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Separation kinetics of an oil-in-water emulsion under enhanced gravity

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A B S T R A C T

The breakup of crude oil emulsions to produce clean oil and water phases is an important task in crude oil processing. We have investigated the demulsification kinetics of a model oil-in-water emulsion in a centrifugal field to mimic the forces acting on emulsion droplets in oil/water separators such as hydrocyclones. The rate of growth of separated oil phase and the change in mean droplet diameter of the emulsion layer was measured as a function of surfactant concentration, centrifugal acceleration and time. Demulsification is enhanced with increasing centrifugal acceleration and time and decreasing surfactant concentration. A kinetic analysis was performed that allows to estimate the characteristic coalescence times between droplets in the emulsion and between a droplet and the separated oil interface. The experimental procedure presented in this work can serve as a simple, but useful test to predict the separation efficiency of emulsions in separators with swirling flow fields.

1. Introduction

Enhanced Oil Recovery (EOR) methods have received considerable attention during the last decades as a means to improve crude oil production from aging oil fields (Thomas, 2008). Application of the proposed procedures increases the mobility of oil in the reservoir. In the EOR method of surfactant flooding, oil production is promoted through a reduction in wettability of the solids in the reservoir with respect to the oil phase, and a decrease in oil/water interfacial tension in the reservoir. The latter effect promotes the formation of crude oil/water emulsions (Schramm, 2010). Depending on the surfactant type and reservoir conditions, stable macroemulsions or microemulsions may be formed (Taylor and Hawkins, 1992). The produced fluid which originates from a newly opened reservoir typically is a water-in-oil (W/O) emulsion. As the oil/water mixture is separated during several stages, the water-rich stream, which needs to be cleaned from excess oil for discharge back into the sea, will eventually invert to an oil-in-water (O/W) emulsion (Gillies et al., 2000). Further, the water volume fraction of the produced fluid will increase with increasing production time for a given oil field, which will ultimately also lead to the formation of O/W emulsions. The breakup of surfactant-stabilized crude oil emulsions (O/W or W/O) to ultimately recover clean separated oil and water, i.e. oil and water which contain only trace amounts of dispersed phase, poses a challenge for current oil/water separation technologies. Gravity-based settling methods will likely not be always successful to break this type of emulsions. The demulsification time of surfactant-stabilized emulsions in a normal gravitational force field may be orders of magnitude larger than their residence time in the separator. Demulsification using chemicals (Krawczyk et al., 1991) or electric fields (Taylor, 1988) is possible, but these methods are costly and require additional equipment. The separation of stable emulsions using swirling flow fields such as in hydrocyclones (Colman and Thew, 1983), or more recently, internal swirl elements (Slot et al., 2010), has not been the subject of much investigation until now. The tangential forces acting on the droplets can be higher than 100 × the normal gravitational acceleration, and thus will concentrate the droplets in the center or at the wall of the pipe, depending on the density difference between the liquids. It might be intuitively expected that the higher forces acting on the droplets will lead to more effective collisions, i.e. that the time for two droplets to approach from an initial given distance to coalesce decreases with increasing interaction force. However, theoretical calculations and experiments suggest an optimal force for a given oil/water mixture (Ivanov et al., 1999). This behavior is caused by increasing deformation of the droplet interface in the contact region with increasing collision force and thus slower drainage of the continuous film between the droplets as compared to rigid spheres (Hartland et al., 1994). Further, even in the absence of deformation, emulsion droplets may be very stable also at high collision forces due to the adsorbed surfactants creating e.g. electrostatic or steric

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barriers against coalescence between approaching droplets (McClements, 2005).

The demulsification of emulsions under normal gravity without added surfactant was investigated by Jeelani and Hartland (1985). The growth of the separated dispersed phase was followed as the droplets settled and a kinetic model was developed to describe the height of the column of coalesced phase as a function of time. The model uses two adjustable lumped parameters to fit the data. The demulsification of emulsions stabilized with sodium *n*-dodecylsulfate (SDS) in centrifuges was studied by Mittal and Vold (1972) and Vold and Groot (1962). The aqueous phase contained no electrolytes other than the surfactant. It was found that the emulsion stability increased with increasing SDS bulk concentration. The relative volume of separated oil in their experiments after 1–2 h of centrifugation at a rotation speed of 40 000 rpm was $\sim 50\%$ at an SDS bulk concentration of 3 mM SDS and $\sim 0\%$ at 8 mM. Tcholakova et al. (2002) investigated the stability of protein-stabilized oil-in-water emulsions in centrifuges. They expressed their results in terms of a critical osmotic pressure p_{crit} of the emulsion, beyond which the formation of a separated oil phase on top of the emulsion layer takes place. The osmotic pressure of an emulsion is caused by a deviation of the water concentration from its equilibrium value due to the centrifugal forces, which squeeze the water from the emulsion. It was found that p_{crit} decreases with increasing droplet size and decreasing protein concentration. It was further established that coalescence between droplets in the emulsion phase proceeds slower than coalescence between a droplet and the separated oil phase in the system under investigation.

In this paper, we present a simple method to emulate the effect of a swirling flow field on the stability of a batch model oil-in-water emulsion using a tabletop centrifuge. We choose hexadecane as a model oil and sodium *n*-dodecylsulfate as emulsifier, as it resembles the molecular structure of the petroleum surfactants that are used in surfactant flooding. Further, the aqueous phase contained 3 wt% of NaCl to emulate the effect of salt water in the oil reservoir. Experimental parameters were surfactant concentration, centrifugation speed and time. From the experimental data we are able to extract characteristic coalescence times between droplets in the emulsion, and between a droplet and the separated oil homophase.

1.1. Rate equations for coalescence

The stages of demulsification of an oil-in-water emulsion in a centrifuge are displayed in Fig. 1. The emulsion is centrifuged immediately after preparation, which leads to formation of a dense layer of oil droplets on top of the emulsion. This layer will be referred to throughout the paper as *creamed emulsion*. Upon centrifugation, a phase of separated oil may form on top of the creamed emulsion. This oil homophase will be referred to as *separated oil* phase throughout the text. The mean droplet size of the creamed emulsion may also increase due to coalescence between emulsion droplets in the cream layer.

The growth rate of the volume of separated oil phase V_s due to coalescence between a droplet and the oil homophase can be expressed as

$$\frac{dV_s}{dt} = V_t \frac{dn_c}{dt} \tag{1}$$

whereas V_t is the average droplet volume of a droplet in the topmost emulsion layer at the oil/emulsion interface and n_c denotes the number of coalescence events at the oil/emulsion interface. The coalescence rate dn_c/dt can be expressed as

$$\frac{dn_c}{dt} = k_{ds} N_t = \frac{N_t}{\tau_{ds}} \tag{2}$$

In Eq. (2), k_{ds} denotes the rate constant for coalescence between a droplet and the separated oil phase. $1/k_{ds}$ can be regarded as a characteristic time for coalescence τ_{ds}, which is the time needed for the film of continuous phase between a droplet and the interface to drain from some initial distance to a critical thickness where coalescence takes place. N_t denotes the number of droplets in the top layer of the emulsion at the emulsion/oil interface and can be written as

$$N_t = \frac{\pi \phi_t d_i^2}{4A_t} \tag{3}$$

d_i denotes the diameter of the emulsion/oil interface, A_t and ϕ_t denote the average cross-sectional area and packing density of the emulsion droplets in the top layer, respectively. Due to the different settling velocities of emulsion droplets with different sizes in normal gravitational and centrifugal fields and the possibility of droplet deformation, the mean droplet size in the top emulsion layer and thus also A_t would be expected to be different than the total average droplet diameter and cross-sectional area of the droplets in the bulk of the emulsion.

Insertion of Eqs. (2) and (3) in Eq. (1) with the shape parameter $q_t = A_t/V_t$ and $V_s = x_s V_o$, whereas V_s is the total volume of oil in the system and x_s the volume fraction of separated oil, yields an expression for the calculation of τ_{ds}

$$\frac{1}{\tau_{ds}} = \frac{4V_o q_t}{\pi d_i^2 \phi_t} \frac{dx_s}{dt} \tag{4}$$

In the case of spherical droplets, $q_t = 3/2d_t$.

Upon centrifugation, coalescence between droplets in the creamed emulsion may also occur, which will increase the mean droplet diameter. A volume element V in the creamed emulsion is given by $V = NV_c + V_{cont}$, whereas N signifies the number of droplets per unit volume, V_c the average droplet volume in the creamed emulsion and V_{cont} the volume of continuous phase. The change of these variables with time is given by the continuity

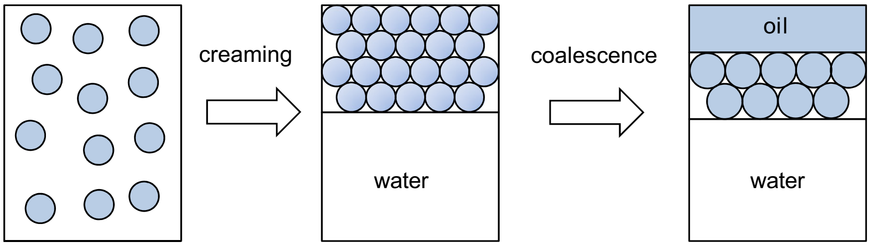

Fig. 1. Stages of demulsification in the centrifuge. After preparation, the distribution of droplets in the emulsion is homogeneous. Upon centrifugation, the droplets will rise to the top of the system, and form a dense layer. At the bottom, an almost pure water phase remains. As a result of coalescence, a phase of separated oil may form on top of the emulsion layer, and the mean droplet size in the emulsion layer may increase. The depiction of the droplet size distribution is only schematic, as the emulsion will be polydisperse.