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Stability of water–Boscan crude oil emulsions: Effect of salts, alcohols and glycols

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ABSTRACT

The stability of oil–water emulsions was studied using salts, alcohols and glycols. The studies of the type and concentration of salt showed that as the charge of the cation or anion increases a greater number of unstable emulsions are obtained. When the number of hydroxyl groups present in the alcohols and glycols increases, emulsions obtained separate quickly and wider compositional ranges are obtained. The demulsifying-glycol–salt synergy showed that a large synergistic zone is obtained when the charge of the anion is increased. The presence of salts, such as sodium sulfate and sodium phosphates, increases the low stability region where the emulsions formulated separates in less than 5 min.

1. Introduction

A variety of operational problems arise during the different stages of oil production. Produced water from oil extraction is one of the most frequent ones. When this two-phase water–oil mixture passes through pumps, valves, elbows and pipeline fittings, sufficient mechanical agitation is created to disperse water droplets in the crude oil thus creating microemulsions, which are thermodynamically unstable colloidal systems in which both the continuous and the dispersed phase are liquid (Mullins et al., 2007). The macroemulsions obtained are stabilized by some crude oil components, such as asphaltenes and resins, thus increasing the stability of the water-in-crude oil emulsions and generating great problems in the oil industry, and increased pumping, transport, storage, and refining costs (Sheu et al., 1992; Kilpatrick and Spiecker, 2001; Marfisi and Salager, 2004; Mullins et al., 2007; Verruto et al., 2009).

Generally, these kinds of emulsions are undesirable in the oil industry, because the commercial sale specifications are strict and the salts, sludge and sand dissolved in the aqueous phase may corrode the equipment, as well as reduce the API gravity, which is one of the main commercial parameters used to establish the quality of a crude oil (Marfisi and Salager, 2004). The dehydration of crude oils may be defined as a process that may reduce the content of water associated to the crude oil up to a percentage equal or smaller than 1% v/v whether as an emulsion or free (Kilpatrick and Spiecker, 2001; Marfisi and Salager, 2004). Currently, there are different crude oil dehydration technologies: those based on the addition of chemical additives, or on the use of mechanical, thermal and/or electrical energy. The most efficient method is the latter, because when an electric field ranging from 1 to 10 kV/cm is applied to the emulsion it causes its electrocoalescence, generating the polarization of the water molecules in the discontinuous phase and thus resulting in the separation of the emulsion (Marfisi and Salager, 2004; Mullins et al., 2007). However, electric dehydration has the drawback that it is very expensive, due to the large amount of energy consumed during the dehydration process; therefore, at an industrial level, chemical dehydration is often combined with some mechanical and/or thermal method to dehydrate crude oil (Kilpatrick and Spiecker, 2001; Marfisi and Salager, 2004; Mullins et al., 2007; Bai et al., 2009).

In this work, we study the chemical dehydration processes, which consist in changing the physical–chemical formulation of the system by adding a dehydrating or demulsifying agent (hydrophilic surfactant dissolved in water) in order to generate an unstable emulsion in which the coalescence of the droplets of the dispersed phase occurs fast, reducing the time needed by the constituent phases to separate under the action of gravity. Breaking of emulsion. One of the emulsion breaking models that has been proposed for the formulation and its relationship with the emulsion stability is the surfactant affinity difference (SAD) or its dimensionless equivalent: the hydrophilic–lipophilic deviation (HLD) (Salager, 1999).

The dehydrating agents added to the system increase the speed at which the droplets approach and the interfacial film drainage. Those agents weaken and/or inhibit the formation of an interfacial film and change the physical-chemical formulation of the system, thus shifting it to the optimal formulation region in the plot, where

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Nomenclature

C_A	asphaltenes concentration
C_D	demulsifier concentration
C_T	total concentration
HLB	hydrophilic–lipophilic balance
NPE 11	nonylphenol with 11 units of ethoxylation
Q/R	radius/charge relation
O/W	oil in water emulsions
W/O	water in oil emulsions

emulsions break, the crude oil is dehydrated, microemulsions are dissolved and enhanced oil recovery occurs (Rondón et al., 2008; Borges et al., 2009). In the optimal formulation region, the stability of the emulsions obtained is minimal and the emulsions separate as if there were no surfactant in the medium. This is due to the fact that bicontinuous microemulsions are generated in which both direct and invert micelles exist and the system does not show a defined interfacial curvature (Salager, 1999).

Several chemical dehydration studies have been carried out using polyetoxylate demulsifiers (Zaki et al., 1996; Salager, 1990; Ramalho et al., 2010; Pereira et al., 2011). Therefore, in this work we studied the chemical dehydration processes of Boscán crude oil, which is easily emulsifiable due to its high content of asphaltenes and resins, by adding a non-ionic nonylphenol surfactant with 11 units of ethoxylation. We also studied the effect of other chemical additives such as salts, alcohols, and glycols in order to change the physical–chemical environment of the system. The systematic change of the concentration of these additives allows obtaining formulation–composition maps that show the type and the stability of the obtained emulsions. This allows identifying the most appropriate conditions for a fast and efficient crude oil dehydration, in order to continue understanding the interfacial phenomena occurring in emulsified systems as we have done in previous works (Rondón et al., 2006, 2008; Borges et al., 2009).

2. Experimental

2.1. Materials

The Boscán crude oil used in this study was supplied by the Hydrocarbon Physical-Chemistry Lab of the Chemistry Department at the Universidad Central de Venezuela. Sodium chloride, magnesium chloride, calcium chloride, ferric chloride, sodium carbonate, sodium sulfate, and sodium phosphate salts were supplied by Riedel-de Haën; alcohols and glycols: ethanol, 2-propanol, 1-butanol, 2-butanol, ethylene glycol, propylene glycol, butylene glycol and glycerol were supplied by Merck and Sigma-Aldrich; analytical grade cyclohexane was bought from Fisher Scientific; while nonylphenol (demulsifier) with 11 units of ethylene oxide was supplied by Witconol.

2.2. General considerations

The next section shows the general considerations taken into account to formulate and measure the stability of the different systems studied.

2.2.1. Oil phase (or organic phase)

The oil phase is constituted by solutions of Boscán crude oil dissolved in analytical grade cyclohexane. This crude oil, with a known concentration of asphaltenes, is mixed with the solvent so that it can be diluted to obtain concentrations of asphaltenes of 2000 ppm. Cyclohexane is used as an aliphatic solvent, because it has an intermediate solubility for asphaltenes and allows better simulating the crude oil matrix. Cyclohexane reduces oil viscosity, which allows for easier handling of the prepared emulsions; additionally, it provides an intermediate solubility to asphaltenes, keeping them close to their precipitation point, and increasing the interfacial activity and, thus, their emulsion-stabilizing capacity. The use of other solvents, such as toluene, would produce the complete solubilization of the asphaltenes in the organic phase, decreasing their interfacial activity and, therefore, their stabilizing capacity; if a different aliphatic solvent, such as n-heptane, is used the total precipitation of asphaltenes, would occur (McLean and Kilpatrick, 1997; Eley et al., 1988). Table 1 shows the most important physical–chemical properties of Boscán crude oil.

2.2.2. Aqueous phase

The aqueous phase is constituted by demulsifier solutions in the presence of salts, alcohols or glycols. The demulsifier is used at concentrations ranging from 4 to 1000 ppm. To study the effect of mono- and polyvalent salts, concentrations ranging from 1 to 10% w/V were used; on the other hand, concentrations ranging from 4 to 1000 ppm are used to study the effect of alcohols and glycols.

2.2.3. Demulsifier

Nonylphenol with 11 units of ethoxylation (NPE 11), a hydrophilic surfactant with a hydrophilic–lipophilic balance (HLB) of 13.8 and a molecular weight of 705 g/mol, is used as the demulsifier. NPE-11 was chosen, because it is a water-soluble surfactant with an intermediate hydrophilicity, a condition under which the higher interfacial activity of the demulsifier is achieved (Rondón et al., 2006).

2.2.4. Mono- and polyvalent salts

Sodium chloride was used as a monovalent salt, while magnesium chloride, calcium chloride, ferric chloride, sodium carbonate, sodium sulfate, and sodium phosphate were used as polyvalent salts.

2.2.5. Alcohols

Ethanol, 2-propanol, 1-butanol, and 2-butanol were used as linear alcohols; ethylene glycol (1,2-ethanediol), propylene glycol

Table 1
Physical–chemical properties of Boscán crude oil (Gutiérrez et al., 2001; Carnahan 1999; Ocanto et al., 2009).

Property	Boscán crude oil
Origin	Boscán field. State of Zulia, Venezuela
% Asphaltenes/(% w/w)[a]	19.0
% Resins/(% w/w)[a]	48.0
°API Gravity	10.1
Density (g/mL)	0.9984
Sulfur content (% w/w)	5.52
Nitrogen content (ppm)	6013–6395
Nickel content (ppm)	150.00
Vanadium content (ppm)	1200.01
Water content (% w/w)	0.45
Neutralization number (mg KOH/g)	0.91
Kinematic viscosity (@ 180 °F) (cSt)	800
Atmospheric residue (590 °F) /(% w/w)	86.7

[a] Percentage determined by precipitation and purification with n-heptane.

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