

# Bitumen-in-water emulsion: Destabilization by electrolyte solutions and rheological evaluation

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## ABSTRACT

*The breaking process of the bitumen emulsion is initiated when put into contact with aggregates during the mixing step. It is due to interactions between the binder and the aggregates and also water loss (evaporation and gravity flow). Some mechanisms are supposed to play a role in the breaking process which highly rules the coating quality of the aggregates by the bitumen binder, the implementation step of the mixture on the pavement and the final mechanical properties of the mixture. However the bitumen emulsion breaking process is not fully understood. It remains difficult to know which parameters have a preponderant role on emulsion breaking and how the kinetics of the different involved phenomena impact the global destabilization.*

*The first part of the presented paper aims to determine the influence of electrolyte solutions, used as emulsion destabilizing agents to simulate ionic species release in the aqueous phase of the emulsion by the aggregates, on concentrated oil-in-water bitumen emulsion stability. Secondly, the evolution of rheological properties of the emulsion during destabilization process, which have been put in evidence in the first part, will be presented and discussed*

*The emulsion destabilization, which included a gelation process, has been evaluated by macroscopic and microscopic observations, as well as size distribution and rheological measurements. An interpretation of the destabilization processes will be drawn using rheology, the emulsion formulation and the electrolyte solutions.*

**Keywords:** Chemical properties, Emulsions, Rheology

## 1. INTRODUCTION

Bitumen emulsions used for road pavement correspond to emulsions where bitumen droplets are dispersed in an aqueous phase containing a cationic emulsifier. The bitumen emulsion breaking is initiated when put into contact with aggregates. It is due to physical-chemical interactions with the aggregates surface and water loss (drying and gravity flow). Some mechanisms supposed to play a role in the breaking process, like emulsifier adsorption at minerals surface, rise in pH or ionic species releases have been studied [1-8]. However bitumen emulsion breaking process is not well understood, it is difficult to determine which parameters have a significant role on emulsion rupture and how the kinetics of the different involved phenomena impact the global destabilization.

Emulsions can be destabilized through different mechanisms: creaming, sedimentation, flocculation, coalescence and Oswald ripening. Ostwald ripening is not observed for bitumen emulsions since the solubility of bitumen in water is almost zero. Creaming and sedimentation are not of prime interest in this case. Flocculation and coalescence will be the two mechanisms principally considered in the article. Flocculation is a reversible process whereby droplets stick together, without losing their individual integrity, and form aggregates of droplets. Coalescence is a breaking process in which droplets fuse together into bigger ones. The presence of electrolytes at sufficient concentration in the aqueous phase can lead to emulsion destabilization by flocculation and coalescence [9-11]. Philip and al. [12] and Bonakdar and al. [13] have demonstrated the gelation phenomenon of calibrated bitumen emulsion when coalescence is initiated by NaOH addition. However the gelation phenomenon is not observed with all bitumen emulsions formulation, indeed it depends on bitumen origin and composition [14] and also on the surfactant used.

The contact between bitumen emulsion and aggregates leads to mineral dissolution phenomena which occurs through hydrolysis reactions at aggregates surface thus ionic species are released in solution ( $\text{Na}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$ ...) [6], [15-17]. In addition, with specific aggregates, a rise in pH is observed which corresponds to an increase of hydroxide anions concentration in solution [18]. In order to study the impact of ionic release in the aqueous phase by the aggregates, different electrolytes solutions were used as emulsion destabilizing agents (NaCl, KBr and NaOH) to simulate this phenomenon. Thus, bitumen was used as oil phase and a quaternary ammonium salt surfactant tetradecyltrimethylammonium bromide (noted TTAB) was used as cationic emulsifier. This type of surfactant can be used to formulate bitumen emulsions for road pavement but contrary to amine type surfactant it does not require the acidification of the aqueous phase since it does not depend on the pH.

The aim of this study is to get a better understanding of how different electrolytes can impact bitumen emulsion stability and to characterize the destabilization evolution with rheological measurements.

## 2. MATERIALS AND METHODS

### 2.1 Emulsions composition

A paraffinic bitumen penetration grade 160/220 was used to prepare the bitumen-in-water emulsion. The acidity penetration and ring and ball softening temperature are presented in Table 1. According to cationic emulsifier, a quaternary ammonium salt tetradecyltrimethylammonium bromide (noted TTAB) critical micellar concentration (noted CMC) of  $3.5 \times 10^{-3}$  M from Fluka was used.

**Table 1: Properties of bitumen used for emulsion**

Penetration (1/10 mm)	R&B softening temperature (°C)	Acid value (mg of KOH)
170 ± 1	40.6 ± 0.1	0.3

### 2.2 Emulsion preparation

Bitumen-in-water emulsions were prepared with a colloidal mill. The apparatus is composed of two containers with controlled temperature: one is for the aqueous phase at 40°C the other is for the bitumen at 130°C. Two distinct circuits lead the different phases toward the mixer in which the bitumen is dispersed in the aqueous phase. The gap between the rotor and the stator is at 1mm and the velocity of the rotor was fixed at 10000rpm. The Flow rates of the aqueous phase and of the bitumen are regulated to obtain an emulsion with a bitumen content of 65 wt %. An emulsifier concentration of 4 Kg/ton of emulsion (i.e. 9.7 CMC) has been chosen and corresponds to typical bitumen emulsion formula used in pavement industry practices. For tests, it could be noted that emulsions with bitumen content of 58 wt % and of 10 wt %, with a concentration of 7 CMC and 0.5 CMC in TTAB respectively, have been used (See paragraph 3.1.1).

The used emulsions remained stable during the experimental period, droplet size distribution measurements were assessed regularly to control emulsion stability.

### 2.3 Emulsion destabilization

The aqueous electrolytes solutions were prepared by dissolving salts (NaCl, KBr and NaOH) in deionized water purified by a Millipore system. Those solutions were used as destabilizing agents for the emulsion. To evaluate the

different electrolytes influence on emulsion stability, the following protocol has been used: first the emulsion of known initial mass fraction is introduced in a 20 ml glass jar, and secondly a known amount of electrolyte is added regarding the concentration targeted. Then the mixture is manually stirred for 2-3s. Finally breaking behavior of the emulsion is macroscopically and microscopically assessed versus time.

## 2.4 Optical microscopy observations and droplet size distribution determination

Microscopic observations and droplets size measurements were done to assess emulsions stability in term of flocculation and coalescence.

Microscopic observations allow determining the droplets packing i.e. possible flocculation, and if coalescence has occurred via the observation of larger droplets apparition. The emulsions were observed with an optical microscope (Olympus BX60) in reflected path. The ANALYSIS software was used for image acquisition. For Optical microscopic observations, emulsions were diluted to target 10 wt % of oil value in the sample to ensure a sufficient contrast, then a drop of the sample is enclosed between a glass slide and a cover glass.

Droplets size measurements are used to follow coalescence progress in time. The size distribution was measured by static light-scattering using a Malvern Mastersizer Hydro 2000 SM apparatus using Mie theory. The samples were diluted (simple scattering) in the measuring cell with distilled water or aqueous surfactant solution to avoid emulsion coalescence during tests and *in-situ* homogenized thanks to the flow generated by the apparatus pump. Oil droplets size distribution was characterized by the volume mean droplet diameter noted  $d_{4,3}$  (1), this definition of average droplet diameter is more relevant to highlight coalescence since it emphasizes larger particles:

$$d_{4,3} = \sum n_i d_i^4 / \sum n_i d_i^3 \quad (1)$$

With  $n_i$  is the total number of droplets with  $d_i$  diameter.

Refractive index for bitumen and distilled water are equal to 1.625, 1.330 respectively and the absorption coefficient of bitumen is equal to 0.0035 (usual values).

## 2.5 Rheology

Rheological measurements were assessed by dynamic oscillatory rheometry using a controlled stress Malvern Kinexus Pro rheometer. In function of the sample type, different geometries were used: a 40 mm diameter cone-plate geometry for the lowest viscosity samples, a plate-plate geometry of 20 mm diameter for measurement on bitumen sample, and a plate-plate geometry of 20 mm diameter sand-blasted, in order to minimized slip wall effects and to allow the water circulation, for the monitoring in time of the emulsion destabilization with an homothetic contraction. The apparatus is equipped with a Peltier module incorporated in the inferior plate which regulates the sample temperature (with a precision of 0.01°C). All the measurements were performed at 25°C. A solvent trap is also used for measurement on emulsions in order to prevent the drying of the sample.

For the emulsion destabilization experiments, the emulsion is placed within the geometry gap after NaOH addition in the sample. Then the measurement is started 3min after the sample deposition. The gap is fixed at 1mm and the frequency at 1Hz.

## 3. RESULTS AND DISCUSSION

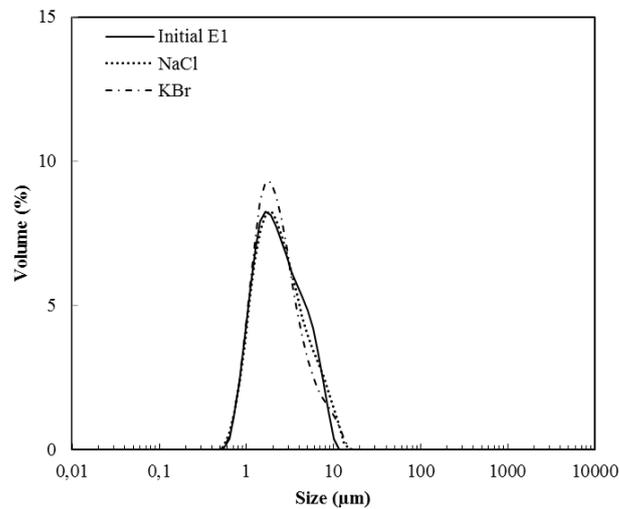
### 3.1 Influence of salts on cationic emulsions stability

To simulate ionic species release from aggregates, electrolyte solutions have been added to the cationic bitumen emulsion and their impact on the emulsion stability has been evaluated.

#### 3.1.1 Bitumen emulsions stabilized with TTAB

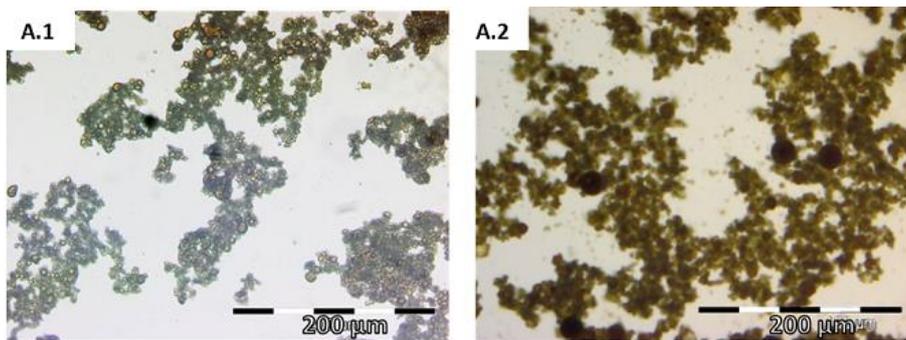
KBr, NaCl and NaOH electrolyte solutions were added to the bitumen emulsion noted E1 and emulsion stability was evaluated.

Figure 1 shows droplet size distributions of the emulsion without salt added (initial  $E_1$ ) and in presence of NaCl or KBr (0.5 M) in solution after 24h. The droplet size distribution doesn't evolve significantly.



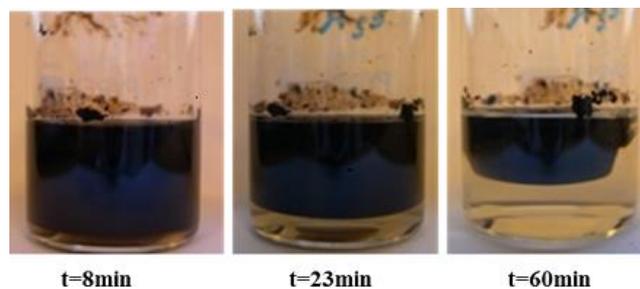
**Figure 1: Size distribution profiles of E<sub>1</sub> without and with KBr and NaCl addition (0.5M) after 24h.**

Figure 2 shows microscopic observations of E<sub>1</sub> emulsion in the presence of KBr and NaCl. Initially the droplets in the emulsion are well dispersed. In presence of salt (0.5 M) an important instantaneous flocculation occurs which leads to the formation of a network of flocculated bitumen droplets. But the emulsion remains liquid like and flows under its own weight.



**Figure 2: Microscopic images of E<sub>1</sub> diluted (10wt % of bitumen) in presence of KBr (0.5 M) (A.1) and NaCl (0.5 M) (A.2).**

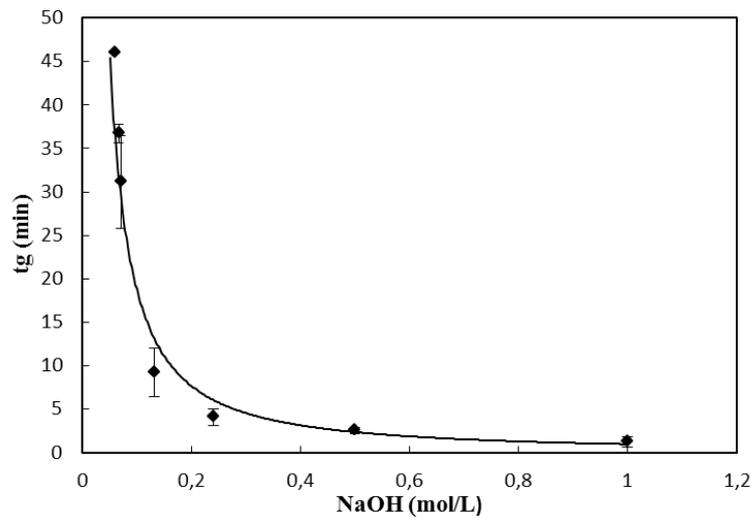
The phenomenon is different when NaOH is added. The gelation process, described in the literature [12-13] and [19], of monodisperse bitumen emulsions diluted between 8% and 20% volume fraction in bitumen, is observed depending on the experimental conditions. We define the gelation time  $t_g$  as the delay between the introduction of the rupturing agent, NaOH, and the moment when the sample does not flow any more. It has been macroscopically determined by regularly and gently tapping the surface of the sample with a thin rod, when gelation occurs the surface of the sample becomes rigid. We checked that this small solicitation does not affect  $t_g$ . Then the gel starts to progressively contract in a homothetic way (see Figure 3).



**Figure 3: Images of E<sub>1</sub> gelation at various time intervals after NaOH addition.**

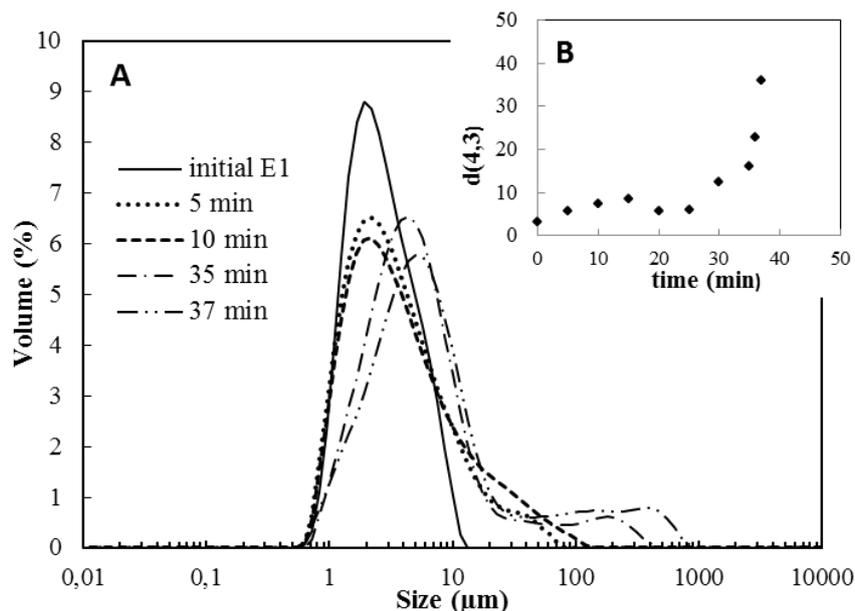
When NaOH is added at 0.5 M in the sample the gelation is observed for a  $t_g$  around 3 min (Figure 4). The gelation in those conditions is too fast to perform size distribution measurement between NaOH addition and gel formation. So,  $t_g$  has been measured for different concentration of NaOH added. Figure 4 represents the evolution of the measured  $t_g$  for

the emulsion at 58 wt % in function of the concentration of NaOH in the sample.  $t_g$  decreases with the increase of NaOH concentration, the gel forms faster when the amount of rupturing agent is increased.



**Figure 4: Gelation time  $t_g$  as a function of NaOH concentration in the sample.**

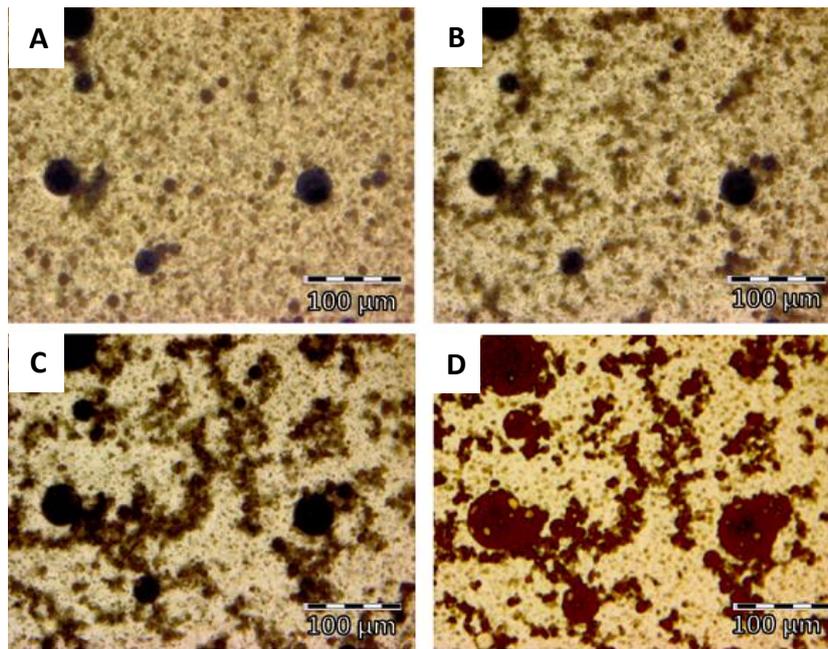
The destabilization evolution of  $E_1$  has been monitored by droplets size distribution measurements. We chose an emulsion sample characterized by a  $t_g$  around 45min, which corresponds to a concentration of 0.06 M according to Figure 4, to study the evolution of the coalescence destabilization. A small amount of emulsion was taken at different times between the rupturing agent addition and  $t_g$ , and was then diluted in approximately 10 mL of aqueous phase (distilled water and surfactant) to stop the destabilization. Figure 5.A represents the evolution of droplet size distribution at different times. In the early stages (from 0 to 20 min) the droplets size distribution doesn't evolve significantly. For longer times, an evolution of the distribution toward the larger droplets is observed (Figure 5.B). However, as we can see on Figure 5.A, the coalescence progression remains limited. Even if, when approaching  $t_g$ , some larger particles appears (between 100 and 1000  $\mu\text{m}$ ) the majority of the droplets population ranges from 1 to 15  $\mu\text{m}$  approximately. In addition, it is possible to break the gel in the first stages, right after its formation, with a strong agitation and to obtain a liquid like behavior again. Then the gel reforms after few minutes. Thus the coalescence can't be the only phenomenon responsible for the gelation process, it's seems that a strong flocculation is also needed.



**Figure 5: Droplet size distributions (A) and  $d(4,3)$  evolution (B) of  $E_1$  at different times after NaOH addition.**

The destabilization evolution with NaOH has also been observed microscopically (Figure 6). The observations have been performed with a concentration of 0.5 M of NaOH. The sample has been observed right after the NaOH addition. The practically instantaneous flocculation is the first phenomenon observed on the images before coalescence occurs. The flocculation is here characterized by the apparition of droplets aggregates. With time the droplets merge with each

other. In comparison with flocculation the coalescence kinetics is much slower, as it takes a lot of time for the droplets to fuse and relax the shape [20].



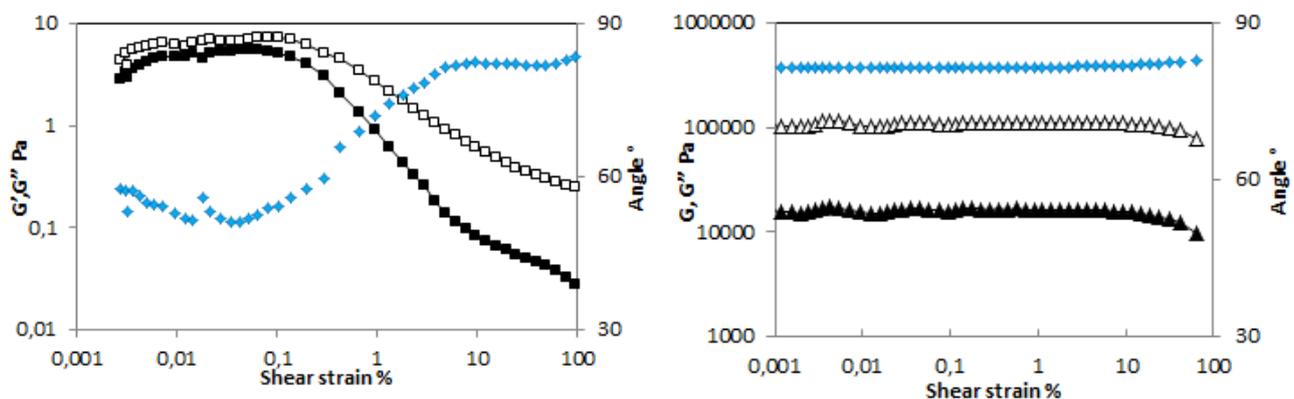
**Figure 6: Microscopic images of the gel formation for E<sub>1</sub> between 3 min and 120 min (A to D) after NaOH addition (0.5 M). 10 wt % in bitumen.**

### 3.2 Rheological behavior of the emulsion throughout destabilization with an homothetic contraction

The destabilization phenomena with NaOH addition is then monitored by rheological measurement. The aim of this rheological assessment is to have a more precise determination of the gelation time and also to follow the return of the bitumen at its initial state (i.e non-emulsified). Thus, a specific protocol has been set up to follow the rheological behavior of the system.

#### 3.2.1 Set up of the rheological protocol

During the destabilization process, the sample evolves with time and so its linear domain can evolve as well. The linear domain corresponds to the range of strain for which no structural modification of the sample is generated.  $\gamma_{LD}$  is defined as the linear domain limit, it is the maximal strain that can be applied to the sample without changing its structure. It is thus necessary to determine the linear domain of both the emulsion without destabilization and the bitumen in order to know the shear stress range that can be applied to the sample to stay in the linear domain throughout the sample evolution. As the rheometer works in stress controlled, a shear stress sweep is applied to the sample, from  $10^{-4}$  Pa to  $10^5$  Pa at 1Hz frequency. The results enabled to established  $\gamma_{LD}$  for the emulsion and the bitumen. For the emulsion the linear domain stops at 0.15% shear stress whereas for the bitumen the domain is much larger and extends to 20% shear stress, see figure 7.



**Figure 7: Evolution of elastic modulus  $G'$  (full square symbol), viscous modulus  $G''$  (empty square symbol) and phase angle (diamond symbol) in function of shear strain for E<sub>1</sub> (left) and for the bitumen (right) .**

An operating method is set up with the rheometer in order to adapt the shear stress value to apply to the sample throughout the destabilization evolution. The shear stress values were chosen so as to stay in the linear domain and also to have a good measurement sensibility, meaning that the shear stress should not be too low. Thus the procedure is decomposed in 5 steps described in Table 1.

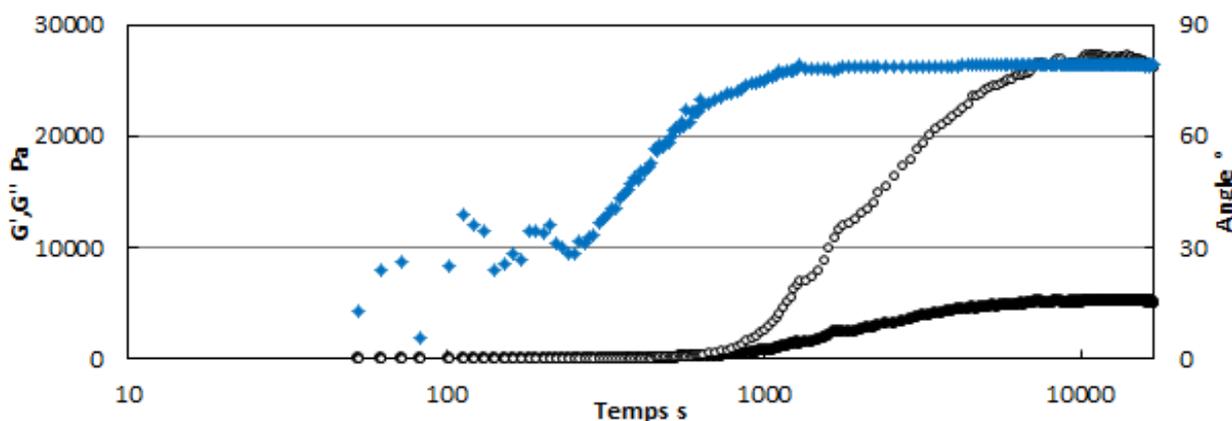
**Table 1 : Experimental conditions applied to the sample for the rheological assessment of the gelation phenomena**

Step	Shear stress	Trigger to the next step
1	$3 \cdot 10^{-3}$ Pa	$\gamma < 1 \cdot 10^{-3} \%$
2	0,05 Pa	$\gamma < 1 \cdot 10^{-3} \%$
3	0,1 Pa	$\gamma < 1 \cdot 10^{-3} \%$
4	0,5 Pa	$\gamma < 5 \cdot 10^{-3} \%$
5	1 Pa	end

### 3.2.2 Rheological properties evolution of the emulsion during destabilization

Rheological assessments of the destabilization with an homothetic contraction of the bitumen emulsion are performed on the emulsion at 58% in bitumen with a NaOH concentration in the sample of 0.07M, which correspond to a  $t_g$  around 35min. The evolution of the viscous modulus ( $G''$ ), elastic modulus ( $G'$ ) as well as the phase angle are followed over time (Figure 8).

In the first stages of the measurement, the sample keeps the rheological behavior of the emulsion, then around 240s the phase angle begin to raise, this change can be attributed to the start of the destabilization process. The phase angle raise progressively until it stabilizes around  $78^\circ$ . We consider that the network of interconnected droplets is irreversibly formed when the phase angle reaches the value of  $78^\circ$  and we define the corresponding time " $t_{gr}$ " as the rheological gelation time. For the sample tested here the  $t_{gr}$  was about 25min whereas the  $t_g$  manually measured was about 32min. For the viscous and elastic modulus a gradual increase is observed until stabilization of values. The viscous modulus increases more significantly than the elastic modulus. With the progress of the destabilization the rheological behavior of the sample tends toward the rheological behavior of the bitumen. Indeed, with the "gel" formation and its contraction the material become denser in bitumen and the modules increase therefore the system gradually gets closer to bitumen properties. However, the modulus values are still lower than those for original pure bitumen as some water remains trapped in the sample.



**Figure 8: Characteristic evolution of  $G'$  (full symbol),  $G''$ (empty symbol) and phase angle (diamond symbol) during destabilization progress for NaOH concentration of 0,07M**

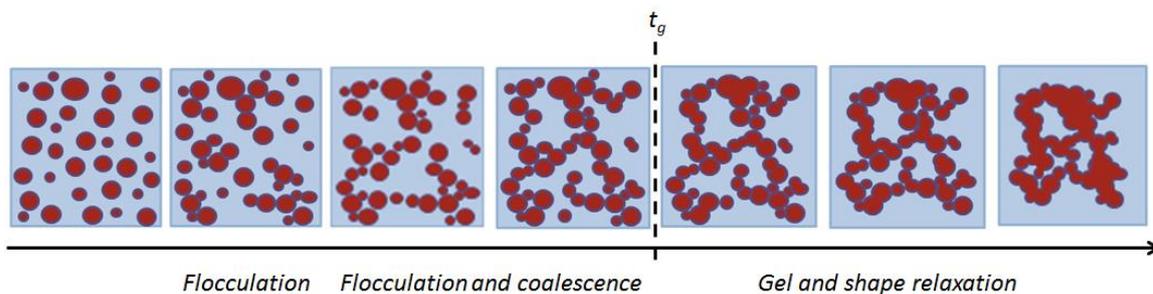
## 4. INTERPRETATIONS

Salt addition on cationic emulsions promotes destabilization by flocculation as a general rule. Indeed, salt addition decreases the Debye length. The result is a reduction of the electrostatic repulsion, which can become weaker than Van der Waals attractive forces.

With NaOH electrolyte, coalescence destabilization is more pronounced than with NaCl or KBr electrolytes. In fact it is the only electrolyte which promotes coalescence. This could be explained by different anions specific effect on TTAB interfacial properties. The effect of electrolytes on ionic surfactant interfacial adsorption and surface tension has been the subject of many studies [21-26]. In the presence of electrolytes surface tension of aqueous phase decreases significantly below the CMC, CMC value is decreased and it has an impact on interfacial adsorption of the surfactant

and counter ions. For the various anions the cationic surfactant interfacial properties is not the same. It has been demonstrated that in the presence of hydroxide anions the CMC of quaternary ammonium salt surfactant is less decreased than with halide anions. This could be explained by the fact that hydroxide ions are less strongly bound to the cationic surfactant than halide ions. As a consequence, hydroxide ions do not promote additional surfactant adsorption at the interface which could densify the monolayer at the air/water interface. Thus a hypothesis could be drawn that in presence of hydroxide ions, emulsion will be less stable against coalescence than in the presence of the others anions for which the interfacial monolayer of surfactant seems more compact and thus more difficult to break.

On the other hand, the gelation phenomena, described elsewhere [12-13] and [19], of bitumen emulsions with NaOH addition was observed with the bitumen emulsion tested (see Figure 9). For the gelation phenomena with a homothetic contraction to occur, flocculation is first required to create a network of droplets. Then coalescence and finally a slow shape relaxation. The shape relaxation characteristic time  $t_r$  depends of viscosity  $t_r \propto \frac{\eta R}{\gamma}$  with  $\eta$  the oil viscosity,  $R$  the droplet radius and  $\gamma$  the surface tension [12]. When the viscosity increases,  $t_r$  increases as well, so when coalescence happens if  $t_r$  is sufficiently high compared to the coalescence kinetics, a network of coalesced droplets can form before shape relaxation is completed which leads to the formation of a gel.



**Figure 9: Schematic representation of E<sub>1</sub> destabilization in presence of NaOH.**

The rheological evaluation of the gelation phenomena indicate that with the destabilization evolution, the rheological behavior tends to the behavior of the bitumen with a  $G''$  much greater than  $G'$ . Moreover the rheological measurements shows that the phase angle is a good indicator for kinetics following. In fact it allows determining from rheology tests a specific gelation time noted “ $t_{gr}$ ”. This method of gelation time determination turned out to be more precise than the manual method, indeed, the repeatability is good and the control over the experimental conditions is better (i.e solvent evaporation, temperature and sample dimensions). However the difference in value between the gelation time measured with the two different methods is important, for example there is a difference around 12 min with for the experiment presented in this paper. This difference could be explain by the difference in the samples geometry and environment, indeed in the rheometer the thickness of the sample is of 1mm and the water can flow more freely outside the gel during contraction contrary to the samples destabilized in the glass jar.

## 5. CONCLUSION

In this paper, the destabilization behavior of a bitumen emulsion, stabilized with a quaternary ammonium salt emulsifier in presence of different electrolytes has been assessed. In general the addition of electrolytes favors flocculation. With NaOH the behavior is different, in addition to flocculation; coalescence also occurs leading to a gelation phenomenon. The gelation phenomenon was rheologically characterized; it appears that the phase angle is a reliable indicator for the following of the kinetics of the destabilization process.

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