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Investigating the effects of salts on the coalescence process in bitumen emulsions

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ABSTRACT

The breaking and coalescence process in bitumen emulsions during their application strongly influences the resulting long-term mechanical performance of the cold mix asphalt. This phase separation process is affected by physico-chemical changes at the bitumen/water interface. This paper describes the effects of addition of different salts on the destabilization of bitumen emulsions. This study is limited mainly to cationic rapid setting (CRS) bitumen emulsions and salts which are very commonly added to these emulsions as a stabilizer. However, a few samples with non-ionic emulsifiers were also prepared and analyzed comparatively to understand the electrostatic force balance with varying concentrations of selected salts. The experimental part includes a bitumen droplet relaxation test, droplet size distribution measurement, microscopy, and evaluation of physico-chemical properties of prepared soap solutions e.g. interfacial tension and density measurements. Some experiments on the effect of selected water-soluble organic solvents on the coalescence process were also carried out. The results showed that coalescence was delayed after the addition of salts, while the water soluble organic solvents proved not to affect the emulsion significantly.

KEYWORDS: Cold Mix Asphalt, Bitumen emulsions, Breaking, Coalescence, Relaxation, Salts, Organic Solvents.

1. Introduction

There are several technologies available for producing cold mixes, including foamed bitumen, cutback bitumen solution or emulsified bitumen. Emulsification of bitumen in a water phase is one of the methods used to reduce its viscosity and make it work as an effective binder. For the pavement industry, the use of Cold Mix Asphalt (CMA) has become an attractive alternative to replace the traditional Hot Mix Asphalt (HMA), due to its reduced energy consumption and environmental impact \cite{1-3}. However, there are still some concerns regarding its usage. For instance, the mechanical strength of cold mixtures in the early stages is known to be lower than that of traditional HMA due to the trapped water in the asphalt mixture after setting of the emulsion has occurred \cite{4} and, as such, this may result in the delayed opening of roads for traffic.
Bitumen emulsions are produced by mixing hot bitumen and a water phase containing emulsifying agents, using very high shear force to disperse the bitumen into small droplets [5-7]. Developing a suitable emulsion formulation requires the selection of the right type of emulsifier and additives, suitable for the intended aggregate type, bitumen type and expected climate conditions. An emulsifier acts as a surface active agent that concentrates at the interphase region between two immiscible liquids such as oil and water [8]. The process of manufacturing bitumen emulsions must be highly controlled to ensure their storability, workability and adhesion.

Bitumen emulsions are mostly oil in water (o/w) type emulsions and contain 60 – 80 % bitumen by weight (wt%), around 0.15 – 2 wt% emulsifier [6] and 20 – 40 wt% water with minor additives (e.g. salts). Generally, in bitumen emulsions, the bitumen droplet size distribution is in the range of a few μm (1 – 20 μm), which is strongly influenced by the emulsion recipe, temperature of the bitumen and water phase, mechanics and the operating conditions of the emulsion manufacturing mill [9]. The application of bitumen emulsions for pavements are varied, ranging from spray applications such as surface dressings or chip seals, fog seals, tack and prime coats, to being mixed with stone materials as in slurries, microsurfacing and cold mix paving.

This study is limited to the CMA bitumen emulsion technology. In the following sections, the mechanisms of these processes are addressed in more detail, followed by a brief description of the effects of salts and the aim of the study, respectively.

1.1. Bitumen Emulsion Setting

Bitumen emulsions are designed to break quickly or slowly, depending on the type of application. The breaking rate is primarily determined by type and amount of emulsifier. The most common types of emulsifier for bitumen emulsions are the cationic amines, which exist in many different varieties. They have the advantage of being adsorbed at the surface of mineral aggregates, causing a destabilization due to depletion in the emulsion followed by flocculation and finally coagulation, through coalescence of the bitumen droplets, ideally forming a bitumen layer coating the stone material. Coalescence is the final stage of the breaking process in which droplets merge into bigger ones and a film of bituminous binder develops, then sets and hardens (“cures”), thereby determining the mechanical strength of the cold asphalt mixture. In ideal conditions, good adhesion can be achieved if bitumen completely coats the stone surface and water is pushed out from the asphalt mixture. However, premature coalescence of bitumen away from the stone surface, or residual moisture at the interface, [10] could lead to poor adhesion and reduction in mechanical strength of the asphalt mixture.

1.2. Effects of Salts

Addition of salt in emulsions has traditionally been used to break emulsions. Previous studies [11-13] have found that salts with various ionization potentials and concentrations cause phase separation in emulsions. In oil/water emulsions, the potential energy barrier for charged oil droplets in a water phase arises due to electrostatic repulsion between these droplets. Electrostatic forces consist of coulombic repulsion, in the case of two similarly polarized head groups, and attractive van der Waals forces.
In stable emulsion systems, an electric double layer with a certain thickness may establish around the dispersed phase droplets. The droplet’ surface potential usually defines the thickness of this electric double layer [14]. The electrostatic double layer has basically two parts, a compact double layer (the Stern layer) very near to the droplet interface and a diffuse layer (the Gouy-Chapman layer), having a boundary with the electrolyte solution. A diffuse double layer is a result of force balance on the counter ions, which are pulled towards the charged surface due to coulombic attraction as well as simultaneously being displaced away from the interface due to osmotic pressure. The formation of the double layer is greatly affected by increased salinity of the water phase, as instead of it reduces the thickness. Outside the diffuse layer, the electrical potential is zero as the net charge in this layer exactly balances the charge on the droplet surface. The height of the droplet surface potential or energy barrier or force experienced by the droplets can be decreased by increasing the concentration of ions in the aqueous phase; it also depends on the charge number of the added counter ions. On the other hand, the Stern layer is quite immobile and the surface charge density is reduced very effectively by the binding of counter ions on the surface groups. This strongly reduces the surface potential of the Stern layer, which is often called zeta potential.

The thickness of the diffuse layer is termed the Debye length (1/κ), which is significantly influenced by the concentration of electrolyte in the solution. At high salt concentrations, the Debye length may be so short that the attractive van der Waals forces overcome electrostatic repulsive forces, leading to flocculation (which is reversible in some cases). However, the shear force due to the relative motion of liquid near the droplet surface also plays a role and may cause interfacial turbulence, damaging the Stern layer and eventually resulting in coalescence of the droplets.

At lower concentrations, added salts have a stabilizing effect especially if the emulsions were stabilized electrostatically. The small addition (0.1 – 0.2M) of salt helps to screen the Coulombic repulsion between surfactant molecules. This enables a higher density of surfactant molecules to pack in an ordered form in the interface which stabilizes emulsions by enhancing film rigidity and mechanical strength.

In the bitumen emulsion industry, it is common practice to add salt (from 0.1 to 0.2M) to stabilize emulsions. There are four main reasons for adding salts. First, it works as a stabilizer to equalize the water density if it is lower than the bitumen phase, which may reduce settling. Second, it helps to control the drastic change in viscosity of bitumen emulsion by reducing the osmosis of water into the bitumen. Bitumen may contain a small amount of salt, which can lead to an osmotic swelling of the droplets in an emulsion, as water is drawn into the droplet [15]. This results in an increase in emulsion viscosity, often followed by a decrease as the salt slowly escapes. Generally, calcium or sodium chlorides are added to reduce the osmosis of water into the bitumen and minimize the changes in viscosity. Third, adding salts to the water phase of the bitumen emulsion means that those salt counter ions quickly react with the surfactant molecules’ polar heads and also with the breaking additive (such as NaOH), which can sometimes be added intentionally to break the bitumen emulsion. Fourth, adding salt to bitumen emulsion stimulates the hydrolysis reactions occurring at the mineral surface when they are in contact with bitumen emulsion. The ionic species such as Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$ etc. contained in the mineral aggregates may be dissolved due to hydrolysis reactions [16-22] with hydrochloric acid in the emulsion, resulting in increased salt content. In the case of reactions with alkaline minerals such as limestone, the result may be a change in pH. These different aspects of chemical and electrochemical processes balance at the oil/water interface, for
example salt concentration and the pH variations, are factors that affect the stability of the emulsion [11, 23, 24].

1.3. Purpose of the Study

As mentioned in section 1.1, the breaking and coalescence of bitumen emulsion takes place in several stages. In a previous paper, we described a new test method [25] developed to investigate the coalescence step of the breaking procedure. In this study, we used the new technique to investigate the effect of different additives in bitumen emulsions. We particularly focused on the influence of salt addition on the coalescence mechanism. In the second part of the study, we investigated how some specific solvents influenced the coalescence process.

Since the newly developed coalescence test is limited to using bitumen droplets in the mm range while real bitumen emulsions have bitumen particles in the range of 1 – 20 μm, more traditional droplet size analyses of bitumen emulsions were included. They were expected to give a measure of the overall stability of the emulsions, partly confirming the observations in the coalescence test, but also giving a better evaluation of the coalescence observations.

2. Experimental Methods

In this work, five experimental methods were selected to investigate the effect of salts on the coalescence process. These were a bitumen droplet relaxation test, a droplet size distribution measurement, light optical microscopy, surface tension measurements and tests to evaluate the density of aqueous mixtures at different temperatures. The basics of each of these test methods are explained now.

A new test method for studying the coalescence of two bitumen droplets was used in this research work. The details of the test set-up and experimental design of this bitumen droplet relaxation test were described in the previous study [25]. In this test, two bitumen droplets of 1 – 2 mm diameter are attached to L-shaped probes and brought into contact with each other to initiate coalescence. The probes are immersed in a glass container filled with relevant solvents (aqueous phase, with and without selected additives). There is no compression force applied while bringing the two droplets into contact; however, the position of the two droplets are positioned close enough for them to be touching each other. The bitumen droplet relaxation test very much follows Frenkel’s theory, where two oil drops diffuse into each other through a shape relaxation that is mainly driven by the surface tension [26]. The characteristic time for shape relaxation is governed by a competition between surface tension and viscous dissipation and can be represented as:

\[ \tau_{\text{relaxation}} \propto \frac{\eta R}{\gamma}, \]

where \( \eta \) is the droplet viscosity, \( R \) is the characteristic radius of the droplet and \( \gamma \) is the droplet surface tension. In bitumen emulsions, the coalescence process as determined by the droplet relaxation test consists of two steps. The first is the penetration through the protective barrier (electrical double layer) and the second the time for shape relaxation. For a material such as bitumen, with a very high viscosity, the latter step tends to take a very long time.
Optical microscopy and droplet size distribution methods have been used in several studies to investigate emulsion stability [1-3, 5-7]. The optical microscopy was carried out with an OLYMPUS BX51. A MALVERN MASTERSIZER 3000E was used for droplet size distribution measurement. Both characterization techniques were used for monitoring the coalescence process over different time frames e.g. 1 hr, 1 day, 1 week and 1 month. The bitumen emulsion samples were diluted (10 times) for optical microscopy and droplet size distribution measurements, as they are otherwise too dense to allow sufficient light through. This dilution was made with the same water phase used in manufacturing to create a real-world emulsion environment.

Density (ρ) and equilibrium SFT-surface tension (γ) or IFT-interfacial tension (γ) of water phase soap solutions were measured using a density meter “DMA 4500 (from Anton Paar)” and a Wilhelmy plate method [27], respectively. In the Wilhelmy technique, a thin plate is used to measure equilibrium surface or interfacial tension at an air/liquid or liquid/liquid interface. The plate is oriented perpendicular to the interface, and the force exerted on a vertically immersed plate is measured. Platinum is chosen as the plate material when measuring the surface tension or interfacial tension, as it is chemically inert and easy to clean, and because it can be optimally wetted on account of its very high surface free energy. It therefore generally forms a contact angle θ of 0° with liquids. The changes in the ratio of SFT or IFT to density of the water phase, with and without additives (salt), were correlated with the coalescence or relaxation time of the bitumen droplets.

2.1. Materials and experimental design

In this study, an emulsion grade of virgin bitumen from Nynas, with penetration grades 160/220, 70/100 and 50/70, was used. Redicote products E-9 and EM44 from AkzoNobel were selected as cationic emulsifiers, with Redicote E-47 NPF (Nonyl Phenol Free) used as the non-ionic emulsifier for this study. Redicote E-9 is a special grade of tallow diamine designed to produce cationic rapid and medium setting bitumen emulsions of the highest quality; it has, for many years, been the standard against which other cationic emulsifiers are judged. Redicote EM44 is basically also an amine-based (N-tallow alkyltrimethylene-diamine, but contains additional functional groups e.g. polymers of ethylene oxide) standard emulsifier for rapid and medium setting cationic bitumen emulsions. Redicote E-47 NPF emulsifier is an ethoxylated alcohol used for producing non-ionic and sometimes anionic slow setting bitumen emulsions, and is typically effective at mixture concentrations between 0.8 and 1.2%.

The selected salts contained monovalent and divalent cations (e.g. Na⁺, K⁺ and Ca²⁺) and monovalent and divalent anions (e.g. Cl⁻, Br⁻, SO₄²⁻). The following salts were used: sodium chloride (NaCl), potassium bromide (KBr), potassium sulfate (K₂SO₄) and anhydrous calcium chloride (CaCl₂), all from Sigma-Aldrich.

Organic solvents are commonly used in bitumen emulsions to improve coalescence. They are usually nonpolar liquids such as kerosene. In our experiment, we decided to select solvents which were mainly water soluble and, to a very small extent, bitumen soluble, to be able to study their effect on coalescence without changing the viscous behavior of the bitumen. For this purpose, the following solvents were selected: Methanol (Reagent grade, VWR), Ethanol (SOLVECO Analytical grade, 99.5%), 2-Propanol (Reagent grade, VWR), and Glycerol (Sigma-Aldrich, Reagent Plus 99%). The ratio for each solvent mixture (e.g. 90% water phase + 10% organic solvent) was based on volume. Among these solvents, adding ethanol to
bitumen emulsion is recommended in rare cases when the temperature is below freezing point (0 °C).

Experimental design factors and levels are shown in a flow chart in Fig. 1 for both bitumen and the water phase. The temperature of the water phase was varied from ambient conditions up to 50 °C. In this work, all three penetration grades bitumen (160/220, 70/100 and 50/70) were used for the droplet relaxation experiment. However, only one bitumen grade 160/220 was selected for preparing real emulsion samples.

![Fig. 1. Experimental design factors and concentrations.](image)

### 2.2. Bitumen emulsion preparation

An emulsion grade bitumen 160/220 was selected to prepare cationic rapid setting (CRS) and non-ionic bitumen emulsions, stabilized using Redicote E-9, EM44 and E-47 NPF, respectively. In the Nynas and AkzoNobel laboratories Sweden, a pilot plant set-up for preparing bitumen emulsion was used to produce different sets of samples, with and without salts. In the emulsion manufacturing mill, the temperatures of bitumen and water phases were set to 140 °C and 40 °C, respectively, resulting in emulsion samples with a temperature between 80 – 90 °C. Water phases containing three selected salts (CaCl₂, NaCl, and K₂SO₄) with molar concentrations (0.1M, 0.3M, 0.5M, 0.7M, 0.9M, 1.0M and 3.0M) were prepared. The required level of surfactants was also added to these salt-containing water solutions followed by hydrochloric acid to activate the surfactant. In the case of Redicote E-9 and EM44, the required level for CRS was 0.17% with a pH = 2.3. However, in the case of non-ionic bitumen emulsion with Redicote E-47 NPF, the minimum required level to stabilize bitumen emulsion was 0.8% with neutral pH. In this case, two types of non-ionic emulsion samples were prepared with 1% E-47 NPF at pH=7 and pH=2.3, respectively.
3. Study Results

In the first set of experiments using the droplet relaxation method, the effect of salt in the water phase was investigated.

3.1. Effects of salts

3.1.1. Relaxation test observation

The shape relaxation test consists of two steps. First, the two droplets coalesce when the protective barrier is penetrated. Then, shape relaxation occurs when the two droplets merge into one. In the case of bitumen at lower temperatures, its viscosity is very high, so the shape relaxation, which is mainly a function of viscosity, can take a very long time. To investigate the relationship between relaxation time and viscosity, the bitumen droplet relaxation test was carried out with selected grades of bitumen (50/70, 70/100 and 160/220) at three different temperatures (30, 40 and 50 °C). The relaxation time as a function of bitumen viscosity was plotted so that the coalescence of different viscosity grades bitumen could be compared (see Fig.2). These tests were carried out using deionized water containing 0.17% Redicote EM44 but without salt. The bitumen droplets were prepared in a silicone mold one day before the relaxation test and stored in a freezer at -20 °C. The method of preparing bitumen droplets and details of the test set-up have been published in our earlier paper [25]. Fig. 2 shows the strong correlation between viscosity and relaxation time. A careful examination shows that there is no linear correlation between log relaxation time and log viscosity. The three measurements for each bitumen type at different temperatures do not fall on a straight line. It can also be seen that two bitumen types (160/220 and 70/100) measured at the same viscosity (but at different temperatures) have relaxation times that differ by more than a factor of ten. For all three bitumen types, the test at the lowest temperature (highest viscosity) yielded a very long relaxation time. From this, we might conclude that temperature is more influential on the relaxation time than viscosity. These results have good repeatability: measurements were within ± 5% of the average value over five test runs under the same experimental conditions e.g. droplets of the same size were selected for the repeated experiments and the test temperature was controlled throughout the experiment.
Fig. 2. Coalescence of bitumen droplets in pure deionized water containing 0.17\% Redicote EM44 and without salt (droplet relaxation time as a function of viscosity of indicated bitumen grades).

It is known that the bitumen surface changes structure over time (ageing) [28, 29]. To investigate whether this surface ageing under water could prevent coalescence, the relaxation test was carried out with the droplets stored in water (see Fig. 3). In this test, droplets were kept in water for some time before starting the relaxation experiment. The results are shown in Fig. 3 for 30 minutes storing time and 62 hours storing time. The results show no significant difference in the coalescence times of two bitumen droplets.

In the next step, the relaxation times of the three penetration grades (160/220, 70/100, 50/70) in a water phase typical for a bitumen emulsion, containing 0.17\% Redicote EM44 with HCl to pH=2.3, without and with added salts, at 50 °C, were investigated. The results are given in Table 1 and show an increase in relaxation time, $\tau_{\text{relaxation}}$ when salts were added.
Table 1. Coalescence or relaxation time [in minutes] for the selected bitumen grades in a water phase (0.17% Redicote EM44@pH2.3) with and without added salts, at 50 °C.

<table>
<thead>
<tr>
<th>Binders</th>
<th>Water phase without salt (Reference)</th>
<th>Addition of calcium chloride (CaCl₂) in water phase</th>
<th>Addition of potassium bromide (KBr) in water phase</th>
<th>Addition of sodium chloride (NaCl) in water phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>160/220</td>
<td>8 mins</td>
<td>12 mins</td>
<td>18 mins</td>
<td>19 mins</td>
</tr>
<tr>
<td>70/100</td>
<td>20 mins</td>
<td>26 mins</td>
<td>42 mins</td>
<td>40 mins</td>
</tr>
<tr>
<td>50/70</td>
<td>55 mins</td>
<td>90 mins</td>
<td>120 mins</td>
<td>140 mins</td>
</tr>
</tbody>
</table>

In Fig. 4, the measured relationships between densities of water and bitumen phases were compared as functions of temperature (Fig. 4a). At lower temperatures, the density of water is a little lower than bitumen, so a small addition of salt may help to raise the water density to prevent precipitation or creaming in bitumen emulsions. The densities of bitumen and water at 50 °C, the testing temperature in the current experiments, are very similar. Fig. 4b shows density meter measurements of the water phase soap solution containing 0.17% Redicote EM44 and hydrochloric acid (pH = 2.3), with and without calcium chloride salt, at selected temperatures. The results in Fig. 4b and calculated data in Fig. 4c are strongly correlated with those given in Table 1 e.g. bitumen droplets in a water phase solution with a higher density have longer relaxation times.

![Density Comparison](image1)

![Relaxation time](image2)

![Buoyancy effects](image3)
20 and 50°C, c) relaxation time as a function of calculated densities of water phases at 50°C, and d) buoyancy effects due to density difference during coalescence of bitumen droplets of indicated grades in water + 0.17% Redicote EM44 + salts + hydrochloric acid (to pH=2.3) at 50°C.

With a higher salt content, the water tends to have a higher density than bitumen, so the buoyancy effect causes the fusing droplets to float. Due to these buoyancy effects, estimation of droplet relaxation time becomes difficult and a coalesced droplet might not be exactly round. This type of situation only occurred in a water phase soap solution with 0.5M CaCl₂ and 0.5M KBr. However, the buoyancy effect was not particularly visible in a solution containing 0.5M NaCl. During repeated measurements of the bitumen droplet relaxation times in solutions with 0.5M (CaCl₂, KBr), only a qualitative comparison of nearly-coalesced droplets is possible (see Fig. 4d). In this case, the error was more than 5% from the average value of measured coalescence time of two bitumen droplets.

3.1.2. Microscopy and droplet size distribution measurements

In the droplet relaxation method, bitumen droplets with a diameter of 1 – 2 mm were used, while bitumen emulsions consist of droplets with sizes ranging from typically 1 to 20 µm. These small droplets could not be monitored with the set-up of the droplet relaxation method. The coalescence in real emulsions was observed using optical microscopy. Emulsions stabilized with Redicote EM44 containing CaCl₂ salt were produced in the laboratory mill. Microscopy and size distribution tests provide only qualitative information about the coalescence process but the relaxation test can actually quantify the coalescence. Though, the relaxation test method did not address the smaller scale droplets at the moment but the parametric relationships using the bigger scale droplets found to be very much consistent with the expected coalescence behavior.

The samples were diluted 10 times with the same water phase and one droplet of ≈ 100 µl was placed on a glass slide. There were two types of glass slides used for optical microscopy. One had a round curved indent in the middle of the glass slide, where a diluted emulsion droplet could be spread and covered with a flat glass coverslip. The other was flat with a glass coverslip. All images taken and presented in this work used transmission mode. During microscopy, bitumen droplet packing, shape and morphology of the agglomerates or flocculates, as well as coalescence processes, were observed.

Fig. 5 shows micrographs of CRS bitumen emulsions with added salt (Fig. 5a and 5c) and without (Fig. 5b and 5d) added salt. These micrographs show that 0.1M CaCl₂ keeps the bitumen emulsion stable compared to that in Fig. 5b and 5d, and droplets retain their original shapes even in big flocculates, after a long period (up to 4 weeks of storage). Emulsion samples without salt show strong aggregation of bitumen droplets and there are more diffused droplets in the central part of agglomerates.
Fig. 5. CRS bitumen emulsions stabilized by 0.17% Redicote EM44 with 0.1M CaCl$_2$ (a,c) and without salt (b,d) [micrographs obtained after 4 weeks of storage].

If the salt content is raised to 0.5M, the stabilizing effect is lost as indicated in Fig 6. Here we can see a strong flocculation followed by tendencies to coalescence. This observation agrees with the expected decrease in stability with higher salt concentrations.
Further investigations of the breaking process were carried out with droplet size measurements using a light scattering technique. The advantage of this was that we could see the size distribution of the droplets. The disadvantage was that the instrument was not able to detect larger (up to 1 mm) coalesced bitumen droplets.

Fig. 7 shows the changes in size and size distribution of bitumen droplets with respect to time in CRS bitumen emulsions, with and without salts. It can be observed that at very low and very high salt concentrations, the droplet size does not change significantly with time as compared to intermediate salt concentrations e.g. 0.3M to 0.7M CaCl\textsubscript{2}. Salt addition in cationic emulsions promotes the breakdown of the emulsion by reducing the thickness of the electric double layer (or Debye length or separation distance). In this way, van der Waal interaction overcomes the electrostatic repulsion potential. This is expected to result in very unstable emulsions at higher salt concentration, in contrast to the results shown in Fig. 8 where there appears to be good stability at high salt concentrations. To further confirm these observations, two more salts, NaCl and K\textsubscript{2}SO\textsubscript{4}, were tested at different concentrations (Fig. 9 a and b). The results confirm a minimum in stability at about the same ionic activity. Two hypotheses were proposed. The first is that the emulsion at higher salt concentrations was mainly broken, and the broken and coalesced bitumen was present in lumps or large droplets which were not detected using the light scattering technique. The second is that the stabilization mechanism using emulsifier Redicote EM44, which consists of both amine groups and ethoxylate groups, is not a pure electrostatic stabilization.
Fig. 7. Effect of salt concentrations on droplet size distribution in CRS bitumen emulsions stabilized by 0.17% Redicote EM44.
As was not expected and seemed contradictive, some additional experiments were planned to understand this unusual behavior of salts. One emulsion was prepared with an emulsifier consisting of only amine groups. For this purpose, Redicote E-9 was selected. A second emulsion was prepared with an emulsifier containing only ethoxylate as a hydrophilic group. For this purpose, Redicote E-47 NPF was selected. The results are shown as time series in Fig. 10.
Fig. 10. Droplet size distributions of bitumen-in-water emulsions produced with different types of emulsifiers, with and without salt of various concentrations. (a,c and e) Emulsion with E-9 at pH=2.3; (b,d) Emulsion with E-47 NPF at pH=7, and (f) Emulsion with E-47 NPF at pH=2.3.

The test confirmed that electrostatic stabilized emulsions (Redicote E-9) showed growth in bitumen droplet size at very high salt concentrations. These concentrations were considerably higher compared to emulsions made with Redicote EM44. It was also noticed that emulsions could not be made using Redicote E-9 and K₂SO₄, which likely is due to formation of amine sulfates which have very low solubility in water. Emulsion samples containing non-ionic emulsifiers (Redicote E-47 NPF) were stable at all salt concentrations.

Emulsions prepared with non-ionic polyoxyethylene (POE) surfactants are stabilized by steric interactions between the adsorbed hydrated polymer chains when the particles of the disperse phase are close [30]. Non-ionic surfactants achieve stabilization of the emulsion by surrounding the bitumen droplet with a hydrated layer of surfactant. This layer acts as a steric barrier to droplet coalescence. POE is one of the most researched synthetic water soluble...
polymers due to its frequent use. POE based emulsifiers is the most common emulsifier in most household detergents. [32]. At the molecular level, two or three water molecules can hydrate one POE monomer and usually water molecules form a sheath around the POE macromolecule. The study of commercial POE specimens indicates that the main impurity ion is Ca$^{2+}$, which is adsorbed by the oxygen atoms of the ethylene oxide groups, attributing a positive electrical charge to the polymer chain [33]. The clustering effect of aqueous POE solutions in the presence of salt (CaCl$_2$) using small angle neutron scattering (SANS) have also confirmed that Ca$^{2+}$ ions bind to the oxygens of POE [34]. These interactions transform the neutral polymer chains to a weakly charged polyelectrolyte and give rise to repulsive interactions between PEO/Ca$^{2+}$ complexes at higher salt concentrations.

A region of instability appears in the emulsion samples prepared with Redicote EM44 (Ethoxylated R-Tallow Amine) with salt containing both monovalent and divalent cations. A possible explanation is based on the structural conformation of emulsifier connected with the types of salt ions and their concentrations. All active emulsifiers generate a layer of the water face on top of the organic phase of the system and the process is called hydration. The molecules in the hydrophilic part of active emulsifier arrange themselves with the neighbouring water molecules. Likewise oxygen in POE chains or alcohol head groups, nitrogen in case of amines head groups interact with water by forming hydrogen bonds. A Stern layer [27] is established due to these interactions and at least present in case of ionic emulsifiers. In case of nonionic emulsifiers, POE chains make a spongy type structure layer which absorbs water molecules. The relative motion of liquid near the droplet surface plays a role in damaging the hydrated Stern layer or water of the spongy layer. Emulsion start to coalesce when the kinetic energy of the emulsified droplets is enough for interfacial turbulence. The region of instability can be visualized from two perspectives or mechanisms that can be the basis for the proposed hypothesis.

Mechanism A is for hydrated systems that contain a standard emulsifier without any additional functional groups e.g. Redicote E-9 (R-Tallow Diamine). In this mechanism, there is a strong electrostatic repulsion between diamine head groups that stay at the bitumen droplet surface and counter ions (Cl$^-$ in the case of CaCl$_2$ with respect to the cationic emulsifier), that cannot diffuse easily (see Fig. 11a).

![Fig. 11](https://example.com/fig11.png)

**Fig. 11.** Mechanisms explaining region of instability. (a) hydrated system represents emulsion prepared with E-9 (R-Tallow Diamine), (b) hydrated system represents emulsion prepared with EM44 (Ethoxylated R-Tallow amine).

By contrast, mechanism B represents a hydrated system as illustrated in Fig. 11b. Micelles are not completely hydrophilic on their surface. The lateral repulsion between the head groups is
usually so strong that in between some of them, the hydrophobic inner part of the micelle is directly exposed to water. In this system, diffusion of counter ions is possible, and diffused regions with negative head groups may change the electrostatic force balance generated by the emulsifier, and the coalescence starts due to Van der Waal interaction between the bitumen droplets which are there all the time. With increasing salt concentrations, water activity changes leads to the loss of some fractions and, as a result, POE chains start to collapse and make POE/Ca\(^{2+}\) complexes. There could be a few hypotheses to explain the instability region. For instance, i) with increasing salt concentrations, both adsorption of surfactant might change and as a result the concentration of surfactant on the bitumen drops might vary; ii) at high salt concentrations water/surfactant activity changes that leads to the loss of some POE/Ca\(^{2+}\) fractions and, as a result, POE chains start to collapse. Salt concentration up to minimum stability (0.5M CaCl\(_2\)), bitumen drops coagulate due to screening of charges with adding salt. But adding more salt, POE head groups regrow and again stabilize the system.

3.2. Effect of organic solvent on coalescence

Different organic solvents may be added to the emulsion to improve emulsification, to reduce settling, improve the curing rate at low temperatures, or to provide the correct binder viscosity after curing. It is common to use non-polar solvents such as kerosene or similar solvents. The presence of organic solvent also ensures that the coalescence process is largely driven by inertia, which improves the stability of early neck formation. However, other factors e.g. the rheological properties of the water/bitumen interface, which, in addition, might evolve with the interface aging, could play crucial roles in the coalescence process.

3.2.1. Relaxation test observation

For this investigation, we selected polar organic solvents which were mainly water soluble and remained in the water phase of the emulsions. The selected solvents were glycerol, methanol, propanol and ethanol, with and without added 0.1M CaCl\(_2\) (see Table 2). For these experiments, the droplet coalescence test was limited to two bitumen grades (160/220, 70/100) of the same crude oil origin.

By adding organic solvents to the water phase, some of the physical properties of the aqueous mixtures change. In Table 2, the density (\(\rho\)) and surface tension (\(\gamma\)) of the aqueous mixtures are listed, as measured in the laboratory. It can be observed in the data shown in Table 2 that addition of methanol, propanol and ethanol resulted in decreasing density of the water phase. However, in the case of glycerol, the density of the aqueous mixture was slightly increased. Salt addition to the aqueous solution resulted in an increase in the density. Furthermore, for the aqueous mixtures containing 10% organic solvents, all except glycerol showed a decrease in surface tension compared to the water phase without solvent. The addition of glycerol had no effect on the surface tension.
Table 2. Measured physico-chemical properties of selected aqueous mixtures.

<table>
<thead>
<tr>
<th>S.Nr</th>
<th>Aqueous Mixtures</th>
<th>Density ρ (g/cm³)</th>
<th>Surface Tension γ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water + Redicote EM44 @ pH=2.3</td>
<td>0.99282</td>
<td>39.608 ± 0.059</td>
</tr>
<tr>
<td>2</td>
<td>Water + Redicote EM44 @ pH=2.3 + 0.1M CaCl₂</td>
<td>1.00162</td>
<td>37.477 ± 0.210</td>
</tr>
<tr>
<td>3</td>
<td>Water+ Redicote EM44 @ pH2.3 + 10% Glycerol</td>
<td>1.01615</td>
<td>39.792 ± 0.273</td>
</tr>
<tr>
<td>4</td>
<td>Water+ Redicote EM44 @ pH2.3 + 10% Glycerol + 0.1M CaCl₂</td>
<td>1.02232</td>
<td>37.249 ± 0.183</td>
</tr>
<tr>
<td>5</td>
<td>Water+ Redicote EM44 @ pH2.3 + 10% Methanol</td>
<td>0.97465</td>
<td>38.554 ± 0.346</td>
</tr>
<tr>
<td>6</td>
<td>Water+ Redicote EM44 @ pH2.3 + 10% Methanol + 0.1M CaCl₂</td>
<td>0.98248</td>
<td>37.529 ± 0.393</td>
</tr>
<tr>
<td>7</td>
<td>Water+ Redicote EM44 @ pH2.3 + 10% 2-Propanol</td>
<td>0.97536</td>
<td>35.824 ± 0.164</td>
</tr>
<tr>
<td>8</td>
<td>Water+ Redicote EM44 @ pH2.3 + 10% 2-Propanol + 0.1M CaCl₂</td>
<td>0.98190</td>
<td>33.911 ± 0.205</td>
</tr>
<tr>
<td>9</td>
<td>Water+ Redicote EM44 @ pH2.3 + 10% Ethanol</td>
<td>0.97487</td>
<td>38.398 ± 0.182</td>
</tr>
<tr>
<td>10</td>
<td>Water+ Redicote EM44 @ pH2.3 + 10% Ethanol + 0.1M CaCl₂</td>
<td>0.98273</td>
<td>36.003 ± 0.305</td>
</tr>
</tbody>
</table>

The results from droplet coalescence experiments at 40 °C in selected aqueous solution containing Redicote EM44, with and without added salt, are shown in Fig. 12a-b, respectively. The coalescence times for the same bitumen droplets in different aqueous environments are not the same, and the coalescence process here can probably be linked with difference in IFT of bitumen and the water phase, respectively, that drives the coalescence. The measured IFTs of three bitumen grades (160/220, 70/100 and 50/70) are (45.9 mN/m, 42.7 mN/m and 38.8 mN/m), respectively [31]. A correlation diagram between the relaxation time and the IFTs of the selected aqueous mixtures at 40 °C is shown in Fig. 13. Results show that there is a weak correlation between the two parameters.

Fig. 12. Coalescence of indicated bitumen grades in 100/90% water + 0/10% (glycerol, methanol, 2-propanol, and ethanol) + emulsifier + hydrochloric acid (to pH=2.3) at 40 °C, (a) without salt, and (b) with 0.1M CaCl₂.
3.2.2. Microscopy and droplet size distribution measurements

To investigate whether the organic solvents had any effect on the stability of real emulsions, the droplet size distribution was measured over three weeks. The samples consisted of a CRS emulsion with 0.17% Redicote EM 44 and pH 2.3. The solvents were added directly to the emulsion. To ensure that any effect was not due to the dilution of the emulsion, a sample diluted with tap water was added as a reference. The results are shown in Fig. 14. There were very small changes in particle size distribution with the addition of organic solvents to the water phase.

**Fig. 14.** Effect of different solvents on droplet size distribution in Cationic Rapid Setting (CRS) bitumen emulsions.
Microscopic observations, shown in Fig. 15, confirmed the results shown in Fig. 14, but also showed that droplets moved around as flocculates after 4 weeks. There seems not to be any major coalescence of the droplets. By comparing Fig. 7 (effects of salts on droplet size distribution) with Fig. 15 (effects of different solvents on droplet size distribution), salt addition at higher concentrations yields far greater effects on droplet size distribution. However, organic solvents have little influence on surfactant molecules and mostly change only the physico-chemical properties of the aqueous phase such as density, viscosity and surface tension. Thus, organic solvents seem to have very little effect on coalescence.

![Fig. 15. CRS bitumen emulsions with addition of solvents leading to flocculation and coalescence. (a. 10% Ethanol, b. 10% 2-Propanol, c. 10% Glycerol, d. 50% Tap Water).](image)

4. Conclusions and Discussions

In this work, we found that addition of salt to bitumen emulsions generally slowed down coalescence, as measured by the shape relaxation test. We also noticed that addition of small amounts of salt, 0.1M – 0.2M, stabilized the emulsion, while addition of large amounts of salt gave different results depending on the type of emulsifier. Particularly strange results were found with Redicote EM-44, which showed a minimum in stability with the addition of 0.5 M CaCl₂. This is contradictory to the results with Redicote EM-9, which showed the expected behavior of being less stable at higher concentrations of salt up to 3M. Redicote EM-9 is a diamine emulsifier and produces emulsions at pH 2.3 which are only electrostatic stabilized. Bitumen emulsions made using a non-ionic emulsifier Redicote EM-47 NPF were shown to be insensitive to salt content. The results with Redicote EM-44, which is a mixture of
emulsifier, are assumed to be due to the particular mixture. Further speculation regarding Redicote EM-44 is not possible since the exact formulation is a trade secret of AkzoNobel.

The use of polar organic solvents, which are mainly water soluble and are expected not to affect the viscosity of the bitumen, improves the coalescence as measured with the shape relaxation test. The largest effect is seen with propanol, which is also the most hydrophobic of the tested solvents. The tests are limited to water phases containing Redicote EM-44. The effect could be different for other emulsifiers.

The following conclusions were drawn:

- The relaxation test results show no significant difference in the coalescence times of two bitumen droplets having small and long water pre-conditioning history.

- In the case of CaCl₂, cationic rapid setting (CRS) bitumen emulsion prepared with Redicote EM44 (Ethoxylated R-Tallow Amine) showed a region of minimum stability of emulsion at a salt concentration of 0.5M. Below and above this minimum concentration, there is normal stability.

- CRS bitumen emulsion prepared with standard emulsifier Redicote E-9 (R-Tallow Diamine) showed normal behavior with increasing concentrations of CaCl₂ and NaCl with emulsions destabilizing at high salt concentrations. Emulsions prepared with non-ionic emulsifier Redicote E-47 NPF were very stable for the selected concentration range of all salts.

- The effect of salts on the coalescence process is more significant compared to the aqueous mixtures containing organic solvents. The presence of salt in a mixed solvent environment prolonged the relaxation process.

In the size distribution and microscopic investigations of bitumen emulsions, one can only characterize flocculates and coalesced droplets but not the other phase separation processes e.g. creaming or sedimentation. However, in the relaxation test method, creaming and sedimentation can be observed to a certain extent. Apart from the electrostatic force imbalance due to salt addition, the density, viscosity and surface tension of the water phase all change with increasing salt concentration whereas bitumen density remains constant.

Investigating the effects of salts on the destabilization of bitumen emulsions has improved the understanding of the factors that impact storage stability and electro-chemical balance at the bitumen-water interface, and this may enable the bitumen industry to design bitumen emulsions under better control.

However, there are some limiting factors in these investigations: (i) the bitumen droplet size in the relaxation test was at the millimeter scale which is bigger than in the real world and (ii) the bitumen emulsion sample used for size distribution and optical microscopy was 10 times more dilute than an actual real emulsion would be.

A study related to the relaxation of bitumen droplets could be further extended by developing a numerical model to investigate more thoroughly the effects of small sized (order μm) bitumen droplets which are difficult to produce and handle using experimental methods. This
would enable the detailed development and control of bitumen emulsions on a larger scale which would contribute to its widespread applicability in cold mix asphalt.

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References


