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Effect of surfactant micelle shape transition on the microemulsion viscosity and its application in enhanced oil recovery processes

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ABSTRACT

Surfactants have already been distinguished as having commercial application in oil industry especially Enhanced Oil Recovery (EOR) processes. During EOR processes, surfactants or a mixture of surfactants and polymers are injected into the reservoir to reduce the interfacial tension of microemulsion typically from about 30 dyn/cm to 10^{-3} dyn/cm. Polymers are added to reduce the mobility by increasing the viscosity of the solution. The geometrical micelle shape of a number of surfactants might change from spherical to cylindrical above a concentration generally known as critical micelle concentration. Although previous studies haven't considered the effect of surfactants on solution viscosity, this shape transition could significantly affect the viscosity of solution. In this study, a previously developed model is used in conjunction with experimental data to investigate the effect of surfactant and salt concentrations on the micelle shape transition. It is found that for some ranges of surfactant and salt concentrations; shape transition from spherical to cylindrical causes a considerable increase in the viscosity of dodecyl ammonium chloride (DeAC) solution. Based on the results of this study, a number of surfactants could be used for simultaneous modification of the IFT and viscosity of the microemulsion rather than using both polymers and surfactant.

1. Introduction

After primary and secondary production from a reservoir, a considerable volume of oil, even up to 70% of the original oil in place, remains in the reservoir rock which could not be produced due to the effect of capillary forces, unfavorable mobility ratio, and reservoir rock heterogeneities [1].

Surfactant flooding is a process during which a slug of surfactant solution referred to as microemulsion is injected into the reservoir from one or several injection wells arranged in a special pattern. Water is injected to sweep the slug of surfactant and the residual oil toward the production wells. In some cases, a slug of polymer is also injected after surfactant slug in order to increase the microemulsion viscosity. The polymer slug reduces the mobility ratio (ratio of the microemulsion mobility to the oil mobility) and subsequently prevents water breakthrough; however, a number of problems are associated with polymer injection including high expenses of the process and degradation of polymer in the reservoir [2]. Surfactant injection is a common method that could be implemented to produce the oil remained in the reservoir via an Interfacial Tension (IFT) reduction mechanism [2]. In this respect, a dimensionless parameter referred to as Capillary Number (Nc) is used to display quantitatively the effects of IFT, viscosity and other parameters on residual oil saturation. Nc is defined as:

$$\mathbf{Nc} = \boldsymbol{\mu}\mathbf{u}/\boldsymbol{\sigma}. \tag{1}$$

In which $\boldsymbol{\mu}$ is the microemulsion viscosity in poises, $\mathbf{u}$ is the apparent velocity of the microemulsion in m/s and $\boldsymbol{\sigma}$ is IFT in dyn/cm [3]. There exists an inverse proportionality between Nc and residual oil saturation (ROS) meaning that an increase in Nc would lead to a reduction in ROS. Surfactants are amphiphilic molecules composed of a hydrophilic head and a hydrophobic tail. These two different characteristics, the polar head (water-loving) and the non-polar tail (water-hating) in a single surfactant molecule result in its amphiphilic behavior toward solvents [4]. Accordingly, surfactants are implemented in a wide range of industrial applications including the food, pharmaceutical, cosmetics, and Enhanced Oil Recovery (EOR) [5]. Based on the charge of the head group, surfactants are categorized into four types: anionic, cationic, nonionic, and zwitterionic surfactants [6]. The two first types are more common in the oil recovery process. Cationic surfactants have proved to be highly efficient in carbonate reservoirs [7]. In this study, dodecyl ammonium chloride (DeAC), a cationic surfactant, is chosen to carry out further investigations together with the experimental viscosity data reported in the literature [8].

At low concentrations, surfactant molecules are in monomer form, but as the concentration exceeds a threshold value, aggregates begin to form in the solution. These aggregations are called micelles, and

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that threshold concentration is known as critical micelle concentration (CMC) [9]. Above the CMC, addition of more surfactants into the solution leads to an increase in micelle concentration while the monomer concentration remains quite constant [4].

Formation of micelles affects the surfactant solution properties including interfacial tension (IFT), equivalent conductivity, osmotic pressure, solubilization, magnetic response and self-diffusion [5]. It has been shown experimentally that micelles possess one of the following geometrical shapes: sphere, cylinder (rod), disk and ellipsoid [10]. A number of parameters are believed to be controlling the micelle morphology including the surfactant structure, surfactant concentration, temperature and additives [11]. It has been observed that usually at low surfactant concentrations above the CMC, micelles are formed in spherical shape, thereby introducing this morphology as the first and most probable shape of the micelles to occur.[10]. Nevertheless, further increases in surfactant concentration might lead to an increase in aggregation number (i.e. number of monomers that are aggregated around a same micelle core) and micelle size which in turn results in shape transition of micelles from spherical to cylindrical (rod like) [10].

Theoretical studies have indicated that micelle size is proportional to the square root of micelle concentration [12]. Furthermore, a review on the experiments carried out on different surfactants including hexadecyl trimethylammonium bromide [13], hexadecyl heptoxyethylene glycol monoether [14] and tetradecyl hexoxyethylene glycolmonoether [15], reveals that there is a strong possibility for cylindrical micelles to form at higher concentrations [16].

Shape transition of micelles as a result of surfactant concentration increase depends to a large extent on the type of surfactant and its structure. Surfactants have been classified into three main types based on shape transition behaviors [17]:

1- Surfactants with high solubility in water, which show no major changes in micelle shape: no considerable changes in microemulsion properties including viscosity are expected
2- Surfactants with high solubility in water, which show shape transition as surfactant concentration increase: dramatic changes in some properties including microemulsion viscosity are expected.
3- Surfactants with low solubility in water: increases in surfactant concentration in this type of surfactants might result in phase separation even at considerably low surfactant concentration. Thus, these surfactants are not suited for EOR processes.

For type 2 surfactants, shape transition occurs after reaching a threshold surfactant concentration, C_{th}. The dominant shape of the micelles is transferred from spherical to cylindrical above this threshold concentration. In addition to surfactant concentration, water salinity (i.e., NaCl concentration) might also influence the shape of micelles [18].

Cylindrical micelles are larger than spherical micelles. The size of cylindrical micelles increases as surfactant concentration increases above the C_{th}. besides, it has been proved that large cylindrical micelles could be treated as rigid instead of flexible cylinders [12]. Hence, it could be pointed out that increasing the surfactant concentration above the C_{th} will result in an increase in microemulsion viscosity. Although increasing the surfactant concentration above the CMC might have no significant influence on the IFT, it could render a possible increase in the microemulsion viscosity.

Taking a look at the literature, it was realized that previous EOR studies have not taken into consideration the potential influence of surfactants on the viscosity. Thus, this work is primarily devoted to investigate the effect of surfactant on the microemulsion viscosity.

A mathematical model has recently been developed for the prediction of microemulsion viscosity assuming that cylindrical micelle shape is dominant. [12]. Nagarajan, R, used this model to calculate K value (one of the model parameters that will be described in the next section) for each surfactant concentration at which experimental viscosity data were available. Obtained results were then implemented to show the rigidity of cylindrical micelles. Taking these results into consideration, we first used the experimental data of a cationic surfactant, dodecyl ammonium chloride (DeAC [8]) [12], to determine the shape transition concentration, C_{th}. The aforementioned mathematical model was then implemented at surfactant concentrations above the C_{th}, to calculate an optimum K value for every salt (NaCl) concentration. In the next step, the predicted values of viscosities were compared with experimental data to corroborate the validity of the model. Finally, the conditions under which microemulsion viscosity is high enough to be employed in the EOR processes were determined. The main objective of this study is thus to investigate the application of a single surfactant instead of using a mixture of surfactant and polymer in EOR processes.

2. Mathematical modeling

The viscosity of microemulsion with cylindrical micelles is usually determined from the following third order equation as a function of surfactant concentration [12,19]:

$$\boldsymbol{\eta r} = \mathbf{1} + \mathbf{m} + \mathbf{k_1} \times \mathbf{m^2} + \mathbf{k_2} \times \mathbf{m^3} \tag{2}$$

Where $\boldsymbol{\eta r}$ and $\mathbf{m}$ in Eq. (2) are defined by Eqs. (3) and (4) respectively:

$$\boldsymbol{\eta r} = \frac{\boldsymbol{\mu}}{\boldsymbol{\mu_{CMC}}} \tag{3}$$

$$\mathbf{m} = \boldsymbol{\upsilon} \times \boldsymbol{\Phi} \tag{4}$$

The motion of a particle in the microemulsion induces a flow field which will be felt by all the other particles. As a result, these particles experience a force which is believed to be the consequence of hydrodynamic interaction with the original particle [20]. The term $k_1 \times m^2$ in Eq. (2) accounts for this hydrodynamic interaction. The parameter k_1 is a constant parameter which its value has been estimated to be 0.75 [21]. The term $\mathbf{k_2} \times \mathbf{m^3}$ used in Eq. (2) accounts for the micelle–micelle interactions and is assumed zero for dilute solutions [12]. Ranges of surfactant concentration for practical EOR applications are less than 4 g/100 mL which is considered within the range of dilute solutions [6]. Therefore, the fourth term of Eq. (2) could be omitted for EOR applications.

Considering a particular surfactant flooding during an EOR process at constant reservoir temperature, the following equations show that the shape factor, υ and the volume fraction of surfactant, Φ are just functions of surfactant concentration. Therefore, the viscosity of microemulsion is only a function of the surfactant concentration.

The volume fraction of surfactant in Eq. (4) is defined as:

$$\boldsymbol{\Phi} = \mathbf{Xm} \times \left(\frac{\mathbf{Vs}}{\mathbf{Vw}}\right) \tag{5}$$

If the surfactant concentration, **C**, is defined in gram per 100 mL, and the surfactant molecular weight, MWs in gram per mole, the Eq. (5) could be rewritten as:

$$\boldsymbol{\Phi} = \left(\frac{10}{55.5}\mathbf{MWs}\right)(\mathbf{Cm}) \times \left(\frac{\mathbf{Vs}}{\mathbf{Vw}}\right) \tag{6}$$

where **Cm** and **Xm** are defined according to the following equations:

$$\mathbf{Cm} = \mathbf{C} - \mathbf{Ccmc} \tag{7}$$

$$\mathbf{Xm} = \mathbf{X} - \mathbf{Xcmc} \tag{8}$$

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