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Study on Characteristics of Micelles Formed by Surfactants and Polymer Mixtures for Enhanced Oil Recovery

Roland Nagy*[a], László Bartha[a] Judit Tóth[b], Árpád Vágó[c]

[a]Department of MOL - Hydrocarbon and Coal Processing, University of Pannonia, Egyetem str 10., Veszprém Hungary
[b]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Pusztaszeri str. 59-67, Budapest, Hungary
[c] Upstream Division, MOL Plc, Oktoberhuszonharmadika str. 6., Budapest, Hungary
nroland@almos.uni-pannon.hu

The bio-degradable vegetable oil based nonionic surfactants are generally used in the oil and petrochemical industry. This publication considers two combinations of various surfactants applied in enhanced oil recovery (EOR). The polymer-surfactants solutions prepared by mixtures of two types of nonionic surfactant and an anionic surfactant and a flow modifier type polymer used in various concentrations were studied.
The physical properties of micelles formed in aqueous solution in terms of viscosity are measured by dynamic shear rate rheometer (DSR). The study was extended to measure the size of micelles formed in aqueous solution of various surfactants mixtures. The results obtained by dynamic light scattering (DLS) technique at different temperatures have been also presented. The influence of the surfactant composition on micelle size and the surface properties of the synthesized surfactants were also considered.
As a results of the rheological measurement were demonstrated that higher viscosity of the surfactant solution was caused by the increased micelle size. The hydrodynamic radius was also calculated based on current measurements, and fitted well with the results. The size distribution of micelles formed in aqueous solution by different surfactant mixtures were examined as a function of temperature, and surfactant concentration.

1. Introduction

Surfactants are prepared on the basis of both natural and synthetic raw materials, and applied for production of several types of foods, agrochemicals, petrochemicals, cosmetics and explosives. Presently, about 50% of the surfactants used in the industry are derived from petrochemical raw materials, and the other 50% are derived from oleo chemicals. Some emulsion-based products need only to remain stable for a short period (e.g. between two processing steps), whereas others must remain stable for relatively long-periods (e.g. a few weeks, months or years). Therefore the developer of surfactants must have a good understanding of the factors that determine their size distribution in order to produce them with the required characteristics (Schramm, 2000.). he most important parameter of the emulsions are the viscosity, the particle size distribution, the other colloidal characteristics and the relationship between the main properties. Numerous of studies have been carried out to investigate these parameters by using experimental and commercial surfactants .
The study of the interaction between polymers and surfactants was the subject of several research efforts, because of both theoretical and practical interest. Understanding of polymer-surfactant interactions is relevant to important industrial processes such as enhanced oil recovery (Maindarkar, 2013.).
According to the EOR experiments published in the literature and our own research it was found that by using certain combinations of different surfactants and flow modifying water-soluble polyacrylic acid derivatives, substantially higher displacement efficiency can be achieved than by the individual components alone. Our research was intended to study this synergism (Adasani, 2011).
The aim of this study was to determine the size distribution of experimental surfactant package and its combination with a commercial flow modifier type polymer in the solution and explore the possible

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interaction between polymer and surfactant used with special interest of enhanced oil recovery. Therefore, our investigation was focused on the influence of temperature and surfactants concentration on the particle size and rheological behaviour of the surfactant and surfactant-polymer mixtures.

2. Materials and methods

2.1 Preparation of the surfactant and surfactant-polymer solutions

For the preparation of the experimental colloid solutions one anionic (MOLANIONIC) and two nonionic (PENONIONIC I and II) surfactants developed and produced by cooperative research groups of University of Pannonia and Hungarian Oil and Gas Company (MOL Plc) were used. Additional partially hydrolysed synthetic polyacrylamide (HPAM) was used as a mobility control polymer type.

Concentration of surfactants were 5, 10, 15, 20 and 25 g/dm^3 and of polyacrylamide 1 g/dm^3. The polymer-surfactants solutions were prepared from water that derived from petroleum reservoir of Algyő.

The surfactant containing emulsions were prepared by mixing of all components (detailing in Table 2.1.) and homogenizing by using ultrasonic equipments. Then the colloidal solutions were stored at 50, 60, 70 and 80 °C temperature for 3 h.

Table 2.1.: Composition of the surfactants and surfactant-polymer mixtures

Symbols of compositions	K-1	K-2	KP-1	KP-2
Components	Ratio of components, %			
MOLANIONIC	55	60	51.56	56.25
PENONANIONIC I	25	40	23.44	37.5
PENONANIONIC II	20	-	18.75	-
HPAM	-	-	6.25	6.25

2.2 Rheology measurement

The rheological properties of surfactant solutions were measured by using Anton Paar dynamic shear rheometer with concentric cylinder measurement cell. The cylinder type of Anton Paar CC27 was used. Samples were placed in the temperature-controlled measurement vessel at 80°C.

2.3 Determination of the size distribution by dynamic light scattering method

Dynamic light scattering experiments were carried out with the solutions by using Malvern Zetasizer Nano ZS instrument. The technique was suitable for measuring the size and size distribution of micelles formed in aqueous solution of various surfactants and polymer mixtures.

2.4 Transmittance

The AvaSpec fiber optic spectrophotometer to characterize the solubility of the surfactants in water was used. In the experimental work an AvaSpec 2048 Standard fiber optic spectrophotometer with AvaLight-DHc Compact Halogenlight source was applied.

The characteristics of the spectrophotometer:

- Optical level; Symmetric Czerny-Turner, 75 mm focal length
- Wavelength 410 nm
- Detector; CCD linear, 2048 pixels

3. Results and discussion

3.1 Dynamic Light Scattering measurements

Dynamic Light Scattering (sometimes referred to as Photon Correlation Spectroscopy or Quasi-Elastic Light Scattering) is a technique for measuring the size of particles typically in the sub micron region. DLS measures Brownian motion and relates this to the size of the particles. The velocity of the Brownian motion is defined by a property known as the translational diffusion coefficient (usually given the symbol, D). The size of a particle is calculated from the translational diffusion coefficient by using the Stokes-Einstein equation. The diameter that is measured in DLS is a value that refers to how a particle diffuses within a fluid so it is referred to as a hydrodynamic diameter.

Based on the dynamic light scattering measurements it was observed that both the tenside and the polymer-tenside solutions have one peak (See Figure 3.1.). In the case of the polymer and the surfactant mixtures in aqueous solution the similar form of the size distribution were obtained.

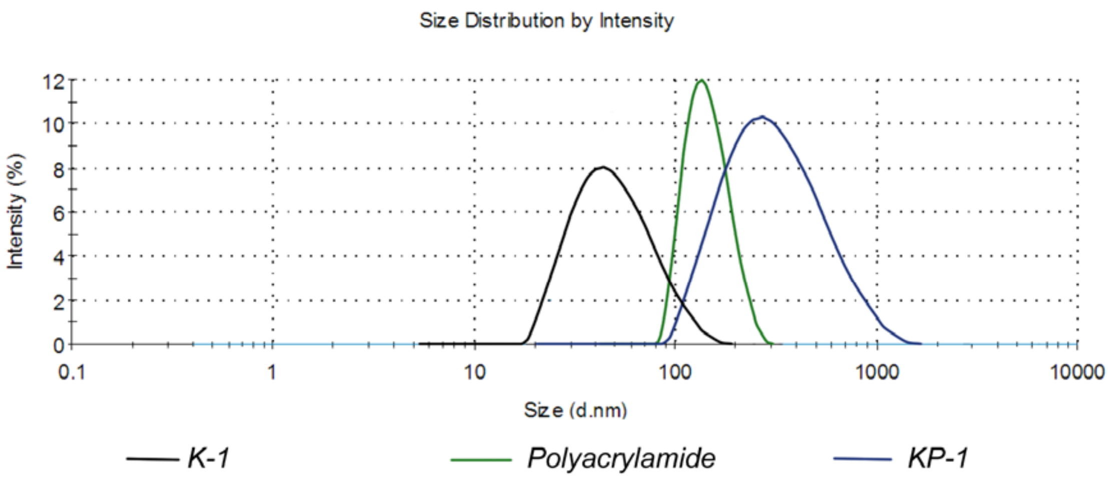

Figure 3.1.: Size distribution of the K-1, Polyacrylamide and KP-1 solution (70 °C)

The average size of the surfactant package micelles was 80 nm with a range of 20-200 nm. The polyacrylamide has a higher average size (180 nm) and a narrow size distribution (100-300 nm). In the case of combination of the surfactants and the polyacrylamide a monomodal size distribution with an average micelles size of 150 nm and a wide size distribution of 100-1,000 nm were obtained. The type of the wide distribution and the higher particle size has proved the interaction of the surfactants and polyacrylamide in the solution.

3.1. Influence of temperature

The polymer-surfactant solutions were treated at 50°C, 60°C, 70 °C and 80 °C temperature for 3 h. The last value of the temperatures is important since these polymer-surfactants mixtures are going to be used in reservoir, where the temperature is about 80 °C. The concentration of the surfactants was 15 and of polymer 1 g/dm^3. The hydrodynamic size of the micelles in different solutions and temperatures is given in Table 3.1. and demonstrated in Figure 3.2.

Table 3.1.: Hydrodynamic radius of the micelles in the mixture solutions in different temperatures

Sample	Hydrodynamic radius, nm	Hydrodynamic radius, nm	Hydrodynamic radius, nm	Hydrodynamic radius, nm
	50 °C	60 °C	70 °C	80 °C
K-1	55.0	53.7	57.1	64.95
K-2	50.6	54.1	59.7	68.45
KP-1	98.2	100.8	112.9	120.4
KP-2	123.2	123.3	139	150.8

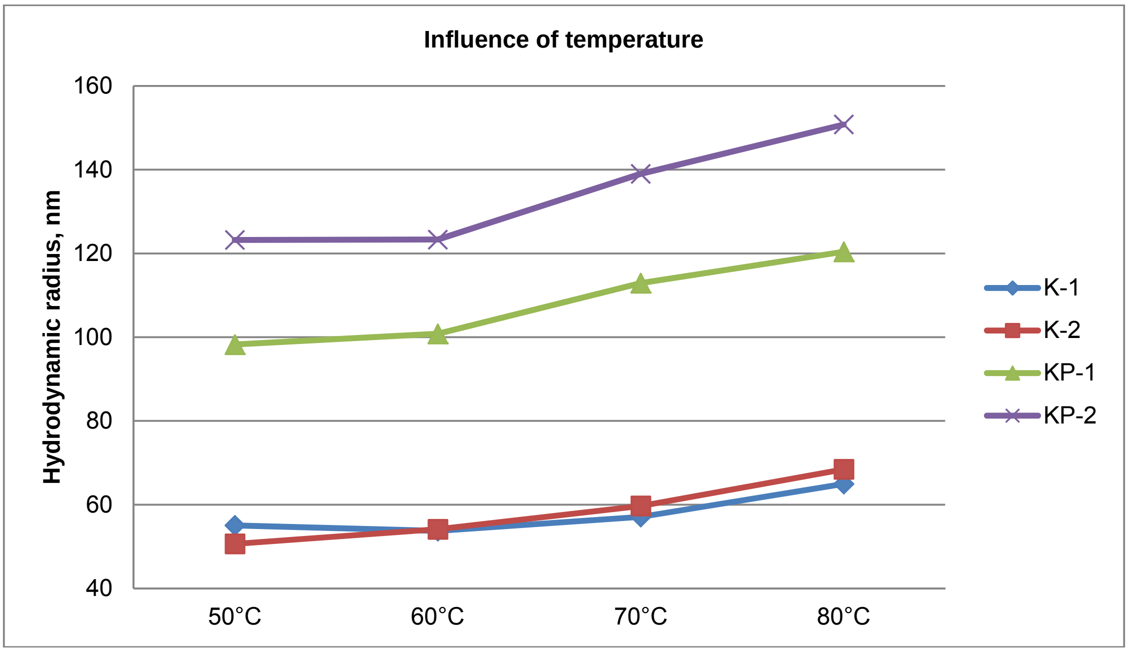

Figure 3.2.: Influence of temperature on hydrodynamic size

It was found that at higher temperature the micelle size significantly increased in both cases, i. e. in the surfactant and surfactant-polyacrylamide mixture solutions.

3.2 Influence of surfactants concentration

It was studied how the concentration of the surfactant influenced the micelle size in the solution. The concentration of the surfactant was 5, 10, 15, 20 and 25 g/dm^3 and of polymer 1 g/dm^3. The temperature of solutions was constant 80°C. The measured hydrodynamic size data are given in Table 3.2. and demonstrated in Figure 3.3.

Table 3.2.: Influence of surfactant concentration on hydrodynamic size

	Concentration, g/dm^3	KP-1	KP-2
Hydrodynamic radius, nm	5	84.1	88.6
Hydrodynamic radius, nm	10	89.9	94.7
Hydrodynamic radius, nm	15	92.1	95.5
Hydrodynamic radius, nm	20	95.1	102.1
Hydrodynamic radius, nm	25	150.9	128.3

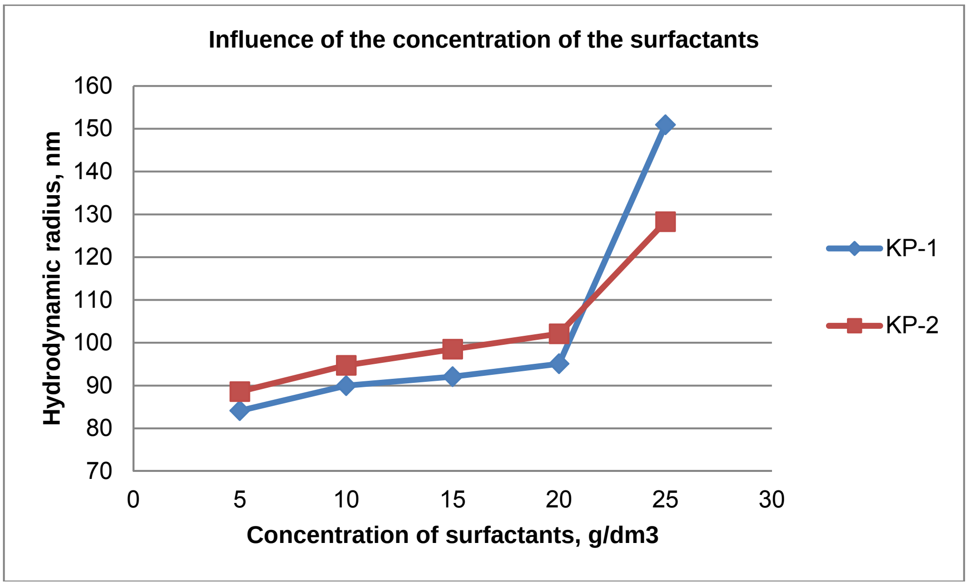

Figure 3.3.: Influence of the concentration of the surfactants on hydrodynamic size

It was found that by increasing concentration of surfactants in the surfactants and polymer mixture solution the micelle size increased. Remarkable increasing of the hydrodynamic diameter was found in case of concentration of 25 g/dm^3, especially of KP-1 solution. That concentration can be a limit of industrial application because of the large size can be reduced the effectiveness of the oil recovery. On the basis of previous investigations the optimal concentration of the surfactant is 15 g/dm^3 taking into consideration the effectiveness of the oil recovery and the cost of the surfactant solution.

3.3 Relation between size and rheology

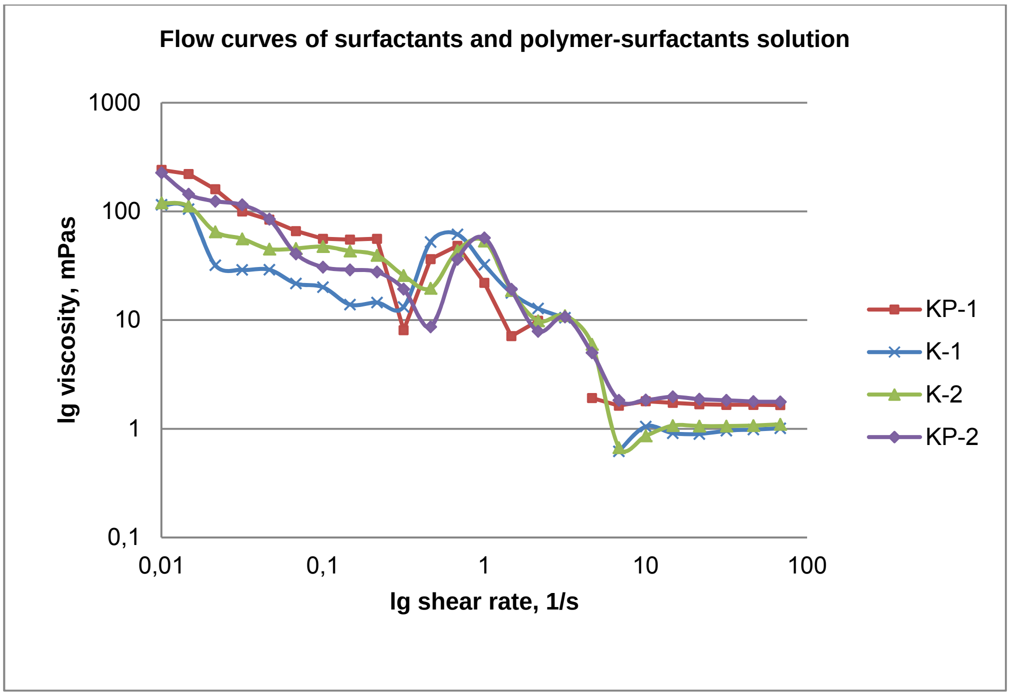

Figure 3.4.: Flow curves of surfactants and polymer-surfactants solution

There was the same trend between the results of the size distribution and the viscosity at low shear rate (See Figure 3.4.). At the middle shear rate the gradual degradation of the micelles structure could be indicated by the characteristic peaks of locally breakpoints. Based on the data it can be supposed that the higher viscosity of the polymer-tenside solutions were caused by the increased micelle size in consequence of the strong interaction between the HPAM and surfactants.

Besides the particle size of the micelles and rheological behaviour of the colloid mixtures the solutions transparency were also determined at 80°C in 15 and 1 g/dm^3 of surfactant and polymer concentration, respectively. The measured data are given in Table 3.3.

Table 3.3.: Transparency of surfactants and polymer solutions

Sample	Transmittancy, %
K-1	18
K-2	58
KP-1	20
KP-2	65

Based on the data it could be concluded that transparency of the colloid solutions is influenced more by the surfactant than by the polyacrylamide.

4. Conclusions

The size and distribution of micelles formed in aqueous solution by different surfactant mixtures and the flow modifier type HPAM polymer were analyzed. The new experimental results were summarized as follows.

- Based on the experimental data a significant level of interaction between the surfactants and the HPAM polymer were found.
- The hydrodynamic diameter of the micelles depends both on the temperature and the composition of the surfactants package used in the colloid solution.
- The results obtained by rheological measurement could be explained with DLS data and confirm the hypothesis, that the higher viscosity of the polymer-tenside solution caused by the increased micelle sizes formed by the interaction of the surfactants and the flow improver polymer.
- The hydrodynamic radius was also calculated based on current measurements, and agreed well with the results.

Based on these results the interaction between the surfactants and the polymer can be stated since significant changes in the hydrodynamic size of micelles and the rheological behaviour were detected in the mixture of surfactant and polymer solutions. This effect has an important contribution to improve the efficiency of polymer-tenside compositions used in the EOR type exploration processes.

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