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Effect of Electrolyte on Synergism of Anionic-Nonionic Surfactant Mixture

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Abstract: In this study, anionic (Sodium Dodecyl Sulfate) and nonionic (Triton X100) surfactants mixture (1:1 mass ratio) were evaluated for synergism in Critical Micelle Concentration (CMC) at different ionic strength values. Interaction between the binary surfactant mixture was studied by surface and interfacial tensions. The composition of mixed micelles and the interaction parameter, β evaluated from the CMC data obtained by both surface and interfacial tensions for different systems using Rubingh's theory were discussed. It has been shown, that the, micellization behavior of the mixture was improved significantly in presence of salt in particular after equilibration with shale.

Key words: Surfactant, surface tension, interfacial tension, CMC, ionic strength, adsorption, synergism

INTRODUCTION

There has been a broad range of research performed on surfactants over the years due to their importance in many fields. An important application of surfactant is oil-contaminated soil washing and enhanced oil recovery. The mechanisms behind surfactant enhanced removal of oil from soil/oil reservoirs have been proposed to occur in two steps: Mobilization and solubilization (Deshpande *et al.*, 1999). If the oil/water interfacial tension is lowered below some critical figure, then the drop of oil will flow out of the pore space between the sand grains. This process is called mobilization. For example, in water-wet rocks, reduction of the interfacial tension to values of the order of 10^{-3} mN m⁻¹ is needed in order to obtain substantial mobilization and recovery of oil (Holmberg *et al.*, 2002). The mobilization mechanism occurs at concentrations below the surfactant CMC (Duffield *et al.*, 2003; Urum and Pekdmeir, 2004; Vreysen and Maes, 2005). Phenomena associated with this mechanism include reduction of surface and interfacial tension, reduction of capillary force, wettability and reduction of contact angle.

Solubilization mechanism occurs at concentrations far above CMCs. The hydrophobic interior of the micelle creates an environment for partition of oils. This results in an increase in apparent aqueous solubility of oils. The apparent solubility increases linearly with an increase in the surfactant concentration above CMC (Rosen, 2004). The solubilization mechanism is quite effective in removing the oil but it requires high concentrations of surfactant and additional separation of the oil from the surfactant solution (Childs *et al.*, 2005).

The adsorption of surfactants on soils/reservoir-matrix may result in the loss and reduction of their concentration, which may render them less efficient or ineffective in practical treatment by both mechanisms (Urum and Pekdmeir, 2004). Thus for a successful oil removal operations by surfactants, several subjects must be addressed: (1) the surfactant must be able to lower oil/water interfacial tension to ultra low values, (2) has a lower CMC, (3) be insensitive to harsh brine environments, (4) sorb less to soil substrate and (5) have high solubilization capacities of oil in hand (Deshpande *et al.*, 2000; Torres *et al.*, 2003).

Recently, mixed nonionic-anionic surfactants were found superior to the relevant single ones mainly due to high solubilization capacity of the mixture as well as the reduction in nonionic surfactant partition and/or sorption to soil. Yang *et al.* (2005) showed that the amounts of both Triton X-100 (TX100) and Sodium Dodecylbenzene Sulfonate (SDBS) sorbed to Ca-montmorillonite are significant. However, the amount of either TX100 or SDBS sorbed can be decreased and minimized when they are mixed with each other.

Furthermore, the extent of TX100 partitioning into the organic phase was found to decrease if the amount of SDBS increased (Zhao *et al.*, 2006a, b). Decreasing loss of surfactant due to partitioning and/or sorption and the greater apparent solubilization of the mixture will reduce surfactant volumes needed and thus the capital expenditure and operation cost (Zhao and Zhu, 2006).

Surfactant mixtures of TX100 and Sodium Dodecyl Sulfate (SDS) also have been studied. The Critical Micelle Concentrations (CMCs) of mixed surfactants were sharply lower than that of sole SDS. With the increase in mole

fraction of TX100, the CMCs decrease continuously from the CMC of pure SDS down to the CMC of pure TX100. Furthermore, the experimental CMCs were lower than the ideal CMCs (Janczuk *et al.*, 1995; Wang and Kwak, 1999; Porcel *et al.*, 2001; Zhu and Feng, 2003; Zhou and Zhu, 2004, 2006; Owoyomi *et al.*, 2005; Zhao *et al.*, 2005; Mata, 2006; Yu *et al.*, 2006).

Anionic-nonionic surfactant mixtures are also found to exhibit cloud points higher than those of the single nonionic surfactant, along with Krafft points lower than those of the single anionic surfactant. Mixed surfactants could be employed over a wide range of temperature, salinity and hardness conditions than the individual surfactants (Gu and Galera-Gomez, 1995; Al-Ghamdi and Nasr-El-Din, 1997; Goell, 1999; Zhou and Zhu, 2004).

Therefore, it is obvious that nonionic-anionic surfactants may perform better than individual surfactants. Generally, most of previous studies focused on nonionic-anionic surfactant mixtures solubilization and desorption of organic compounds compared to corresponding individual surfactants of each mixture (Zhu and Feng, 2003; Zhou and Zhu, 2004; Zhou and Zhu, 2005; Zhao *et al.*, 2005; Zhou and Zhu, 2006; Yu *et al.*, 2006; Zhao *et al.*, 2006a, b). However, to the best of our knowledge, no studies have been conducted to investigate synergism in CMC for anionic-nonionic surfactant mixtures in presence and absence of shale, oil phase and an electrolyte. An electrolyte is necessary to reduce CMC of anionic surfactant, hence CMC of anionic-nonionic mixture. It will also allow transition of surfactant from Winsor Type I to Winsor Type III where lower interfacial tension is exhibited (Wisnor, 1948). However, the electrolyte has a detrimental effect on cloud point of nonionic surfactants. Furthermore, presence of anionic surfactant in anionic-nonionic mixtures will increase the cloud point of nonionic surfactant. These interactions make overall effect difficult to expect.

This study is intended to investigate the simultaneous losses of SDS, TX100 and their mixture by partitioning in an oil phase (Sarapar147), adsorption to shale and abstraction by multivalent cations (Ca^{++} , Mg^{++}). Surface/interfacial tensions of individual surfactants and their mixture are studied to determine adsorption and micellization properties in presence and absence of an electrolyte (NaCl). Synergism between mixed surfactants is also investigated.

MATERIALS AND METHODS

Materials

Surfactants: Triton X-100 (TX100) extra pure, was purchased from Scharlau Chemie, Spain. Sodium Dodecyl Sulfate (SDS) was obtained from BDH Chemicals Ltd. (Poole, England), with purity of 90%. Electrolyte, Sodium

Chloride (NaCl), used for controlling the ionic strength was purchased from Fisher Scientific with analytical purity (99.98%). Sarapar147, surrogate oil phase was supplied by Kota Minerals and Chemical Sdn. Bhd. (KMC). Sarapar147 is a colourless mineral oil ranging from C14 to C17 and is derived from petroleum crude oil. All chemicals were used as received without further purification. Selected physicochemical properties of the compounds were presented in Table 1.

Rock matrix surrogate: Rock samples were collected from an outcrop of a local shale formation (Batu-Arang, Selangor, Malaysia). The shale comprises of the most adsorbing shale minerals mainly montmorillonite, illite, kaolinite and saturated with both Mg^{++} and Ca^{++} which cause abstraction to anionic surfactants. Rock samples were disintegrated into small pieces by hammer then grounded using rock pulverizer (Fritsch, Germany).

Rock cuttings were air dried for 24 h followed by oven drying at 105°C for 24 h. The difference between the initial and final weights is the moisture content of the shale ($\sim 3.3\%$). Density of shale was determined to be 1.94 g cc^{-1} . Dried rock samples were sieved to obtain particles less than 2 mm and larger than 1mm in all experiments.

Methods: The surfactant solutions were prepared in a standard 1000 mL volumetric flasks. Surfactants were weighed on mass basis and emptied into the volumetric flask then double distilled water was used to complete the solution to the final weight (1 kg). After the preparation of the stock solution, it was diluted to obtain desired concentration.

TX100 and SDS Solutions were prepared at concentrations ranged from 0.0025 to 1 wt% corresponding to molar concentrations of $0.039\text{-}15.47 \text{ mM L}^{-1}$ for TX100 and $0.0867\text{-}34.68 \text{ mM L}^{-1}$ for SDS. Mixed surfactant solutions were prepared by mixing SDS and TX100 solutions of the same weight concentrations with 1:1 volume ratio. This results in a mole fraction of 0.691 SDS in the total mixture. Mixed surfactant solutions were allowed to equilibrate for at least 5 h before any measurements were made.

Surface tension measurements: The surface tension technique was applied to determine the CMC in various combinations of shale and/or surfactant systems. The surface tension measurements were carried out with Krüss tensiometer (Krüss GmbH, Hamburg, Instrum. Nr, K6) using a platinum-iridium ring at constant temperature ($25\pm 1^{\circ}\text{C}$). The tensiometer was calibrated using method described in ASTM Designation: D 1331-89. Surface and interfacial tension measurements were undertaken according to the method described in ASTM Designation: D 1331-89.

Table 1: Physicochemical properties of chemicals

Chemical	Structure/Composition	MW ^a	CMC ^b (mg L ⁻¹ /mM L ⁻¹)	HLB ^c	D ^d (g mL ⁻¹)	BP ^e (°C)
TX100	C ₃₄ H ₆₂ O _x (x-11)	646.37	130-200/0.2-0.31	13.5 [§]	1.070 [#]	270 [#]
SDS	C ₁₂ H ₂₅ NaSO ₄	288.4	963-2420/3.32-8.4	40.0 [§]	0.400 [#]	-
Sarapar147	95wt% n-paraffin and 5wt% iso-paraffin	NA	-	-	0.773 [#]	258-293 [#]
Sodium Chloride	NaCl	58.46	-	-	-	-

^a Molecular Weight, g mol⁻¹; ^b Critical Micelle Concentration; ^c Hydrophile-Lipophile Balance; ^d Density; ^e Boiling Point; [§] Zhou and Zhu (2004); [#] Provided by company; NA = Not Available

Krüss tensiometer operates on the Du Nouy principle, in which a platinum-iridium ring is suspended from a torsion balance and the force (in mN m⁻¹) necessary to pull the ring free from the surface film is measured. Surface tension value was taken when stable reading was obtained for a given surfactant concentration, as indicated by at least three consecutive measurements having nearly the same value. The average of a series of consistent readings for each sample was then corrected to account for the tensiometer configuration, yielding a corrected surface tension value (Zuidema and Waters, 1941). A correction factor, F is multiplied by the average dial reading (pull on the ring in dynes) in order to obtain the corrected value for surface/interfacial tension (ST/IFT). Zuidema and Waters (1941) proposed the following empirical correlation to calculate the correction factor:

$$F = 0.725 + \sqrt{\frac{9.075 \times 10^{-4} (\text{STorIFT})}{\pi^3 \Delta \rho g R^3} - \frac{1.679r}{R} + 0.04534}$$

Where:

- F = the correction factor; R = the radius of the ring, cm;
- r = the radius of the wire of the ring, cm;
- ST/IFT = the apparent value or dial reading, dyne/cm (mN m⁻¹);
- Δρ = the density difference between the lower and upper phases, g cc⁻¹;
- g = acceleration due to gravity, 980 cm sec⁻².

The Equation is applicable only when 0.045 ≤ ΔρgR³/(STorIFT) ≤ 7.5.

Interfacial tension measurements: Equal volume of Sarapar147 and surfactant solution was poured into a glass beaker of diameter 6 cm and the resulting mixture used for the interfacial tension studies. The same procedure used for the surface tension measurement was used for the interfacial tension study except that the balance of the tensiometer reading for zero was checked with the platinum-iridium ring completely immersed in the oil phase and not in the surface or interface of oil-surfactant. The platinum ring was then completely immersed in the surfactant phase before the platform was

gradually adjusted until a force necessary to detach the platinum ring upward from the surfactant-oil interface was exerted.

CMC measurements: The CMC values were obtained through a conventional plot of the surface/interfacial tension versus the logarithm value of the surfactant concentration. The CMC concentration corresponds to the point where the surfactant first shows the lowest surface/interfacial tension. The surface/interfacial tension remains relatively constant after this point.

Adsorption to shale: Adsorption to shale was determined by batch equilibrium adsorption procedure. Ten grams of shale cuttings are added to 60 mL surfactant in a 100 mL glass vials (1:6 w/v ratio) and allowed to equilibrate at 25±1 °C. The vials are then shaken on a gyratory shaker at 100 rpm (wrist orbital shaker) for 3 h and allowed to rest for 16 h. Preliminary experiments indicated that within 3 h-shaking almost all adsorption takes place. Sixteen hours contact time at rest was long enough for equilibrium and complete separation to be obtained. Surfactant sample aliquots are taken for surfactant concentration determination before and after adsorption. All experiments were conducted with 3 replicates at 25±1 °C.

Cloud point measurements: Cloud point measurements were taken for Triton X-100 at two concentration namely, 0.05 and 0.5 wt% in presence of different salt concentrations (0, 2, 4 and 6 wt%). Measurements are also taken for 1:1 TX100- SDS mixture at 0.05 and 0.5 wt% total concentration at different salt concentrations (0, 2, 4 and 6 wt%). The Cloud Point (CP) was taken as the temperature at which the immersed portion of the thermometer suddenly became invisible on heating and fully visible on cooling. For this purpose, the test tubes were placed in a transparent water bath equipped with a control unit which permitted temperature increases at the rates of 5°C min⁻¹. CP measurements were made in triplicate.

RESULTS AND DISCUSSION

Effect of salt on SDS and TX100

Before equilibration with shale: Figure 1 shows the effect of added electrolyte on surface and interfacial tensions of

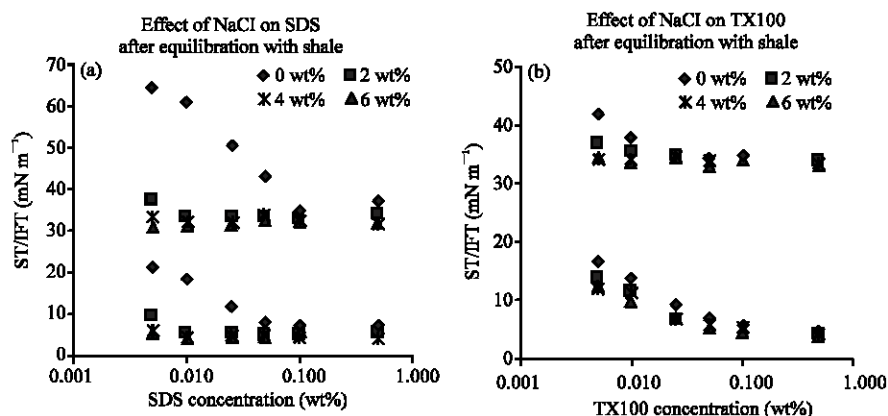


Fig. 1: Surface/interfacial tensions for fresh solutions

SDS and TX100. The upper trends stand for Surface Tensions (STs) while the lower trends stand for interfacial tensions (IFTs). This will be the case for all figures in this paper unless otherwise stated. Surface tension between water and air was measured as 72.57 mN m⁻¹ while interfacial tension between water and Sarapar147 was measured as 29.64 mN m⁻¹. As the surfactant solution is introduced, this value was reduced as shown in Fig. 1. Surface/interfacial tension is concentration dependent, i.e., as the surfactant concentration increases, surface/interfacial tension decreases until the surfactant CMC value is reached and remains constant there afterwards. The CMC of SDS can be estimated from Fig. 1a at 0.1 wt% (3.468 mM L⁻¹) SDS using surface and interfacial trends. The CMC of TX100 is shown from surface tension trend to be at 0.0125 wt% (0.193 mM L⁻¹) TX100 (Fig. 1b). While the CMC was not achieved in presence of Sarapar147 oil until a concentration of 0.07 wt% (1.083 mM L⁻¹) TX100 was reached. CMC of surfactants obtained here were compared with those in literature. CMC of SDS compares well with those reported in Yang *et al.* (2005), Zhu and Feng (2003), Zhou and Zhu (2004, 2006) and Zhao *et al.* (2005).

The CMC value of TX100 obtained by surface tension measurement (0.0125 wt%) was much lower than that obtained by interfacial tension vs. concentration (0.07wt%). The first value was comparable well with values reported in previous published studies. The second value however, was not reported in literature. This is because surface tension technique is often used to determine surfactant CMCs. It is worthy to note that, surface tension technique ignores the effect of oil phase on micellization behavior.

When NaCl salt was added to the systems surface and interfacial tensions has been reduced sufficiently for SDS. The CMC of SDS can now be obtained at a concentration of only 0.005 wt% SDS when 4 and 6 wt%

NaCl was added. As shown in Fig. 1a, reduction in surface and interfacial tension increases with amount of NaCl added until CMC is reached. This result is expected and well documented in literature. Salts tend to screen electrostatic repulsions between head groups and make the surfactant effectively more hydrophobic. This increases hydrophobic interactions among the surfactant monomers and cause them to aggregate at lower concentration, thereby the CMC decreases (Lange, 1999).

The effect on TX100 was not as significant and seems not to alter greatly surface and interfacial tensions. The CMC value has been reduced from 0.0125 wt% TX100 to 0.005 wt% TX100 when 4 and 6 wt% NaCl was added as indicated by surface tension measurements (Fig. 1b). Similarly, CMC value has been reduced from 0.07 to 0.05 wt% TX100 when NaCl was added as indicated by interfacial measurements.

After equilibration with shale: As seen in Fig. 1 and 2, surface/interfacial tension and CMC values for SDS have not been changed before and after equilibration with shale in absence of ionic strength. However, it is clear that salt has loss it significant effect on SDS in presence of shale (Fig. 2a). Nevertheless, salt presence at the lowest concentration of SDS was seen to increase surface and interfacial tension instead. At higher concentration of SDS (0.025 and 0.05 wt%), salt addition resumes it effect and slight reductions in surface and interfacial tensions are shown particularly for 4 and 6 wt% NaCl dosages. It seems that presence of shale has negated salt effects on SDS particularly at lower concentrations of SDS.

Surface and interfacial tensions for TX100 has been increased significantly after equilibration with shale. This indicating a significant loss of TX100 attributed most probably to adsorption to organic matter/clay minerals in shale and partitioning into Sarapar147. The CMC of TX100 as determined by surface tension measurement is

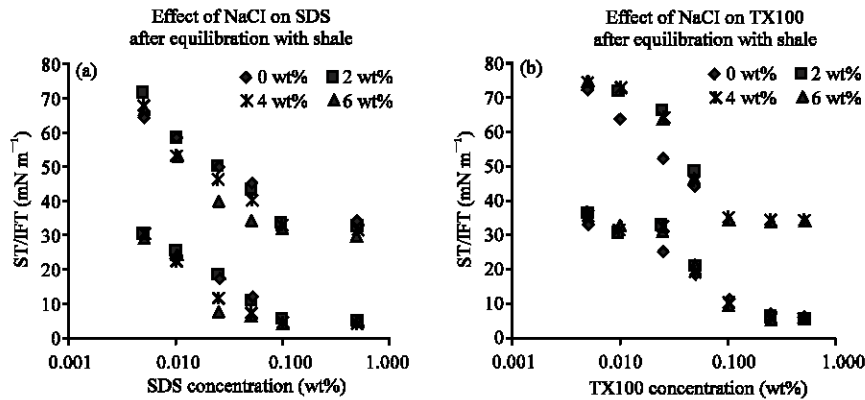


Fig. 2: Surface/interfacial tensions after equilibration with shale

at 0.1 wt%. However, the CMC of TX100 was attained at 0.25 wt% in presence of Sarapar147. This is a perceptible detrimental change in TX100 behavior in presence of oil phase. The result shows that both shale and Sarapar147 are responsible for loss of TX100.

More importantly, is the detrimental effect of salt on surface and interfacial tensions in presence of shale. It seems that salt assisted sorption of TX100 to shale. This is in agreement with previous results (Verkruijse and Salter, 1985; Lewis *et al.*, 1986; Travalloni-Louvisse and Gonzalez, 1988). It expected that salt has lowered the cloud point of TX100. It has been previously shown that adsorption of nonionic surfactants, at a given temperature, depends on the difference between this temperature and the cloud point of the surfactant at the same conditions (Verkruijse and Salter, 1985; Lewis *et al.*, 1986; Travalloni-Louvisse and Gonzalez, 1988). Presence of salt was found to reduce greatly the cloud point of nonionic surfactant. Accordingly, the cloud point of TX100 as a function of salt has been determined and shown in Fig. 3.

It has been clear that addition of salt has lowered the cloud point of TX100. The effect seems linear, with the greater effect on higher concentration. The CMCs of SDS have not been notably changed before and after equilibration with shale in presence and absence of salt. This indicates a minor loss of this surfactant either as sorption or precipitation to divalent-cations rich shale. In contrast, the CMC value of TX100 has been shifted to higher concentrations. The surfactant was adsorbed heavily to shale and salt was seen to assist adsorption by lowering the cloud point of TX100 particularly in the pre CMC region.

Effect of salt on SDS-TX100 mixture

Before equilibration with shale: Figure 4 shows the surface/interfacial tension curves as total surfactant

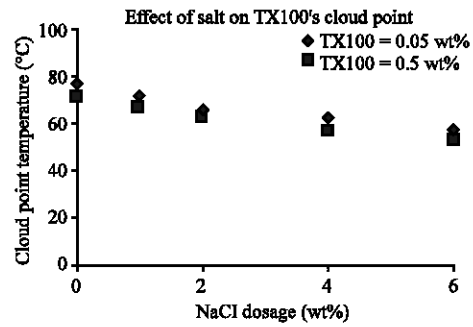


Fig. 3: Effect of salt on TX100 cloud point

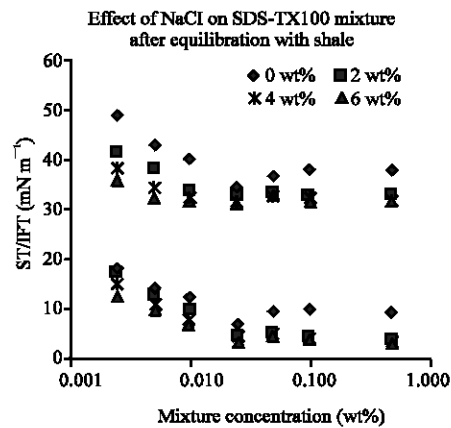


Fig. 4: Mixing effects before equilibration with shale

concentration for the mixed SDS-TX100 system in which the molar fraction of SDS was 0.691 and the salt dosage added ranged from 0 to 6 wt%. The surface/interfacial tensions decreased with increasing total surfactant concentration and added salt. Each surface/interfacial tension curve had a breaking point that was taken as the mixed CMC.

The effect of salt was more pronounced for surface tension trends and the CMC has been reduced from 0.025 to 0.01 wt% when 2 and 4 wt% salt has been added. Further decrease in CMC value has been found when the salt dosage was 6 wt%, the CMC has been reduced to 0.005 wt%. Similar reductions in interfacial values were found, however, the CMC value exhibits no change with addition of salt dosages and remained constant at 0.025 wt%. This may be explained by loss of TX100 concentration to the Sarapar147 oil phase which affects total mixture concentration and behavior.

Compared to individual surfactants (Fig. 1), the mixture shows better performance in surface/interfacial and micellization behaviours than stand alone surfactants. It is clear that presence of both surfactants form mixed micelles which behave differently from individual surfactants.

After equilibration with shale: Figure 5 depicts surface/interfacial tension curves of SDS-TX100 mixture in presence and absence of salt after equilibration with shale. It is obvious that the mixture at all salt dosages show a superior behavior than in absence of salt. Both surface and interfacial trends are similar. Different salt dosages have a much similar effect. CMC value was seen to decrease from 0.1 in absence of salt to 0.025 in presence of salt.

Compared to individual surfactants (Fig. 2), the SDS-TX100 mixture in absence of salt performed similar in micellization and sorption behavior to SDS. The mixture however, out performs interfacial, micellization and sorption behavior of TX100. In presence of salt the mixture was superior to individual ones nearly in all aspects. This result attributed in part to the mixed micelle formation. One possible reason behind this result is the enhanced behavior of TX100 in presence of anionic surfactant (SDS) which is expected to retard decreased cloud point of TX100 caused by salt addition. An overall improvement was seen in the behavior of the mixture. To investigate this part further, cloud point temperatures of SDS-TX100 mixture at concentrations of 0.05 and 0.5 wt% in presence of 2, 4 and 6 wt% salt were measured. The cloud point was increased significantly in presence of SDS and was not possible to measure below 100°C unless for 0.5 mixture at 6 wt% NaCl (cloud point = 75°C). Sodium chloride does not affect the cloud point of TX100 until a very high concentration of it is built up in the system. This is in agreement with literature (for example, Al-Ghamdi and Nasr-El-Din, 1997; Goell, 1999). Anionic surfactants form mixed micelles with nonionics and increase the charge repulsion between micelles, thus leading to their stabilization (Goell, 1999). This result

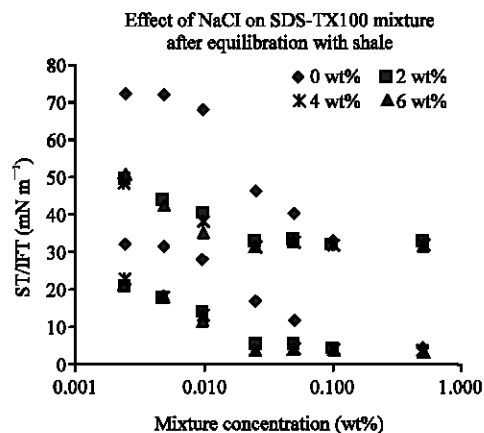


Fig. 5: Mixing effects after equilibration with shale

increased solubility of nonionic surfactant at a given temperature or equivalently, an increase in the cloud point of nonionic solution with a fixed concentration is obtained.

Synergism: Surface/interfacial tension measurements and nonideal solution theory have been used to investigate the micelle formation of mixed nonionic-anionic surfactants and the degree of synergism or antagonism. In an ideal mixed system, the ideal CMC of mixed surfactant solutions at any mole ratio of SDS to TX100 can be predicted with ideal solution theory (Rosen, 2004).

$$\frac{1}{\text{CMC}_{\text{ideal}}} = \frac{\alpha}{\text{CMC}_{\text{TX}}} + \frac{1-\alpha}{\text{CMC}_{\text{SDS}}} \quad (1)$$

Where α is the mole fraction of TX100 in the mixed solutions and thus $1-\alpha$ is the mole fraction of SDS. Due to the interaction between TX100 and SDS in mixed solutions, the experimental CMC of a mixed surfactant solution (CMC_{exp}) is always different from $\text{CMC}_{\text{ideal}}$. According to nonideal solution theory of Rubingh (1979), the deviation of CMC_{exp} from $\text{CMC}_{\text{ideal}}$ can be represented by the parameter β , which also represents the interaction between TX100 and SDS in mixed solutions. The more negative β value of the mixed system indicates the stronger attraction and synergism between the TX100 and SDS. Synergism in mixed micelle formation exists when the CMC of a mixture is less than that of individual surfactants. The conditions for synergism to exist in the mixture are as follows: (a) β must be negative; (b) $|\beta| > \left| \ln(\text{CMC}_{\text{TX}}^M / \text{CMC}_{\text{SDS}}^M) \right|$ (Rosen, 2004). A negative value of β , indicates synergism in mixed micelle formation. A positive value indicates antagonism and if $\beta = 0$ then mixed micelle formation is ideal. β can be calculated as follows (Rosen, 2004):

$$\beta = \frac{\ln((\alpha CMC_{exp}) / (X_{TX}^M CMC_{TX}))}{(1 - X_{TX}^M)^2} \quad (2)$$

where X_{TX}^M is the mole fraction of TX100 in the total surfactant in the mixed micelles.

X_{TX}^M can be determined from a relationship derived by Rubingh (1979):

$$1 = \frac{(X_{TX}^M)^2 \ln((\alpha CMC_{exp}) / (X_{TX}^M CMC_{TX}))}{(1 - X_{TX}^M)^2 \ln(((1 - \alpha) CMC_{exp}) / ((1 - X_{TX}^M) CMC_{SDS}))}$$

Rubingh equation was solved it relatively to obtain the value of X_{TX}^M , from which the interaction parameter β was evaluated using Eq. 2.

CMC_{TX}^M and CMC_{SDS}^M are calculated from the following relationships:

$$CMC_{TX}^M = X_{TX}^M CMC^* \text{ and } CMC_{SDS}^M = X_{SDS}^M CMC^*$$

$$\frac{1}{CMC^*} = \frac{\alpha}{f_{TX} CMC_{TX}} + \frac{1 - \alpha}{f_{SDS} CMC_{SDS}}; \quad f_{TX} = \exp[\beta(1 - X_{TX}^M)^2]$$

$$\text{and } f_{SDS} = \exp[\beta(1 - X_{SDS}^M)^2]$$

Using surface tension data: SDS-TX100 mixture CMCs at different salt dosages are either equal or lower to those obtained from ideal mixing theory as indicated in Table 2 (A). Hence synergism is missing with respect to critical micelle concentration in presence and absence of salt. However, after equilibration with shale salt addition assisted mixed micellization at lower concentration and hence synergism was found as the experimental CMCs were lower than ideal CMCs (Table 2B). β -values are negative and the synergism is stronger after equilibration with shale (Table 3).

Using interfacial tension data: Before equilibration with shale, SDS-TX100 mixture CMC in absence of salt is lower than that obtained from ideal mixing theory (Table 4A). When 2 wt% salt was added to the surfactant mixture, dramatic improvement in CMC of SDS was realized (from 0.1 to 0.01 wt%). Corresponding, reduction in CMC of SDS-TX100 mixture as obtained from ideal mixing theory

Table 2: CMCs obtained from ST measurements
A: Before equilibration with shale

NaCl (wt%)	Mole fraction		CMC			
			Experimental		Ideal	
	α (TX100)	$1 - \alpha$ (SDS)	wt%	mM L ⁻¹	wt%	mM L ⁻¹
0	1	0	0.0125	0.193	0.0125	0.193
	0.31	0.69	0.025	0.627	0.032	0.557
	0	1	0.1	3.468	0.1	3.468
2	1	0	0.01	0.155	0.01	0.155
	0.31	0.69	0.01	0.251	0.01	0.251
	0	1	0.01	0.347	0.01	0.347
4	1	0	0.005	0.077	0.005	0.077
	0.31	0.69	0.01	0.251	0.005	0.125
	0	1	0.005	0.173	0.005	0.173
6	1	0	0.005	0.077	0.005	0.077
	0.31	0.69	0.005	0.125	0.005	0.125
	0	1	0.005	0.173	0.005	0.173

B: After equilibration with shale

NaCl (wt%)	Mole fraction		CMC			
			Experimental		Ideal	
	α (TX100)	$1 - \alpha$ (SDS)	wt%	mM L ⁻¹	wt%	mM L ⁻¹
0	1	0	0.1	1.547	0.1	1.547
	0.31	0.69	0.1	2.507	0.1	2.507
	0	1	0.1	3.468	0.1	3.468
2	1	0	0.1	1.547	0.1	1.547
	0.31	0.69	0.025	0.627	0.1	2.507
	0	1	0.1	3.468	0.1	3.468
4	1	0	0.1	1.547	0.1	1.547
	0.31	0.69	0.025	0.627	0.1	2.507
	0	1	0.1	3.468	0.1	3.468
6	1	0	0.1	1.547	0.1	1.547
	0.31	0.69	0.025	0.627	0.1	2.507
	0	1	0.1	3.468	0.1	3.468

Table 3: Synergism parameters from ST data

After equilibration with shale

NaCl (wt%)	X_{TX}^M	X_{SDS}^M	β	f_{TX}	f_{SDS}	CMC*	CMC ^M _{TX}	CMC ^M _{SDS}	$ \ln(CMC_{TX}^M/CMC_{SDS}^M) $
0	NA	NA	NA	NA	NA	NA	NA	NA	NA
2	0.500	0.500	-5.545	0.250	0.250	0.535	0.267	0.267	0
4	0.500	0.500	-5.545	0.250	0.250	0.535	0.267	0.267	0
6	0.500	0.500	-5.545	0.250	0.250	0.535	0.267	0.267	0

Table 4: CMCs obtained from IFT measurements

A: Before equilibration with shale

NaCl (wt%)	Mole fraction		CMC			
			Experimental		Ideal	
	α (TX100)	1- α (SDS)	wt%	mM L ⁻¹	wt%	mM L ⁻¹
0	1	0	0.07	1.083	0.07	1.083
	0.31	0.69	0.02	0.501	0.088	2.065
	0	1	0.1	3.468	0.1	3.468
2	1	0	0.05	0.774	0.05	0.774
	0.31	0.69	0.025	0.627	0.013	0.418
	0	1	0.01	0.347	0.01	0.347
4	1	0	0.05	0.774	0.05	0.774
	0.31	0.69	0.025	0.627	0.007	0.228
	0	1	0.005	0.173	0.005	0.173
6	1	0	0.05	0.774	0.05	0.774
	0.31	0.69	0.025	0.627	0.007	0.228
	0	1	0.005	0.173	0.005	0.173

B: After equilibration with shale

NaCl (wt%)	Mole fraction		CMC			
			Experimental		Ideal	
	α (TX100)	1- α (SDS)	wt%	mM L ⁻¹	wt%	mM L ⁻¹
0	1	0	0.25	3.868	0.25	3.868
	0.31	0.69	0.1	2.507	0.123	3.582
	0	1	0.1	3.468	0.1	3.468
2	1	0	0.1	1.547	0.1	1.547
	0.31	0.69	0.025	0.627	0.1	2.507
	0	1	0.1	3.468	0.1	3.468
4	1	0	0.1	1.547	0.1	1.547
	0.31	0.69	0.025	0.627	0.1	2.507
	0	1	0.1	3.468	0.1	3.468
6	1	0	0.1	1.547	0.1	1.547
	0.31	0.69	0.025	0.627	0.1	2.507
	0	1	0.1	3.468	0.1	3.468

Table 5: Synergism parameters from IFT data

A: Before equilibration with shale

NaCl (wt%)	X_{TX}^M	X_{SDS}^M	β	f_{TX}	f_{SDS}	CMC*	CMC ^M _{TX}	CMC ^M _{SDS}	$ \ln(CMC_{TX}^M/CMC_{SDS}^M) $
0	0.524	0.476	-5.736	0.273	0.207	0.525	0.275	0.250	0.096

B: After Equilibration with Shale

NaCl (wt%)	X_{TX}^M	X_{SDS}^M	β	f_{TX}	f_{SDS}	CMC*	CMC ^M _{TX}	CMC ^M _{SDS}	$ \ln(CMC_{TX}^M/CMC_{SDS}^M) $
0	0.375	0.625	-1.609	0.533	0.797	1.470	0.605	0.677	0.511
2	0.501	0.499	-5.575	0.250	0.247	0.532	0.266	0.265	0.004
4	0.501	0.499	-5.575	0.250	0.247	0.532	0.266	0.265	0.004
6	0.501	0.499	-5.575	0.250	0.247	0.532	0.266	0.265	0.004

was shown (from 0.088 to 0.013 wt%). At this salt dosage, the experimental CMC of mixture was higher than the ideal CMC. As the salt dosage was increased to 4 and 6 wt%, further decrease in CMC of SDS was obtained

accompanied by a further decrease in CMC of mixture as obtained by ideal mixing theory. The experimental mixture CMCs, however, do not show any reduction than that obtained in absence of salt. Hence, synergism of the

mixture was only shown in absence of salt. β values are negative for this case and are shown in Table 5A. The activity coefficients f_{TX} and f_{SDS} are obviously less than unity in absence of salt. As shown in the Table 5A, the condition of synergism in CMC is fulfilled. After equilibration with shale, all the systems showed synergism in presence and absence of salt (Table 4B). The experimental CMCs of mixture are similar at all salt dosages (0.025 wt%). Ideal CMCs of mixture are also similar at all salt dosages (0.1 wt%). The CMC of SDS do not experienced any change with salt addition, however, it is the TX100 CMC which has been lowered (0.25 to 0.1 wt%).

CONCLUSION

Behavior of individual surfactants widely differs from their respective mixture. Furthermore, individual surfactants and their mixture behave differently in presence and absence of salt, shale and oil phase. Therefore, it is stressed here to do a pre-investigation and screening of surfactants at all possible conditions that will be met in real application. With respect to addition of salt, results obtained in this study showed that addition of salt in SDS-TX100 mixture resulted in superior behavior of mixture than in absence of it, particularly after equilibration with shale. Experimental mixture CMCs obtained from surface/interfacial tensions data are similar (0.025 wt%) and were far lower than those of ideal mixing theory (0.1 wt%). For this reason strong synergism was found where $\beta = -5.575$.

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