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Investigation of alkaline–crude oil reaction



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ABSTRACT

One of the mechanisms of alkaline flooding relies on alkaline reaction with organic acids (saponifiable components) in the crude oil to produce an in situ surfactant called soap that lowers interfacial tensions. However, this mechanism is not quantified in the literature. For example, what is the fraction of acid components which react with alkaline solution to generate soap? How much soap can be generated?

In this paper, this mechanism and related issues are discussed, analyzed or quantified. In particular, the numerical simulation approach is used. The results show that only a fraction of acid components can be converted into soap; the amount of generated soap could be low. A minimum pH (e.g. 9) is needed for the acids to be converted to soap. The literature information on the effect of amount of acid components (total acid number) on oil recovery is also discussed.

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1. Introduction

Several mechanisms in alkaline flooding have been summarized by Ref. [16]: emulsification and entrainment [30], emulsification and entrapment [15], wettability reversal (oil-wet to water-wet [20,21], or water-wet to oil-wet [5]), emulsification and coalescence [2]. These mechanisms are all related to the generated soap.

Another mechanism which is not related to soap generated but related to alkaline reaction with rock and formation is that alkaline solution reacts with a divalent to form precipitates. The precipitates preferentially reduce high-permeability channels, thus sweep efficiency is improved, as suggested by Ref. [26]. This process is known as mobility controlled caustic flood (MCCF). Also, addition of alkalis increases pH and lowers the surfactant adsorption so that very low surfactant concentrations can be used to reduce cost.

The above discussion shows that most of mechanisms of alkaline flooding is related to in situ generation of soap. Then an important question is, how much soap can be realistically generated in alkaline flooding? We will address this question in this paper. First, we will introduce how the soap is generated and how the acid number is measured. Then we will use a simulation model to quantify the amount of soap is generated. Finally, we will further discuss the relationship between acid number and oil recovery in alkaline flooding.

2. In situ generation of soap

In alkaline flooding, an injected alkali reacts with the saponifiable components in the reservoir crude oil. These saponifiable components are described as petroleum acids (naphthenic acids). Naphthenic acid is the name for an unspecific mixture of several cyclopentyl and cyclohexyl carboxylic acids with molecular weight of 120 to well over 700. The main fractions are carboxylic acids [29]. Other fractions could be carboxyphenols [27], porphyrins [7], and asphaltene [23]. The naphtha fraction of the crude oil raffination is oxidized and yields Naphthenic acid. The composition differs with the crude oil composition and the conditions during raffination and oxidation [25]. Details of alkali–oil chemistry related to saponification will not be discussed in this paper. A highly oil-soluble single pseudo-acid component (HA) is assumed in oil. The alkali–oil chemistry is described by partitioning of this pseudo-acid component

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between the oleic and aqueous phases and subsequent hydrolysis in the presence of alkali to produce a soluble anionic surfactant A^- (its component is conventionally denoted by $RCOO^-$), as schematically described by Ref. [6]. The overall hydrolysis and extraction is given by



and the extent of this reaction depends strongly on the aqueous solution pH. This reaction occurs at the water/oil interface. A fraction of organic acids in oil become ionized with addition of an alkali, while others remained electronically neutral. The hydrogen-bonding interaction between the ionized acids and neutral acids can lead to the formation of a complex called acid soap. Thus the overall reaction, Eq. (1), is decomposed into a distribution of the molecular acid between the oleic and aqueous phases,



and an aqueous hydrolysis [6],



Here HA denotes a single acid species, A denotes long organic chain, and the subscripts o and w denote oleic and aqueous phases, respectively. The acid dissociation constant for Eq. (3) is

$$K_A = \frac{[H^+][A^-]}{[HA_w]}, \quad (4)$$

and the partition coefficient of the molecular acid is

$$K_D = \frac{[HA_w]}{[HA_o]}, \quad (5)$$

where brackets indicate molar concentrations. Additionally, the dissociation of water is



and the dissociation constant of water is

$$K_w = [H^+][OH^-]. \quad (7)$$

Water concentration is essentially a constant. An increase in $[OH^-]$ results in a decrease in $[H^+]$. pH is defined as $-\log[H^+]$. At high pH, the concentration of anionic surfactant (soap) in the aqueous phase is

$$[A^-] = \frac{K_A K_D [HA_o]}{[H^+]} = \frac{K_A K_D [HA_o] [OH^-]}{K_w}. \quad (8)$$

Thus, for a fixed acid concentration in the oil phase and for a given pH, Eq. (8) estimates the amount of surface-active agent (A^-) present in the aqueous phase. This equation also reveals that K_A , K_D , K_w and pH regulate the amount of surface-active agent in the aqueous phase. K_D must be small enough so that the acid is not extracted into the aqueous phase by normal low-pH water-flooding [6]. used $K_w = 5 \times 10^{-14}$, $K_D = 10^{-4}$, and $K_A = 10^{-10}$. Using these numbers, for 1% NaOH, $[A^-]$ is about 5% of $[HA_o]$. Or a very high pH (close to 14 which is not practical) is required for the surface-active agent to be totally soluble in the aqueous phase. However, more $[A^-]$ is accumulated at the oil/water interface which instantaneously reduces IFT.

3. Measurement of acid number

For the convenience of later discussion, measurement of acid number is described here. A measure of the potential of a crude oil to form surfactants is given by the acid number (sometimes called total acid number TAN). This is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of crude oil. Usually, acid number determined by non-aqueous phase titration [9] is used to estimate the soap amount. However, short chain acids, which also react with alkali, may not behave like a surfactant because they are too hydrophilic. Also phenolics and porphyrins in crude oil will consume alkali and will not change the interfacial properties as much as a surfactant. Asphaltene and/or resin may have carboxylate functional groups but not be extracted into the aqueous phase. Total acid number determined by non-aqueous phase titration could not distinguish the acids that can generate natural soap and those that can consume alkali without producing surfactant. Another fact which could stimulate a question about the non-aqueous phase titration is that acid number does not always correlate with oil recovery, which will be discussed later.

Liu [18] introduced another method called soap exaction to quantify acid number. Since the anionic surfactant can be accurately determined by potentiometric titration (see Appendix A in Ref. [18] with Benzethonium Chloride (hyamine 1622), it is reasonable to use this method to find the natural soap amount. Since this potentiometric titration is for aqueous phase, the soap should be extracted into aqueous phase as the first step. As an anionic surfactant, the natural soap may stay in the oleic phase and form Winsor type II microemulsion when the electrolyte strength is high. To extract the soap into aqueous phase, NaOH was used to keep the pH high with low electrolyte strength. Also isopropyl alcohol is added to make the system hydrophilic so that soap will partition into aqueous phase.

Since those acids that cannot generate soap will not be detected by the potentiometric titration, the acid numbers obtained by the soap extraction are less than the acid numbers determined by non-aqueous phase titration as expected. There is no general ratio between those two acid numbers, i.e., the natural soap amount of an oil cannot be determined just by non-aqueous phase titration. Oils with high acid number by non-aqueous phase titration usually have high soap content. But it is not always true [18]. Liu [18] compared the acid numbers measured from the two methods. The data showed that the acid number from the soap extraction was about one half of the value from the non-aqueous phase titration.

For acid numbers, >1.0 is generally considered high, 0.3–1 is intermediate, and 0.1–0.25 is low. The acid numbers of Daqing oils are low, in the order of 0.1 mg/g. Most crude oils have acid number lower than 5 mg KOH/g oil. Practically, the minimum acid requirement to be effect in ASP flooding is 0.3 mg KOH/g in oil [4].

Assume the acid number of a crude oil is accurately measured, the generated soap may be estimated by further assuming (1) the required alkali is available which is generally true; (2) the total surface-active agents are converted into soap. Based on the definition that acid number (AN) is the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of oil, the soap concentration, C_{soap} , in meq/mL is

$$C_{\text{soap}} \left[\frac{\text{meq}}{\text{mL}} \right] = \frac{(AN)\rho_o}{(MW)_{\text{KOH}}(\text{WOR})}, \quad (9)$$

where $(MW)_{\text{KOH}}$ is the molecular weight of KOH which is 56 g/mole, ρ_o is the oil density in g/mL, WOR is the water to oil ratio in

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