

ISSN 1996-3343

Asian Journal of
Applied
Sciences

Investigating Synergism in Critical Micelle Concentration of Anionic-Nonionic Surfactant Mixtures: Surface Versus Interfacial Tension Techniques

¹Mazen Ahmed Muherei and ²Radzuan Junin

¹ Department of Petroleum Engineering, Faculty of Engineering,
Hadhramout University for Science and Technology (HUST),
50511 Mukalla, Yemen

²Department of Petroleum Engineering, FKKKSA, UTM,
81310 Skudai, Johor, Malaysia

Abstract: In this research, anionic (SDS) and nonionic (TX100) surfactant mixtures (1:2, 1:1, 2:1; TX100: SDS mass ratios) were evaluated for possible synergism in Critical Micelle Concentration (CMC). Synergism of both surfactants was sought in presence of shale and/or oil phase. The composition of mixed micelles and the interaction parameter, α evaluated from the CMC data obtained by both Surface Tension (ST) and Interfacial Tension (IFT) for different systems using Rubingh's theory were discussed. Both techniques give comparable conclusions regarding synergism in CMC. However, using IFTs to determine CMCs before and after equilibration with shale showed greater losses of nonionic surfactant than using ST technique. For the interfacial tension data, β -values ranges from -5.803 to -5.917 before equilibration with shale and from -1.286 to -2.045 after equilibration with shale for the mixtures with TX100 mole fractions of 0.18 and 0.47, respectively. This result suggested that synergism was always stronger before equilibration with shale and/or contact with oil phase. Among the mixtures studied, the mixture with higher TX100 mole ratio exhibit more synergism than others. This is particularly true after equilibration with shale and/or contact with oil phase pointing out to the role, the losses of TX100 may have on synergism of TX100-SDS mixtures.

Key words: Surfactant, CMC, adsorption, partition, mixed surfactants

INTRODUCTION

The use of surfactants to decontaminate groundwater aquifers, enhance residual oil recovery and in soil-clean up operations is well established and both anionic and nonionic surfactants have been used to remediate land polluted with oils and hydrocarbons as well as many other organic contaminants. A fundamental property of surfactants is their ability to form micelles (colloidal sized clusters) in solution. This property is due to the presence of both hydrophobic and hydrophilic groups in each surfactant molecule. It is the formation of micelles in solution which gives surfactants their excellent detergency and solubilization properties. Hence, the most important parameter in terms of the ability of a surfactant to mobilize or solubilize hydrophobic contaminants in contaminated soil is the surfactant Critical Micelle Concentration (CMC). In general, concentrations of surfactant in soil-water below the CMC have little or no effect on solubilization of hydrophobic materials. Only when micelles are present does significant desorption of such pollutants from soil surfaces occur (Haigh, 1996).

Corresponding Author: Mazen Ahmed Muherei, Department of Petroleum Engineering, Faculty of Engineering, Hadhramout University for Science and Technology (HUST), 50511, Mukalla, Yemen
Tel: 009675303320

Nonionic surfactants are often used because of their lower CMCs as compared to ionic surfactants, their higher degree of surface-tension reduction and their relatively constant properties in the presence of salt, which result in better performance and lower concentration requirements. In particular, the non-ionic ethoxylate surfactants have been suggested for the removal of organic contaminants from soil because of their high solubilization capacity and biodegradability (Paria and Yuet, 2007). However, some concerns with these surfactants are their significant loss to soil and partitioning to organic phase during practical applications (Zhao *et al.*, 2006, 2007). Nevertheless, under some conditions, usually at concentration well below CMC, the adsorption of these surfactants to soil can enhance the adsorption of hydrophobic contaminants to soil. This has been attributed to partition of hydrophobic contaminants into surfactant hemi-micelle formed on soil surface (Edwards *et al.*, 1994; Sun *et al.*, 1995; Haigh, 1996).

Anionic surfactant on the other hand, sorb less to soil but they form micelles at higher concentrations in aqueous solutions than nonionic surfactants with an equivalent hydrophobic group (Rosen, 2004) and are more prone to precipitate in presence of multivalent cations (Ca^{++} , Mg^{++}). Substantial loss of surfactant by such mechanisms will definitely reduce their active concentration in aqueous solution, which would greatly reduce the surfactant solubilization and flushing efficiency.

The interaction between surfactants in mixtures can produce marked interfacial effects due to change in adsorption as well as in the charge density of the surface. In most cases, when different types of surfactants are purposely mixed, what is sought is synergism, i.e., the condition when the properties of the mixture are better than those attainable with the individual components by themselves. Surfactant mixtures of practical interest include like-charge surfactants, for instance mixtures of anionic surfactants, or mixtures of cationic surfactants, but the more common case involves mixture of ionic and nonionic surfactants (Wang and Kwak, 1999). Mixing of cationic and anionic surfactants often tends to form precipitates (Joshi *et al.*, 2005; Zhang and Somasundaran, 2006), consequently they are of no practical value. Similarly, mixtures of nonionic surfactants tend to behave ideally (Joshi *et al.*, 2005).

A typical feature of the adsorption of ionic (anionic/cationic)-nonionic mixtures is the synergy or anti-synergism (antagonism) at interfaces. For example, the adsorption of one surfactant is either enhanced or retarded by the addition of a small amount of the other surfactant. Furthermore, mixing anionic and nonionic surfactants may raise or lower the CMC from that obtained by ideal mixing.

This study deals with an experimental study on the interaction and micellization of nonionic surfactant, Triton X 100 (TX100), with anionic surfactant, Sodium Dodecyl Sulphate (SDS). The CMC values of the corresponding binary mixtures in the whole range of composition were obtained by both surface and interfacial tension and then the result have been analyzed in terms of interaction parameter, β , using Rubingh's regular solution theory.

Surfactant binary mixtures of nonionic surfactant, TX100 and anionic surfactant, SDS or SDBS (sodium dodecylbenzene sulfonate) have been studied (Janczuk *et al.*, 1995; Zhu and Feng, 2003; Zhou and Zhu, 2004; Owoyomi *et al.*, 2005; Zhao *et al.*, 2005; Joshi *et al.*, 2005; Yang *et al.*, 2005; Zhao *et al.*, 2006, 2007). The Critical Micelle Concentrations (CMCs) of mixed surfactants were sharply lower than that of sole anionic surfactant (SDS or SDBS). With the increase in mole fraction of TX100, the CMCs decrease continuously from the CMC of pure SDS/SDBS down to the CMC of pure TX100. Furthermore, the experimental CMCs were lower than the ideal CMCs. It is noteworthy however, to point out that the CMC measurements and synergism calculations in these studies were taken from surface tension measurements.

Recently, mixed surfactant was found superior to the relevant single ones mainly due to the reduction in nonionic surfactant partition and/or sorption to soil as well as the high solubilization capacity of the mixture. Yang *et al.* (2005) showed that the amounts of both TX100 and 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 oil phase was found to decrease if the amount of SDBS increased (Zhao *et al.*, 2006, 2007). Decreasing loss of surfactant due to partitioning and/or sorption and the greater apparent solubilization of the mixture will reduce surfactants volumes needed and thus the capital expenditure and operation cost (Zhao and Zhu, 2006).

Since, TX100 is the surfactant with the lower CMC its contribution in the mixed micelle formation is important, particularly if its composition in the aqueous phase is lower than the other surfactant with the large CMC (ex. SDS). It is expected that probable loss of TX100 monomers in aqueous phase solution upon equilibrium with soil (through adsorption mechanism) or in presence of oil phase (through partition mechanism) will affect greatly the degree of synergism in mixed micelle formation and may render the mixture exhibiting less synergism.

Accordingly, it becomes important to investigate whether the synergism of both surfactants still holds after equilibration with soil and/or contact with oil phase. In this study, it is intended to use CMCs as measured from interfacial tension trends to probe the state of interaction after equilibration with soil and/or contact with oil phase. Comparison with CMCs measured with surface tension trends is provided.

MATERIALS AND METHODS

Surfactants

Triton X-100 (TX100) extra pure, was purchased from Scharlau Chemie, Spain. Sodium Dodecyl Sulfate (SDS) was obtained from Merck with a high grade of purity (99%). The oil, Sarapar147, 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 are presented in Table 1.

Soil Surrogate Samples

Samples were collected from an outcrop of a local shale formation (Batu Arang, Selangor, Malaysia). Rock samples were disintegrated into small pieces by a jaw crusher and then ground using rock pulverizer (Fritsch, Germany). Rock samples were air dried for 24 h followed by oven drying at 105°C for 24 h. The density of shale was measured as 2.1 g cc⁻¹ using a calibrated 50 mL pycnometer. Dried rock samples were sieved to obtain particles less than 2 mm and larger than 1 mm in all experiments.

Preparation of Surfactant Solutions

The surfactant solutions were prepared in a standard 1000 mL volumetric flasks. Surfactants were weighed on mass basis and emptied into the volumetric flask and 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.

Table 1: Physicochemical properties of chemicals

Chemical	Structure/ composition	MW ^a (g mol ⁻¹)	CMC ^b (mg L ⁻¹ , mM L ⁻¹)	HLB ^c	D ^d (g mL ⁻¹)	BP ^e (°C)
TX100	C ₂₄ H ₄₂ O _x (x-11)	646.37	130-200 (0.2-0.31)	13.5 [§]	1.070 [#]	270 [#]
SDS	C ₁₂ H ₂₄ NaSO ₄	288.4	963-2420 (3.32-8.4)	40 [§]	0.400 [#]	-
Sarapar147	95wt.% n-paraffin and 5wt.% iso-paraffin	NA	-	-	0.773 [#]	258-293 [#]

^aMolecular weight, ^bCritical micelle concentration, ^cHydrophile-lipophile balance, ^dDensity, ^eBoiling point, [§]Zhou and Zhu (2004), [#]Provided by company; NA: Not Available

TX100 and SDS solutions were prepared at concentrations ranges from 0.0025 to 1 wt.% corresponding to molar concentrations of 0.039-15.47 mM for TX100 and 0.0867-34.68 mM for SDS. Mixed surfactant solutions were prepared by mixing SDS and TX100 solutions of the same weight concentrations with different volume ratios (1:2, 1:1 and 2:1 SDS:TX100). This results in a mole fraction of TX100 in the total mixtures of 0.47, 0.31 and 0.18, respectively. 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, Instrument 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: D1331-89. Surface and interfacial tension measurements were undertaken according to the method described in ASTM Designation: D1331-89.

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.

Interfacial Tension Measurements

Equal volume (15 mL) of Sarapar147 and surfactant solution was poured into a glass beaker of 6 cm diameter 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 surfactant solution phase and not in the surface or interface of Sarapar147-surfactant. Hence, the platinum ring must be completely immersed in the surfactant phase before the platform is gradually adjusted until a force necessary to detach the platinum ring upward from the surfactant-oil interface is exerted.

CMC Measurements

The CMC values were obtained through a conventional plot of the surface/interfacial tension versus 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 isotherms were determined by batch equilibrium adsorption procedures. Ten gram of shale were added to a set of 60 mL surfactant solutions (surfactant initial concentrations spans from 0.0025 to 1 wt.%) in a 100 mL glass vials (1:6 v/v ratio) and allowed to equilibrate at $25\pm 1^\circ\text{C}$. The surfactant solution-to-soil ratio was designated as 6:1 (v/w) to reach the optimal washing performance (Chu and Chan, 2003; Urum and Pekdemir, 2004). The vials were then agitated on a gyratory shaker at 100 rpm (wrist orbital shaker) for 3 h and allowed to rest for 16 h. Surfactant sample aliquots were taken for surfactant concentration determination before and after adsorption. To determine the maximum sorption of surfactants into shale, a surface/interfacial tension method was used. Each adsorption experiment involved 10 batch test samples in 100 mL glass vials. The amount of surfactant

adsorbed and/or abstracted was computed from the difference of CMC values before and after adsorption. All experiments were conducted with 3 replicates at 25±1°C and means of three replicates were used.

RESULTS AND DISCUSSION

Theory of Mixed Micelles

Surface tension measurements and Rubingh's regular solution theory have been proven to be remarkably successful in expressing the characteristics of mixed surfactant solutions used to investigate the micelle formation of mixed nonionic-anionic surfactants. The condition for synergism in surface tension reduction efficiency is fulfilled when the total concentration of the mixed surfactant required to reduce the surface tension of the system to a given value is less than that of either individual surfactant. Rosen (1986) have reached similar analogous equations for the presence of another hydrocarbon liquid, i.e., use of interfacial tension trends for CMC measurement and examination of synergism in mixed monolayer and mixed micelle formation.

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 among the mixture. The conditions for synergism to exist in the mixture are as follows: (a) β must be negative; (b) $|\beta| > |\ln(\text{CMC}_{\text{TX}}/\text{CMC}_{\text{SDS}})|$ (Rosen, 2004; Zhou and Zhu, 2005; Rosen, 1986; Rubingh, 1979). 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 (Rubingh, 1979):

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

where, X_{TX}^{M} is the mole fraction of TX100 in the total surfactant in the mixed micelles and can be determined from the following relationship which was derived by Rubingh (1979):

$$1 = \frac{(X_{\text{TX}}^{\text{M}})^2 \ln((\alpha \text{CMC}_{\text{exp}})/(X_{\text{TX}}^{\text{M}} \text{CMC}_{\text{TX}}))}{(1 - X_{\text{TX}}^{\text{M}})^2 \ln(((1 - \alpha) \text{CMC}_{\text{exp}})/((1 - X_{\text{TX}}^{\text{M}}) \text{CMC}_{\text{SDS}}))} \quad (3)$$

Rubingh's equation was solved iteratively to obtain the value of X_{TX}^{M} , from which the interaction parameter \hat{a} was evaluated using Eq. 2. Therefore, according to Rubingh's regular solution theory for mixed micelles, the mixed CMC (CMC^*) for TX100+SDS systems obtained by mixing the surfactants can be estimated from the following equations:

$$\frac{1}{\text{CMC}^*} = \frac{\alpha}{f_{\text{TX}} \text{CMC}_{\text{TX}}} + \frac{1-\alpha}{f_{\text{SDS}} \text{CMC}_{\text{SDS}}} \quad (4)$$

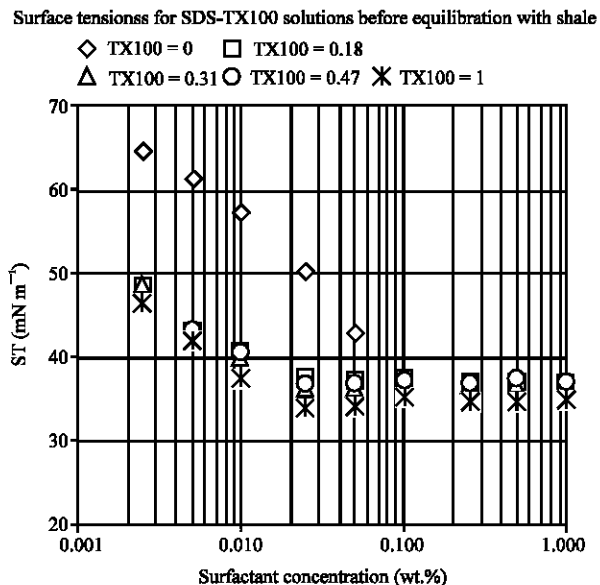


Fig. 1: Mixing effect on CMCs before equilibration with shale

$$f_{TX} = \exp[\beta(1 - X_{TX}^M)^2] \text{ and } f_{SDS} = \exp[\beta(1 - X_{SDS}^M)^2] \quad (5)$$

where, f_{TX} and f_{SDS} are the activity coefficients of surfactants in mixed micelle. In case of ideal behaviour, $f_{TX} = f_{SDS} = 1$ and hence Eq. 4 reduces to Eq. 1.

Evaluating Synergism Using Surface Tension Data Before Equilibration with Shale

Figure 1 shows surface tension trends (STs) and depicts the surface tension curves as total surfactant concentration for the mixed SDS-TX100 system in which the molar fractions of TX100 were 0, 0.18, 0.31, 0.47 and 1, respectively. The two outer surface tension curves are for the pure components. Surface tension between water and air was measured as 73 mN m^{-1} . As the surfactant solution is introduced, this value was reduced as shown in Fig. 1. Surface tension is concentration dependent, i.e., as the surfactant concentration increases, surface tension decreases until the surfactant CMC value is reached and remains constant there after wards. CMC of pure surfactants obtained were compared with those in literature. CMC values of SDS obtained from both surface tensions vs. concentration are similar at 0.1 wt.% (3.468 mM L^{-1} or 1000 mg L^{-1}). CMC of SDS compares well with those reported by Zhu and Feng (2003), Zhou and Zhu (2004, 2007) and Zhao *et al.* (2005).

The CMC value of TX100 obtained by surface tension measurements was about 0.025 wt.%, much lower than that obtained by SDS. This value is comparable well with values reported in previous published studies (Zhu and Feng, 2003; Zhou and Zhu, 2004, 2007; Zhao *et al.*, 2005).

This is because anionic surfactants normally possess higher CMCs than nonionic surfactants. For nonionic surfactants, aggregation or micellization is mainly due to hydrophobic interaction among hydrocarbon chains. This is more feasible because the hydrophobic groups are easily separated from the aqueous environment, whereas for ionic surfactants, high concentrations are necessary to overcome the electrostatic repulsion between ionic head groups during aggregation (Joshi *et al.*, 2005).

Table 2: Synergism data for surfactants before equilibration with shale

Mole fraction		CMC					
		Experimental		Ideal			
α (TX100)	$1-\alpha$ (SDS)	wt.%	mM L ⁻¹	wt.%	mM L ⁻¹		
(A) CMCs obtained from ST measurements							
1	0.00	0.025	0.387	0.025	0.387		
0.47	0.53	0.025	0.547	0.041	0.906		
0.31	0.69	0.025	0.627	0.052	1.302		
0.18	0.82	0.025	0.707	0.065	1.828		
0	1.00	0.100	3.468	0.100	3.468		
(B) Synergism parameters from ST data							
α TX100	X_{TX}^M	X_{SDS}^M	β	f_{TX}	f_{SDS}	CMC*	$ \ln(CMC_{TX}/CMC_{SDS}) $
Before equilibration with shale							
0.47	0.7501	0.2499	-1.888	0.8888	0.3456	0.5517	2.1934
0.31	0.6585	0.3415	-2.361	0.7593	0.3592	0.6228	2.1934
0.18	0.5684	0.4316	-2.865	0.5864	0.3963	0.7148	2.1934

Referring to Fig. 1, there is neither surface tension value nor CMC value for the mixture lower than that obtained by TX100. This is in agreement with Mata (2006), Janczuk *et al.* (1995) and Paria *et al.* (2003). The critical micelle concentrations of mixed surfactants are lower than that of sole SDS and very close to that of pure TX100. In this respect, this experimental results for fresh solutions agrees with those observed by Mata (2006), who found a decrease in CMC of mixture with increase in mole fraction of TX100, however, the CMC of the mixed system at any composition could not be reduced than that of pure TX100.

Data for all systems obtained from the surface tension measurements are shown in Table 2 along with interaction parameters. It can be said that before equilibration with shale, synergism was found between all mixtures (Table 2). As shown in Table 2A the experimental CMCs for mixtures are lower than those obtained by ideal mixing. β -values are negative as shown in Table 2B showing interaction between mixed surfactants. As mentioned before, the β -values demonstrate the extent of interaction between the two surfactants, which leads to deviation from the ideal behaviour. The larger the value of β , the stronger the mixing nonideality and the corresponding synergism.

Therefore, a bit stronger synergism is found for the lower TX100 mole fraction mixture as indicated in Table 2B. Yang *et al.* (2005) studied synergism of TX100 and SDBS at comparable mass ratios and found an opposite trend, i.e. the interaction increases with increasing the mass ratio of nonionic surfactant to anionic. At TX100:SDBS mass ratios of 3:7, 5:5 and 7:3, Yang *et al.* (2005) found respective interaction parameters of -2.93, -3.14 and -3.67. Zhao *et al.* (2006) studied the same surfactants at the same mass ratios and found interaction parameter values of -3.03, -2.89 and -3.35, respectively which do not follow the same trend. Mata (2006) found the interaction parameter for TX100 mole fractions of 5, 2 and 1 in the solution mixture to be -3.97, -4.22 and -3.10, respectively. Generally, the synergistic behavior can be explained assuming that in the mixed micelle ethoxylated chains of the nonionic surfactant coil around the charged head groups of the anionic surfactant, screening the electrostatic repulsions and thereby favoring micelle formation resulting in lower CMCs (Joshi *et al.*, 2005).

The calculated values of the mole fraction of surfactants in the mixed micelle (X_{TX}^M, X_{SDS}^M) at different mole fractions in the bulk (α) are recorded in Table 2B. A marked deviation from the ideal behavior can be observed. For all the mixed systems, α TX100 and X_{TX}^M are found to be different. The mole fraction of TX100 in mixed micelle, X_{TX}^M are always higher and reveal that the contribution of nonionic surfactant, TX100, is significant in the mixed micelle compared to that of anionic, SDS, surfactant.

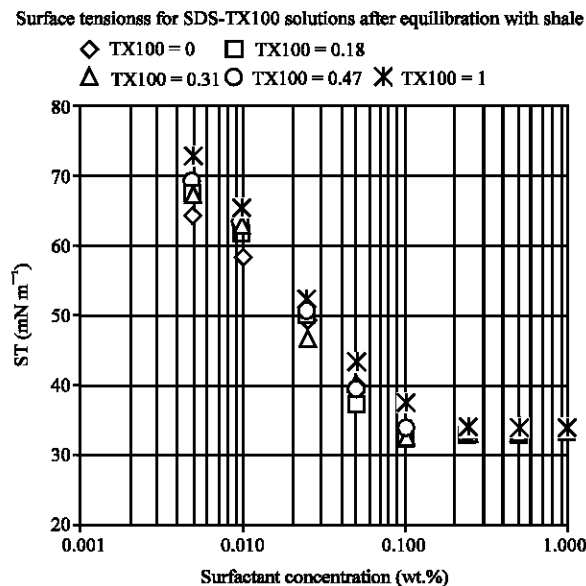


Fig. 2: Mixing effect on CMCs after equilibration with shale

The activity coefficient f_{TX} and f_{SDS} are also shown in Table 2B. As mentioned earlier, the activity coefficient shows the effect and contribution of individual component in mixed micelles, hence necessary to be calculated. The much lower mole fraction (X_{SDS}^M) of SDS is reflected in its small activity coefficient (f_{SDS}) values, which suggests that SDS in the mixed micelle is far away from its standard state. The (f_{TX}) values of TX100 are obviously higher (closer to unity) which represents that TX100 in the mixed micelle is near to its standard state.

However, Rubingh (1979) and Rosen (1986, 2004) had indicated another condition for synergism in CMCs which must be fulfilled, i.e., $|\beta| > |\ln(CMC_{TX}/CMC_{SDS})|$. As shown in Table 2B, the second condition of synergism in CMCs is fulfilled for mixture systems with lower TX100 mole ratio (0.31 and 0.18), which showed higher synergism. However, the synergism is not fulfilled for the mixture with higher TX100 mole ratio, α TX100 = 0.47.

After Equilibration with Shale

Figure 2 shows surface tension curves of SDS-TX100 mixtures after equilibration with shale. It is obvious that the mixture at all SDS molar fractions did improve behavior of TX100 surfactant. The CMC of pure TX100 have been notably reduced, i.e., all mixtures' CMCs are similar to pure SDS CMC at 0.1 wt% and less than that of pure TX100 CMC at 1.5 wt%. It can be said that the presence of SDS (at molar ratios used here) did reduce sorption of TX100 to shale. This is comparable to the observations made by other researchers (Zhou and Zhu, 2007; Yu *et al.*, 2007). A reduction in TX100 sorption to soil was found and hence, a reduction in CMCs of mixtures after equilibration with soil from that of pure TX100. As shown in Table 3A, the CMCs of SDS: TX100 mixtures are less than those obtained from ideal mixing theory. Hence synergism is maintained with regard to critical micelle concentration even in presence of shale. β -values are again negative as shown in Table 3B but not as negative as the previous case indicating less interaction and synergism. Contrary to the previous case, stronger synergism is observed for mixtures with higher TX100 mole fraction indicating that shortage in TX100 monomers is the cause behind decrease in synergism and interaction.

Table 3: Synergism data for surfactants after equilibration with shale

Mole fraction		CMC					
		Experimental		Ideal			
α (TX100)	$1-\alpha$ (SDS)	wt.%	mM L ⁻¹	wt.%	mM L ⁻¹		
(A) CMCs obtained from ST measurements							
1	0.00	0.15	2.321	0.15	2.321		
0.47	0.53	0.10	2.187	0.12	2.595		
0.31	0.69	0.10	2.507	0.11	2.795		
0.18	0.82	0.10	2.827	0.11	3.010		
0	1.00	0.10	3.468	0.10	3.468		
(B) Synergism parameters from ST data							
α TX100	X_{TX}^M	X_{SDS}^M	β	f_{TX}	f_{SDS}	CMC*	$ \ln(CMC_{TX}/CMC_{SDS}) $
After equilibration with shale							
0.47	0.5465	0.4535	-1.005	0.8133	0.7407	2.1949	0.4016
0.31	0.4279	0.5721	-0.763	0.7790	0.8696	2.5002	0.4016
0.18	0.2956	0.7044	-0.575	0.7518	0.9510	2.8371	0.4016

Similar to the case before equilibration with shale, a deviation from the ideal behavior can also be observed in Table 3B. For all the mixed systems, the mole fraction of TX100 in mixed micelle, X_{TX}^M , are always higher than α TX100 however, to a lesser degree than the case before shale equilibration. This may indicate the probable loss of TX100 monomers to shale through adsorption mechanism. The activity coefficient f_{TX} and f_{SDS} are again shown in Table 3B. In this case, the mole fraction of SDS in the mixed micelle (X_{SDS}^M) and its activity coefficient are higher than the case before equilibration with shale. Furthermore, both increase as the mole fraction of TX100 (α TX100) decreases. This suggests that SDS in the mixed micelle plays a greater role than TX100. Most importantly, Table 3B shows that the second condition of synergism in CMCs is fulfilled for all the mixture systems. This result suggested that with further losses of TX100 monomers, the mixtures may no longer behave synergistically.

Evaluating Synergism Using Interfacial Tension Data

Before equilibration with shale and at sub-CMC concentrations, interfacial tension values for mixtures are similar or slightly lower than individual surfactants (Fig. 3). However, their CMCs are lower (0.02 wt.%) than those of individual surfactants (0.1 wt.%). After equilibration with shale, CMC values for surfactants mixtures are closer to that of pure SDS at 0.1 wt.% (Fig. 4).

CMC of SDS has not been changed before and after equilibration with shale indicating minimum losses of the surfactant. However, the TX100 CMC has been increased significantly at 0.25 wt.%. This significant increase in TX100 CMC is mainly due to a remarkable loss of surfactant monomers (13.5 g TX100) by both adsorption to shale and partition into the oil phase.

After equilibration with shale and in presence of oil phase, SDS-TX100 mixtures experienced low CMCs compared to TX100 revealing minor losses of mixed monomers by both mechanisms (sorption and partition). It is clear that the addition of SDS has reduced the amount of TX100 adsorbed to shale or partitioned into the oil phase. It is widely accepted among researchers that SDS surfactant is less likely to adsorb to shale and far less likely to partition into an oil phase. However, TX100 surfactant is more liable to sorb onto shale and partition into oil phase (Harusawa *et al.*, 1980; Rosen, 2004; Zhao and Zhu, 2006; Zhao *et al.*, 2006, 2007). Mixing SDS with TX100 may therefore retard the affinity of TX100 to sorb onto shale or partition into oil phase. It is needed to point out that sorption and/or partitioning of any surfactant proceeds through the sorption and/or partitioning of surfactant monomers and micelle formation limits surfactant adsorption and partitioning, i.e., the micelles are not directly sorbed or partitioned (Harusawa *et al.*, 1980). In mixed surfactant solution,

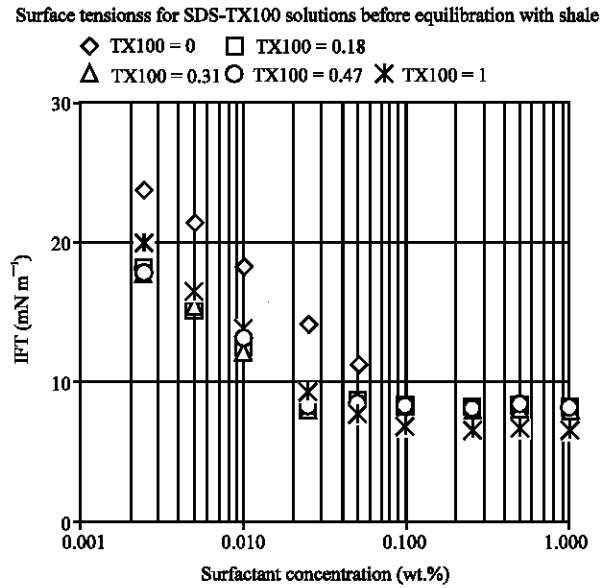


Fig. 3: Mixing effect on CMCs before equilibration with shale

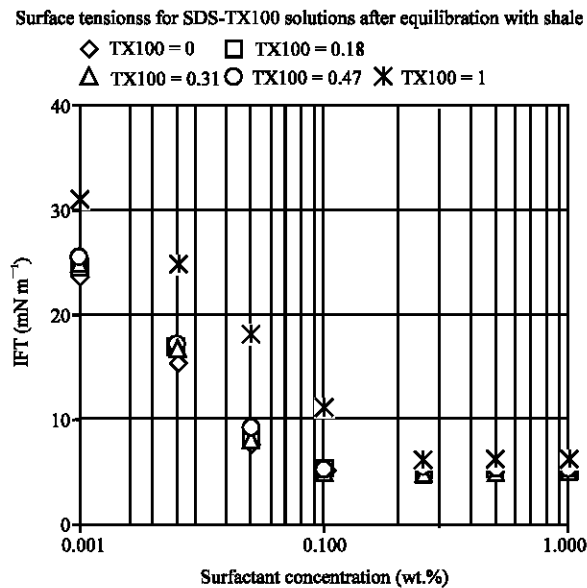


Fig. 4: Mixing effect on CMCs after equilibration with shale

the formation of mixed micelles affect the CMC, i.e., mixing will result in a lower CMC. This will reduce the monomer concentration of component surfactant in mixed solution and hence their sorption onto shale and partition to oil phase (Zhou and Zhu, 2007).

Similar results have been found by other researchers, i.e., the sorption of nonionic surfactant was strongly restricted with the presence of anionic surfactant in the mixed micelle. Yang *et al.* (2005) showed that the amount of TX100 was decreased when it was mixed with anionic surfactant, Sodium

Table 4: CMCs obtained from IFT measurements

Mole fraction		CMC			
		Experimental		Ideal	
α (TX100)	1- α (SDS)	wt.%	mM L ⁻¹	wt.%	mM L ⁻¹
Before equilibration with shale					
1	0.00	0.07	1.083	0.070	1.083
0.47	0.53	0.02	0.437	0.083	1.820
0.31	0.69	0.02	0.501	0.088	2.215
0.18	0.82	0.02	0.565	0.093	2.622
0	1.00	0.10	3.468	0.100	3.468
After equilibration with shale					
1	0.00	0.25	3.868	0.250	3.868
0.47	0.53	0.10	2.187	0.139	3.050
0.31	0.69	0.10	2.507	0.123	3.077
0.18	0.82	0.10	2.827	0.112	3.175
0	1.00	0.10	3.468	0.100	3.468

Table 5: Synergism parameters from IFT data

α TX100	X_{TX}^M	X_{SDS}^M	β	f_{TX}	f_{SDS}	CMC*	$ \ln(CMC_{TX}/CMC_{SDS}) $
Before equilibration with shale							
0.47	0.5666	0.4334	-5.803	0.3362	0.1552	0.4391	1.1638
0.31	0.5236	0.4764	-5.723	0.2728	0.2083	0.4996	1.1638
0.18	0.4779	0.5221	-5.917	0.1993	0.2589	0.5695	1.1638
After equilibration with shale							
0.47	0.4718	0.5282	-2.045	0.5652	0.6343	2.1932	0.1092
0.31	0.3753	0.6247	-1.612	0.5329	0.7968	2.5003	0.1092
0.18	0.2664	0.7336	-1.286	0.5005	0.9128	2.8366	0.1092

Dodecyl Benzene Sulfate, SDBS. Zhao *et al.* (2006, 2007) concluded that the extent of TX100 partitioning into the oil phase decreased when the amount of SDBS increased. Therefore, it can be said that the presence of SDS significantly reduced adsorption and partitioning of TX100 to shale and oil phase.

As shown in Table 4, the CMCs of surfactant mixture before and after equilibration with shale are significantly lower than those obtained from ideal mixing theory. Hence, synergism is clear with respect to interfacial tension in presence and absence of shale. β -values are negative and the synergism is stronger before equilibration with shale than after equilibration with shale (Table 5).

The values of the mole fraction of surfactants in the mixed micelle (X_{TX}^M and X_{SDS}^M) at different mole fractions in the bulk (α) are calculated according to the CMCs from IFT data and are shown in Table 5. For all the mixed systems particularly before equilibration with shale, X_{TX}^M are found to be higher than α TX100 revealing that the contribution of nonionic surfactant is significant. After equilibration with shale, X_{TX}^M are found to be nearly identical to that of α TX100 revealing less contribution of nonionic surfactant.

Before equilibration with shale, the mole fraction (X_{SDS}^M) of SDS is more or less identical to the mole fraction of Triton X100 (X_{TX}^M). This is reflected by their more or less identical activity coefficients (f_{SDS} and f_{TX}) values. Before equilibration with shale, all activity coefficients are dramatically lower than 1 indicating greater deviation from standard state (Table 5). However, after equilibration with shale, the (f_{SDS}) values of SDS are obviously higher which represents that SDS in the mixed micelle is near to its standard state particularly for the mixture with the lowest degree of synergism ($\beta = -1.286$). For all mixed systems before and after equilibration with shale, the condition of synergism in CMCs is fulfilled since $|\beta| > |\ln(CMC_{TX}/CMC_{SDS})|$ (Table 5).

CONCLUSION

The experimental data from surface tensions of solutions before equilibration with shale showed that CMCs of mixed surfactants are close to that of pure TX100 and much lower than that of pure SDS. However when using interfacial tension data to probe mixture interaction after contact with oil phase, the CMCs were close to SDS's CMC and are far lower than TX100's CMC. The CMCs of mixed surfactants as obtained from surface/interfacial tension are lower from those of ideal mixing theory, hence synergism was found.

After equilibration with shale, CMCs of mixtures as indicated by both surface and interfacial tension data were very close to that of pure SDS but much lower than that of pure TX100. More importantly, mixture CMCs are lower than those of ideal mixing theory and so synergism was obtained. However, the synergism was less significant than the one obtained in the case before equilibration with shale. For the interfacial tension data, β -values ranged from -1.286 to -2.045 after equilibration with shale meanwhile, β -values ranged from -5.803 to -5.917 before equilibration with shale. The weight of current evidence suggested that the mixture with higher TX100 mole ratio exhibited more synergism than others particularly after equilibration with shale and/or contact with oil phase. Furthermore, considering interfacial tension data to predict nonionic-anionic mixture interaction and degree of synergism in real environments are more reasonable since it takes into account probable loss of surfactant to either soil or oil phase.

ACKNOWLEDGMENT

This research was financially supported by UTM (University Teknologi Malaysia).

REFERENCES

- Chu, W. and K.H. Chan, 2003. The mechanism of the surfactant-aided soil washing system for hydrophobic and partially hydrophobic organics. *The Sci. Total Environ.*, 307: 83-92.
- Edwards, D.A., Z. Adeel and R.G. Luthy, 1994. Distribution of nonionic surfactant and phenanthrene in a sediment/aqueous system. *Environ. Sci. Technol.*, 28: 1550-1560.
- Haigh, S., 1996. A review of the interaction of surfactants with organic contaminants in soil. *The Sci. Total Environ.*, 185: 161-170.
- Harusawa, F., S. Taeko, H. Nakajima and S. Fukushima, 1980. Partition isotherms of nonionic surfactants in the water-cyclohexane system and type of emulsion produced. *J. Colloid Interface Sci.*, 74: 435-440.
- Janczuk, B., J.M. Bruque, M.L. Gonzalez-Martin and C. Doradu-Calasan, 1995. The properties of mixtures of ionic and nonionic surfactants in water at the water/air interface. *Colloids Surf. A: Physicochem. Eng. Aspects*, 104: 157-163.
- Joshi, T., J. Mata and P. Bahadur, 2005. Micellization and interaction of anionic and nonionic mixed surfactant systems in water. *Colloids Surf. A: Physicochem. Eng. Aspects*, 260: 209-215.
- Mata, J.P., 2006. Hydrodynamic and clouding behaviour of triton X-100 + SDS mixed micellar systems in the presence of sodium chloride. *J. Dispersion Sci. Technol.*, 27: 49-54.
- Owoyomi, O., I. Jide, M.S. Akanni, O.O. Soriyan and M.K. Morakinyo, 2005. Interaction between sodium dodecylsulphate and triton X-100: Molecular properties and kinetics investigations. *J. Applied Sci.*, 5: 729-734.
- Paria, S. and P.K. Yuet, 2007. Adsorption of nonionic surfactants onto sand and its importance in naphthalene removal. *Ind. Eng. Chem. Res.*, 46: 108-113.

- Paria, S., C. Manohar and K.C. Khilar, 2003. Experimental studies on adsorption of surfactants onto cellulosic surface and its relevance to detergency. *J. Inst. Eng. Singapore*, 43: 34-44.
- Rosen, M.J., 1986. Molecular Interaction and Synergism in Binary Mixtures of Surfactants. In: *Phenomena in Mixed Surfactant Systems*. ACS Symp. Series 311. Scamehorn, J.F. (Ed.). Am. Chem. Soc., Washington, DC, ISBN-10: 0841209758, pp: 144-162.
- Rosen, M.J., 2004. *Surfactants and Interfacial Phenomena*. 4th Edn., Chapter 11., Wiley-Interscience New York, ISBN-10: 0471478180 .
- Rubingh, D.N., 1979. *Solution Chemistry of Surfactants*, Vol. 1., Plenum Press, New York, ISBN 0-306-401 74-6, pp: 337-354.
- Sun, S., W.P. Inskip and S.A. Boyd, 1995. Sorption of nonionic organic compounds in soil-water systems containing a micelle-forming surfactant. *Environ. Sci. Technol.*, 29: 903-913.
- Urum, K. and T. Pekdemir, 2004. Evaluation of biosurfactants for crude oil contaminated soil washing. *Chemosphere*, 57: 1139-1150.
- Wang, W. and J.C.T. Kwak, 1999. Adsorption at the alumina-water interface from mixed surfactant solutions. *Colloids Surf. A: Physicochem. Eng. Aspects*, 156: 95-110.
- Yang, K., L. Zhu and B. Zhao, 2005. Minimizing losses of nonionic and anionic surfactants to a montmorillonite saturated with calcium using their mixtures. *J. Colloid Interface Sci.*, 291: 59-66.
- Yu, H., L. Zhu and W. Zhou, 2007. Enhanced desorption and biodegradation of phenanthrene in soil-water systems with the presence of anionic/nonionic mixed surfactant. *J. Hazardous Mater.*, 142: 354-361.
- Zhang, R. and P. Somasundaran, 2006. Advances in adsorption of surfactant and their mixtures at solid/solution interfaces. *Adv. Colloid Interface Sci.*, 123-126: 213-229.
- Zhao, B., L. Zhu, W. Li and B. Chen, 2005. Solubilization and biodegradation of phenanthrene in mixed anionic-nonionic surfactant solutions. *Chemosphere*, 58: 33-40.
- Zhao, B. and L. Zhu, 2006. Solubilization of DNAPLs by mixed surfactant: Synergism and solubilization capacity. *J. Hazardous Mater.*, B136: 513-519.
- Zhao, B., L. Zhu and K. Yang, 2006. Solubilization of DNAPLs by mixed surfactant: Reduction in partitioning losses of nonionic surfactant. *Chemosphere*, 62: 772-779.
- Zhao, B., X. Chen, K. Zhu and L. Zhu, 2007. Micellar solubilization of TCE and PCE by mixed surfactant: Effects of surfactant partitioning and DNAPL mixing. *Colloids Surf. A: Physicochem. Eng. Aspects*, 296: 167-173.
- Zhou, W. and L. Zhu, 2004. Solubilization of pyrene by anionic-nonionic mixed surfactants. *J. Hazardous Mater.*, B109: 213-220.
- Zhou, W. and L. Zhu, 2005. Solubilization of polycyclic aromatic hydrocarbons by anionic-nonionic mixed surfactants. *Colloids Surf. A: Physicochem. Eng. Aspects*, 255: 145-152.
- Zhou, W. and L. Zhu, 2007. Enhanced desorption of phenanthrene from contaminated soil using anionic/nonionic mixed surfactant. *Environ. Pollut.*, 147: 350-357.
- Zhu, L. and S. Feng, 2003. Synergistic solubilization of polycyclic aromatic hydrocarbons by mixed anionic-nonionic surfactants. *Chemosphere*, 53: 459-467.