Original article

Investigation of alkaline–crude oil reaction

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A B S T R A C T

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.

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 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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Peer review under responsibility of Southwest Petroleum University.

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

$$HA_o + NaOH \leftrightarrow NaA + H_2O, \tag{1}$$

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,

$$HA_o \leftrightarrow HA_w, \tag{2}$$

and an aqueous hydrolysis [6],

$$HA_w \leftrightarrow H^- + A^-. \tag{3}$$

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

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

and the partition coefficient of the molecular acid is

$$K_D = \frac{[HA_w]}{[HA_o]}, \tag{5}$$

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

$$H_2O \leftrightarrow H^+ + OH^-, \tag{6}$$

and the dissociation constant of water is

$$K_w = [H^+][OH^-]. \tag{7}$$

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

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

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 waterflooding [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

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

where $(MW)_{KOH}$ 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

Table 1
Formation water and injection water analysis.

Ion	Formation water (FW)		Injection water (IW)		Ion	FW	IW
	mg/L	meq/mL	mg/L	meq/mL		mmol/mL	meq/mL
Na^+	2272.6	0.098809	47.0	0.002043			
K^+	214.0	0.005487	11.0	0.0002821	$Na^+ + K^+$	0.104296	0.002326
Mg^{2+}	34.5	0.002840	11.5	0.0009498			
Ca^{2+}	57.2	0.002860	67.1	0.0033565	$Ca^{2+} + Mg^{2+}$	0.002850	0.004306
Cl^-	2091.0	0.058901	138.5	0.003901	Cl^-	0.058901	0.003901
HCO_3^-	2623.4	0.043006	150.5	0.0024672			
CO_3^{2-}	240.0	0.008000	7.0	0.0002333	$CO_3^{2-} + HCO_3^-$	0.047006	0.005168

laboratory pipette tests, and it is the ratio of water saturation to oil saturation, S_w/S_o. Since surfactant concentration is generally expressed in volume percent in water, C_{soap} in vol.% is

$$C_{soap}[vol.\%] = \frac{(MW)_{soap}(AN)\rho_o(10^{-3})}{(MW)_{KOH}(WOR)\rho_{soap}} \times 100\%$$
$$= \frac{0.1(AN)(MW)_{soap}\rho_o}{(MW)_{KOH}(WOR)\rho_{soap}}\%, \qquad (10)$$

where $(MW)_{soap}$ is the soap molecular weight. If $\rho_o/\rho_{soap} = 1$, and $(MW)_{soap}/(MW)_{KOH} = 10$, then the soap concentration in the volume percent in water is AN/WOR %. Further, if WOR = 1, the soap concentration is simply AN % without need of calculation. The discussion here shows that the concentration of generated soap is linearly proportional to the acid number. This calculation assumes that the surface-active agents are fully soluble in the aqueous phase, but they are not in reality.

Here we use acid number to characterize a crude oil. Sometimes, we use equivalent alkane carbon number (EACN) to describe a crude oil [3]. Oils having characteristics similar to the lower straight chain hydrocarbons tend to form three-phase regions over a narrow salt concentration range and at a relatively low salt concentration, but the relative uptake of oil and brine per unit volume of surfactant into type III phase increases [11]. This is because oils having different EACN's may generate different amount of soap. The soap has a different type III salinity range than a synthetic surfactant. Thus the type III salinity range is affected by EACN.

4. Analysis of alkaline flooding performance

In this section, we use an alkaline model to investigate the effect of generated soap on alkaline flooding performance. In this

model, only soap effect is actually functioning. We first describe setting up an alkaline model and then discuss the results.

4.1. Set up the EQBATCH model

To simulate alkaline flooding, first we need to have initial conditions (concentrations) of species. This is done by a geochemistry program called EQBATCH. EQBATCH estimates the initial equilibrium based on the formation and water composition, the acid number of crude oil, and water and oil saturations. The initial equilibrium data from EQBATCH batch calculation are then input into the UTCHEM alkaline model. UTCHEM is a chemical simulator. The UTCHEM model continues simulation of the oil recovery process. For a detailed description of EQBATCH, see Ref. [1]. Now we briefly describe how to set up an EQBATCH model.

The concentrations of formation water and injected water are shown in Table 1 (left side). The initial formation water pH is 8.1. The acid number is 0.81 mg KOH/g oil. The initial water and oil saturations are 0.383 and 0.617, respectively.

To simplify the problem, monovalents Na^+ and K^+ are combined into a single pseudo-monovalent Na^+. Similarly, the divalents Ca^{2+} and Mg^{2+} are combined into a single pseudo-divalent Ca^{2+}, and CO_3^{2-} and HCO_3^- are combined into a single pseudo-carbonate CO_3^{2-}. The elements, independent species, dependent species, solid species, adsorbed cations on matrix and surfactant associated cations are defined and listed in Table 2. For this case, 6 elements ($N = 6$), 6 independent species and 8 dependent species with total 14 fluid species ($J = 14$), 2 solid species ($K = 2$), 3 adsorbed cations on matrix ($I = 3$) and 2 surfactant associated cations ($M = 2$) are defined. Note that the subscripts a and s for $Ca(OH)_2$ and $CaCO_3$ mean in aqueous and solid states, respectively. A^-, HA_o and HA_w represent petroleum acid anion, petroleum acid in oleic phase and petroleum acid in

Table 2
List of elements and reactions species.

Order #	Elements or pseudoelements	Independent fluid species	Dependent fluid species	Solid species	Adsorbed cation on matrix	Surfactant associated cations
1	Calcium	H^+		$CaCO_{3\,(s)}$	$\overline{H}^+$	$\overline{Na}^+$
2	Carbonates	Na^+		$Ca(OH)_{2\,(s)}$	$\overline{Na}^+$	$\overline{Ca}^+$
3	Sodium	Ca^{2+}			$\overline{Ca}^+$	
4	Hydrogen	CO_3^{2-}				
5	Petroleum acid	HA_o				
6	Chlorine	H_2O				
7			$Ca(OH)^+$			
8			$Ca(HCO_3)^+$			
9			A^-			
10			$(OH)^-$			
11			HCO_3^-			
12			H_2CO_3			
13			$CaCO_{3(a)}$			
14			HA_w			

Aqueous reaction	Definition	Species	Equilibrium constant
	K_1^{eq}	H^+	1
	K_2^{eq}	Na^+	1
	K_3^{eq}	Ca^{2+}	1
	K_4^{eq}	CO_3^{2-}	1
	K_5^{eq}	HA_o	1
	K_6^{eq}	H_2O	1
$Ca^{2+} + H_2O \xrightarrow{K_4^{eq}} Ca(OH)^+ + H^+$	$K_7^{eq} = \frac{[Ca(OH)^+][H^+]}{[Ca^{2+}]}$	$Ca(OH)^+$	1.2050E−13
$Ca^{2+} + H^+ + CO_3^{2-} \xrightarrow{K_5^{eq}} Ca(HCO_3)^+$	$K_8^{eq} = \frac{[Ca(HCO_3)^+]}{[Ca^{2+}][CO_3^{2-}][H^+]}$	$Ca(HCO_3)^+$	1.4142E+11
$HA_w + OH^- \xrightarrow{K_2^{eq}} A^- + H_2O$	$K_9^{eq} \equiv K_A = \frac{[A^-][H^+]}{[HA_w]}$	A^-	1.0000E−12
$H_2O \xrightarrow{K_1^{eq}} H^+ + OH^-$	$K_{10}^{eq} \equiv K_w = [H^+][OH^-]$	$(OH)^-$	1.0093E−14
$H^+ + CO_3^{2-} \xrightarrow{K_3^{eq}} HCO_3^-$	$K_{11}^{eq} = \frac{[HCO_3^-]}{[H^+][CO_3^{2-}]}$	HCO_3^-	2.1380E+10
$2H^+ + CO_3^{2-} \xrightarrow{K_6^{eq}} H_2CO_3$	$K_{12}^{eq} = \frac{[H_2CO_3]}{[H^+]^2[CO_3^{2-}]}$	H_2CO_3	3.9811E+16
$Ca^{2+} + CO_3^{2-} \xrightarrow{K_7^{eq}} CaCO_{3(a)}$	$K_{13}^{eq} = \frac{[CaCO_{3(a)}]}{[Ca^{2+}][CO_3^{2-}]}$	$CaCO_{3(a)}$	1.5849E+03
$HA_o \xrightarrow{K_D} HA$	$K_D = \frac{[HA_w]_{water}}{[HA_o]_{oil}}$	HA_w	1.0000E−04

Dissolution/precipitation reaction	Definition	Solubility product	
$CaCO_{3(s)} \xrightarrow{K_1^{sp}} Ca^{2+} + CO_3^{2-}$	$K_1^{sp} = [Ca^{2+}][CO_3^{2-}]$	8.7E−09	
$Ca(OH)_2 \xrightarrow{K_2^{sp}} + Ca^{2+} + 2OH^-$	$K_2^{sp} = [Ca^{2+}][H^+]^{-2}$	4.7315E+22	

Exchange reaction on matrix	Definition	Exchange constant	
$2\overline{Na}^+ + Ca^{2+} \xrightarrow{K_1^{ex}} 2Na^+ + \overline{Ca}^{2+}$	$K_1^{ex} = \frac{[\overline{Ca}^{2+}][Na^+]^2}{[\overline{Na}^+]^2[Ca^{2+}]}$	2.623E+02	
$\overline{H}^+ + Na^+ + OH^- \xrightarrow{K_2^{ex}} \overline{Na}^+ + H_2O$	$K_2^{ex} = \frac{[\overline{H}^+][Na^+]}{[\overline{Na}^+][H^+]}$	1.460E+07	

Exchange reaction on micelle	Definition	Exchange constant	
$2\overline{\overline{Na}}^+ + Ca^{2+} \xrightarrow{K_1^{exm}} 2Na^+ + \overline{\overline{Ca}}^{2+}$	$K_1^{exm} = \frac{[\overline{\overline{Ca}}^{2+}][Na^+]^2}{[\overline{\overline{Na}}^+]^2[Ca^{2+}]}$	$K_1^{exm} = \beta_1^{exm}([A^-]+[S^-])$ based on Ref. [13] model, $\beta_1^{exm} = 2.5$	

aqueous phase, respectively. The last fluid species must be HA_w. In principle, we can arbitrarily select N independent species. Practically, we select the species which are similar to the elements. And they are simple species (not combined species like HCO_3^-) so that other dependent species can be defined from them with equilibrium constants. Chlorine is a non-reactive species, therefore, it is not selected as an independent species. Of course, it will not appear in any reaction equation.

After defining the species, write down the relevant reaction and equilibrium equations below. The cation exchanges with $\overline{Na}^+$ on matrix and $\overline{\overline{Na}}^+$ in micelle are defined. Note that the salinity in the surfactant solution will affect the salinity adsorbed in matrix and associated with micelles. The resultant salinity will affect the coefficients of Langmuir equation for surfactant adsorption, and thus the effect of salinity on surfactant precipitation or adsorption is simulated in UTCHEM [31]. The constants and coefficients below have been cross-checked from different sources. These data should be typical for most of applications. These data are for 25 °C. The data at any other reservoir temperature can be estimated, or obtained from

available databases or softwares like Geochemist's Workbench® [10] or PHREEQC [24].

Next, list stoichiometric coefficients, exponents and charges in equations based on the above reaction equations and equilibria, and input some of the initial species concentrations. EQBATCH uses these initial input values and the other input constants listed in the above to regulate their final output values. The output will be copy/pasted into the UTCHEM model as the input.

4.2. Set up the UTCHEM model

The initial species concentrations in the reservoir are from the EQBATCH output. The injection water compositions are shown in Table 1. Table 3 shows the injection scheme and the detailed components of injection water. Slug 1 is 0.7 PV water injection with 1.5% NaCl added in the injection water, followed by Slug 2 of 0.3 PV alkali injection, and Slug 3 of 0.5 PV water injection with 0.5% NaCl added. In addition to the BATCH input parameters listed in the above, the key parameters used in the UTCHEM

Table 3
Injection scheme.

	(IW) meq/mL	Slug 1 (0.7 PV)		Slug 2 (0.3 PV)		Slug 3 (0.5 PV)	
		IW + 1.5% NaCl		IW + 1.6% Na$_2$CO$_3$		IW + 0.5% NaCl	
		1.5% NaCl	Total	1.6% Na$_2$CO$_3$	Total	0.5% NaCl	Total
Cl^-	0.003901	0.2564	0.260301		0.003901	0.085467	0.089368
Ca^{2+}	0.004306		0.004306		0.004306		0.004306
CO_3^{2-}	0.005168		0.005168	0.3019	0.307068		0.005168
Na^+	0.002326	0.2564	0.258726	0.3019	0.304226	0.085467	0.087793

Table 4
Key parameters in the alkaline flood simulation model.

| Parameters	Parameter value
Grid blocks	80, 1, 1
Grid block sizes	0.011, 0.11, 0.11
Components	W, O, S, P, Cl, Ca, alcohol 1, alcohol 2, CO_3, Na^+, H^+, acid
Porosity	0.1988
Permeability	236, 236, 118
Initial water saturation	0.383
Initial salinities and hardness	0.059, 0.0057
C_H	0.35
T_p for water, oil and microemulsion	1965, 8000, 364.2
Residual saturations at low N_c	0.382, 0.3803, 0.382
Endpoint relative permeabilities	0.03, 1.0, 0.03
Relative permeability exponents	1.12, 1.3, 1.12
Residual saturations at high N_c	0.0, 0.0, 0.0
Endpoint relative permeabilities	0.5, 1.0, 1.0
Relative permeability exponents	1.1, 1.1, 1.1
Water and oil viscosities, cP	0.995, 24.3
Production pressure	14.5
Injection rate	0.05

model are listed in Table 4. Basically it is a one-dimensional model.

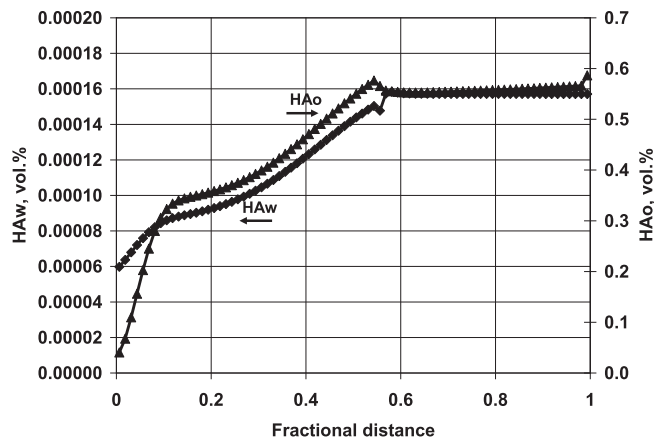### 4.3. Justification of the model validity

The UTCHEM model is based on a model template (ex06) and the EQBATCH model is simplified from the model described in Appendix C of UTCHEM Technical manual by combining some species into pseudo-species. Some physical constants like equilibrium constants and solubility products are cross-checked from several sources. More importantly, this model is used to have matched the salinity scan experimental data presented in Table 7.2 in Ref. [28] by using very small acid number and very low alkaline concentrations, which will be presented later.

4.4. Results and discussion

In this model, alkaline injection is from 0.7 PV to 1.0 PV. The profiles of concentrations at 0.9 PV during alkaline injection are presented. Fig. 1 shows the pH and generated soap concentration profiles. The soap concentration profile is parallel to that of pH except near the injection end of the core. This figure also shows that pH higher than 9.5 is required to generate soap. This high-pH front is at the fractional distance (x/L for this one-
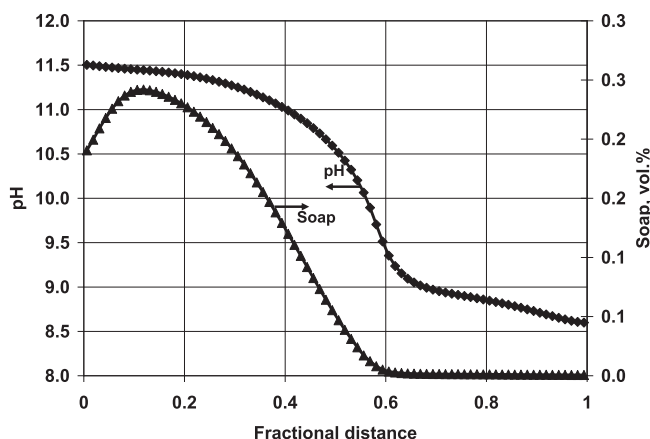

Fig. 2. Profiles of petroleum acids in water and oil phases, HA_w and HA_o, at 0.9 PV.

dimensional model) of 0.6. Fig. 2 shows the profiles of petroleum acids in water and oil phases, HA_w and HA_o, at 0.9 PV injection. Both of the concentrations are converted to the volume fractions in the aqueous phase. These two profiles parallel each other. HAw is almost four orders of magnitude lower than HA_o. Near the injection end, these two concentrations are lower because some acid components are dissociated as soap, thus the acid components is depleted.

Fig. 3 shows water, oil and microemulsion phase saturation profiles at 0.9 PV injection. The oil bank ahead of the high-pH front is almost invisible (0.02 saturation jump) at the fractional distance of 0.6. The significantly reduced oil saturation region is only near the injection end, although the effective salinity is in the type III region (optimum salinity condition) along the whole core at this time (Fig. 4). In other words, even at the optimum salinity condition, the oil bank formed by the soap generation is not significant. Fig. 5 shows the pressure profiles at 0.9 PV injection. The pressure gradient behind the high-pH front is lower than that before. That means the flow mobility behind the front is higher than that before the front. Thus the front moves at an adverse mobility ratio. A mobility control agent like polymer is needed.

Fig. 6 shows the IFT profiles of water/microemulsion and oil/microemulsion. Behind the high-pH front, the oil/microemulsion is in the range of 0.0001–0.01 mN/m. The IFT before the front is 20 mN/m. In other words, the alkaline–crude oil reaction zone does show ultra-low IFTs.

Fig. 1. pH and soap concentration profiles along fractional distance at 0.9 PV injection.
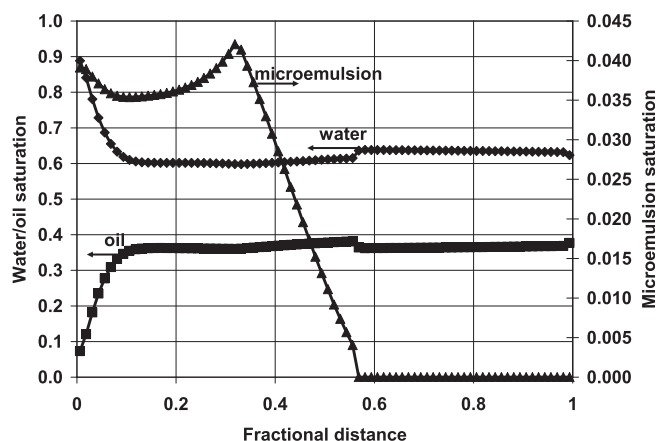
Fig. 3. Saturation profiles (water/oil/microemulsion) at 0.9 PV injection.
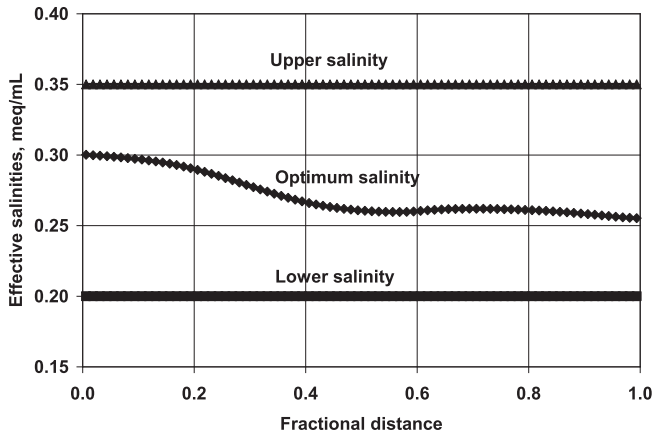
Fig. 4. Effective salinity and the effective salinity limits for Type III at 0.9 PV injection.
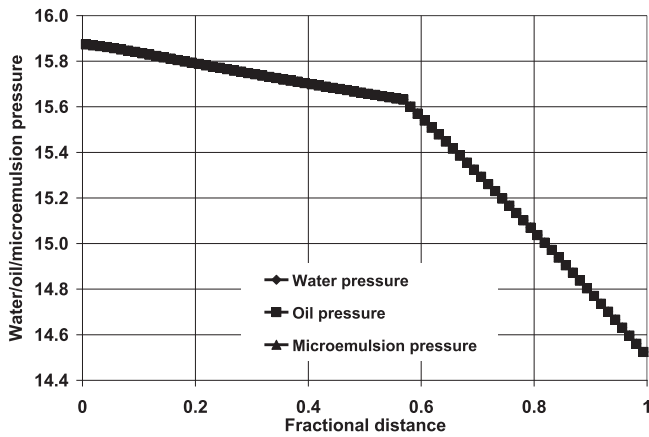

Fig. 5. Phase pressure (water/oil/microemulsion) at 0.9 PV injection.

The oil recovery factor is shown in Fig. 7. From this figure, the incremental oil recovery factor of alkaline flooding over water flooding is about 2.5% (from 41.5% for waterflooding to 44% for alkaline flooding). Such low incremental oil recovery factor is consistent with the field project data surveyed by Ref. [19]. From their data, the incremental oil recovery factors from alkaline
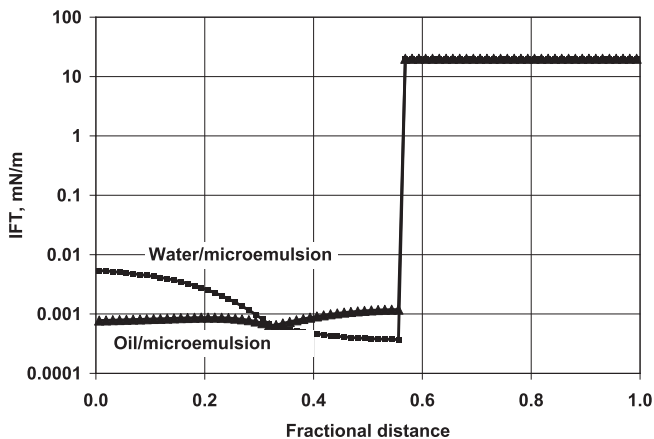

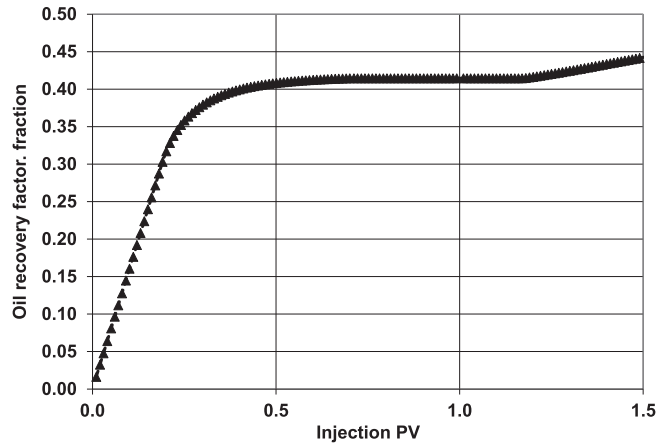Fig. 6. Profiles of IFTs (water/microemulsion, oil/microemulsion) at 0.9 PV injection.

Fig. 7. Oil recovery factor in the alkaline flooding.

flooding projects were 1—2% for most of the projects and 5—6% for few projects.

5. Analysis of alkaline-surfactant (AS) phase behavior

In situ generated soap usually has low optimum salinity. To reach an optimum salinity condition, alkaline concentration has to be low. The problem is, if the injected alkaline concentration is low, alkali may not be able to further transport in deep formation because of alkaline consumption. To solve this problem, a synthetic surfactant is injected, since a synthetic surfactant generally has a higher optimum salinity so that the optimum salinity for the mixture of soap and synthetic surfactant will have a higher optimum salinity. Then a higher-concentration alkaline solution can be injected to meet the requirements of the optimum salinity and consumption [22]. Therefore, it is suggested that a synthetic surfactant be injected in a practical alkaline project. In this section, the amount of soap is evaluated in AS flooding. Before that, we need to set up an EQBATCH model.

5.1. Set up of alkaline-surfactant phase behavior model

The difference between the phase behavior model and the flow model of an alkaline-surfactant system is that matrix does not exist in the phase behavior test tube. Thus there is no ion exchange on matrix in the phase behavior model. An UTCHEM AS phase behavior model is built based on the proceeding alkaline model by removing the ion exchange on matrix and adding a synthetic surfactant. To validate this AS model, we check whether this model could reproduce the surfactant salinity scan data presented in Table 7.2 of [28] by simply setting a negligible acid number in the model and zero alkaline concentrations. Fig. 8 shows that the calculated data from the alkaline-surfactant (AS) model match the experimental data (points). Thus the AS model is validated.

5.2. Amount of soap generated

The first question is, how much acid content in the crude oil can be converted into soap which helps to solubilize oil and water. Based on the above AS model and the input data in Table 5, a new AS phase behavior model is built.

Fig. 9 shows the converted fraction of acid into soap at different alkali concentrations. It shows that up to 15 wt.% sodium carbonate, less than half of the acid component is
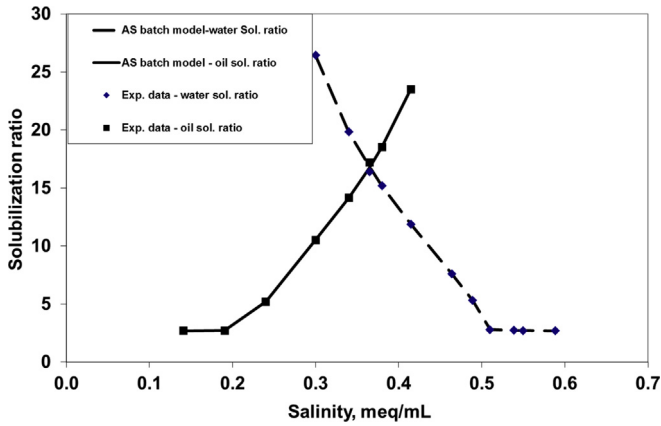
Fig. 8. Comparison of the experimental data with the calculated from the AS batch model.
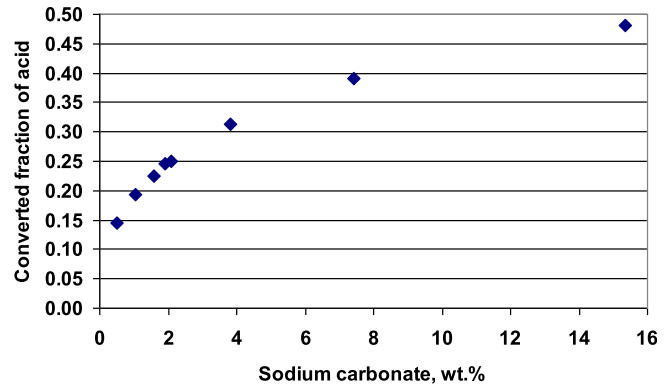

Fig. 9. Converted fraction of acid into soap at different alkali concentrations.

Fig. 10. Molar fraction of soap in the total amount of surfactants at different alkali concentrations.

converted into soap. In practice, alkaline concentration is less than 2%. Then only about quarter of acid can be converted into soap according to Fig. 9. Karpan et al. [17] assumed that acid components are completely converted into soap by reacting with alkaline solution in their simulation model. As discussed earlier, some acid components consume alkali but may not generate soap. Obviously, the assumption of complete conversion is invalid.

The next question is: what is the molar fraction of soap in the total surfactant? Fig. 10 shows the molar fraction of the generated soap in the total moles of surfactants at different alkali concentrations. It shows that up to 15 wt.% sodium carbonate, the generated soap is less than half of the total moles of surfactants. In a practical alkaline concentration of 2%, the generated soap is less than one third of the total moles of surfactants. In this model, the concentration of synthetic surfactant is only 0.2%. Then the actual soap concentration is less than 0.1%. This example shows that the generated soap concentration in practice could be low.

When an alkali is injected into a reservoir, a fraction of acid components are converted into soap which helps to solubilize oil and water into the microemulsion phase. How much does the soap change the solubilization? Fig. 11 shows that the water and oil solubilization ratios at different effective salinities, based on the two definitions. One definition is the ratio of water or oil volume solubilized (V_w or V_o) to the volume of injected synthetic surfactant in the microemulsion phase. The other definition is

the ratio of water or oil volume solubilized (V_w or V_o) to the total volume of injected synthetic surfactant and the generated soap in the microemulsion phase. We generally use the former definition for convenience, because the volume of soap is unknown without using an AS model. This figure shows that the solubilization ratios in the latter definition are lower than those in the former definition. However, the differences is not obviously visible. Fig. 12 shows the ratios of water and oil solubilization ratios based on the two definitions. In the figure, (SR)$_{total}$ is the solubilization ratio when the total volume of surfactant and soap

Table 5
Input data of the base AS model.

|	
Injection water	
NaCl, %	0.6
Na$_2$CO$_3$, %	1.9
Ca^{2+}, meq/mL	0.001
Water/oil ratio	1
Acid number, mg KOH/g oil	0.467
Surfactant concentration, vol.%	0.2
Surfactant phase behavior data	
Lower salinity limit, meq/mL	0.55
Upper salinity limit, meq/mL	1.1
Maximum height of binodal curve at zero salinity	0.030
Maximum height of binodal curve at optimum salinity	0.015
Maximum height of binodal curve at twice optimum salinity	0.030
Soap behavior data	
Lower salinity limit, meq/mL	0.1
Upper salinity limit, meq/mL	0.2
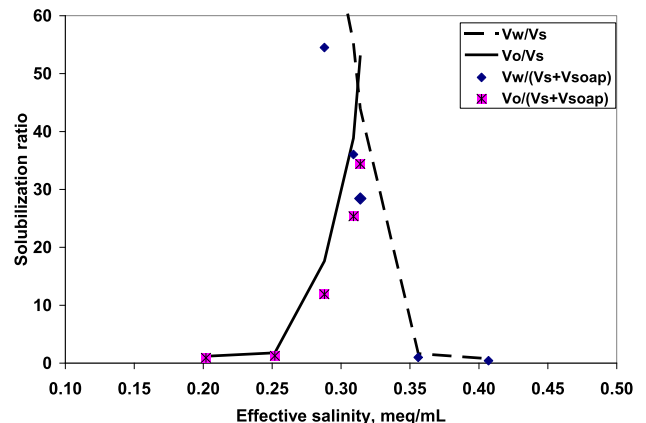
Fig. 11. Water and oil solubilization ratios at different effective salinities.
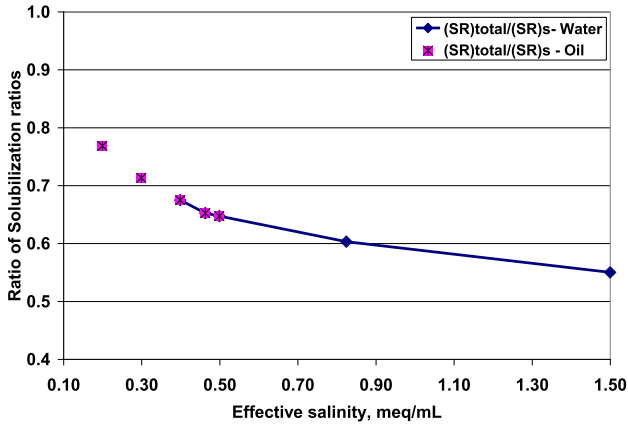
Fig. 12. Ratios of water and oil solubilization ratios based on the two definitions.
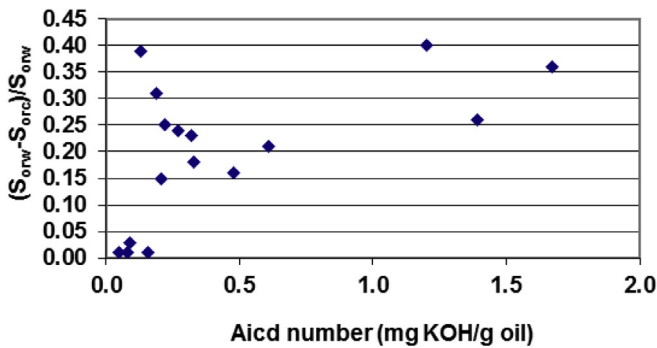

Fig. 13. Reduction in residual oil saturation vs. acid number.

Fig. 14. Equilibrium IFT vs. acid number.

Fig. 15. Reduction in residual oil saturation vs. IFT.

is used to define the ratio, and $(SR)_s$ is the solubilization ratio when only the surfactant volume is used. This figure shows that the ratios of SR are from 0.55 to 0.77. The differences in solubilization ratios should be taken into account when using [14] equation or [12] equation to calculate interfacial tensions. Without including the soap generated, the calculated interfacial tensions from those equations would likely be lower than the actual values.

6. Discussion of acid number in alkaline flooding

Alkalis react with naphthenic acid in the crude oil to generate soap. The soap reduces the IFT, which leads to high capillary number so that the residual oil saturation is reduced. It is intuitive to infer that higher acid number will lead to a higher oil recovery.

Fig. 13 shows the reduction in residual oil saturation by alkaline flood at different acid numbers. The data were calculated from the data presented by Ref. [8]. The alkali used was 0.1% NaOH. It shows that these two variables were not correlated. Fig. 14 shows that the equilibrium IFT between alkaline solution and oil was not strongly related to acid number, and Fig. 15 shows that the S_{or} reduction was not correlated with the IFT. Interestingly, Li's (2007) data shows that even when the acid number was zero, the IFT decreases with alkaline concentration. The alkaline flooding results from Castor et al. (1981b) show that the recovery efficiencies could be better correlated with the stability of emulsions and wettability alteration rather than with the IFT.
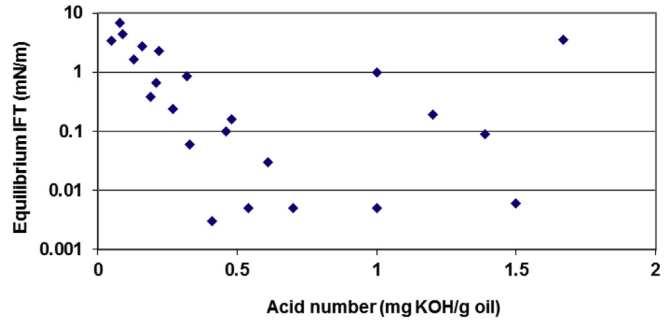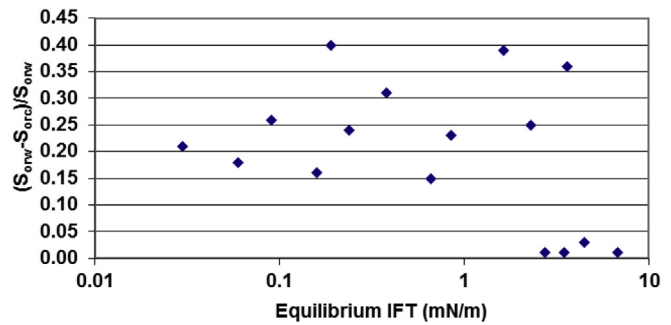
7. Concluding remarks

The simulation study in this paper shows that only a fraction of acids in the crude oil can be converted to in situ surfactant (soap). The amount of generated soap is not much, the soap molar fraction being one third of the total surfactants in the example calculation presented in this paper. To generate soap, pH in the system must be high (e.g. higher than 9.5). The simulation calculation in this paper shows that the incremental oil recovery in alkaline flooding is low, which is consistent with the field projects. The incremental oil recovery in alkaline flooding projects is not correlated to acid number for several reasons: (1) probably different methods were used to measure acid numbers; (2) some acid components may not be able to generate soap; (3) the application conditions may not provide optimum salinity conditions to generated soap. In other words, a synthetic surfactant may need to be injected to improve the phase behavior. It is also implied that the reduced IFT may not be the dominant mechanism in alkaline flooding. Other mechanisms like emulsification may be even more important.

Nomenclature

A^-	in situ generated anionic surfactant (soap)
AN	acid number, mg KOH/g oil
C	concentration, m/L^3, meq/mL
C_H	empirical constant in the Huh IFT equation
HA_o	pseudo-acid component in oil, m/L^3, mol/L
HA_w	pseudo-acid component in water, m/L^3, mol/L
K	equilibrium constant or product constant
K_A	acid dissociation constant
K_D	partition coefficient of the molecular acid
K_w	water dissociation constant
L	unit of liter, or outlet distance from the inlet, L
MW	molecular weight, Dalton (Da)

N_C	capillary number
SR	solubilization ratio
T_p	parameter in a capillary desaturation curve equation
V	volume solubilized in microemulsion
x	distance, L, m, cm
ρ	density, m/L^3, g/cm^3

Superscript

eq	equilibrium
ex	exchange
exm	exchange associated with micelles
—	adsorption associated with matrix through ion exchange
ˆ	adsorbed
=	associated with micelles

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