Influence of HPAM on W/O Emulsion Separation Properties

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ABSTRACT:

The present study reports on the influence of partially hydrolysed polyacrylamide (HPAM) on essential w/o emulsion properties. The characterization has been undertaken with low field NMR to follow droplet sizes and distributions, sedimentation and coalescence kinetic, bench-scale electrocoalescence (Ecrit) experiments to follow emulsion stability changes and electrorheology to detect changes in the viscosity upon applying an external electric field.

The result is that HPAM is basically not influencing the DSD and stability level of the emulsions as can be expected of bulk polymer. However there seems to be an interaction between added demulsifier either through direct molecular interaction or via an interfacial complexation.

# Introduction

Enhanced Oil Recovery (EOR) is a widely considered technique to increase the production of crude oil from the reservoirs[1](#_ENREF_1), [2](#_ENREF_2). Surfactant EOR is widely proposed to recover the residual crude oil. The main modus operandi of these surfactant molecules is to reduce the interfacial tension between oil and water, and to alter the wetting conditions in the reservoir from oil-wet to water-wet. However when using only aqueous surfactant solutions a fingering might take place in the reservoir which will lead to an uneven propagation of the surfactant front. To balance the viscosity and to increase the sweep efficiency polymers have been used since late 1950s. Standnes has compiled most of the known field cases in his extensive review[3](#_ENREF_3) with summarizing comments. He reports an overwhelming use of partially hydrolysed polyacrylamide (HPAM) for this purpose. According to Standnes et al.[3](#_ENREF_3), 40 of the reported polymer projects were clarified as successes while 6 were considered less successful. A complete statistic show that USA reports 46 projects (64 %), Canada and China 6 (8 %), Germany 4 (5.6 %) etc. Of these 6 cases were offshore while 66 were implemented on-shore. HPAM was by far the most frequently used polymer (92 %).

The challenges in the polymer flooding test seem to be related to injectivity during the operation, corrosion of process equipment and water-in-oil (w/o) emulsion formation.

To introduce polymers to increase the EOR efficiency can have severe consequences later on in the production profile. In this paper we focus on how the HPAM will influence the separation of water and oil by changing the stability of the water-in-oil emulsions.

Literature deals with different aspects of separation problems. Mostly the reported studies view systems consisting of alkali/surfactant/polymer with o/w emulsions. There seems to be a wide agreement that in these systems the alkali and surfactant components have a stabilizing effect on the dispersed oil droplets in the dispersion / emulsion. Obviously there is synergy effect of the alkali and added surfactant. The alkali will raise the pH and activate the fatty acids in the crude oil droplets creating an indigenous anionic surfactant that strengthens the function of the added EOR surfactant (in most cases a petroleum sulfonate or a nonionic surfactant)[4-6](#_ENREF_4). Some authors try to differentiate the mechanisms behind the impact on the o/w emulsions. Generally the major effect is attributed to the surfactant blend while the HPAM seems to have a smaller impact, mostly to increase the viscosity and influence the oil-droplet interaction (via collision)[4](#_ENREF_4). Addition of HPAM influences negatively the emulsion stability when added in concentrations below 300 mg/L for a high molecule weight (1.2 x 107 MW) polymer, and 800 mg/L for a 3.0 x 106 MW HPAM for oil-in-water emulsions[4](#_ENREF_4). For higher molar masses the destabilization seems to pass through a flocculation stage, while at higher polymer concentrations the increased water viscosity seems to reduce the droplet collision.

The literature in the field of w/o emulsion seems to be much scarcer and there is obviously a need for fundamental work to clarify effects. Our study should be seen as screening study where central separation parameters are identified and studied. It is our purpose to show how HPAM influences emulsion stability, droplet size distribution, and the influence of an external electric field. The study also covers the influence of mixing parameters on the structure and viscosity of the HPAM solutions. For this purpose we have chosen a set of experimental bench-scale techniques developed at the Ugelstad Laboratory. These include low frequency NMR to determine droplet sizes and distributions, sedimentation and coalescence kinetics of emulsions. The rheological properties of emulsions[7](#_ENREF_7), [8](#_ENREF_8) under influence of external electric field (AC) have also been investigated. In addition to the influence of HPAM we have also studied how some commercial demulsifiers influence the separation process when applied to emulsions with HPAM. Based on data from the characterization above on realistic production fluids we discuss the influence of HPAM on central parameters for an up-scaled separation process.

# Fundamentals

## Formation of Emulsions[9](#_ENREF_9)

Emulsions are not thermodynamically stable, and as such will always eventually phase separate. Some of the kinetic stability of an emulsion is derived from the droplet size since only small droplets (μm range) will have kinetic energy comparable to the gravitational energy. As such, information about droplet size and droplet size distribution is of vital importance to evaluate the stability of an emulsion[10](#_ENREF_10). The emulsion droplet size is essentially determined by the internal Laplace pressure and the (shearing) energy input into the mixture when the emulsion was formed. This can be expressed in the Weber number

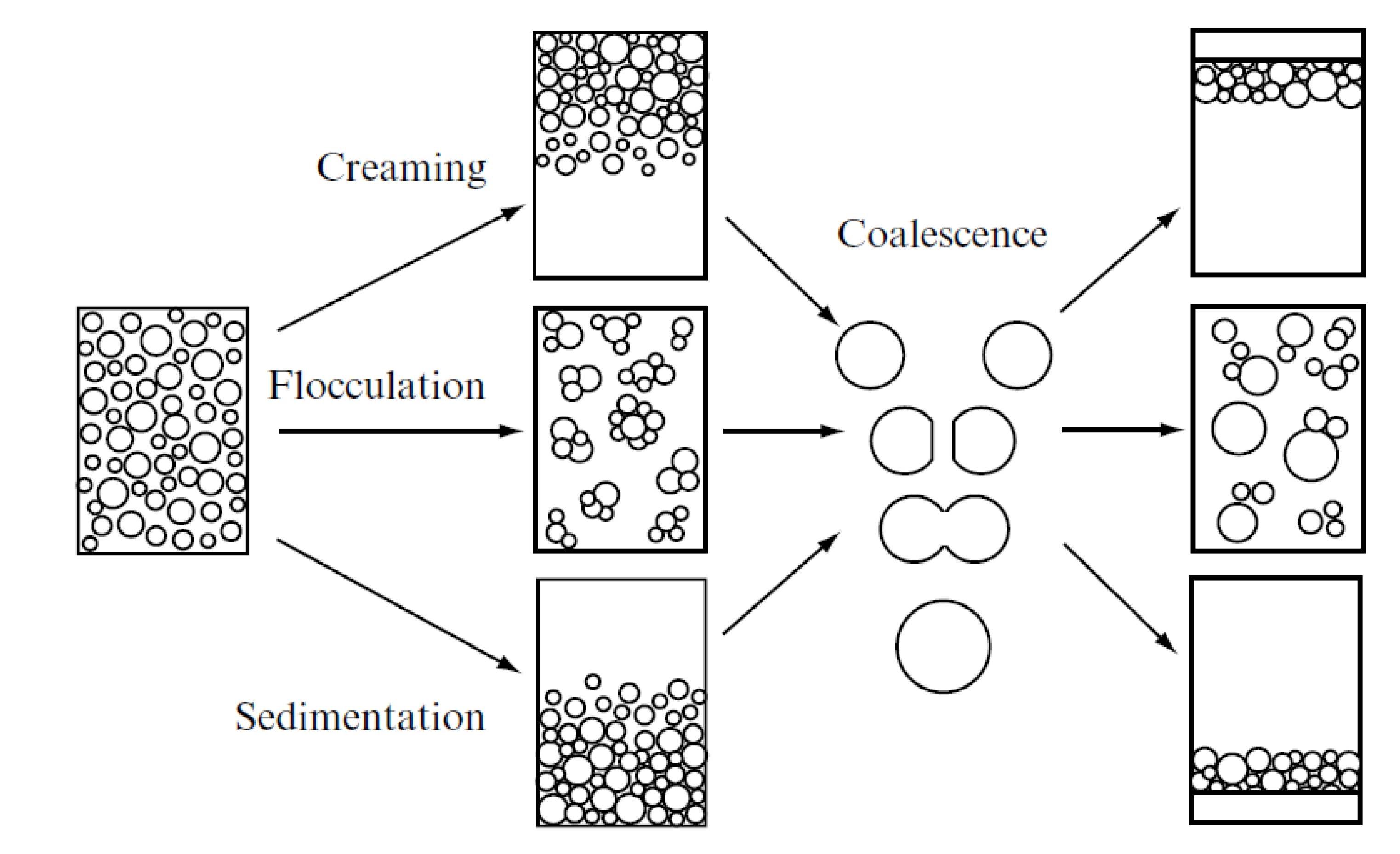
(1)



in which G is the shear rate, ηc is the viscosity of the continuous phase, r is the droplet radius, and γ is the interfacial tension. As such, the Weber number shows the ratio between shear forces and the interfacial tension. If the Weber number is above some critical value, dependent on the ratio of the viscosity of the continuous and dispersed phase (ηD/ηc), then droplets will break up. Since HPAM is a bulk polymer and water soluble (and not interfacially active), eq (1) shows to a first approximation that HPAM might affect the droplet size in a w/o emulsion with HPAM, mainly through the effect on the viscosity of the dispersed phase.

## Destabilization of Emulsions

Since emulsions are kinetically stabilized systems they will as function of time break down to an equilibrium state with a water phase and an oil phase. The main processes preceding equilibrium are sedimentation (creaming) and coalescence (Figure 1).



**Figure 1:** Schematic representation of emulsion flocculation, sedimentation, and coalescence phenomena[11](#_ENREF_11). Reprinted with permission from Holmberg et al. Copyright 2003 John Wiley & Sons, Ltd.

Sedimentation is the process causing a gradient in the number of water droplets due to a gravity accumulation of droplets. A simple approach to sedimentation (creaming) is Stokes law for settling velocity, i.e.

(2)



where vs is the droplet’s settling velocity (m/s) (vertically downwards if ρp > ρf, upwards if ρp < ρf ), g is the gravitational acceleration (m/s2), ρp is the mass density of the droplets (kg/m3), ρf is the mass density of the fluid (kg/m3), and μ is the dynamic viscosity (kg /m\*s). This also means that vs is dependent on the droplet size distribution.

A simple approach to evaluate the influence of HPAM on sedimentation would be to evaluate how HPAM influences the individual parameters in Stokes law, and in which direction this would drive sedimentation (creaming) qualitatively. Since HPAM is a bulk component in the water phase with a density higher than water, Δρ should increase since the density of the dispersed phase would be higher. Since HPAM is located exclusively in the water phase, ηc would be constant. The influence of HPAM on the radius of the droplets must be evaluated for each individual case. As such, the major impact HPAM could have on the sedimentation (creaming) rate would be through Δρ, and as such accelerate the sedimentation.

Coalescence is the process when droplets form larger entities and finally result in phase separation. The coalescence is a complex process dependent on a number of different factors, such as collision frequency, velocity, and coalescence probability, the surface tension of the droplet, and the surface rheology of the droplet, with main experimental parameters being interfacial tension and interfacial rheology, since qualitatively the coalescence rate is determined by the properties of the thin films separating the droplets[9](#_ENREF_9), [12](#_ENREF_12), [13](#_ENREF_13).

In a first approximation, HPAM being a bulk polymer without any influence on interfacial parameters, there should be no influence on the coalescence process. However, the application of an external electric field might change this situation as seen below. Also the efficiency of added demulsifiers can depend on presence of HPAM.

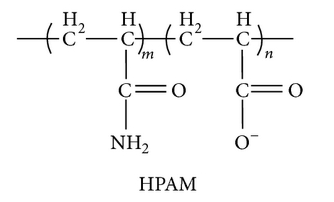
The influence of an external electric field on an emulsion is two folded; first it will induce a time dependent deformation on the individual water droplets. This response is frequency and field dependent and motivates an investigation at different electrical field frequencies. The second response is related to the ionic transport through thin films. Since HPAM is a high molecular weight polyelectrolyte, it should be confined to the droplets independent of the electric field, although it might have an effect on the distribution of the small electrolytes (salts) in the water droplet. As such, the HPAM might not have a direct effect of the emulsion stability under an electric field, but might anyway have an indirect effect by influencing the small ions polarizing the water droplets in the external field.

The background given above is qualitative and represents a first approximation of expectations. However, since the systems and their interfaces are very complex an extensive experimental campaign is motivated in order to clarify the influence of HPAM on w/o emulsions in detail.

# Experimental

## Chemicals

Two heavy crude oils, one from the Middle East and one from the North Sea, were used in this study. HPAM (partially hydrolyzed polyacrylamide, figure 2) used was Flopaam 3230S and 3630S, supplied by SNF Floerger. Demulsifier has been developed for North Sea conditions. Synthetic produced water (Table 1) was used as water phase.



**Figure 2:** Structure of the partially hydrolyzed polyacrylamide HPAM.

**Table 1:** Synthetic produced water composition

|  |  |
| --- | --- |
| Constituent | Concentration (g/L) |
| CaCl2 2 H2O | 0.272 |
| MgCl2 6 H2O | 0.059 |
| NaCl | 5.9006 |
| NaHCO3 | 0.2545 |
| Na2SO4 | 0.7199 |

## Preparation of Samples

### HPAM Solution Preparation

Water (milli-Q or SPW) and HPAM was stirred with a four bladed propeller at 400-600 rpm, and after 3h the polymer particles were dissolved. The solution was transferred to a shaker where it was shaken at 100-200 rpm for minimum 17 h.

### Emulsion Preparation

Different parameters, such as temperature, mixing speed, mixing device, mixing time, water cut, water composition, and mixing device were screened before a final selection of experimental emulsion parameters facilitating stable enough systems to be analyzed by electro rheology, NMR and Ecrit experiments. w/o emulsions were prepared by mixing synthetic produced water (SPW) and crude oil, always adding to a total volume of 30 mL. The mixing was performed with a four bladed propeller at 2000 rpm for 15 minutes at a temperature of 40 °C.

## Techniques and Procedures

### ****Viscosity Measurements****

The viscosity was determined using a Physica MCR 301 rheometer from Anton Paar, fitted with cylinder-cup (CC27) geometry. The measuring cup of CC27 had a radius of 14.4600 mm, while the measuring bob had a radius of 13.3235 mm, the cone angle is 120° and the measure gap was 1.137 mm. 20 ml sample was run in two parallels with a constant temperature and shear rate from 0.1 s-1 to 1000 s-1 and back down to 0.1 s-1.

### Interfacial and Dilatational Rheology Measurements

Interfacial tension and dilatational rheology were measured using profile analysis tensiometer (PAT-1) from Sinterface, Germany. The instrument was calibrated with a sphere of known diameter and the surface tension of water was measured to check the calibration as well as to ensure that there is no contamination in the system.

The cuvette was filled with the HPAM buffer solution (no salt). A drop of oil phase was then introduced into the cuvette at the tip of a hook using a dosing pump. The experiments were carried out at room temperature (ca. 22°C). The volume of the oil droplets were monitored and adjusted continuously by the software to ensure that it is maintained at 25 μl. The aging time before starting oscillations was set at 2 hours. The periods chosen for the oscillations were 100s, 80s, 60s, 40s and 20s with a total of 5 periods for each sequence while the amplitude of oscillation was 7%. All the experiments were performed at least twice to ensure reproducibility of results.

In dilatational measurements, the rheological properties of the adsorbed film are investigated by changing the interfacial area while keeping the shape of interface nearly unaltered. Thus, the interfacial area A is given by:

(3)



represents the amplitude area, is the equilibrium interfacial area, ∆A is the area change at any time t and ω is the frequency of oscillations. The interfacial rheological properties are characterized by the complex interfacial dilatational modulus ε, which is defined as the increase in interfacial tension γ for a unit of relative increase in interfacial area A.



(4)



When the area is deformed, the change in interfacial tension can be written as:

(5)



where, = interfacial dilatational elasticity and = interfacial dilatational viscosity



Thus, the complex interfacial dilatational modulus can then be written as:

(6)



Or,

(7)



where, the first term E’ represents the elastic contribution while the second term E” represents the viscous contribution.

### Nuclear Magnetic Resonance (NMR)

#### Water Distribution

Figure 3 shows the NMR sequence used for measuring the amount of water at different locations in the test samples. Initially, the NMR signal contains a crude oil and water contribution. Because of a significantly lower transverse relaxation time for the crude oil, one may use the C1 loop to suppress the contribution from the crude oil. The first gradient echo is then from water only, and a Fourier transform of this echo yields a water profile. The second loop is used to measure a gradient echo at an even longer observation time, which gives another water profile. These two profiles may then be used to correct for transverse relaxation of the water signal, ending with a third water profile, which is unaffected by transverse relaxation processes. This profile is proportional to the water content along the sample, and by calibrating with a sample that contains 100% water; one can measure the water content along the height of the emulsion. C1 is determined by measuring the signal for pure oil phase and determining at which C1 value the entire oil signal has vanished.

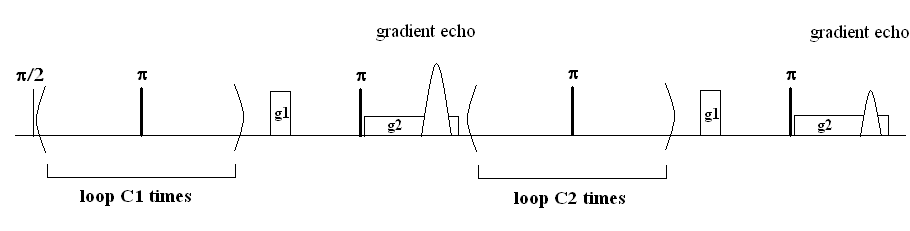


Figure 3*:* NMR sequence used for acquiring the water profile.

The NMR measurements were performed on a low field NMR spectrometer supplied by Anvendt Teknologi AS (Norway). The magnetic field is 0.48 T, capable of delivering a gradient strength up to 4 T/m. The duration of the sinusoidal gradient pulse is 0.8 ms, and the direction of the gradient is along the length of the tube. The NMR sample tubes of 18 mm diameter were filled with ~4 mL of the emulsion.

Some uncertainties are introduced from approximations in the NMR theory and the sensitivity of the NMR. These measurement uncertainties are dependent on the viscosity of the continuous phase, and decreases with increase in viscosity. For heavy oils (like the ones used in this study) the error in the NMR measurements can be approximated around 5 %. Details about the NMR procedure can be found in Opedal et al.[14](#_ENREF_14) and Simon et al.[15](#_ENREF_15)

#### Droplet Size Distributions by NMR

The method for acquiring droplet size distributions by NMR is thoroughly treated in Sørland[16](#_ENREF_16), and here we sketch the solution which combines diffusion and relaxation time measurements. Restricted diffusion measurements at short observation times is a situation where the surface relaxation term is absent in the solution of the diffusion propagator, i.e. the short time expansion[17](#_ENREF_17). By assuming piecewise smooth and flat surfaces and that only a small fraction of the particles are sensing the restricting geometries, the restricted diffusion coefficient can be written as[17](#_ENREF_17):

 (8)

where *D*(*t*) is the time dependent diffusion coefficient, *D*0 is the unrestricted diffusion coefficient, in bulk fluid, and *t* is the observation time. The higher order terms *in t, φ (ρ , R, t)*, hold the deviation due to finite surface relaxivity and curvature (*R*) of the surfaces. At the shortest observation times these terms may be neglected such that the deviation from bulk diffusion depends on the surface to volume ratio alone. In a porous system a large span in pore sizes must be assumed, and thus eq. 3 must be expected to be valid also for a heterogeneous system. If *ξi* is the volume fraction of the droplets with surface to volume ratio (*S*/*V*)*i*, eq. 8 can be expressed as (9)

 (9)

Measurements of the early departure from bulk diffusion combined with a linear fit of the experimental data to the square root of time will thus result in a value for the average surface to volume ratio [18-20](#_ENREF_18).



Assuming that the water molecules probe the droplets within the sample, there is a simple relation between *T*2 values and the droplet sizes



(10)

This couples the surface to volume ratio to the surface relaxivity, *ρ*, and makes it difficult to assign the T2 distribution to a (V/S) distribution. However, if the assumption made in equation 10 holds for any droplet size, with *ξi* being the volume fraction of pores with surface to volume ratio (S/V)i and corresponding relaxation time *T*2*i* , it may be written



(11)

Here the basic assumption that the surface relaxivity *ρ* is independent of droplet size is made use of. The left hand side of equation 11 is the harmonic mean of the *T*2-distribution weighted by the fraction *ξi* of nuclei with relaxation time *T*2*i* and *n* is the number of subdivisions of droplet sizes. This average can be calculated from the *T*2-distribution obtained in a CPMG measurement where the magnetization attenuation is converted into a *T*2 distribution by solving an inverse problem using e.g. an Inverse Laplace Transform (ILT) routine. Then the surface relaxivity *ρ* can be calculated from equation 11 if the average surface to volume ratio is already found from the diffusion experiment. Finally, the measured *T*2-distribution can be transformed into an absolute droplet size distribution (*V*/*S*) by means of the relationship inherent in equation 11.

### The Ecritical cell

The electric field cell consists of two brass plate electrodes separated by a thin Teflon plate. The thickness of the Teflon plate is 0.25 mm and it has a 10 mm diameter sample hole in the center[21](#_ENREF_21).

The brass plate electrodes are connected to a power supply (Agilent 6634B) that can increase voltage stepwise up to 100 V DC and measure the current through the emulsion. A sudden increase in current running through the sample indicates that the electric field has broken the droplet state. The corresponding electric field is the Ecrit value. In these experiments the increase was 0.2 V/step (1 second per step).

### Electrorheology

The rheological properties of emulsions in an external field were measured with a Physica MCR-301 rotational rheometer (Anton Paar) in controlled shear mode, using the RheoPlus software. This commercial rheometer, equipped with an electro rheological temperature device, was modified to allow the connection with an AC source[22](#_ENREF_22). The electric part of the equipment consists of a high voltage generator, a function generator, a digital oscilloscope and an amplifier. Measurements of viscosity during exposure of electric field were performed on crude oil emulsions (w/o). In the electro rheology experiments the cup is grounded. The rotating bob is the high potential electrode, with a spring directly connected to the generator slide. Thus, at low shear rates, the quality of the measurements may be affected by interference effects even if the mean values of the rheological variables are clearly identifiable. At higher shear rates this problem disappears. The original measuring bob was modified to give uniform electric field inside the cup[7](#_ENREF_7), [22](#_ENREF_22), [23](#_ENREF_23). In order to allow for an effective electric field application, the rheometer cup is insulated with PVC tape (3M, Super 33+) 0.178 mm thick and designed to perform up to 105 ºC which induces a slight overestimation of the emulsion viscosity.

All the experiments were run at 40 °C for Crude oil with an electric field applied for 10 s. The strengths of the electric fields were 1, 1.5, 3 and 5 kV/cm and the frequencies tested were 100 Hz, 500 Hz and 1000 Hz. All analyses were conducted with sinusoidal waveform.

# Results

We present the results in two sessions where the first session is dealing with polymer HPAM solutions and their properties and the second session is devoted to bulk and interfacial properties of emulsions.

## Influence of Shear Rate on HPAM Stability

The rheological properties of HPAM solutions, with or without mixing at 2000 rpm for 15 minutes after sample preparation, were determined by analyzing the viscosity change with shear rate (1-1000 s-1 and back) at 40 °C.



**Figure 4**: Viscosity of 300 ppm HPAM 3630S in synthetic produced water at 40 °C with and without stirring at 2000 rpm for 15 min (2 parallels).

Both shear rate and temperature will influence the rheological properties of the HPAM solutions[24](#_ENREF_24). Figure 4 gives a representative presentation of these changes at 40°C. The figure reveals that the difference between the stirring (2000 rpm) and no stirring is small while the shear rate gives a much larger impact on the viscosity. The reproducibility is very good and we cannot observe any hysteresis effects when going from low to high shear rate and vice versa.

## Interfacial Tension and Interfacial Rheology Measurements

Figure 5 shows the influence of different concentrations of HPAM on the variations of the interfacial tensions with time for the systems toluene + crude oil / water. The figure shows that the influence of HPAM is very limited.



**Figure 5:** Dynamic interfacial tension as function of time measured at the water containing different concentrations of HPAM / 50 % toluene + 50 % crude oil interface.

Figure 6.a. presents the influence of HPAM on the interfacial moduli E’ and E’’ under similar conditions as in figure 5. There seems to be a strong influence of HPAM on the interfacial rheology parameters. However in order to check to what degree of viscosity enhancement of the bulk will play a role, we performed experiments on system with pure toluene and water and HPAM i.e. a system where we do not have any surface active component. The results of these experiments are shown in figure 6.b. This system presents similar interfacial rheology moduli as in figure 6.a. That means that the increase of interfacial rheology parameters in presence of HPAM is a pure artifact originating from the increase of the bulk viscosity.

(b)

(a)



**Figure 6:** E’ and E’’ moduli measured at a period of 100 s after 2 hours of ageing for (left): 50 % toluene + 50 % crude oil / water + HPAM interfaces or (right): 50 % toluene + 50 % crude oil or pure toluene / water + HPAM 500 ppm interfaces.

## Influence of HPAM on DSD

Figure 7 presents the DSD of emulsion prepared with and without HPAM. The distributions display only one mode centered around 10 µm. The distribution shows that HPAM alone had no effect on the droplet size distribution. These results are in line with the interfacial tension measurements presented in figure 5.



**Figure 7:** Cumulative (left) and differential (right) size distribution determined right after and 20 min after emulsion preparation with and without 3230S or 3630S HPAM. Conditions: 40 % WC, no demulsifier added.

Figure 7 summarizes the influence of several parameters on the DSD for 40 % water cut as measured by NMR. As seen in figure 7 the HPAM type, i.e. 3230S or 3630S with different molecular weights, did not influence the result. Further overall the addition of HPAM did not influence the distribution, neither did an ageing of the samples to 20 minutes. Obviously the stability level was so high that essentially no coalescence did occur in this time period.

## Influence of Demulsifiers on DSD

The same set of experiments was repeated for the samples, now in presence of demulsifier. The level of added demulsifier was 100 and 200 ppm. In presence of the demulsifier the distribution curve is significantly shifted to higher droplets, i.e. from 8 to 13 µm. Obviously the initial effect of the demulsifier was rather imminent and after 10-20 minutes the coalescence process had stopped. Though the differentiated curve (8b) reveals that the position of the large droplets is much high in presence of demulsifier. However the influence of HPAM is so limited that it could not be detected.



**Figure 8:** Cumulative (left) and diff erential (right) size distribution determined right after and 20 min after emulsion preparation with and without 100 or 200 ppm demulsifier. Conditions: 40 % WC, no HPAM.

## Electrocoalescence experiments

### Small scale Ecrit Cell

The emulsions were analyzed by electro coalescence experiments directly after preparation and 1 hour after preparation to determine and compare the stability level and to investigate how addition of HPAM influenced the emulsion stability. The sample was injected into the Ecrit cell before the electric field was applied stepwise up to max 100 V DC.

**Table 2:** Ecrit (kV/cm) of water in oil emulsions with and without 3230S or 3630S HPAM measured right after and 1 hour after emulsion preparation.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| WC v/v | Without HPAM | | With HPAM 3630S 500ppm | | With HPAM 3230S 500 ppm | |
| Initial | 1 hour | Initial | 1 hour | Initial | 1 hour |
| 15 % | 1.68 +/- 0.19 | 1.67 +/- 0.17 | 1.34 +/- 0.08 | 1.34 +/- 0.10 | 1.48 +/- 0.18 | 1.62 +/- 0.18 |
| 30 % | 0.91 +/- 0.14 | 1.01 +/- 0.07 | 0.80 +/- 0.08 | 1.12 +/- 0.09 | 0.91 +/- 0.11 | 0.88 +/- 0.10 |
| 40 % | 0.70 +/- 0.14 | 0.71 +/- 0.11 | 0.75 +/- 0.05 | 0.87 +/- 0.05 | 0.76 +/- 0.05 | 0.71 +/- 0.15 |

Table 2 presents the Ecrit values for emulsions prepared with and without HPAM for different amounts of water. The results show that for a given water cut, the Ecrit is not influenced by the presence of HPAM which is in good agreement with the DSD experiments presented in figure 7, i.e. with a constant droplet size the stability level remains intact and Ecrit will be constant. The Ecrit increase when the water cut decreases. This result has previously been explained by Hemmingsen et al.[25](#_ENREF_25). The result can be qualitatively explained by larger droplet-droplet distances at lower concentrations. This will increase the flocculation time and hence the whole coalescence process.

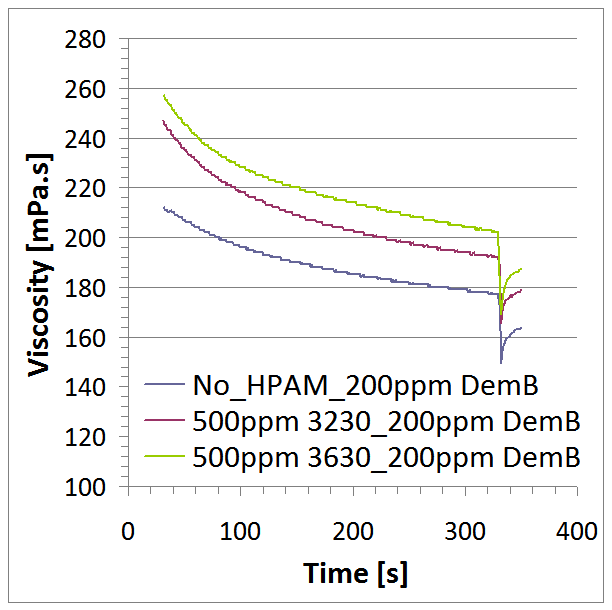
It should be pointed out that the Ecrit value is very sensitive to different kinds of emulsions with different chemical compositions of bulk and interfaces. This has been very clearly documented by Sjöblom et al.[21](#_ENREF_21), [25](#_ENREF_25).

A schematic explanation to the observed behavior of water droplets in an external electric field would include the following processes and the mechanism behind coalescence involves under these conditions several distinct steps. First the applied field gives rise to a polarization inside the individual water droplets. This process will give an alignment of positive and negative charges (electrolytes) inside the droplets in accordance with the applied electromagnetic field. In this way the charge separation creates dipoles where the size of the dipole depends on the size of the water droplets, amount of electrolyte and strength and frequency of the applied field. With the charge separation there will be a natural attraction/repulsion between the droplets and a tendency to line up in a linear floc between the electrodes. The next step involves changes in the interstitial film between the droplets. The system will show a gradual depletion of liquid from the film separating the droplets. Gradually the film becomes very thin and the final breakage will depend on both electrostatic and molecular forces to promote the coalescence and the breakdown of the emulsion. Processes in thin films are very complex and the drainage is not ideal. This has been clearly pointed out in recent publications[26-28](#_ENREF_26).

### Electrorheology

In addition to small scale Ecrit cell, the stability of crude oil emulsions subjected to electric field was analyzed by electrorheology. The larger volume used in this technique (19 mL) allows to determine the droplet size distribution by NMR after electric field treatment. Moreover this technique allows to measure the emulsion viscosity before, during and after electric field application.

Figure 9 presents typical variations of emulsion viscosity with time for emulsions subjected to an electric field. The data showed a slight decrease in the viscosity before the electric field was applied, followed by an immediate drop in the viscosity corresponding to coalescence when applying the field. Figure 9 shows a difference in starting values of the viscosity of the different emulsions. Most likely this reflects the consequences of the sedimentation process. This process is more pronounced for the HPAM systems. This is also confirmed by figure 12. The viscosity increase after the applied electric field was turned off, could be explained by convection, since there is probably free water. When crude oil and water were placed directly into the rheometer sample cup showed that the rheological conditions used in this study are such that no emulsification took place.



**Figure 9:** Viscosity as a function of time for emulsions subjected to an electric field of 5 kV/cm at 500 Hz for 10 seconds, 330 seconds after start of the experiment in presence of 200 ppm of demulsifier with and without HPAM. WC=30 %.

### DSD by NMR in presence of demulsifier and HPAM and after electrorheology treatment

DSDs were determined by NMR before and after electro rheology treatment of emulsions to study the effect of HPAM in the absence of demulsifier (Figure 10). Results show that HPAM has little influence on emulsion DSD as seen in part 4.3. The electrorheology treatment per say has also a negligible influence on the DSD and does not induce droplet coalescence.

On the contrary Figure 11 shows that HPAM in combination with demulsifier could induce the formation of larger droplets than with only demulsifier. The initial modes of the DSD are 8 µm in absence of HPAM and 30 µm in presence of 200 ppm demulsifier B and 500 ppm of HPAM. The increase again in amounts of droplets larger than 80 µm seems to be very pronounced. Moreover it appears that the presence of HPAM can strengthen the action of demulsifier used in this study. Indeed the modes and the amount of droplets larger than 80 µm are more important in presence of a mixture of demulsifier and HPAM than with only demulsifier. This behaviour could be explained by the presence of interaction between the demulsifier and HPAM that would enhance the coalescence process. However in absence of knowledge of the demulsifier structure, further explanation is precluded.



**Figure 10:** Cumulative (left) and differential (right) size distribution determined before and after electrorheology treatment (3 kV/cm at 100 Hz for 10 seconds) with and without 500 ppm of 3630S HPAM. Conditions: WC=30 %, no demulsifier.



**Figure 11:** Cumulative (left) and differential (right) size distribution determined before and after electrorheology treatment (5 kV/cm at 500 Hz for 10 seconds) in presence of 200 ppm of demusifier with and without 500 ppm of 3230S or 3630S HPAM. Conditions: WC=30 %.

### Separation after electrorheology treatment in presence of demulsifier and HPAM

In addition to the determination of emulsion DSD, the NMR technique allows to follow up the kinetic of separation between oil and water as explained by Opedal *et al.*[*14*](#_ENREF_14)*,* [*29*](#_ENREF_29) and Simon *et al.*[*15*](#_ENREF_15). In this situation NMR allows to determine the position of the sedimentation front as well as the free water appearance kinetic. The latter represents the percentage of water released as a free water layer at the bottom of the test tube compared with the initial water amount. This curve allows to define the time required to have the first appearance of the free water layer named coalescence induction time. The figure also shows the position of the sedimentation front with time. The sedimentation rate calculated from the linear part of the curve can be determined from this curve.

Figure 12 presents the sedimentation and coalescence profiles for crude oil emulsion in presence of 200 ppm of demulsifier with and without 3630S HPAM after electrorheology treatment i.e. the same conditions as presented in figure 11. All the samples display both sedimentation of droplets (decrease of the position of the sedimentation front with time) and appearance of free water at the bottom of the tubes. After one hour the free water phase represents ca. 30 % of the total volume of the sample i.e. the water cut of the sample. This means that the separation is close to completion.

Figure 12 also shows that both the sedimentation rate and the free water appearance kinetic are higher for systems containing both HPAM and demulsifier than only demulsifier. This result, consistent with DSD reported in figure 11, shows that the efficiency of demulsifier to separate oil and water is strengthened by HPAM possibly because of the presence of interaction between the demulsifier and HPAM.



**Figure 12:** Sedimentation and coalescence profiles for crude oil emulsion with WC=30 % in presence of 200 ppm of demulsifier with and without 3630S HPAM after electrorheology treatment (5 kV/cm at 500 Hz for 10 seconds). Fill symbols: sedimentation. Empty symbols: free water appearance kinetic.

# Conclusions

The present study reveals some important features on how an addition of HPAM to the water phase will influence the separation process involving w/o emulsions.

Obviously the presence of HPAM has no detectable influence on the size and size distribution of water emulsion droplets in the size interval studied. Also an electrochemical treatment revealed basically no influence of HPAM.

However a combined effect of HPAM and a demulsifier revealed interesting features and clear effects of on both sedimentation and coalescence of the corresponding emulsions.

The obvious conclusion seems to be an interaction between the interfacially bound demulsifier and the HPAM molecules. This interplay is important for the whole destabilization process of the w/o emulsions and for the separation profile of the system.

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