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Evaluation of oil-in-water emulsions with cationic–anionic surfactants mixtures for potential use in the oil industry

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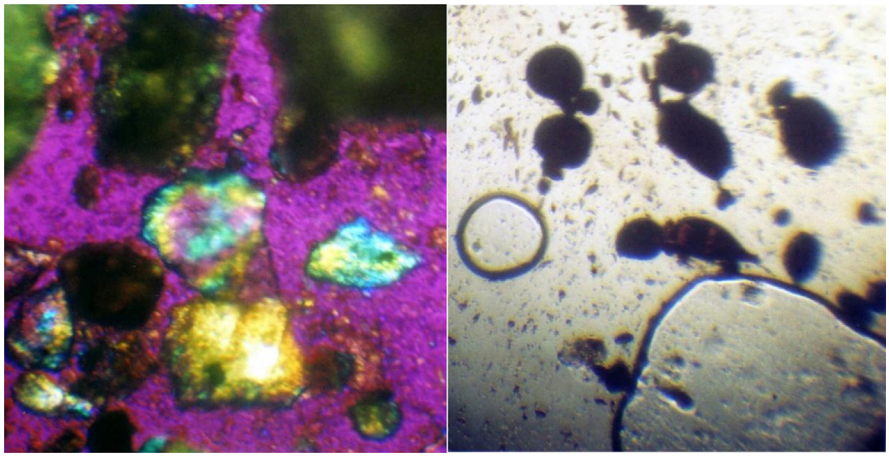
HIGHLIGHTS

- The emulsifier properties of sodium oleate (NaOl)–hexadecyltrimethylammonium bromide (HTAB) aqueous mixtures were studied.
- The formation of O/W and W/O emulsions was explored and their properties were determined.
- It was found that all emulsions were stable on ageing and to temperature rise.
- The emulsions were destroyed by contact with quartzite stones.
- These mixtures have high potential applicability in the asphalt emulsification for pavement production or sand fixation.

GRAPHICAL ABSTRACT

Left: stones with crude oil emulsion. ×100, Crossed polaroids and 1 λ retardation plate intercalated, showing interference colours in the quartzite stones and sensitive pink of non-birefringent (water) medium. The black zones correspond to stones covered by hydrocarbon. Right: crude oil emulsion, unpolarised light. The emulsion used in both photos was diluted to improve visualization.



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ABSTRACT

The emulsifier properties of sodium oleate (NaOl)-hexadecyltrimethylammonium bromide (HTAB) aqueous mixtures were studied using different proportions of the surfactants. The formation of O/W and W/O emulsions was explored and their properties (viscosity, stability and droplets size distribution) were determined. The mixture with 0.75 mole fraction of HTAB without considering the solvent formed very stable and concentrated O/W emulsions, which were destroyed via heterocoagulation by quartzite sand. Thus, these mixtures have high potential applicability in the asphalt emulsification for pavement production or sand fixation.

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1. Introduction

Stable emulsions of heavy oils or bitumen in water are widely used to extract, transport and store petroleum. These emulsions are an alternative to the increase of temperature for the mixing of asphalt with light oils, which involve high costs and technical complexity [1,2]. O/W bitumen emulsions have been also employed as combustible in electricity power plants [3]. Desire features of these emulsions are high stability and low viscosity.

Other applications of asphalt emulsions are road construction and roof water-proofing. In particular, these emulsions have many advantages for road reparation compared to melted asphalt: easier implementation, fewer precautions and no need of special equipment, as well as their applicability to wet surfaces, a very attractive characteristic. The speed of rupture of the asphalt emulsion on the mineral substrate is of primary importance. On the one hand, enough time must be allowed for proper mixing of the various components of the system but, on the other hand, the breaking time must be short enough to permit a rapid re-opening of the road to traffic [4].

Bitumen is a high viscosity mixture of hydrocarbons (>10^4 cP). "Synthetic" bitumen is best known as asphalt and is a petroleum-like material obtained as a residue from the distillation of petroleum [5] with a consistency varying from viscous liquid to glassy solid. Asphalt is commonly employed as a binder of aggregates for road pavement [6].

Asphalt emulsions are commonly either anionic or cationic. Their rupture in contact with stones is caused by the destabilization of the emulsifier. Polyvalent cations, such as Ca^{+2} and Mg^{+2} (in basic stones such as calcareous ones), react with anionic surfactants producing uncharged insoluble soaps while the negative charge of acid siliceous surfaces reacts with cationic surfactants causing electrostatic adsorption. The adsorbed cationic surfactants show their hydrocarbon chains out of the stones' surface, causing its hydrophobization and thus increasing the tendency of asphalt to adsorb on the stones, promoting the adhesion between the hydrocarbon and the mineral surfaces. Moreover, the surfactant monolayer reduces the affinity of the stones' surface towards water, thus reducing its tendency to destroy the pavement. Water penetration causes stripping of the bitumen from the aggregate particles, consequently endangering the subgrade layer as well as the base course [7].

A catanionic (anionic–cationic surfactant mixture) emulsifier will have both the advantages of cationic and anionic emulsions. However, in general cationic–anionic surfactant mixtures tend to precipitate in some proportions. We have previously studied a catanionic mixture which does not precipitate in any proportion [8–10]. Sodium oleate (NaOl)–hexadecyltrimethylammonium bromide (HTAB) mixtures form soluble systems at all NaOl–HTAB proportions. This mixture does not precipitate at any composition because to steric hindrances, which were attributed to the affinity of the NaOl double bond to water *via* hydrogen bonding. Thus NaOl acts as a surfactant having two hydrophilic groups, the carboxylate and the double bond. This causes a curvature of the aggregate/water surface which favours the O/W emulsification [6–8]. NaOl is a natural, biodegradable soap which is innocuous for the environment. HTAB has bactericide capacity but it is not dispersed in the environment because it is strongly adsorbed by the negative stones' surface and remains below the asphalt layer. Thus, the system NaOl–HTAB seems to have interesting features that makes it attractive for practical applications, especially in the petroleum industry.

In the present work the emulsifier capability of different mixtures of NaOl–HTAB with Argentine crude oil (CO) and with model liquid paraffin (LP) has been studied. The behaviour of the emulsions in contact with a petrous substrate has been also studied in order to evaluate their possible use in pavement production. Our findings are of practical and theoretical interest in the oil emulsions field and set the basis for the future study of the emulsification properties for heavy oil.

2. Experimental

2.1. Materials

For paraffin emulsions, extra dense liquid paraffin (LP) EWE with viscosity Seyboldt 340 s and 75 centi-Stokes was used as purchased. Hexadecyltrimethylammonium bromide (HTAB, $C_{16}H_{32}N(CH_3)_3Br$ > 99%) was from Fluka. Sodium oleate (NaOL, $C_{18}H_{33}O_2Na$ > 99%) was from Aldrich. Both chemicals were of analytical grade and were used as purchased.

The crude oil (CO) of 35° API (0.870 g cm^{-3}) has kinematic viscosity 10.7 mm^2 s^{-1} and dynamic viscosity 96.7 cp (both at 20 °C) and does not contain aromatic compounds, asphaltenes or other chemicals [11]. It has been kindly supplied by the Petrobras Bahia Blanca refinery and is from the Neuquen oil field (Argentina).

The stones were from the Pigüé quarry (Argentina) and were selected because of their poor performance to produce pavements with commercial asphalt emulsions. Their treatment with a commercial asphalt emulsion achieved only an incomplete coverage of the stones' surface, which leaves the pavement vulnerable to water penetration [12].

LP and CO were selected because of their easier manipulation than heavy oils and bitumen. Once the possibility of using the mixture for emulsifying hydrocarbons is stated, it is possible to study the formation of bitumen emulsions. We used Argentinian crude oil, which is free of asphaltenes, due to a matter of availability.

Tri-distillated water was used and the measurements were performed twice.

2.2. Emulsions

Aqueous emulsifier solutions of HTAB and NaOL with 0.1 M were prepared at the mole fractions of HTAB in the surfactant mixture without considering the solvent (α_{HTAB}) 0.1; 0.25; 0.3; 0.50; 0.7; 0.75; 0.9 and 1.

Each emulsion was stirred for 15 min with a steel helix stirring electric device at 800 rpm after the addition of the second phase.

Emulsions of Argentine petroleum were prepared according to two procedures:

a) The aqueous surfactant solution (50 mL) was added in aliquots of 2 mL to 50 mL of CO under stirring. Then, 15 mL of each sample was put in a graduate tube and stoppered. The volume of the emulsion was determined immediately, after 24 h and after a week's time. The emulsions were observed by means of a microscope.
b) The CO (50 mL) was added to 50 mL of the aqueous surfactant solution in aliquots of 2 mL under stirring and the emulsions were observed as in procedure *a*. An additional observation was made after 14 months.

Since the Argentine petroleum was paraffinic (see below), we used for the main determinations a model emulsion with liquid paraffin which facilitates the observation because it is colourless. The model emulsions were prepared with surfactant mixture (0.1 M in water) with α_{HTAB} = 0.1; 0.25; 0.50 and 0.75. Then, 60 mL of liquid paraffin was added to 40 mL of the aqueous surfactant solutions and stirred during 15 min. The systems were transferred to graduated tubes and the volumes of emulsion, remnant water and remainder paraffin were recorded. Samples of the freshly prepared emulsions for microscopic observation were kept in separated sealed vials.

Samples with α_{HTAB} = 0.25; 0.50 and 0.75 were observed in a microscope Nikon Eclipse E-200 POL Polarizing, Tokyo, Japan.

Table 1
Volumes of W/O emulsion and remnant (non-emulsified) water in 10 mL samples as a function of the surfactant composition. A week old samples after centrifugation.

αHTAB	0	0.1	0.3	0.5	0.7	0.9	1
$V_{W/Oemulsion}$/mL	2.9	1.2	0.3	3.3	0.2	0.5	0.2
V_{water}/mL	7.1	8.8	9.7*	6.7	9.8**	9.5	9.8***

* W/O/W emulsion.
** O/W emulsion.
*** Multiple emulsion.

Unless stated otherwise, all observations were made with ×100 magnification. Nonetheless, scale bars were added to the photos. As both phases are transparent and colourless, a drop of aqueous solution of methylene blue was added to determine the nature of the emulsion. In all cases the dye diffused amongst the emulsion droplets, thus all emulsions were O/W. The emulsions remained stable during the microscope observations although no stabilizer was added (such as a gelatine solution) [13].

The viscosity (η) of emulsions was measured with a Vibro Viscometer SV-10/SV 100 calibrated with tri-distilled water (η = 0.89 cP at 25 °C).

The hydrocarbon/water volume ratio in the emulsions was measured using a modified Dean-Stark apparatus [2].

To evaluate the effectiveness of stones in destructing the emulsion and the hydrocarbon deposition on the stones' surface, a powder of the stones was put in contact with the different emulsions and observed under the microscope. In order to reproduce the procedure in real working conditions, the mineral substrate was used as received, without any pre-treatment.

The X-ray diffraction spectrum of the stones employed in the test of stability of emulsion was made in a Phillips PW 1710 diffractometer with Cu anode and curved graphite monocromator operated at 54 kW and 30 mA.

FT-IR measurements were performed with an Infrared Spectrophotometer (Nicolet FT-IR, Model Nexus 470) to test the CO structure.

The size distribution of droplets was determined with a computer program (Pixcavator IA). As a size reference, the width of the hair in Fig. 3a was used (a similar method was used for other magnifications).

Averages and variances values were computed by the minimum variance linear unbiased method [14] and the Student t function was employed to compute the error intervals. Confidence level was 0.90. Errors of derived data were computed with the error expansion method.

3. Results

The X-ray diffractogram (Fig. 1 in Supplementary information, SI) indicates that the stones' nature is clastic sedimentary rock—S0, formed by silica (ortho-quartzite).

The petroleum FT-IR spectrum (not shown) showed only paraffinic hydrocarbon peaks (—CH_3; —CH_2— stretching vibrations at 3000–2850 cm^{-1} and —CH_3; —CH_2— bending vibrations at 1480–1350 cm^{-1}).

3.1. Petroleum emulsions

Changing the order of addition of the components while stirring produced two different kinds of emulsions. The addition of the surfactant aqueous solution to crude oil produced a W/O emulsion (see Fig. 1). Freshly prepared samples did not show significant phase separation. The emulsion could be separated by centrifugation at 2000 rpm only after a week from preparation. Due to the petroleum colour, a Cole-Palmer Iluminator 41720-series was used. Table 1 shows the relative volumes of emulsion as a function of the mixture composition. Pure NaOl (α_{HTAB} = 0) had poor emulsifying capacity, but the addition of a small amount of HTAB (α_{HTAB} = 0.1) produced a good W/O emulsion with small polydisperse droplets (Fig. 1a). Further addition of HTAB produced a very polydisperse W/O emulsion (Fig. 1b and c). With α_{HTAB} = 0.3 two kinds of emulsions appeared: the W/O and a multiple emulsion O/W/O, and with α_{HTAB} = 0.7 there coexist W/O and O/W emulsions.

As we desired O/W emulsions we employed procedure *b*: addition of the crude oil to the surfactant solution under stirring. Fig. 2 shows microscopic images of two of the emulsions obtained with α_{HTAB} = 0.75. The concentrated emulsion was diluted with water to improve the observation.

3.2. Paraffin emulsions

Owing to the difficulty caused by the strong colour of the crude oil to the visual examination and microphotographs analysis, we decided to make model emulsions with liquid paraffin, which is colourless and whose composition and viscosity are similar to that of the crude oil. Since the amount of surfactant affects the size of the droplets, we have used the same amount of surfactant in all the emulsions to compare the effect of the mixture composition.

On the basis of the preceding results, we used only surfactant solutions having α_{HTAB} = 0.1; 0.25; 0.5 and 0.75. Since we were interested in O/W emulsions, these were prepared by dropping the paraffin to the aqueous emulgent solution under stirring. The nature of the emulsion (O/W) was determined by diffusion of a drop of a methylene blue aqueous solution in the continuous phase, viewed through the microscope (Fig. 2 in the SI).

Fig. 3 shows the emulsions obtained with different surfactant compositions. The size distribution of droplets was graphically determined using a computer program (Pixcavator IA) on the photomicrographs.

The freshly prepared emulsions did not show remnant water or paraffin. The viscosity (η) of the emulsion at 25 °C were 13.20 cP for α_{HTAB} = 0.25; 47.00 cP for α_{HTAB} = 0.5 and 382.00 cP for α_{HTAB} = 0.75. The droplets size distribution is shown in Fig. 4.

The particle size of an emulsion is one of the most important characteristics [13]. Droplets size and droplets size distribution can be used as indexes of state of an emulsion and are intimately related to their stability, resistance to creaming, rheology, and chemical reactivity [15]. Two emulsions may have the same average droplet diameter and yet exhibit quite dissimilar behaviours because of differences in their distribution of diameters.

The droplet size distribution for α_{HTAB} = 0.25 is unimodal and broad while that for α_{HTAB} = 0.50 is multimodal with lower maxima. When α_{HTAB} is 0.75 the distribution is a narrow, unimodal and centred in the smaller size. Emulsions with a droplet-size distribution with a maximum of low diameter droplets and with this maximum sharply defined represent a situation of maximum stability [16].

To study the stability of the emulsions, these were aged in sealed graduated tubes. The separation of emulsion and water when the systems were aged can be seen in Fig. 5. The emulsions still remained stable after 14 months. (Fig. 3 in SI).

The aged emulsion with α_{HTAB} = 0.75 had a LP content 73% V/V. Natural bitumen emulsions contain between 70 and 80% V/V of bitumen separated by tiny layer of water, while asphaltic emulsions usually contain about 60% V/V [9].

The size distribution is shifted towards smaller droplets when aged, as shown in Fig. 6 for α_{HTAB} = 0.25 (the other surfactant compositions showed similar behaviour).

To determine the efficiency of the surfactant mixtures to emulsify LP, 20 mL of emulsion having α_{HTAB} = 0.25 was completed to 100 mL with liquid paraffin and stirred. After a day, there was 1 mL of supernatant paraffin, i.e. 1.412 g of surfactant mixture was capable of emulsifying 91 mL of paraffin. The size distribution of droplets

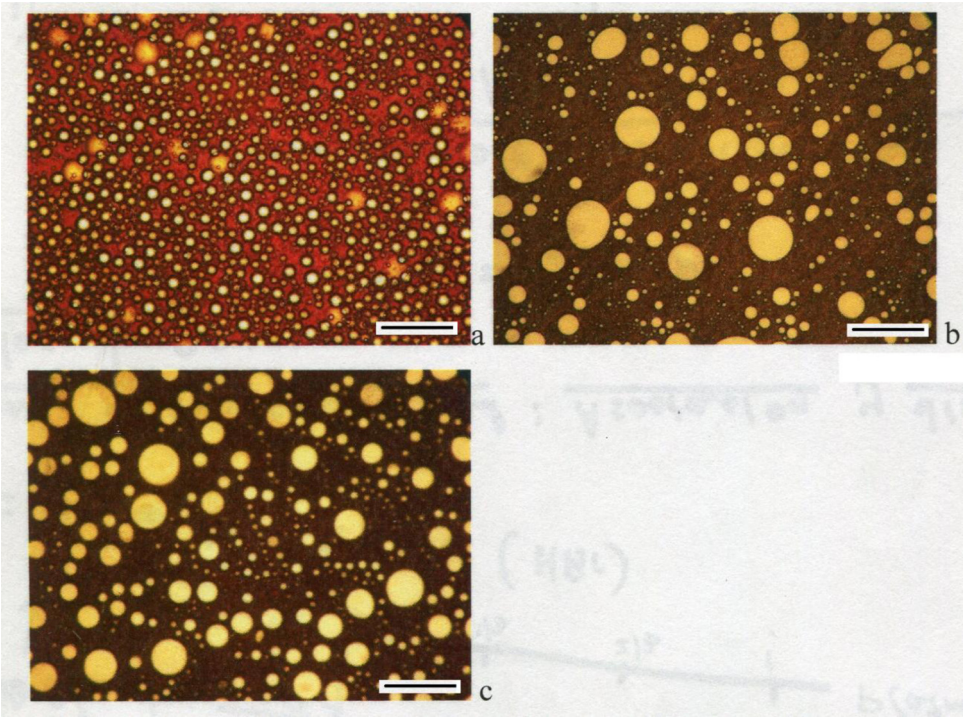

Fig. 1. W/O emulsions produced by dropping aqueous surfactant solution to crude oil under stirring. ×100. (a) $\alpha_{HTAB} = 0.1$, (b) $\alpha_{HTAB} = 0.7$, (c) $\alpha_{HTAB} = 1$. The bar corresponds to 0.2 mm.

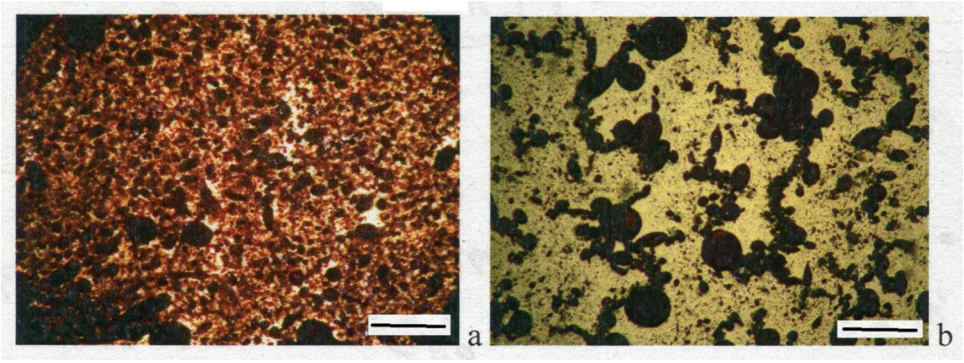

Fig. 2. O/W emulsion obtained by dropping crude oil to the aqueous surfactant solution under stirring. $\alpha_{HTAB} = 0.75$, ×100. (a) emulsion diluted with 25% water, (b) emulsion diluted with 50% water. The bar corresponds to 0.2 mm.

was almost unimodal and is shown in Fig. 7. After one year only 20 mL of paraffin was separated while the remaining emulsion was stable (see Fig. 3 in SI) with the separation of the remnant water (below) and paraffin (above). Similar results were obtained with the other compositions.

No agglomeration or coalescence was observed during the microscope observations, even after one hour of preparing the samples.

To test the temperature stability of emulsions, samples of the three emulsions (with $\alpha_{HTAB} = 0.25$, 0.5, and 0.75) were placed between slides and heated with a temperature-controlled stage at the microscope. Photos were taken at different temperatures up to the ebullition of water (Fig. 8). Vapour bubbles and LP droplets differentiate by the aspect of their borders as a consequence of the different refractive index: the borders are black and thick in the vapour bubbles and light grey in the LP droplets.

Emulsion with $\alpha_{HTAB} = 0.25$ became more fluid at 83 °C and the larger droplets disappeared but the smaller ones were retained. At 111.5 °C the emulsion flowed and the water started to boil. Fig. 8b and c shows the vapour bubbles that grew with increasing temperature. The oil droplets are smaller. At a temperature of 118 °C the emulsion started to break, to be almost completely broken at 119 °C. Fig. 9 shows the evolution of the droplets size with the raising temperature: the multimodal distribution of larger droplets trends to form a bimodal distribution of smaller droplets.

Emulsions with $\alpha_{HTAB} = 0.5$ remained stable up to 103 °C, when vapour bubbles appeared. At 115 °C the system flowed and at 124.5 °C it collapsed. Fig. 10 shows the evolution of the size distribution of droplets with raising temperature: it remained multimodal but shifted towards smaller droplets.

Emulsion with $\alpha_{HTAB} = 0.75$ became fluid at 83.6 °C and the excess of water was separated forming small domains that started to disappear at 104 °C. Some bubbles of vapour appeared and grew with the increasing temperature. Some emulsion was remained up to 122 °C. The size of oil droplets was reduced when the temperature was increased from 37.5 °C to 67.5 °C, and the distribution became narrower. Further increase of temperature did not affect

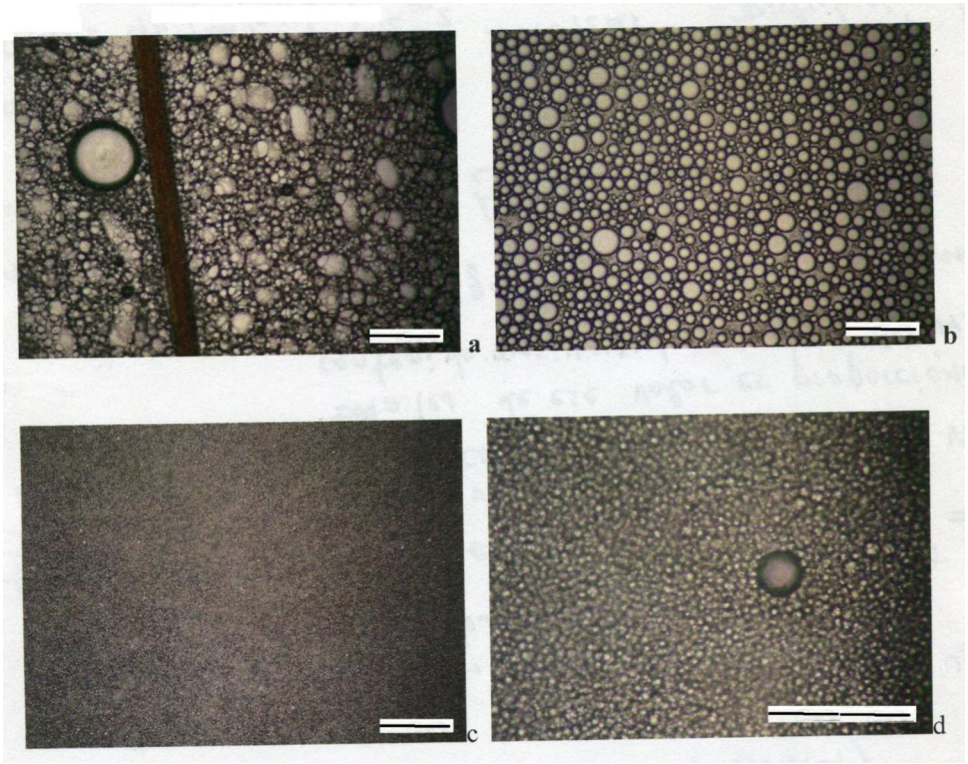

Fig. 3. microscope photos of fresh emulsions having α_{HTAB} = 0.25 (a) ×100, 0.5 (b) ×100, 0.75 (c) ×100 and 0.75 (d) ×400. The line in photo (a) is a hair, having 0.090 mm in width, and used to calibrate the size of droplets. Bars in photos a–c correspond to 0.2 mm, in photo d, to 0.1 mm.

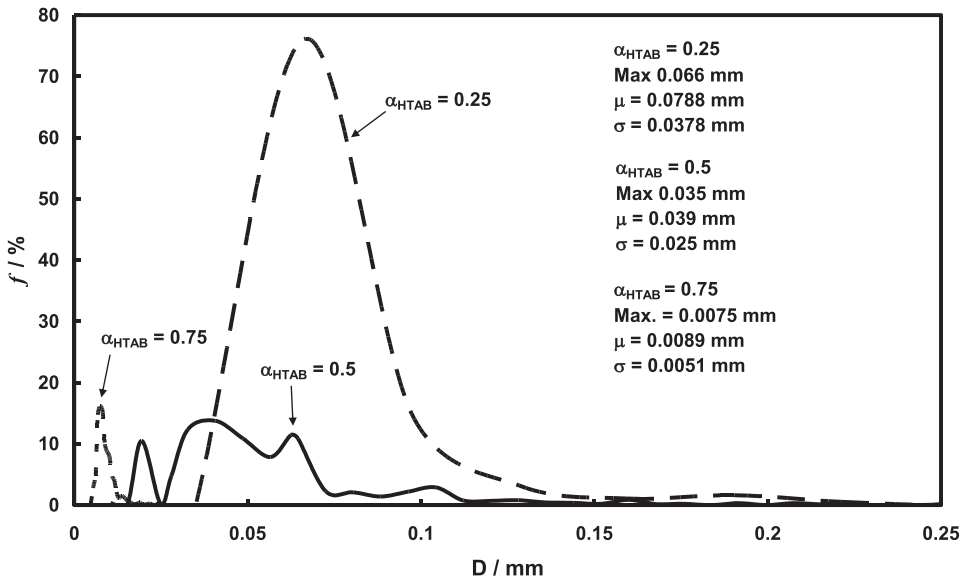

Fig. 4. size distribution of freshly prepared emulsion having α_{HTAB} = 0.25, α_{HTAB} = 0.50 and α_{HTAB} = 0.75. Distribution parameters: μ: number average, σ standard deviation, Max: maximum.

the size distribution. Fig. 11 shows the size distribution of droplets as a function of temperature.

The stability of the emulsions was not affected by two freeze–thaw cycles between −5 and 25 °C, with 8 h in each temperature.

In conclusion, the three compositions gave emulsions stable up to the temperature of water boiling. The size distribution in all cases is shifted to smaller droplets when temperature is increased.

The size behaviour on ageing and heating of emulsions is rather unusual. A possible explanation may be creaming of large oil droplets and therefore shifting the size distribution of the remaining emulsion down. Since samples were taken from different parts of the emulsion, the large droplets probably collapse giving rise to the narrow non-emulsified oil layer. Another possible explanation may be a rearrangement of the surfactant molecules in the droplets interface. Oleate molecules can fold to expose the double bond at the interface, since they tend to form hydrogen bonds with water with their π electrons [17]. This may lead to an average packing parameter of the mixture of surfactants that favours the formation of a hydrocarbon droplet with a given curvature generating a nar-

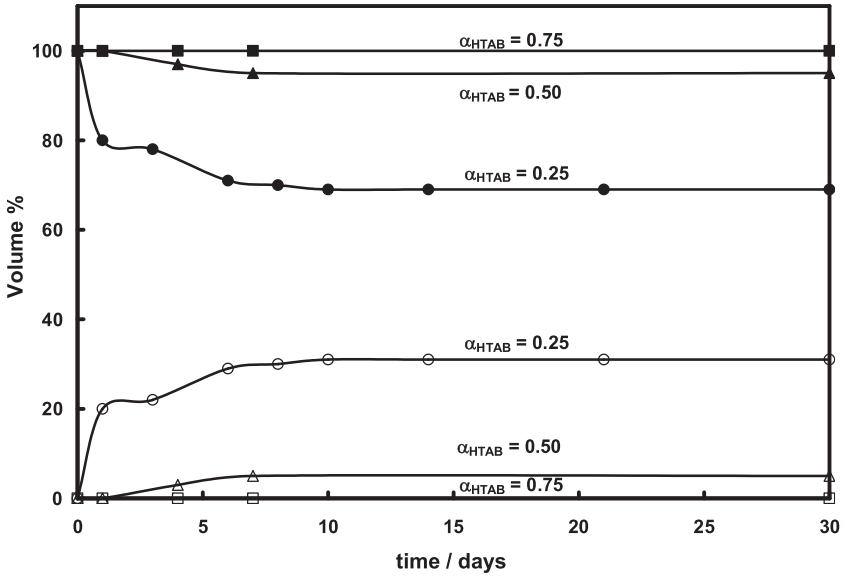

Fig. 5. Dependence on time of the volume percent of remnant emulsion (full symbols) and water (open symbols), ■□: α_{HTAB} = 0.75; ▲△: α_{HTAB} = 0.50; ●○: α_{HTAB} = 0.25.

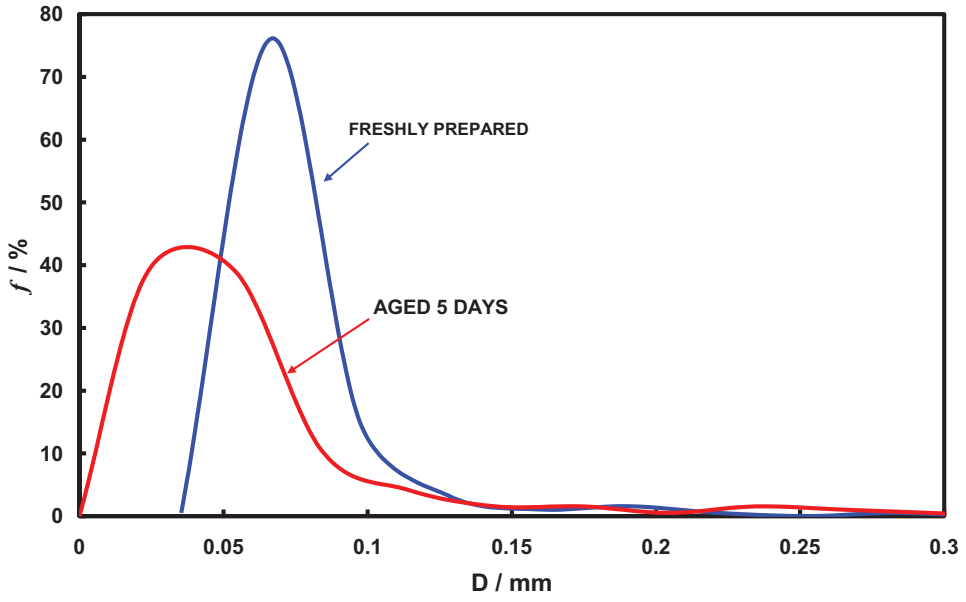

Fig. 6. Evolution with time of emulsion prepared with α_{HTAB} = 0.25.

rower size distribution. This mechanism needs some time, and will be accelerated with temperature.

As suggested by Anton et al. [18] mixtures of anionic and cationic surfactants may be considered as 1:1 complexes and the remainder molecules of the surfactant in excess. The Ol.HTA complex has a large hydrophilic part formed by one $-N(CH_3)_3^+$ group from HTA^+ ion, and the $-COO^-$ and $-CH{=}CH-$ groups of Ol^- ion. As previously mentioned it has been found that the double bond has affinity to water, forming H-bonds with the π electrons [19–21]. The tail of the oleate ion is thus folded to put the $-CH{=}CH-$ group in contact with water in aggregates such as micelles or air/water monolayers [6–8]. This produces a structure of the complex like a cone with the hydrophilic part at the basis, i.e. favouring a curved surface convex to the water. The behaviour of another cationic–anionic surfactant mixture which does not precipitate at any proportion (although it forms a coacervate in some proportions), sodium 10-undecenoate-dodecyltrimethylammonium bromide [19,22,23], was explained by the same phenomenon. This explains why the O/W emulsion is favoured and why the system does not precipitate even at the 1:1 proportion. Similar reasons have been proposed in literature for other cationic/anionic surfactant mixtures which do not precipitate [24].

The mixture with α_{HTAB} = 0.75 is the best to produce O/W emulsions, i.e. once the 1:1 complex was formed, two thirds of the hydrophilic HTAB molecules remain free. Then, the system is formed by an excess of hydrophilic surfactant which promotes O/W emulsion formation, and the complex which has a structure that accommodates to the same oil/water interface geometry.

The droplets size decreases with time and with increasing temperature probably due to that part of the surfactant that remained in the aqueous phase and migrate by diffusion to the droplets surface. This takes time but is accelerated by the temperature rise. The molecules and 1:1 complexes arriving to the oil/water interface must accommodate increasing the surface area, what may only occur with a diminution of the droplets' size when the total oil volume is constant.

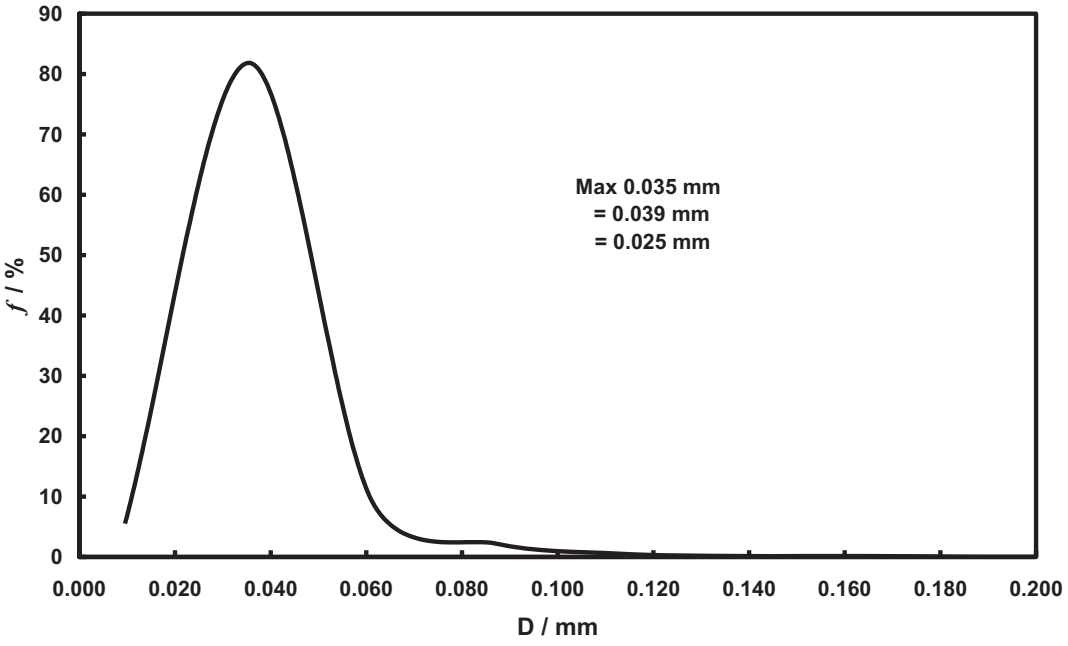

Fig. 7. size distribution of droplets for α_{HTAB} = 0.25 saturated with paraffin.

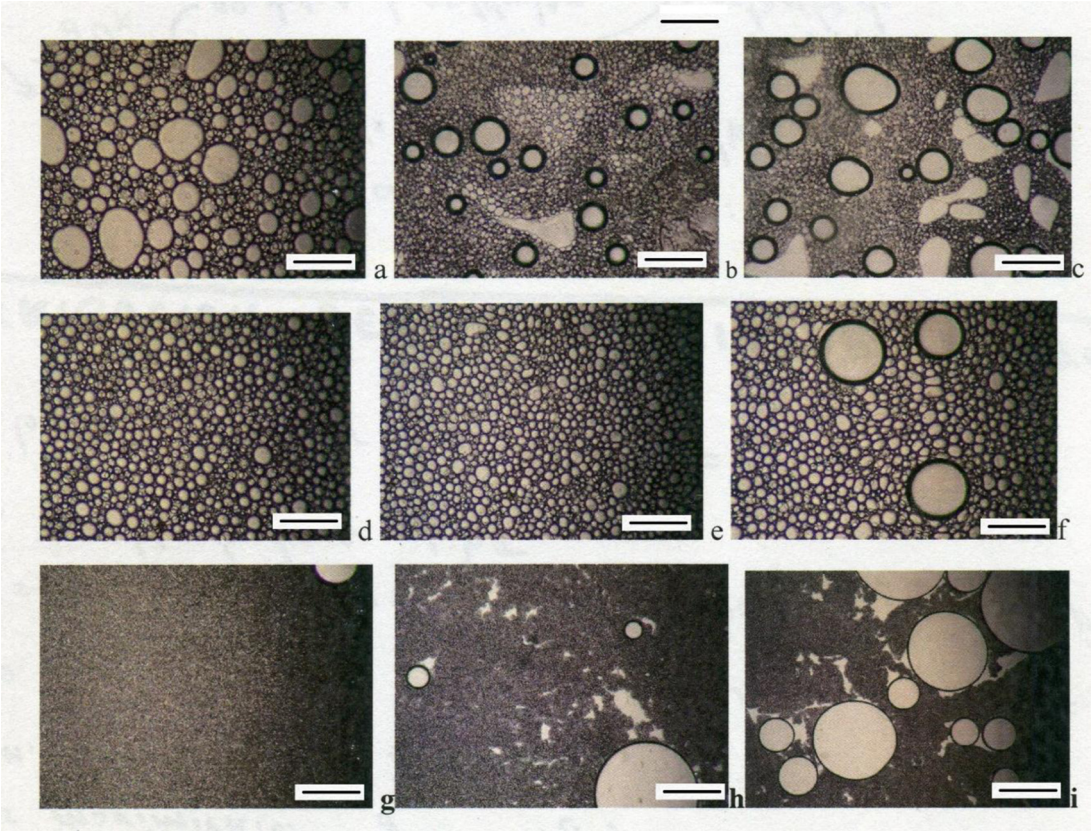

Fig. 8. Evolution of emulsions with temperature, microscope photos ×100 of emulsion width α_{HTAB} = 0.25 (a) at 48 °C, (b) 102 °C, (c) at 111.5 °C. Emulsion with α_{HTAB} = 0.5 (d) at 38 °C, (e) at 100 °C, (f) at 103 °C. Emulsion with α_{HTAB} = 0.75 (g) at 37.7 °C, (h) at 83.5 °C, (i) at 109 °C. The bars correspond to 0.2 mm.

3.3. Destruction of emulsion by stones

The emulsions were put in contact with powdered stones and observed under microscope to determine their applicability in the production of pavements. The emulsion with α_{HTAB} = 0.75 showed the best performance in the previous experiments so it was the only one evaluated for this purpose. The droplets were clustered on the stones' surface and were subsequently destroyed. The destruction of the emulsion was very rapid and finished in 15 min. Fig. 12 shows the evolution of the CO emulsion with α_{HTAB} = 0.75 in contact with the powdered stones which were almost completely covered.

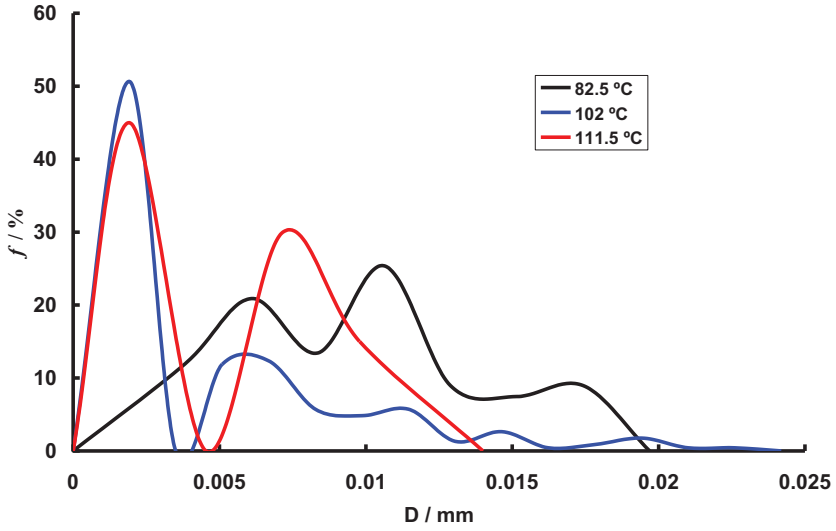

Fig. 9. Evolution of the size distribution of droplets with temperature for $\alpha_{HTAB} = 0.25$

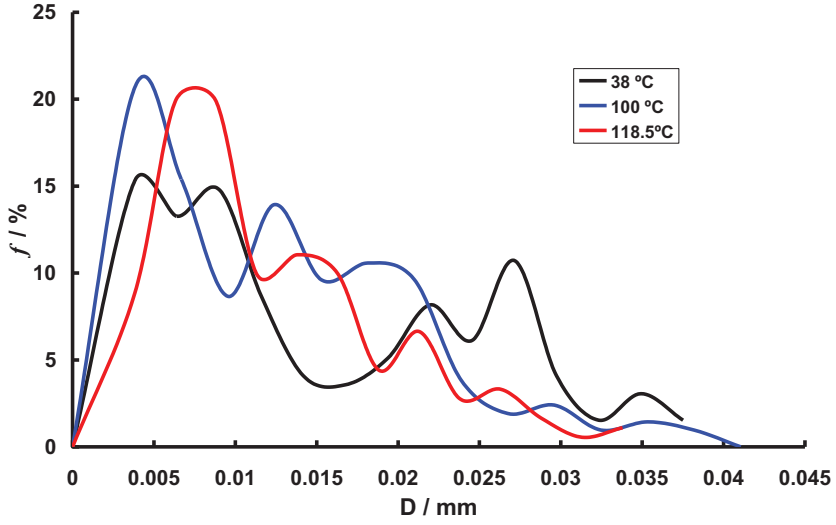

Fig. 10. Evolution of the size distribution of droplets with temperature for $\alpha_{HTAB} = 0.50$.

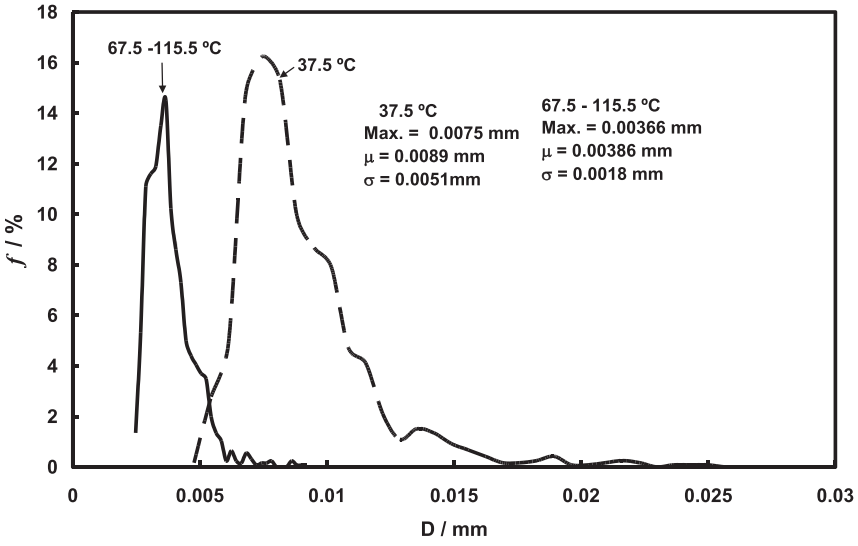

Fig. 11. Size distribution of droplets having $\alpha_{HTAB} = 0.75$ as a function of temperature.

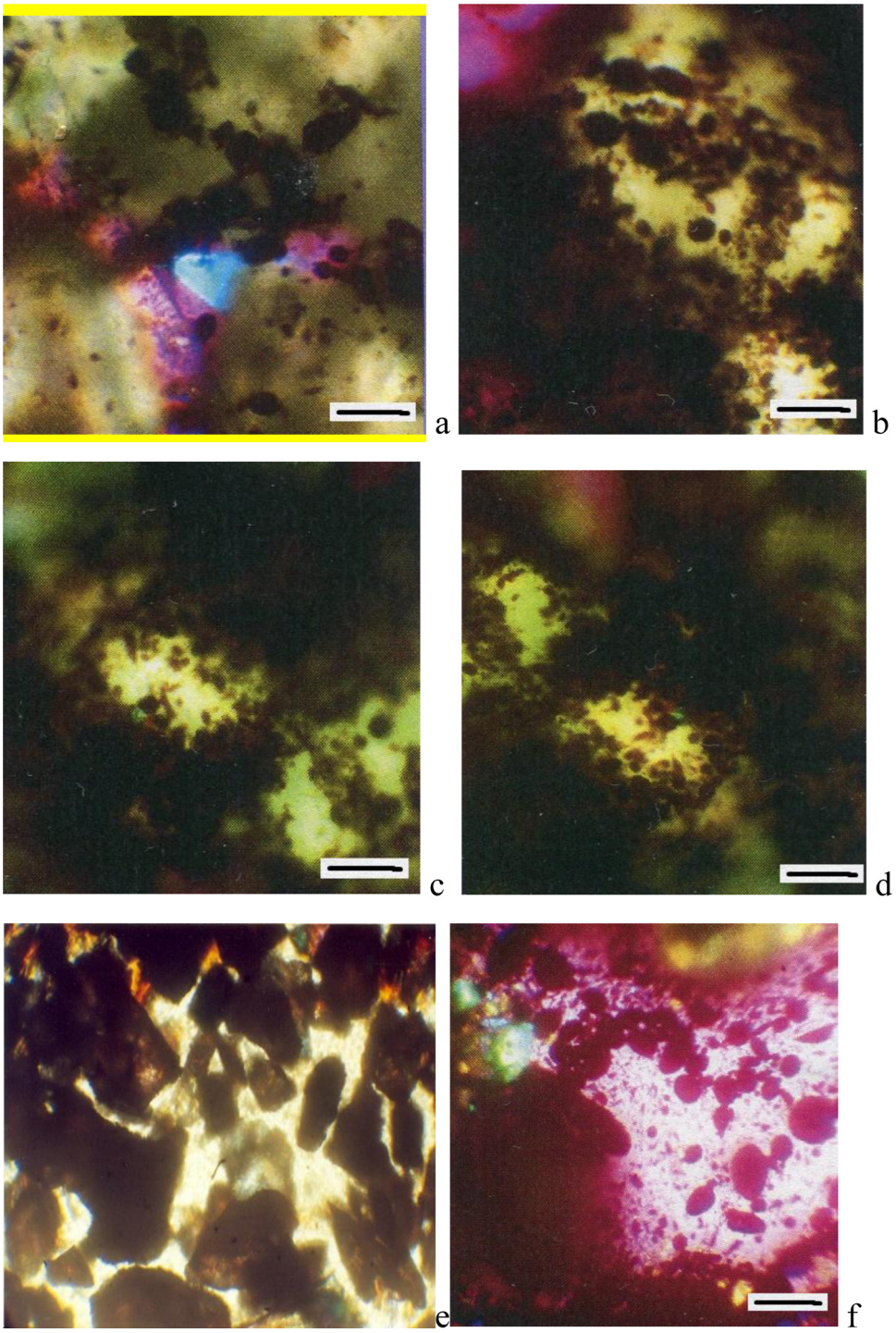

Fig. 12. Photomicrographs of the emulsion destruction in contact with stones. ×100, α_{HTAB} = 0.75. (a) Diluted CO emulsion just added to the stones, (b) after 5 min, droplets were aggregated close to the stones, (c) after 10 min, (d) after 30 min, (e) after 24 h, (f) commercial cationic emulsion after 30 min. Photos a, b and f with polarized light and 1 λ retardation plate intercalated. The other photos are with unpolarised light. Bars indicate 0.2 mm.

The crude oil emulsion was previously diluted with 20% water to improve visualization. The clear regions are water between stones.

The destruction of the emulsion by stones seems to follow the mechanism called heteroflocculation [25], i.e. the oil droplets cluster together around the stones followed by their coalescence on the solid surface. In this sense, some HTAB molecules dissolved in the aqueous phase may hydrophobize the rock surface improving the adherence of the oil.

The breaking time of emulsions is known to be affected by the nature of the aggregate and its specific area, humidity, surfactant concentration, pH, and temperature [4], therefore the speed of breaking in roads industry may be different to that found in our laboratory conditions. Due to the short time of breaking, this emulsion may be useful as an imprinting irrigation, i.e. irrigation of surfaces to produce a transition surface with the new asphaltic layer ensuring the anchoring of this layer, or to stabilize sands [26].

4. Conclusions

NaOl–HTAB mixtures revealed to be good O/W emulsifiers. The system having $\alpha_{HTAB} = 0.75$ gave the largest volume of emulsion having a narrow unimodal size distribution with smaller droplets. This emulsion has a relatively high viscosity. All emulsions were stable on ageing and to temperature rise. The emulsions were destroyed by contact with quartzite stones. These properties may be useful for different applications in petroleum industry such as their use as fuels, transport and pavement production.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfa.2015.11.023.

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