig. 1. The charge density of this cationic polymer is 10%. This polymer was produced by *SNF Floerger* in a solid granular state with a molecular weight of 6 million Da.

Two solvents were used to prepare the polymer solutions in this study: (1) de-ionized (DI) water, and (2) 0.34 M Sodium Chloride (NaCl).

Traces (100 ppm) of Sodium Azide (NaN₃) were added to the solvents as a stabilizer. The solvents were filtered through 0.22-μm Millipore filters to remove any particulate impurities prior to use in the capillary flow experiments.

2.1. Preparation of the polymer solutions

The procedure followed in the preparation of the polymer solutions is critical and has been proven to be vital in the interpretation of the experimental results (Sorbie, 1991). Hence, the procedure followed in the preparation of the polymer

solutions used in the experiments of this study is described in detail below.

The aqueous solvent, either water or 0.34 M NaCl was put in a beaker and stirred vigorously using a magnetic stirrer. The polymer granules were then slowly sprinkled onto the shoulder of the well-developed vortex caused by the stirrer. The solution was magnetically stirred for 24 h under milder stirring after observing the dissolution of the polymer granules. The polymer solutions were then stored at room temperature.

Prior to the use of the polymer solutions in the flow through the capillaries, the solutions were filtered through 3-μm Millipore filters. This removes any polymer microgels that can be formed in these high molecular weight solutions. The flow rate of the polymer solution during the filtration process was adjusted to 6 cm³/min as has been advised by Chauveteau and Kohler (1980). All polymer solutions presented have a polymer concentration of 1000 ppm.

2.2. Flow and time curves

Flow and viscosity-time curves were obtained using a Paar Physcia (US100) rheometer with a cone-and-plate configuration (MK 24; 75 mm cone,1°). The flow and viscosity–time curves were obtained at a temperature of 20 °C.

The polymer solution samples were poured into the rheometer geometry and then allowed to rest for 10 min prior to the start of the measurements to eliminate any time dependant shear behaviour of the polymer solutions caused by placing the polymer samples in the rheometer. The shear rate was continuously ramped up and down in the range 0.1–2500 s^{-1} in 10 min.

The hysteresis between the increasing and decreasing shear rate curves for a particular polymer solution was used to identify the possible thixotropic (or anti-thixotropic) behaviour.

The viscosity–time curves for polymer solution samples were obtained by subjecting the polymer sample to a continuous, constant shear rate over a certain period of time. Fresh samples were used for each shear rate run and the samples were allowed to rest for 10 min before the start of shear. These curves are presented in relative viscosity versus time plots. Hence, before the presentation and discussion of the results, two terms have to be defined: (1) *Initial viscosity* is the viscosity obtained after 2 s of flow of the polymer solution at a constant shear rate. The viscosity obtained after 1 s was found to be very high which is likely to be a start-up effect of the rheometer. (2) *Normalized viscosity* (η_N) is the viscosity at a certain time (t) divided by the initial viscosity. This parameter will help in showing the behaviour of the viscosity at a certain shear rate irrespective of any viscosity values.

2.3. Capillary flow experiments

The flow of solvent and polymer solutions through micro-scale, single, silica capillaries was studied mainly to determine the residual effective hydrodynamic thickness (EHT) of the adsorbed
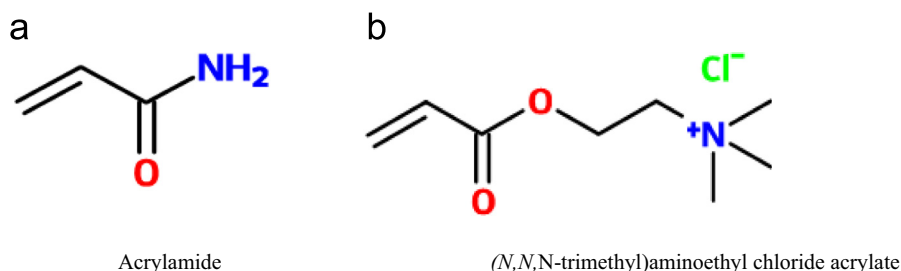

Fig. 1. Structure of the monomers composing PAM (100% a) the CPAM (90% a, 10% b).