

Journal of Applied Chemical Research, 14, 1, 91-107 (2019)

Journal of A p p l ied C hemical R esearch jacr.kiau.ac.ir

Experimental study of salinity and ionic strength effects on Critical Micelle Concentration of a cationic surfactant (HTAB)

Naser Akhlaghi¹, Siavash Riahi^{*2}

¹Department of Petroleum Engineering, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran ²Institute of Petroleum Engineering, School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran (Received 05 May 2019; Final revised received 18 Aug. 2019)

Abstract

The interfacial tension of surfactant solutions is decreased with increasing surfactant concentration to obtain the critical micelle concentration (CMC). After that, the CMC value does not alter much. So this concentration is a critical point during surfactant flooding that is one of the chemical EOR techniques. The reduction of the CMC value is taken into consideration, since the surfactant flooding is very expensive. The surfactant evaluated in this study is a cationic HTAB surfactant that is more appropriate for carbonated oil reservoirs. This research investigates the effect of four different salts (CaCl₂, MgCl₂, Na₂SO₄, and NaCl) at different concentrations (0, 0.1, 0.5, and 1 wt%) on the CMC value. All the experiments were conducted by surface tension technique to measure the CMC values. Also, the ionic strength was calculated for all solutions. Results imply that the addition of all of the salts reduced the CMC value and Na₂SO₄ had the best performance comprise the others. Increasing the salt concentration leads to declining the CMC value for NaCl, and for other salts this behavior was continued till 0.5 wt%. Then it is elevated. The cost consideration indicates addition of slats can reduce the amount of surfactant flooding cost over 12 times.

Keywords: Surfactant flooding, HTAB, EOR, CMC, Salinity.

^{*}*Corresponding author*: Siavash Riahi, Institute of Petroleum Engineering, School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran. Email: Riahi@ut.ac.ir.

Introduction

The injection of surfactants into oil reservoirs is one of the methods of chemical enhanced oil recovery (cEOR), which is a very expensive method in this field. Surfactant is a significant category of chemical compounds used in different sections of industry, namely cosmetics, pharmaceutical, petroleum upstream and downstream industries. Surfactants can decrease surface and interfacial tensions, and also can stabilize of water in oil or oil in water emulsions. These are amphiphilic molecules with polar hydrophilic heads vs. nonpolar hydrophobic tails. The polar head section can be ionic (cationic / anionic) or nonionic [1-2]. Surfactants improved oil recovery by reducing the interfacial tension between residual oil and injected solution. One of the important properties of surfactants is the critical micelle concentration (CMC) which is unique to any material. The CMC is defined as the concentration of surfactants in which the first micelle is formed. Micellization of surfactants occurs after the CMC that this phenomenon depends on the structure of surfactants, hydrophobic structure (such as Length of the hydrocarbon, branched or non-branching chain, saturated or unsaturated chain), pressure, pH, temperature, organic additives and electrolytes [3]. The CMC of surfactant is a point where below and upper of which the behavior of surfactant changes. According to EOR, with increasing surfactant concentration, surface tension (ST) and interfacial tension (IFT) are reduced before the CMC reached; while the ST and IFT remain more or less constant above the CMC point [4]. Extensive studies were applied on surfactant flooding above the CMC due to the enhancement of phase behavior in the reservoir rock porous media and decreased IFT [5-6]. Another advantage of the injection of surfactant in a concentration above CMC, where solution is micellar is that micelles emulsify the residual oil and recover crude oil droplets at the surface of oil-in-water emulsion [6-8]. Also, the highest adsorption of a surfactant on the reservoir rock surface happens at the CMC, over which adsorption stays almost constant. That is why CMC is an important criterion to be considered in EOR applications [9].

With the arrival of surfactants in solution, the interaction between water molecules and hydrophilic groups increases and consequently the micellization free energy rises. On the other hand, with the formation of the micelle, the surface tension decreases. Also, the molecular entropy of the aqueous phase grows (agree factor with the formation of micelle), the entropy of monomers is also reduced due to their accumulation (opposite factor with the formation of micelle) and the interaction of hydrophilic and hydrophilic groups decreases and free energy diminishes (agree factor with the formation of micelle). Therefore as the agree factors overcome to the opposite one, micelle is formed. By amplifying the molecular concentration of surfactant, the number of micelles increases, but the number of free monomers remains unchanged and approximately equal to their amount at the CMC point [10].

For all types of surfactants, the chain length of the nonpolar hydrophobic tail, temperature, and salinity changes affect the CMC. CMC is typically determined by plotting a physicochemical property against the surfactant concentration. CMC can be determined by surface tension and conductivity measurement, voltammetry, IR spectroscopy, and nuclear magnetic resonance spectroscopy [9].

Still, successful surfactant flooding encounters with challenges such as high salinity at the reservoir porous media due to the potency of micelle formation under this situation and usual surfactant injection methods have not shown good results in these reservoirs [6, 11-13]. Surfactant applied in the presence of low salinity called as smart water surfactant flooding has revealed a better outcome of residual oil mobilization. But, the surfactants show enormously limited tolerance to hard salinity. The presence of monovalent cations such as sodium ion alone in the formation water can also prevent the successful surfactant flooding. Divalent cations like calcium and magnesium ions are extremely unfavorable and can lead to surfactant precipitation [6,14-17].

Salt ions feeble the electrostatic repulsion of the solution when exceeding 0.5M so adsorbed on micelles and thus micelles are aggregated in the aqueous solution [6, 18].

Several researchers have reported the effect of electrolytes on CMC. Their results show that increasing of electrolyte mostly moderate micellization of ionic surfactants, because of a reduction in electrostatic repulsion between the charged head group, which induced a decrease in CMC [19-22].

Karnanda and et al. were investigated the effect of salt composition on CMC values of Zonyl FSE and Triton X-405 at 60 $^{\circ}$ C and 2,000 psi. Their experiments show that salt composition has no effect on CMC values for Triton X-405. On the other hand, the CMC value of anionic Zonyl FSE fluorosurfactant increments as Ca²⁺ divalent ions amount grows [23].

Javadian and et al. reported that the presence of ionic liquids in surfactant solution has been modified the CMC and micellization behavior of ionic surfactant (CTAB) [24].

Esan and et al. considered the different concentration of tetramethylammonium bromide salt on CMC values of a cationic surfactant (CTAB). They indicated that the CMC amount of CTAB reduced by increasing salt concentration at different temperatures [22].

Naskar and et al. determined the effects of two different salts on two representatives surfactants (SDS and DTAB) with two methods of conductometry and calorimetry. Their results show that The CMCs of both surfactants were reduced by increasing studied salt concentration amounts [25].

Bera et al. experiments indicate that increasing NaCl concentration from 0.04 to 0.06 mass fractions reduces the CMC of a cationic surfactant (HTAB) [26].

Abbas and et al. were studied the micellar behavior of an ionic surfactant (AOT) in presence of high salinity of Na⁺ ion concentration at a different temperature from 25–105 °C by surface tension (ST) method [27].

The surfactants used for EOR flooding are always more than CMC, because of formation of micelles is necessary to mobilize residual oil molecules. For nonionic surfactants, the concentration around the CMC is required for successful operation, while, for ionic surfactants, it is essential to use these molecules over than CMC. CMC has to be investigated before surfactant flooding to consider the economic concentration desirable especially for ionic surfactants to form enough micelles. This is important in specifying the adsorption of surfactant at the interface of oil/injected solution [2, 28].

Since the HTAB surfactant has an acceptable IFT values as a commercial and conventional surfactant in the EOR flooding, and also motivated by the limitations of the previous studies on the effect of predominant salts that present at the reservoir rock porous media, this research is designed to experimentally study the influence of CaCl₂, MgCl₂, Na₂SOo₄, and NaCl salts on the CMC of HTAB surfactant to optimize the surfactant flooding operational and economical. These salts represent the main monovalent and divalent anions and cations found in the reservoir formation water and sea water, which are the main candidates of aqueous phase to injection toward the oil reservoirs. The CMC of surfactant was measured at different mentioned salts concentrations with surface tension (ST) technique. Also, an economic evaluation performed to evaluate the effect of salts on the optimization of the surfactant injection process.

Experimental

Materials

The cationic surfactant Hexadecyltrimethylammonium Bromide (HTAB) with 390 kg/m³ and 55 g/l bulk density and solubility respectively used in this study was 97 % pure product from Merck Company. The salts used were CaCl₂, MgCl₂, Na₂SO₄, and NaCl from Merck Company. Double distilled water was applied to prepare all surfactant solutions.

Solution preparation

Surfactant solutions were prepared on a mass basis. A 1000 ml standard beaker with distilled water, the desired concentration of surfactant, and the desired concentration of different salts, with a degree of purity of this material, reached the desired concentrations using a stirrer and magnet. After reaching the desired concentrations and diluting the solutions, all the solutions were waited for 24 hours to make the equilibrium is reached [29].

Methodology

The influence of mentioned salts on CMC was measured at the salinities of 0, 0.1, 0.5, and 1 wt% for each of them at ambient temperature and pressure.

All experiments were carried out using a surface tension technique with a pendant drop, which will be described below.

Surface Tension (ST) technique

The surface tension measurements of surfactant solutions were measured using the pendant drop method. The CMC values were determined at the breakpoint of nearly two straight line portions in the surface tension versus surfactant concentration plots [27]. The surface tension of the surfactant solution at different concentrations of surfactant with specific concentrations of salts in the air was measured.

In this research, the pendant drop method was used to measure ST between the aqueous phase and air (Figures 1-3). In this method, the ST is easily calculated from dimensions of a suspended drop photographed by a camera [30]. The assumptions used in this method are :

1. The drop is symmetric and is suspended from a central vertical axis.

2. The drop is static. It means that the interfacial tension and gravity are the only forces available [31].

This study made use of IFT-PDSA-02 apparatus which belongs to APEX Co. as drop shape analysis equipment to calculate the CMC value of surfactant.



Figure 1. Typical setup of the pendant drop method [32].



Figure 2. Associated parameters of pendant drop method [33].



Figure 3. IFT-PDSA-02 apparatus which belongs to APEX Co. as a drop shape analysis equipment.

In this apparatus, a drop of a fluid in the other fluid is formed, and the surface tension is calculated by measuring the drop shape and solving a form of the Laplace equation [34]. The following equation is used to calculate interfacial tension:

$$\Delta P = \sigma + (\frac{1}{R_1} + \frac{1}{R_2})$$
 Eq. 1

 ΔP is the pressure difference between the inside and outside of the droplet, σ is the interfacial tension or surface tension, and R₁ and R₂ are the main radii of the curvature. By setting the camera in front of the cell, the drop formed on the monitor screen can be seen. By using the apparatus software, the drop form is analyzed and ultimately the output of the software is ST amount.

Results and discussion

Salinity Effects on the CMC Value

In this section, the effects of calcium chloride, magnesium chloride, sodium sulfate, and sodium chloride salts, which are commonly found in the reservoir rock porous media and considered as dominant salts in this environment, on the CMC value will be discussed.

To understand the effect of these parameters on the CMC values, four types of brine with different concentration of 0, 0.1, 0.5 and 1 wt% were designed to dissolve in the different surfactant concentration solutions. Then, the efficiency of them was considered by measuring CMC values with the ST method. In order to evaluate the effect of ionic strength on CMC variations, ion strength was calculated for each solution. The ionic strength equation is as follows:

$$I = \frac{1}{2} * \sum_{i=1}^{n} (C_i * Z_i^2)$$
 Eq.2

Where one half is because we are including both cations and anions, c_i is the molar concentration of ion i (M, mol/L), z_i is the charge number of that ion, and the sum is taken over all ions in the solution.

Surfactant ability from perspective of EOR

One of the major reasons for surfactant flooding is the reduction of IFT between injected fluid and residual oil in the reservoir. The IFT of surfactant in EOR is more important to be less than 1 mN/m. in order to investigate the effect of the studied surfactant on reducing the interfacial tension between the surfactant solutions and crude oil (oil sample from Karanj oil field), for example, IFT values were measured in surfactant concentration higher than CMC (400 ppm) and in the presence of mentioned salts at 0.5 wt%. All experiments of this stage were carried out at ambient temperature and pressure.

Figure 4 shows the IFT values at 400 ppm concentration of cationic HTAB surfactants with four types of salts with a concentration of 0.5 wt% in solution.



Figure 4. IFT values vs. 0.5 wt% of CaCl₂, MgCl₂, Na₂SO₄ and NaCl.

Measurement of CMC

For example, the plot of surface tension with increasing of surfactant concentration at 0.5 wt% of CaCl₂ to determine the CMC is shown in Figure 5. For this purpose, CaCl₂ salt was dissolved in specified concentrations in Dobell distilled water, and then cationic HTAB surfactant at concentrations of 25, 50, 100, 200, 300, 400, and 500 ppm was dissolved in the desired brine and the amount of ST between solution and the air was obtained. So the concentration at which the breaking point occurred at this plot is the CMC.



Figure 5. CMC value at 0.5 wt% CaCl₂.

Influence of CaCl₂

The divalent cation of calcium is from abundant ions found in the porous medium of the reservoir. This ion has a significant effect on the chemical processes of the reservoir fluids. For this reason, the effect of this ion on the CMC of studied surfactant should be investigated before injection into the reservoir. Four concentrations of $CaCl_2$ salt were used to prepare of surfactant solutions. The concentrations of salt were 0, 0.1, 0.5, and 1 wt%. Different concentrations of surfactant applied to measure the CMC values in the presence of this salt.

Figure 6 shows the CMC and ionic strength variations against increasing calcium ion concentration. As illustrated in this figure, increasing the amount of $CaCl_2$ concentration leads to decreasing the CMC until the medium concentration of this salt is gained (from 0 to 0.5 wt%) and after that with increasing the concentration of it, the CMC value was sharply increased (from 0.5 to 1 wt%). However, this increase was not as great as when salt was not in solution at all. Also, it can be seen, by rising salt concentration the ionic strength was increased and the CMC value was declined with increasing ionic strength till the moderate amount of it was obtained (from 0 to 0.135 M) and after that, this value was grown by increasing the ionic strength (from 0.135 to 0.27 M) too.



Figure 6. CMC values and Ionic strength vs. CaCl₂ wt%.

Influence of MgCl₂

Another salt that was studied in this research was $MgCl_2$. Mg^{2+} was other influential divalent cations, which is present in the porous media of reservoir rock. As in the previous section, this salt is in four concentrations of 0, 0.1, 0.5, and 1 wt% was used to prepare surfactant solutions and ionic strength of these salt concentrations was determined to compare the CMC values with the ionic strength of solutions.

The variations of CMC and ionic strength with salt concentrations were illustrated in Figure 7. As can be seen in this figure, raising the concentration of $MgCl_2$ lead to decreasing the value of CMC until the mediocre amount of salt concentration obtained (from 0 to 0.5 wt%) and then the CMC value was increased with rising salt concentrations to the high salinity of this salt (from 0.5 to 1 wt%). And also, increasing the salt concentration caused rising the ionic strength amount, but the growing ionic strength led to declining the CMC value till the average amounts of ionic strength (from 0.157) and rising the CMC value till the highest value of it (from 0.157 to 0.315).

The behavior of CMC variations with increasing ionic strength and salt concentration for MgCl₂ is very similar to CaCl₂. With the difference that the CMC values for magnesium chloride were slightly higher than calcium chloride at concentrations of 0.1 and 1 wt% and at a concentration of 0.5 wt% for calcium chloride, it was slightly higher than magnesium chloride. At mentioned salt concentrations the ionic strength of magnesium chloride is more than calcium chloride and as the salt concentration increases, the ionic strength difference of these two salts raises. The differences between CMC values of these two divalent cations can be attributed to the salting out and salting in effects. At the lowest and highest salt concentrations, increasing the ionic strength leads to an increase in the solubility of surfactant in the aqueous phase. So that, surfactant molecules were surrounded with opposite electrical charged ions and this caused to the reduction of electrostatic free energy and also increasing the solution activity and thus leads to raising the solubility. Salting in effect occurred at the lowest and highest concentrations of salt (0.1 and 1 wt%) and so the CMC of magnesium chloride was more than calcium chloride. At salting-out effect, salt compounds are separated in the aqueous phase and some of the water molecules are attracted from salt ions and caused to decreasing the available water molecules to interact with surfactant charged head group. Therefore, the hydrophobic interaction becomes stronger and micelles are formed faster as to the reduction of free energy of micellization. At the moderate salt concentration (0.5 wt%), a fewer value of the CMC of magnesium chloride than calcium chloride can be attributed to the salting out effect.



Figure 7. CMC values and Ionic strength vs. MgCl₂ wt%.

Influence of Na₂SO₄

 Na_2SO_4 is a salt commonly found in the formation water and also sea water. SO_4^{2-} can be affected the chemical reactions in the reservoir environment as a divalent anion. As in the two preceding parts, the effect of this salt on the CMC value is investigated at four mentioned salt concentrations. Figure 8 indicates the CMC and ionic strength alterations with changes in salt concentrations. As can be observed from this figure, the CMC values decrease with arise in salt concentration from low to the moderate amounts (from 0 to 0.5 wt%) of salt and after that it starts to grow (from 0.5 to 1 wt%). Although, the amount of this increase, after doubling the concentration of salt in the solution is very low and subtle (from 30ppm at 0.5wt% to 31ppm at 1 wt%). Moreover, by raising the amount of salt concentration, the ionic strength increases and the CMC value decreases till a moderate amount of ionic strength and after that, it is starting to grow.



Figure 8. CMC values and Ionic strength vs. Na₂SO₄ wt%.

Influence of NaCl

NaCl is a common salt that can be found at the majority of the reservoir brine and forms a large portion of the salinity of formation and sea water usually. Studies show addition of this salt usually leads to reduce the amount of surfactant CMC.

Variations of the CMC value and ionic strength with alterations of salt concentrations were demonstrated in Figure 9. The CMC value declines as salt concentration increases from 0 to 1 wt%, while the ionic strength increases after salt concentration decreases. Also the CMC value diminished with raising ionic strength, so they have contrary relations.



Figure 9. CMC values and Ionic strength vs. NaCl wt%.

Addition of salt to surfactant solutions leads to reduce the electrostatic repulsion between surfactant polar head groups and cause the formation of micelles at lower concentrations of surfactant. At concentrations from 0 to 0.5 wt% of any salts, the electrostatic repulsion between surfactant polar head groups is more reduced; therefore, the CMC values are more decreased. Regarding the release of ion from the hydrophilic head of the surfactant molecules, the presence of salt can cause interactions between surfactant molecules in the micelle single layers. Addition of cationic electrolytes such as NaCl to ionic surfactants causes reduction of the CMC value and increases the lyotropic number [35]. The reduction of CMC value is mainly due to the reduction of the molecular head group area in the presence of additional electrolytes and, consequently, the reduction of electrical repulsion between them in the micelles and promoting micellization. As pointed out before, the interactions between ions are weaker than the interactions between ions and surfactant charged head groups [35-38]. In addition, the reduction of the repulsive forces between the same absorbed charged ions allows the formation of the closest arrangement and hence the reduction of the CMC [35]. Moreover, HTAB has large hydrophobic volume. Thus, it was supposed that under the synergistic hydrophobic interaction, salt was accommodated into the micellar interior. The decrease in the CMC value can be attributed to the synergistic hydrophobic interaction between the nonpolar hydrogen chain of surfactant and salt, and effectual decrease in the electrostatic repulsion between the charged head group which improved the HTAB micellization [22, 39-40]. Also ionic micelles bind counter-ions by electrostatic interaction between the micelle surface charge and the counter-ions formed by the dissociation of the surfactants in solution. By adding salt, the double electric layer of the surfactant polar head amasses. This leads to a screen in electrostatic repulsion between adjoining hydrophilic head groups and, so, enables the aggregation to a lower surfactant concentration and lowering the CMC value [41-45]. Accordingly, by adding salt to HTAB solutions

and increasing ion concentration, declining electrostatic repulsion between cationic head groups and micellization occurs from 0 to 1 wt% of NaCl and 0 to 0.5 wt% of CaCl₂, MgCl₂, and Na₂So₄.

Findings of the present study are in agreement with results of Abezgauz and et al. that their experiments were done with different salts that were NaCl, NaBr, NaClO₃, NaNO₃, and NaSal by concentration range of 0 to 0.01 M [35]. Also Javadian and et al. indicated that increasing the concentration of NaBr slat leads to decreasing the CMC of mixed cationic-anionic (CTAB-SDS) surfactants. Fernandes and et al. reported the addition of this slat caused the CMC of mixed cationic surfactants initially remains stable but for NaBr 0.1 mmol kg–1, the normal screening influence is observed and the CMC declined that was similar to the results of this study [46-47].

The elevating of salt concentrations for divalent anion and cations led to raising the CMC value that can be attributed to salting out and in effects. At concentrations between 0.5 to 1 wt% (high salinity) salting-in effect was occurred and caused increasing the amount of the CMC. As to the low amount of NaCl ionic strength between 0.5 to 1 wt%, the salting-in effect did not emerge. In equal ionic strengths, calcium chloride reduces the CMC of ionic surfactant more than sodium chloride that it can be seen in figures 6 and 9. As can be understood from figures 6 to 9, the intersection point amount (In the direction of the x-axis) of two lines of ionic strength and CMC for sodium chloride differs from other salts. This amount for CaCl₂, MgCl₂, and Na₂SO₄ in the range of 0.1 to 0.2 wt% and for NaCl is 0.1 to 0.3 wt%. the ionic strength amount for NaCl at the concentration of 1 wt% is almost equal to the CaCl₂, MgCl₂, and Na₂SO₄ at the concentration of 0.5 wt%. This shows that at the amount of ionic strength above the range of 0.1 to 0.2 M, the salting-in effect is appeared in the HTAB solution and leads to an increase the CMC value, but not more than the free salt aqueous solution. The lowest value of the CMC is for Na₂SO₄ at a concentration of 0.5 wt% (31 ppm). Also among all the salt concentrations that were studied in this research, Na₂SO₄ had the smallest value of CMC with compared to other salts.

Cost Consideration

The CMC is a critical point at surfactant flooding, and with considering this issue that it is a more expensive EOR method, it may not be an economical project. So it is essential to decrease and optimize the cost of surfactant injection is prerequisite as an EOR method.

Before that applying any method of EOR, determining the costs of it is necessary. Since the main oil reservoirs of Iran are carbonated and the cationic surfactant can be a suitable option to these reservoirs, the cost of cationic HTAB surfactant injection that has the low amount of IFT should be computed and minimized as much as possible.

In this section, the cost of HTAB surfactant for higher injection than CMC value reported and compared with injection surfactant in the presence of salt.

If it is assumed that the HTAB surfactant is to be injected with a 0.5 pore volume (PV) to Karnj oil field with a volume of 9.6 billion barrels. the optimal concentration of injection of this surfactant is 2CMC, considering the cost of this surfactant per kg, 293.5 \$, the approximate cost of injections in an aqueous solution without salt for this reservoir with this hypothetical conditions is approximately 430.8 billion \$. Table 1 shows the values of CMC and injection costs with the above conditions for different studied salts.

Number	Salt Concentration	CMC Value (ppm)	Cost Value of 2CMC
			(billion \$)
1	Free Slat	375	430.8
2	0.1 wt% CaCl ₂	60	68.9
3	0.5 wt% CaCl ₂	38	43.6
4	1 wt% CaCl ₂	100	114.9
5	0.1 wt% MgCl ₂	70	80.4
6	0.5 wt% MgCl ₂	31	35.6
7	1 wt% MgCl ₂	110	126.4
8	0.1 wt% Na ₂ SO ₄	60	68.9
9	0.5 wt% Na ₂ SO ₄	30	34.5
10	1 wt% Na ₂ SO ₄	31	35.6
11	0.1 wt% NaCl	105	120.6
12	0.5 wt% NaCl	54	62
13	1 wt% NaCl	31	35.6

Table 1. CMC amounts and the cost of surfactant injection at 2CMC concentration for different salinities.

As can be understood from this table, reducing CMC at the highest level $(0.5 \text{ wt}\% \text{ Na}_2\text{SO}_4)$ leads to a reduction in the injection costs in this prototype oil reservoir more than 12 times (from 430.8 to 34.5 billion \$).

Conclusion

In this work, the micellar behavior of a cationic HTAB surfactant and the effect of four types of salts (CaCl₂, MgCl₂, Na₂So₄, and NaCl) was studied. The concentrations of salts that were evaluated were 0, 0.1, 0.5 and 1 wt%. The CMC value of this surfactant without salt was 375 ppm. Outcomes reveal the addition of each salt decreased the value of CMC compared with a free salt solution. The increasing salt concentration led to decreasing the CMC value for NaCl, whereas the CMC value

decreased by increasing salt concentrations from 0 to 0.5 wt%. Then, it was increased by raising salt concentrations for CaCl₂, MgCl₂, and Na₂SO₄. All the CMC values were measured by surface tension (ST) technique. The ionic strength of solutions was calculated and it had a proportional relationship with salt concentration and so had the same behavior with the CMC value for studied salts as their concentrations. The lowest value of CMC was 30 ppm for situations of 0.5 wt% Na₂SO₄. Considering the cost evaluation, the addition of salt to HTAB surfactant solution can be lowered the costs of surfactant flooding project more than 12 times. Regardless of the type of salt, the CMC values highly depend on the ionic strength.

References

[1] J. F.B. Pereira, E. J. Gudiña, R. Costa, R. Vitorino, J. A. Teixeira, J. A. P. Coutinho, L. R. Rodrigues, *Fuel*, 111, 259 (2013).

[2] M. S. Benzagouta, I. M. AlNashef, W. Karnanda, K. Al-Khidir, *Korean J. Chem. Eng.*, 30, 2108 (2013).

[3] L. Schramm, Surfactants: Fundamentals and Applications in the Petroleum Industry, CUP, Cambridge (2010).

[4] J. J. Sheng, Modern Chemical Enhanced Oil Recovery, Theory and Practice, GPP, Netherland (2013).

[5] G. Hirasaki, C.A. Miller, M. Puerto, SPE J., 16, 889 (2011).

[6] R. Goswami, K. R. Chaturvedi, R. Sh. Kumar, B. H. Chon, T. Sharma, *J. Petrol. Sci. Eng.*, 170, 49 (2018).

[7] M. Nedjhioui, N. Moulai-Mostefa, A. Morsli, A. Bensmaili, J. Des., 185, 543 (2005).

[8] T. Tichelkamp, H. H. Khanamiri, M. Nourani, J. A. Stensen, O. Torsæter, G. Øye, *Energy Fuels*, 30, 2919 (2016).

[9] M. Sh. Kamal, I. A. Hussein, A. S. Sultan, *Energy Fuels*, 31, 7701 (2017).

[10] K.L. Mittal, D. O. Shah, Adsorption and Aggregation of Surfactants in Solution, CRC, Florida (2002).

[11] R. Tabary, B. Bazin, F. Douarche, P. Moreau, F. Oukhemanou-Destremaut, *SPE Conference*, SPE 164359 (2013).

[12] A. Bera, A. Mandal, H. Belhaj, T. Kumar, Petrol. Sci., 14, 362 (2017).

[13] M. Puerto, G. J. Hirasaki, C. A. Miller, J. R. Barnes, SPE J., 17, 11 (2012).

[14] H. H. Khanamiri, M. Nourani, T. Tichelkamp, J. A. Stensen, Ø. Gisle, T. Ole, *Energy Fuels*, 30, 984 (2016).

[15] R. Tabary, B. Bazin, F. Douarche, P. Moreau, F. Oukhemanou-Destremaut, *SPE Conference*, SPE 164359 (2013).

- [16] R. N. Healy, R. L. Reed, SPE J., 17, 129 (1977).
- [17] C. Negin, S. Ali, Q. Xie, Petrol., 3, 197 (2017).
- [18] H. Iyota, R. Krastev, Colloid Polym. Sci., 287, 425 (2009).
- [19] S. K. Mehta, K. K. Bhasin, R. Chauhan, S. Dham, *Colloids Surf. A: Physicochem. Eng. Aspects*, 255, 153 (2005).
- [20] J. Aguiar, J. A Molina-Boli, J. M. Peula-Garci, R. C. Carnero, *J. Colloid Interface Sci.*, 255, 382 (2002).
- [21] J. Patel, D. Varade, P. Bahadur, Indian J. Chem., 43A, 715 (2004).
- [22] O. S. Esan, O. M. Olubunmi, A. C. Olumuyiwa, O. Olarenwaju, *Inter. J. Thermodynamics*, 18, 246 (2015).
- [23] W. Karnanda, M. S. Benzagouta, A. AlQuraishi, M. M. Amro, Arab. J. Geosci., 6, 3535 (2013).
- [24] S. Javadian, V. Ruhi, A. A. Shahir, A. Heydari, J. Akbari, *Industry Eng. Chem. Research*, 52, 15838 (2013).
- [25] B. Naskar, A. Dey, S. P. Moulik, J. Surfact. Deterg., 16, 785 (2013).
- [26] A. Bera, A. Mandal, B. B. Guha, J. Chem. Eng. Data, 59, 89 (2014).
- [27] A. H. Abbas, W. R. W. Sulaiman, M. Z. Jaafar, A. A. Aja, *Arab. J. Sci. Eng.*, 43, 2515 (2018).
- [28] A. S. Hanamertani, R. M. Pilus, S. Irawan, *ICIPEG*, Kuala Lumpur (2016).
- [29] H. Maeda, S. Muroi, R. Kakehashi, J. Phys. Chem. B, 101, 7378 (1997).
- [30] A. K. Manshad, M. Olad, S. A. Taghipour, I. Nowrouzi, A. H. Mohammadi, *J. Molecular Liq.*, 223, 987 (2016).
- [31] J.M. Andreas, E.A. Hauser, W.B. Tucker, J. Phys. Chem., 42, 1001 (1938).
- [32] J.D. Berry, M.J. Nesson, R.R. Dagastine, C. D. Y. C., R.F. Tabor, *J. Colloid Interface Sci.*, 454, 226 (2015).
- [33] J. Drelich, C. Fang, C.L. White, Encycl. Surf. Colloid Sci., 3, 3152 (2002).
- [34] C. M. Chen, C. H. Chang, Y. M. Yang, J. R. Maa, *Colloids Surf. A: Physicochemical Eng. Aspects*, 174, 357 (2000).
- [35] L. Abezgauz, K. Kuperkar, P. A. Hassan, O. Ramon, P. Bahadur, D. Danino, J. Colloid Interface Sci., 342, 83 (2010).
- [36] M. Thongngam, D. J. McClements, *Langmuir*, 21, 79 (2005).
- [37] K. D. Collins, *Biophys. J.*, 72, 65 (1997).

[38] N. Vlachy, B. Jagoda-Cwiklik, R. Vacha, D. Touraud, P. Jungwirth, W. Kunz, *Adv. Colloid Interface Sci.*, 146, 42 (2009).

- [39] M. Almgren, S. Swarup, J. Phys. Chem., 87, 876 (1983).
- [40] M. Manabe, H. Kawamura, A. Yamashita, S. Tokunaga, *J. Colloid Interface Sci.*, 115, 147 (1987).
- [41] J. L. Salager, Surfactants in Aqueous Solution, FIRP, Venezuela (1993).

[42] T. D. Gurkov, D. T. Dimitrova, K. G. Marinova, C. Bilke-Crause, C. Gerber, I. B. Ivanov, *Colloids Surf. A: Physicochemical Eng. Aspects*, 261, 29 (2005).

- [43] S. Bae, K. Wantke, and H. Motschmann, J. Phy. Chem. B, 103, 1045 (1999).
- [44] L. Zhai, X. Tan, T. Li, Y. Chen, X. Huang, *Colloids Surf. A: Physicochemical Eng. Aspects*, 276, 28 (2006).
- [45] F. K. G. Santos, E. L. B. Neto, M. C. P. A. Moura, T. N. C. Dantas, A. A. D. Neto, *Colloids Surf. A: Physicochem. Eng. Aspects*, 333, 156 (2009).
- [46] S. Javadian, H. Gharibi, Z. Bromand, B. Sohrabi, J. Colloid Interface Sci., 318, 449 (2008).
- [47] R. M. F. Fernandes, E. F. Marques, B. F. B. Silva, Y. Wang, *J. Molecular Liq.*, 157, 113 (2010).