

Investigation of Interaction Between Viscosity-Modifier Polymers and Surfactants Based on Vegetable Oil for Chemical Enhanced Oil Recovery

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Chemical enhanced oil recovery (CEOR) is surely a topic of interest. The process of chemical flooding with solutions of polymers and surfactants can be used for developing oil recovery. The bio-based surfactants have much attention from both scientific and industrial point of views due to their renewable and environment friendly nature and the bio-based surfactants has lower toxicity and better biodegradability. The theory of interactions between polymers and surfactants have been markedly studied. This is particularly important for understanding the mechanism of chemical enhanced oil recovery. The interaction between various surfactant mixtures and flow-modifying polymers in brine solutions was investigated (in practical terms) using various analytical methods, including interfacial tension, emulsification capacity, rheological properties, and oil displacement measurements. Based on the experimental data a significant level of interaction between the surfactants and the polymers were found. It was obtained that by applying flow modifier polymer together with the investigated surfactants the additional oil production could increase.

1. Introduction

The extensive exploration of interactions between polymers and surfactants stems from their broad industrial applications. The particular focus on polymer-surfactant systems arises from their crucial relevance in the chemical enhanced oil recovery process (Khan et al., 2008).

Various authors have provided insights into Surfactant-Polymer Injection and the influence of salt on these interactions. Numerous laboratory experiments, simulations, and field data have demonstrated that Surfactant-Polymer and Alkali-Surfactant-Polymer flooding are among the most effective techniques for recovering medium and low viscosity oils, with applicability extending to high viscosity oil fields as well. Kwak (1998) summarized the existing knowledge of interactions between polymers and surfactants in his book, which lays the foundation for the subject area. Hamouma et al. (2021) investigated the negative effects arising from interactions between polymers and surfactants in their work. Afolabi et al. (2022) provided a review article on polymeric surfactant systems. Druetta and Picchioni (2018 and 2020) mathematically described polymer-surfactant systems under various injection schemes. Firozjahi and Saghafi (2020) compiled numerical and experimental simulations in their detailed review. Yang and Pal (2020) examined the interaction between polymers and surfactants through rheological and interfacial tension studies. Gradzielski (2022) investigated the technological implications of interactions in his work. Studies have identified interactions between surfactants and polymers for numerous surfactants. Interactions in solution between surfactants and water soluble macromolecules have been under study for 70 years or more (Amran et al. 2022; Goddard and Hannan 1977).

In the current study, various experiments were undertaken to characterize the interaction between a flow modifier polymer and different surfactant mixtures developed in-house. This characterization involved measuring the properties of colloidal particles and the rheological characteristics of their solutions. The investigation included examining viscosities at different shear rates and interfacial tension of the polymer-surfactant mixture solutions, providing valuable insights into the robustness of the network formed between the polymer and surfactant.

2. Materials and methods

2.1 Materials

To create the experimental colloid solutions, an anionic surfactant (PEANION) and three nonionic surfactants (PENONION I-III) were utilized, developed, and produced through collaboration between research groups at the University of Pannonia and the Hungarian Oil and Gas Company. Additionally, a partially hydrolyzed synthetic polyacrylamide (HPAM) was employed as a mobility controller-type polymer. Properties of the used surfactants shown in Table 1.

Table 1: Main proprieties of used surfactants

	Ionic charge	Type	Producer
MOLANION	Anionic	Gemini surfactant	MOL-LUB Ltd.
PENONION I	Non-ionic	Diethanolamine and fatty acid methyl ester reaction product	MOL-LUB Ltd.
PENONION II	Non-ionic	Diethanol amine and vegetable oil reaction product	MOL-LUB Ltd.
PENONION III	Non-ionic	Polyethylene-glycol and vegetable oil reaction product	MOL-LUB Ltd.

The concentrations used were 15 g/L for surfactants and 1 g/L for polymer solutions. These solutions were prepared using natural brine sourced from the Algyő petroleum reservoir. The surfactant-containing solutions were created by homogenizing the components in different ratios using UD 11 type ultrasonic equipment (Schoeller and Co., 250W, 20 kHz). The detailed composition of the mixtures is provided in Table 2.

Table 2: Composition of the surfactants and polymer-surfactant mixtures

Samples	SURF-1	SURF-2	SURF-3	P+SURF-1	P+SURF-2	P+SURF-3
Components	Concentration of components, w/w %					
MOLANION	8.25	9	8.25	7.73	8.44	7.73
PENONION I	3.75	6	3.75	3.52	5.63	3.52
PENONION II	3	-	-	2.81	-	-
PENONION III	-	-	3	-	-	2.81
HPAM	-	-	-	0.94	0.94	0.94

2.2 Methods

Determination of interfacial tension (IFT)

The oil-water interfacial tension (IFT) was determined using the spinning (or rotating drop) method. IFT measurements were conducted using the Data Physics Spinning Drop Video Tensiometer SVT 20 device at a temperature of 40 °C with a total concentration of 1 g/L for surfactants and polymer-surfactant mixtures.

Determination of the size distribution by dynamic light scattering (DLS) method

The hydrodynamic radius of the complexes was determined through photon correlation spectroscopy, specifically dynamic light scattering. The size was estimated based on the diffusivity of particles using the Stokes–Einstein relationship. Further information about the technique can be found in (Duretta and Picchioni, 2018). To measure particle size, the prepared colloidal solutions were stored at 80 °C for 3 hours. The measurements were conducted in a PCS8501 glass cuvette at a temperature of 80 °C using Malvern Zetasizer Nano ZS equipment.

Emulsification effect measurement

For the investigation of emulsifying effects, a shaking cylinder with a nominal volume of 25 ml was utilized. The measurement of the required quantity of the tested phases was conducted using this cylinder. For the entire examination, a total of 20 ml of sample is required. In the case of samples with a 50-50% volume ratio, this corresponds to 10 ml of oily phase and 10 ml of aqueous phase. The homogenization of the phases was carried out by flipping the shaking cylinders 30 times after their closure. Following the homogenization, a drying oven

was utilized for the tempering of the samples. After the expiration of the test period, the determination of individual phases is performed through visual inspection.

Rheology measurement

The rheological properties of surfactant solutions were assessed using an Anton Paar dynamic shear rheometer equipped with a concentric cylinder measurement cell and CC27 marked cylinder type. The samples were placed in a temperature-controlled measurement vessel maintained at 80 °C.

Oil displacement test

The core flooding tests were conducted using a method designed to simulate high-temperature oil reservoirs. The crude oil used originated from Algyó, Hungary, and the testing temperature was set at 80°C. The tests were carried out in a core with an inner diameter of 2.5 and a length of 30 cm. The heterogeneity of the formation was simulated using a consolidated core sample. The total oil recovery and the oil recovery through water flooding were calculated, and the difference between them was considered as the tertiary oil recovery factor by polymer or polymer/surfactant hybrid flooding.

3. Results

Surfactant and surfactant-polymer flooding is an EOR technique in which the phase behavior inside the reservoir can be manipulated by the injection of surfactants and cosurfactants, creating advantageous conditions in order to mobilize trapped oil. The IFT values of the prepared samples were measured at 40°C, because at higher temperatures bubbles were formed which disturbed the measurements. The results of IFT values are given in Table 3.

Table 3: IFT values of surfactant mixtures and polymer and surfactant mixtures

	IFT, mN/m
SURF_1	0.062
SURF_2	0.039
SURF_3	0.091
P+SURF-1	0.039
P+SURF-2	0.021
P+SURF-3	0.028

The data showed that the IFT decreased when the solutions contained also flow modifier type polymer and not only a mixture of different surfactants. The difference was 37-69 %. Therefore these polymer-surfactant mixtures with low interfacial tension can be good candidate for chemical enhanced oil recovery.

DLS is a technique for measuring the particle size. The size of a particle is calculated from the translational diffusion coefficient by using the Stokes-Einstein equation. The diameter calculated by DLS is a value what refers how a particle diffuses within a fluid so it indicates the hydrodynamic diameter. The hydrodynamic sizes of the surfactant mixed micelles and of polymer are given in Table 4.

Table 4: Hydrodynamic radius of surfactant mixtures and polymer and surfactant mixtures

	Hydrodynamic radius, nm
SURF-1	89
SURF-2	80
SURF-3	94
P	182
P+SURF-1	291
P+SURF-2	262

The smallest size had the SURF-1 and SURF-2 samples, which contained only surfactants. The HPAM alone had higher size (182 nm) and narrower distribution. In case of the combination of the surfactants and the HPAM, a monomodal size distribution with an average micelles size of above 200 nm and a wide range of size distribution (100–300 nm) were obtained. The type of the wide distribution and the higher particle size indicated the interaction between the surfactants and HPAM in the solution. It was found that the hybrid micelle size obtained from the surfactant mixtures by adding flow modifier polymer significantly increased. The increase in the hydrodynamic diameter was less than an order of magnitude, so it does not cause any problems in terms of

applicability Emulsification effect was tested by bottle test. A bottle test is an analytical procedure in which a chemical is added to samples of a water-oil emulsion to determine the most effective and quantity of chemical needed to separate the emulsion into oil and water fractions. The results are summarized in Table 5.

Table 5: Emulsification effect of surfactant mixtures and polymer and surfactant mixtures

	Emulsification effect (middle phase), V/V%
SURF-1	60
SURF-2	50
SURF-3	55
P+SURF-1	90
P+SURF-2	85
P+SURF-3	90

The smallest middle phase had the SURF-2 and SURF-3 samples, which contained only surfactants. The combination of the surfactants and the HPAM had amount of middle phase above 85 v/v%. By using polymers, it was possible to increase the amount of oil that can be emulsified using a unit of surfactant.

Simulating the real conditions the measurement was performed after water flooding and the additional oil production was determined after emulsion breaking. The results are summarized in Table 6.

Table 6: Additional oil recovery, % (OOIP) of surfactant mixtures and polymer and surfactant mixtures

	Additional oil recovery, %
SURF-1	60
SURF-2	50
SURF-3	55
P+SURF-1	90
P+SURF-2	85
P+SURF-3	90

Polymer and surfactant flooding consist in mixing different surfactants and long chain polymer molecules with the injected water in order to increase the water viscosity. Investigating the rheological properties of the flooding solutions is very important. The measure of viscosity as a function of shear rate gives information about the behaviour of the solution during the flooding process (i.e., low velocity of shear rate) is comparable to the conditions in a reservoir (it can be used to characterize the flow in the pores of the rock), the high velocities to the injection well (it can be used to characterize the flow in the well tube). At slow share rates the viscosity is higher for P+SURF-1, P+SURF-2 and P+SURF-3 than for HPAM, which is favourable for the flooding process (see Figure 1). The increase in viscosity can be explained by the increased micelles size obtained by DLS measurements. At high shear rate there is a decrease in viscosity of the mixed solutions close to the HPAM solution viscosity, which is also wanted during the injection of the solution.

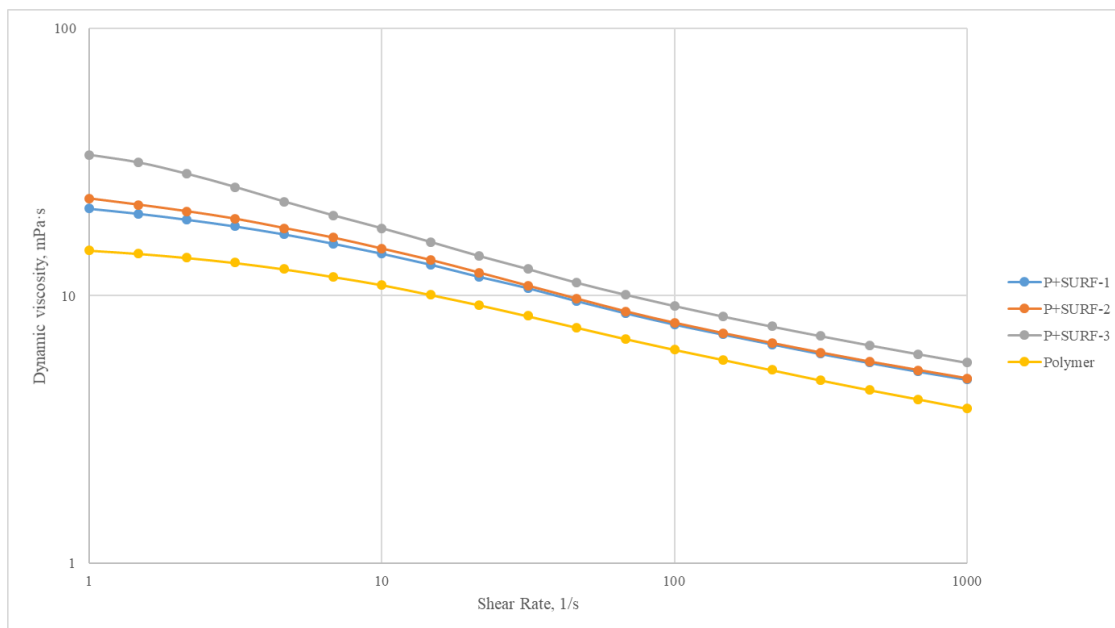


Figure 1: Rheological properties of polymer and polymer-surfactants solutions

The increase in viscosity can be explained by the increased micelles size obtained by DLS measurements. At high shear rate there is a decrease in viscosity of the mixed solutions close to the HPAM solution viscosity, which is also wanted during the injection of the solution.

Four different techniques were used to demonstrate the interaction between the investigated surfactant compositions and the applied flow modifier type polymer.

4. Conclusion

The interaction between different surfactant packages and the flow modifier type polymer in brine solutions were analysed by different methods. The new experimental results are summarized as follows:

- It was found that in the presence of flow modifier type polymer a significant decrease of IFT values created in the crude oil/brine emulsions using different mixtures of own developed surfactants.
- Based on the experimental data a significant level of interaction between the surfactants and the HPAM polymer were found: the hydrodynamic size of the mixed surfactant-polymer composites was higher than alone the size of the polymer or self the surfactant mixtures.
- The results obtained by rheological measurement could be explained by DLS data and confirm the hypothesis, that the higher viscosity of the polymer-surfactant solution can be caused by the increased hybrid micelle size formed by the interaction of the surfactants and the flow improver polymer.
- Based on the experimental data a significant level of interaction between the surfactants and the polymer were found, the emulsification effect of surfactants and polymer-surfactant mixtures was higher than alone the surfactant mixtures.
- It was obtained that by applying flow modifier polymer together with the own developed surfactants the additional oil production could increase.

We managed to improve the properties of surfactant compositions by adding polymers. Examining the surfactant-polymer compositions together, the results of the efficiency tests of the solutions improved, which was also confirmed by the results of the oil displacement tests. Based on these outcomes it can be stated that significant and advantageous interactions between surfactants and flow improver polymer were detected which caused increased viscosity in flooding solutions. This favourable viscosity change effect can be an important contribution to improve the efficiency of polymer-surfactant compositions used in the EOR type exploration processes.

Nomenclature

DLS – dynamic light scattering

EOR – enhanced oil recovery

HPAM – partially hydrolysed polyacrylamide

IFT – interfacial tension

OOIP – original oil in place, %

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