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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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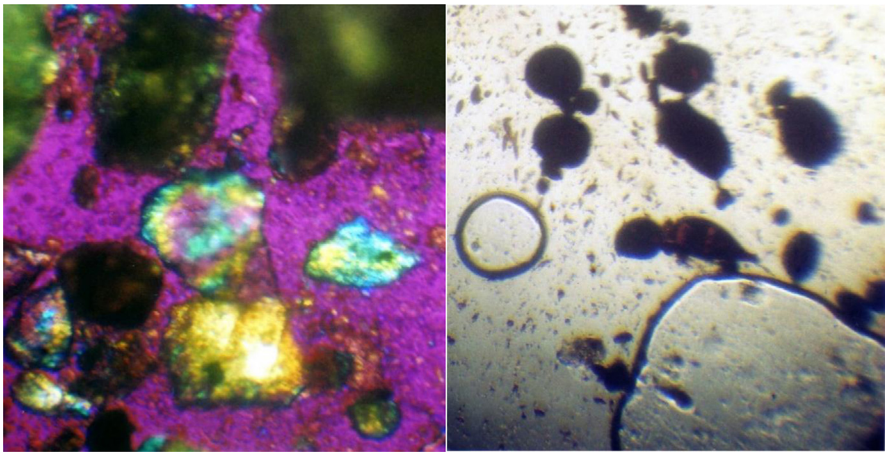
HIGHLIGHTS

- 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 $\alpha_{HTAB} = 0.1$; 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 $\alpha_{HTAB} = 0.25$; 0.50 and 0.75 were observed in a microscope Nikon Eclipse E-200 POL Polarizing, Tokyo, Japan.