

Potential of Palm Kernel Alkanolamide Surfactant for Enhancing Oil Recovery from Sandstone Reservoir Rocks

Parichat Traiwiriyawong and Suratsawadee Kungsanant*

Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Hat-Yai, Songkhla 90110, Thailand

ARTICLE INFO

Received: 6 Mar 2020
Received in revised: 30 Jun 2020
Accepted: 10 Jul 2020
Published online: 29 Jul 2020
DOI: 10.32526/ennrj.18.4.2020.32

Keywords:

Alkanolamide surfactant/
Adsorption/ Crude oil
solubilization/ Solubilization
Equilibrium constant/ EOR

* Corresponding author:

E-mail: suratsawadee.k@psu.ac.th

ABSTRACT

The interest in using benign surfactants has been steadily increasing in the context of enhanced oil recovery (EOR). Palm kernel alkanolamide surfactant (PKA), a nonionic surfactant synthesized from palm kernel oil, was preliminarily assessed for EOR from sandstone reservoir rocks. The performance factors determined were surfactant loss due to adsorption on silica surface and crude oil solubilization for oil solubilizing efficiency. The performance of PKA was compared to two commercial ionic surfactants, SDS (anionic surfactant) and CTAB (cationic surfactant). The results show that PKA was less adsorbed on silica than CTAB or SDS. The adsorption kinetics was well fit with a pseudo-second order model for all three surfactants. The adsorption equilibrium data for CTAB and PKA were fitted with a Langmuir isotherm, while a Freundlich isotherm fit well for SDS, indicating multilayer SDS adsorption on silica surfaces. The adsorption of PKA was not significantly affected by added NaCl or increased temperature. In addition, the solubilization equilibrium constant (K_s) had the rank order PKA>CTAB>SDS, and proportionally increased with added NaCl. PKA performance was also compared to two commercial nonionic surfactants, Tergitol 15-S-9 and Tergitol TMN-6, and the results indicate that PKA was the least adsorbed, and had the highest K_s among the tested nonionic surfactants.

1. INTRODUCTION

Nowadays, enhanced oil recovery (EOR) by surfactant flooding is continuously developed and widely used. The surfactant molecules used in EOR have amphipathic structures. The head part of the surfactant molecule is polar and hydrophilic, whereas its tail is non-polar and hydrophobic. When adding surfactants to the system, they tend to adsorb at crude/water or crude/rock interfaces, lowering interfacial tension, and this can release and mobilize crude oil from the pores of reservoir rocks. These phenomena can increase the amount of crude oil production significantly, by up to 60% (Belhaj et al., 2019; Emadi et al., 2017). In addition, surfactants can form micelles by pointing hydrophobic tails inwards and hydrophilic heads outwards. This phenomenon creates a hydrophobic region for crude oil partitioning and can make crude oil appear water soluble (Rosen, 1989).

However, there are some limitations to surfactant flooding techniques, such as the high cost of surfactants, surfactant loss during operation due to adsorption by reservoir rocks, and their toxicity to the environment, leading to high production costs and toxicity, especially in a sea environment (Bera et al., 2017). Thus, many studies have suggested that surfactants synthesized from natural resources could avoid the negative environmental impacts from surfactant loss during surfactant flooding, and still provide high recovery rate (Arabloo et al., 2015; Barati-Harooni et al., 2016; Iglaue et al., 2010).

Natural surfactants are typically synthesized from plants, seeds, or vegetable oil, depending on availability by locality. This facilitates agricultural waste minimization and can effectively generate value-added products. For example, Arabloo et al. (2015) studied adsorption of a saponin surfactant synthesized from *Glycyrrhiza Glabra* onto sandstone.

The results show that *Glycyrrhiza Glabra* saponin decreased interfacial tension between oil and water from 31.6 mN/m to 6.5 mN/m and could be utilized in EOR. Barati-Harooni et al. (2016) studied adsorption of a nonionic surfactant synthesized from seeds of *Trigloea foenum-graceum* (TFG) on sandstone minerals in EOR. The adsorption of TFG was lower than of other natural nonionic surfactants in controlled conditions. In addition, the price of TFG is lower than those of surfactants commonly used in the crude oil industry. Furthermore, TFG is available in the country of that study and is not harmful to the environment. Iglauer et al. (2010) studied new surfactant classes for their tertiary oil recovery potential. This study examined the adsorption of di-tridecyl sulfosuccinic acid ester, coconut diethanolamide, alkyl polyglycoside, and alkylpropoxy sulfate sodium salts on kaolin clay, with a view to surfactant loss. The results show that coconut diethanolamide was the least absorbed and increased tertiary oil recovery by up to 75%. The study suggested coconut diethanolamide as a new alternative surfactant with high tertiary oil recovery potential.

Therefore, this current work studied the potential of alkanolamide nonionic surfactant (palm kernel alkanolamide, PKA) synthesized from palm kernel oil for EOR. PKA is a natural nonionic surfactant with structure similar to coconut diethanolamide, which has been proven an effective surfactant for EOR (Iglauer et al., 2010). Typically, the alkanolamine synthesized from palm kernel oil is used as an additive in personal care products and has no significant effects on the environment (Wetchakul, 2013). Besides, the study of alkanolamine as EOR surfactant could support palm oil industry, especially in the Southeast Asian countries that are the main palm oil producers (Mukherjee and Sovacool, 2014).

Thus, the performance of PKA in EOR was studied and compared with four commercial surfactants. The selected surfactants are of anionic type, namely sodium dodecyl sulfate (SDS), of cationic type namely cetyltrimethylammonium bromide (CTAB), and of nonionic type, namely secondary alcohol ethoxylate (Tergitol 15-S-9) and a branched secondary alcohol ethoxylate (Tergitol TMN 6). All these surfactants are widely applied as good candidate surfactants in EOR studies. The experiment was divided into two parts, which are surfactant loss due to adsorption on reservoir rock surfaces, and crude oil solubilization ability of the surfactants. For surfactant adsorption, silica was applied as the model

adsorbent representing reservoir rock. The studied factors interacting with surfactant adsorption were salinity and temperature. The surfactant adsorption behaviors were fit by models for both kinetics of adsorption and for equilibrium adsorption isotherm. In the crude oil solubilization study, all the surfactants were tested for crude oil solubilization performance in controlled conditions and compared. The influence of salinity on crude oil solubilization is discussed.

2. METHODOLOGY

2.1 Materials

The anionic surfactant, sodium dodecyl sulfate (SDS, 98% purity) was purchased from Sigma-Aldrich. The cationic surfactant cetyltrimethylammonium bromide (CTAB, 98% purity) was purchased from Ajax Finechem. Regarding the three nonionic surfactants, PKA (80% content) was supplied by Thai Flavour and Fragrance Co., Ltd.; and Tergitol 15-S-9 (90% content), and Tergitol TMN-6 (90% content) were both purchased from Sigma-Aldrich. The properties of the surfactants are summarized in Table 1. Additionally, silica (98% purity, particle size 18 μ m) was purchased from Ajax Finechem. Crude oil was supplied by the Petroleum Authority of Thailand. Sodium chloride (NaCl) purchased from Ajax Finechem was used for brine solution preparation.

2.2 The study of surfactant adsorption on silica surface

2.2.1 Adsorption kinetics

The experiment was conducted by adding a 4-g quantity of silica in 50-mL of distilled water. These samples were combined individually with CTAB, PKA, and SDS. The initial surfactant concentrations were controlled above the CMC values of all surfactants to 15.6 mmol/L, in order to ensure full coverage of surfactant on silica surfaces. The sample bottles were shaken in an incubator with a shaking rate of 170 rpm at 30°C. The liquid samples of surfactant solution were collected for free surfactant concentration measurement using UV-vis spectrophotometry for CTAB ($\lambda=195$ nm) (Atia and Radwan, 1997; Park et al., 2015) or chemical oxygen demand (COD) (Bera et al., 2013) measurement method for PKA and SDS. The blank solution was prepared using 4-g of silica in 50-mL of distilled water to avoid interference of silica on surfactant concentration measurement. The equilibrium times were recorded from observing constant surfactant concentrations in

the supernatant liquid. The experimental results were used to fit models for adsorption kinetics.

The effects of NaCl and temperature on the adsorption of surfactants on silica were tested in 0.1

mol/L NaCl solution and 50°C. The blank solution was prepared without adding a surfactant. The experiment was similar as in prior literature (Bera et al., 2013).

Table 1. Properties of the selected surfactants

Surfactant (Trade name)	Chemical formula	MW (g/mol)	CMC (mmol/L)
Anionic surfactant			
SDS ^a	C ₁₂ H ₂₅ NaO ₄ S	288	8.2
Cationic surfactant			
CTAB ^b	C ₁₉ H ₄₂ BrN	364	0.82
Nonionic surfactants			
PKA ^c	C ₁₃ H ₂₇ ON(CH ₂ CH ₂ OH) ₂	309	0.23
Tergitol 15-S-9 ^d	C ₁₂₋₁₄ H ₂₅₋₂₉ O(CH ₂ CH ₂ O) ₉ H	596	0.09
Tergitol TMN-6 ^d	C ₁₂ H ₂₆ O(C ₂ H ₄ O) ₆	540	1.48

Remark: Letters a, b, c, and d indicate literature data from NCBI (2005), NCBI (2004), Wetchakul (2013), and Parthong et al. (2018), respectively.

2.2.2 Adsorption isotherm

A 4-g silica sample was added in 50-mL of surfactant solution. The initial concentration of CTAB was controlled in the range of 0.274-15.6 mmol/L. The sample bottles were shaken with a shaking rate of 170 rpm at 30°C. As the system reaches equilibrium, liquid samples of surfactant solution were collected and centrifuged. The supernatant liquid was analyzed for surfactant concentration in the bulk solution (Ahmadi and Shadizadeh, 2015; Arabloo et al., 2015; Barati-Harooni et al., 2016). The experiments were performed for PKA and SDS using similar procedures as above using PKA and SDS solutions at concentrations in the ranges 0.162-15.6 mmol/L and 1.734-15.6 mmol/L, respectively. The relationship of bulk surfactant concentration to the initial surfactant concentration was fit with Langmuir and Freundlich adsorption isotherm models.

2.3 Crude oil solubilization study

A 25-mL sample of crude oil and 25-mL of surfactant solution with a concentration of 1 CMC were mixed in 100-mL sample bottle. In addition, several similar sample bottles but without surfactant were prepared as controls. The sample bottles were shaken in an incubator shaker with a shaking rate of 170 rpm at 50°C. Then, the liquid phase was sampled every 2 h and analyzed for crude oil concentration using the COD technique (Siddiqui et al., 2014). The effects of salinity on crude oil solubilization were evaluated using distilled water and 0.1 mol/L NaCl solution (Spildo et al., 2014). No silica was added to the sample bottles to avoid surfactant loss from

adsorption. The crude oil concentration was assessed using COD technique. Samples prepared without adding a surfactant were conducted and determined for unsolubilized crude oil concentration. A blank solution of surfactant was also prepared for baseline data. The equilibrium time for both systems was observed within 24 h.

2.4 Comparing surfactant adsorption and crude oil solubilization behaviors of PKA with selected commercial nonionic surfactants

The surfactant adsorption and crude oil solubilization of PKA were compared with Tergitol 15-S-9 and Tergitol TMN-6. The experimental procedures were as in section 2.2 above, except that the initial concentration was controlled to 1 CMC for each individual surfactant. Since the CMCs of tested nonionic surfactants were quite low, and present in similar range. The concentration of a nonionic surfactant was analyzed by the COD method. For crude oil solubilization, the experimental procedures are similar to those in section 2.3, except that the initial concentration of surfactants was controlled to 1 CMC in 0.1 mol/L NaCl solution, in all cases. The sample bottles were shaken for 24 h.

The experiments were randomized and performed in triplicate, and the standard deviation was less than 5%. The error bars of results are shown in the figures.

2.5 Data analysis

The amount of surfactant adsorption (q , mol/g adsorbent) was calculated as shown in Equation (1):

$$q = \frac{(C_i - C_e) \times V}{m_{\text{silica}}} \times 10^{-3} \quad (1)$$

Here, C_i (mol/g) and C_e (mol/g), respectively, are the initial concentration and the free surfactant concentration in bulk aqueous solution, V (mL) is the volume of the surfactant solution, and m_{silica} (g) is mass of silica (Bera et al., 2013).

Then, the surfactant adsorption was fit with pseudo-first order and pseudo-second order models, presented in Equations (2) and (3), respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Here, q_e (mol/L) and q_t (mol/L) are the amounts of adsorbed surfactants on silica at equilibrium, and that at time t (h^{-1}), respectively. k_1 (h^{-1}) is the rate constant of pseudo-first order. k_2 (g/mol/h) is the rate constant of pseudo-second order (Ahmadi and Shadizadeh, 2015).

The adsorption of surfactant at equilibrium was modeled with the Langmuir and Freundlich adsorption isotherms, according to Equations (4) and (5), respectively:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

Here, q_e (mol/L) is the amount of adsorbed surfactant on silica at equilibrium; q_m (mol/L) is maximum adsorption of surfactant; C_e (mol/g) is free surfactant concentration in bulk aqueous solution at equilibrium; K_L (L/mol) is Langmuir constant indicating the strength of the adsorption force; K_F (mol/g) is Freundlich constant related to adsorption capacity; and n is Freundlich exponent accounting for adsorption intensity (Bera et al., 2013).

The surfactants present in a reservoir can lower the interfacial tension of crude oil/water or crude oil/rock, mobilizing the oil from reservoir rocks. Then crude oil tends to partition into surfactant micelles due to hydrophobic attraction forces. The micelles are subsequently mobilized from source rock by water flooding. Therefore, this experiment observes the crude oil solubility with each surfactant using the solubilization equilibrium constant (K_s) that can be calculated from Equations (6) and (7).

$$X_0 = \frac{C_{\text{sol}}}{C_m + C_{\text{sol}}} \quad (6)$$

$$K_s = \frac{x_0}{C_0} \quad (7)$$

Here, X_0 is the mole fraction of crude oil in micelles, C_{sol} (mol/L) is the solubilized crude oil concentration, C_m (mol/L) is the surfactant concentration in micellar form, K_s (mL/g) is solubilization equilibrium constant, and C_0 (mol/L) is the unsolubilized crude oil concentration (Rosen, 1989).

3. RESULTS AND DISCUSSION

3.1 Surfactant adsorption

3.1.1 Adsorption equilibrium time

The amount of an individual surfactant adsorbed on silica was determined as a function of time, and is shown in Figure 1. As time progresses the amount of adsorbed surfactant on silica rapidly increases, and then tends to become constant within 12 h for PKA, 15 h for SDS, and 20 h for CTAB, respectively. The maximum adsorption quantity was observed as 27.48 $\mu\text{mol/g}$ for CTAB, 25.08 $\mu\text{mol/g}$ for SDS, and 15.20 $\mu\text{mol/g}$ for PKA.

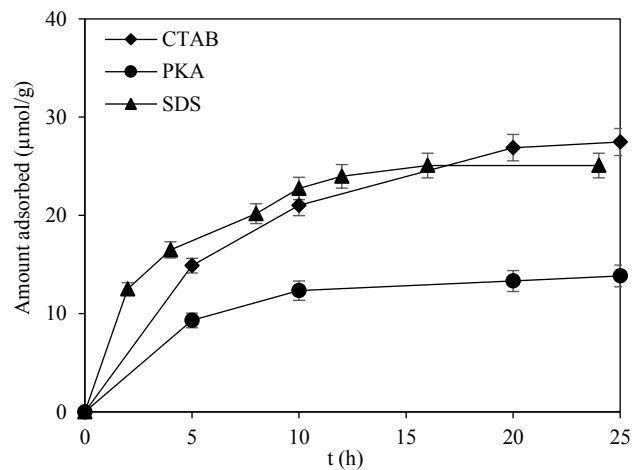


Figure 1. Adsorption kinetics of surfactants on silica in water at 30°C.

It can be seen that CTAB is adsorbed on silica more than SDS or PKA. Typically, the bare surface charge of silica is negative (Lee et al., 2007). The head group of CTAB exhibits a positive charge and is adsorbed on silica surface by ion pairing (Paria and Khilar, 2004). On the other hand, SDS has negatively-charged head group with repulsion from the silica surface. The adsorption of SDS on silica might be induced by weak ionic interactions. However, the SDS

adsorption is slightly below that of CTAB and higher than of PKA. Possibly SDS could form a second layer by tail-tail hydrophobic interactions. Similar results for anionic adsorption have been reported by [Park et al. \(2015\)](#). They observed that high adsorption of anionic surfactant could be brought by the alkyl-alkyl hydrophobic interactions at high surfactant concentrations. Additionally, PKA was less adsorbed on silica than CTAB and SDS. PKA has no charge on its head group and tends to adsorb on silica by van der Waals forces between the hydrophilic head group and

the silica site, having the weakest adsorption on silica surface ([Paria and Khilar, 2004](#)). The order of adsorption by surfactant type is consistent with prior reports ([Rabiu et al., 2016](#); [Bera et al., 2017](#)).

3.1.2 Kinetics of surfactant adsorption

The adsorption data for each surfactant were fitted with pseudo-first order and pseudo-second order models, and the kinetic parameters of adsorption are shown in [Table 2](#).

Table 2. Kinetic parameters of selected surfactants adsorption in water at 30°C

Surfactant	Pseudo-first order			Pseudo-second order		
	k_1 (h ⁻¹)	q_e (μmol/g)	R^2	k_2 (g/μmol/h)	q_e (μmol/g)	R^2
CTAB	0.194	32.6	0.981	0.004	35.3	0.997
PKA	0.162	10.9	0.961	0.021	15.5	0.999
SDS	0.238	23.7	0.971	0.035	28.2	0.994

The coefficient of determination R^2 indicates that the pseudo-second order model is preferable for modeling the adsorption of CTAB, PKA and SDS. The predicted amount of adsorbed surfactant (q_e) reveals that CTAB adsorption is the highest, followed by SDS and PKA in this order. This rank order of surfactant adsorption matches well the adsorption equilibrium profiles shown in [Figure 1](#). Besides, the k_2 values indicating the adsorption speed reveal that the adsorption rate of SDS is higher than those of PKA or

CTAB. The adsorption rate increases inversely with the surfactant molecular weight ([Table 1](#)); SDS has the lowest molecular weight and a comparatively high rate constant ([Liu, 2008](#)).

3.1.3 Adsorption isotherm

The equilibrium data of adsorbed surfactant and free surfactant concentration were fitted with Langmuir or Freundlich isotherm models and the identified parameters are listed in [Table 3](#).

Table 3. Identified parameters in Langmuir and Freundlich equilibrium isotherm models for the selected surfactants

Surfactant	Langmuir			Freundlich		
	q_{max} (μmol/g)	K_L (L/μmol)	R^2	K_F (μmol/g)	n	R^2
CTAB	30.4	7.98E-04	0.9984	0.291	1.938	0.9085
PKA	17.6	5.72E-04	0.9879	0.140	1.892	0.8875
SDS	76.9	5.77E-05	0.9163	0.014	1.198	0.9961

The R^2 values reveal that the adsorption isotherms of CTAB and PKA are well fitted with Langmuir isotherm, indicating monolayer coverage on silica. The maximum amount of the adsorbed surfactant (q_{max}) demonstrates that CTAB is more adsorbed on silica than PKA is. The data are consistent with the q_e values predicted from the pseudo-second order models earlier. In addition, K_L indicates the energy of adsorption or the strength of adsorption forces between silica sites and surfactants. A greater K_L represents stronger interactions between the silica sites and adsorbed surfactant molecules ([Markandeya](#)

[et al., 2017](#)). This is consistent with the fact that the interactions by van der Waals forces observed for PKA-silica adsorption are weaker than that those by ion-pairing in oppositely-charged CTAB-silica adsorption ([Atkin et al., 2003](#); [Eriksson et al., 2002](#); [Somasundaran et al., 1964](#)). Moreover, the R^2 value indicates that the adsorption of SDS should be fitted with the Freundlich isotherm, indicating multilayer adsorption of SDS on silica and that possibly the silica surface is heterogeneous ([Mi et al., 2016](#)). This is consistent with the fact that multilayer adsorption has

been established in prior literature, especially at high SDS concentrations (Park et al., 2015).

3.1.4 Effect of NaCl on surfactant adsorption

The influence of salinity on surfactant adsorption behaviors was examined in 0.1 mol/L NaCl solution. The results were compared with those in water system and are illustrated in Figure 2. Adding NaCl to the system causes competitive adsorption of positively-charged sodium (Na^+) and CTAB on silica, and also increases the electrical repulsion for CTAB. This decreases the CTAB adsorption (Rabiu et al.,

2016). On the other hand, the increase in the positive charge from Na^+ ions on silica surfaces could reduce the negatively-charged repulsion arising between SDS and silica, contributing to SDS adsorption on silica surfaces (Bera et al., 2013). Moreover, NaCl has no effect on PKA because it contains no charge and adsorbs on silica with hydrophobic attraction forces. The results match well other reports indicating that nonionic surfactants are relatively stable in electrolyte or high salinity solutions (Bera et al., 2013; Belhaj et al., 2020; Rabiu et al., 2016).

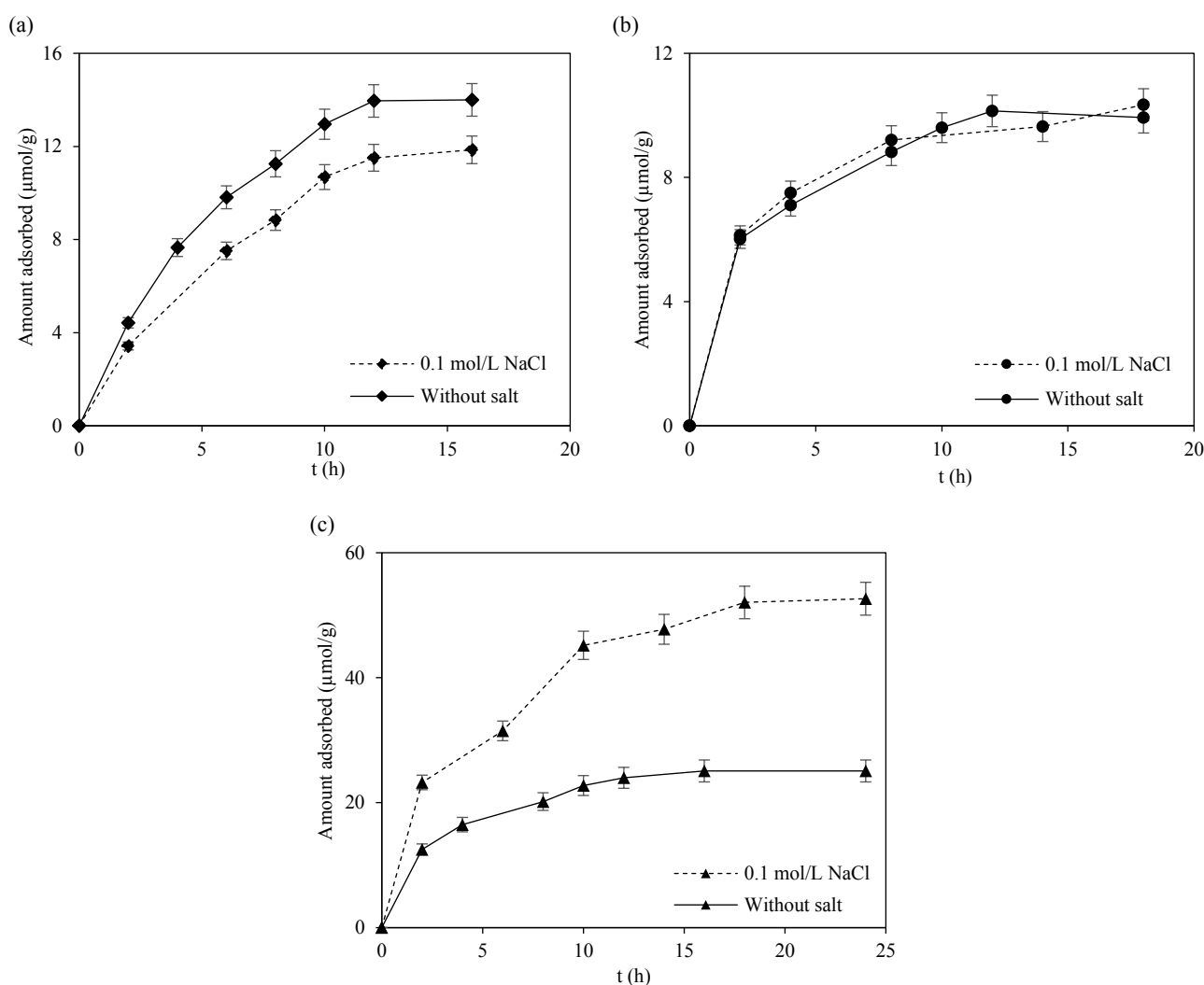


Figure 2 .Surfactant adsorption profiles on silica in 0.1 mol/L NaCl solution and water at 30°C for (a) CTAB, (b) PKA, and (c) SDS.

3.1.5 Effect of temperature on surfactant adsorption

The influences of temperature on adsorption behaviors of the surfactants in reservoir rocks are demonstrated in Figure 3. It was found that the adsorption of all surfactants decreased with temperature. The dominant impacts were observed for

CTAB and SDS, while a minor effect was noted on the absorption of PKA. As the temperature increases, the kinetic energy of surfactant molecules increases, and this possibly facilitates surfactant diffusion from the surfaces, leading to lesser surfactant adsorption on silica (Wiśniewska, 2012).

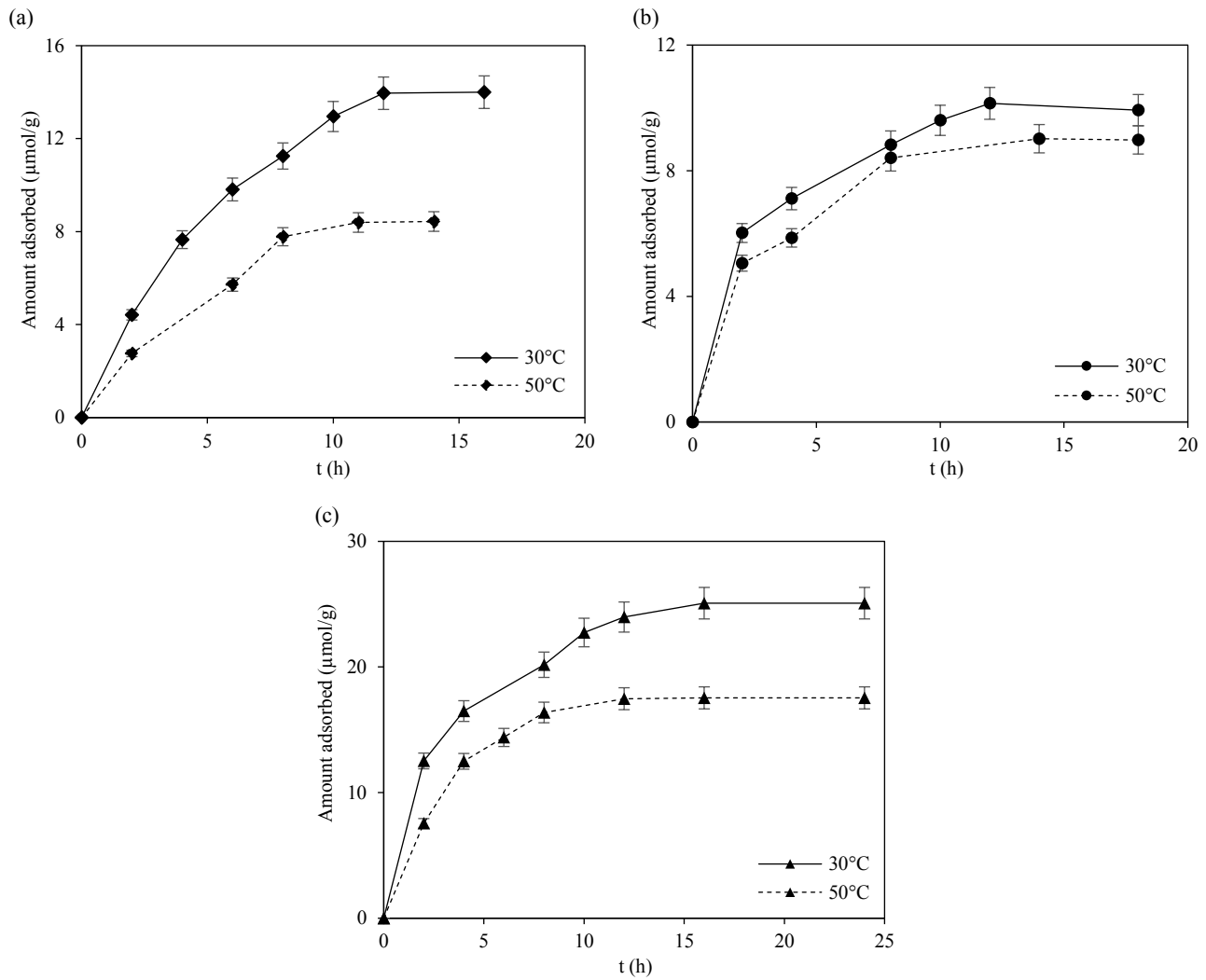


Figure 3. Effect of temperature on surfactant adsorption profiles for (a) CTAB, (b) PKA, and (c) SDS.

Additionally, the change of surfactant adsorption with temperature could be described by thermodynamics, including the changes in enthalpy (ΔH° , KJ/mol), entropy (ΔS° , KJ/mol/K), and standard Gibbs free energy (ΔG° , KJ/mol) (Bera et al., 2013). The ΔH° refers to the amount of heat that passes in or out of the system at constant pressure. The ΔS° indicates the disorder of the system, and the feasibility of the adsorption is clarified by ΔG° . The correlation of parameters was determined according to the Van't hof equation in Equation (8).

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

Here, R (8.314 J/K/mol) is the gas constant, T (K) is the temperature, and K_L (L/mol) is the Langmuir constant at controlled temperature (Juang et al., 2006). The data for K_L estimates from Langmuir isotherm were for 30°C and 50°C. Table 4 is a summary of K_L

values for individual surfactant's equilibrium adsorption at these temperatures.

Table 4. The K_L values for individual surfactant's equilibrium adsorption at two tested temperatures.

Temperature (°C)	K_L (L/mol)		
	CTAB	PKA	SDS
30	797.98	572.39	57.70
50	323.00	191.00	32.90

Then, the data were plotted for $1/T$ versus $\ln K_L$, so that the intercept and slope of correlation represent the values of ΔS° and ΔH° , respectively. Then, ΔG° for each temperature was determined using Equation (9). All these thermodynamic parameters are reported in Table 5.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

Table 5. Thermodynamic parameters of surfactant adsorption on silica surface.

Surfactant	Temperature (°C)	Thermodynamic parameter		
		ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol/K)
CTAB	30	-16.83	-36.80	-0.07
	50	-15.52		
PKA	30	-16.00	-44.65	-0.09
	50	-14.10		
SDS	30	-10.22	-22.85	-0.04
	50	-9.32		

A negative ΔG° indicates that the surfactant adsorption on silica surface occurs simultaneously. The ΔS° is negative, and this demonstrates that surfactant molecules tend to uniformly adsorb on the water/silica interfaces rather than stay disorganized in water above the surface. Furthermore, the negative ΔH° reveals that the adsorption process for all these surfactants is exothermic. Thus, the adsorption of surfactant decreases with increasing temperature. The calculated thermodynamic parameters agree well with the aforementioned experimental results and are consistent with prior studies (Ijagbemi et al., 2009; Juang et al., 2006; Wiśniewska, 2012).

3.2 The study of oil solubilization

The amount of crude oil partitioned into the surfactant solution at 1 CMC, 50°C, and 0 mol/L NaCl is shown in Figure 4. It can be seen that the largest amount of crude oil dissolved in surfactant solution was observed for SDS, followed by PKA, and CTAB in this order. SDS has the highest CMC and the largest amount of monomer in the bulk solution. This phenomenon means it has the most surfactant molecules available for adsorption at crude oil and surfactant solution interfaces, and facilitates the

reduction of interfacial tension between crude oil and surfactant solution, treating the most crude oil (Tehrani-Bagha and Holmberg, 2013). The results agree well with the fact that anionic surfactants have commonly been suggested as effective for reducing interfacial tension between seawater and crude oil (Negin et al., 2017; Belhaj et al., 2020). In addition, it can be seen that PKA slightly outperformed CTAB.

Moreover, from Figure 4, it should be noted that adding NaCl could increase crude oil partitioning in the PKA, CTAB and SDS systems. Typically, adding salt reduces electrical repulsion of ionic heads, or steric repulsion of nonionic heads, resulting in closer packing at air-water interfaces and facilitating low interfacial tension enabling crude oil partitioning to increase (Karnanda et al., 2013; Rostami et al., 2019). Moreover, adding electrolyte in solution could reduce the repulsion forces between the similarly charged head groups, and consequently decrease the CMC (data shown in Table 6), increasing surfactant aggregation numbers and micelle volume. This facilitates the extent of micelle formation and solubilization of crude oil into micelles (Rosen, 1989; Dutkiewicz and Jakubowska, 2002; Qazi et al., 2017).

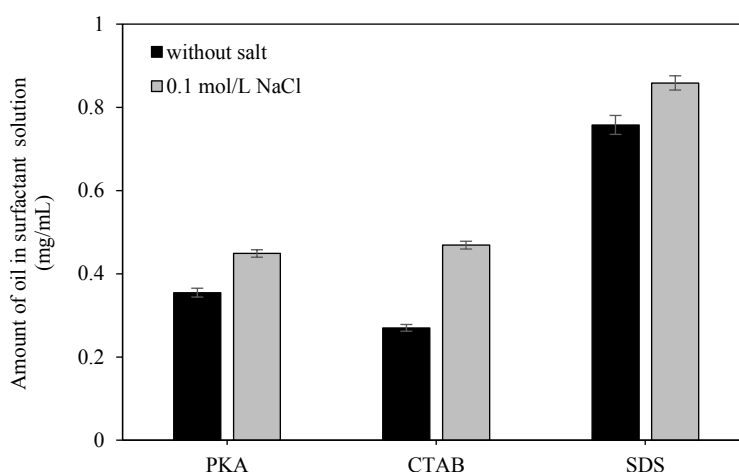
**Figure 4.** The effect of salinity on crude oil partitioning into the surfactant solution at 1 CMC and 50°C.

Table 6. The K_s values for crude oil solubilization in selected surfactant solutions at 0.1 mol/L NaCl and 50°C.

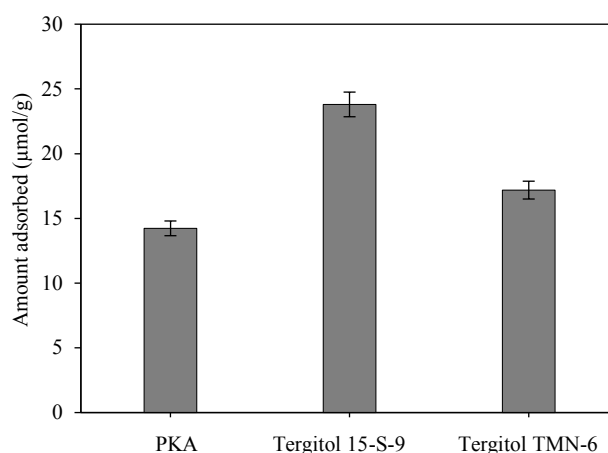
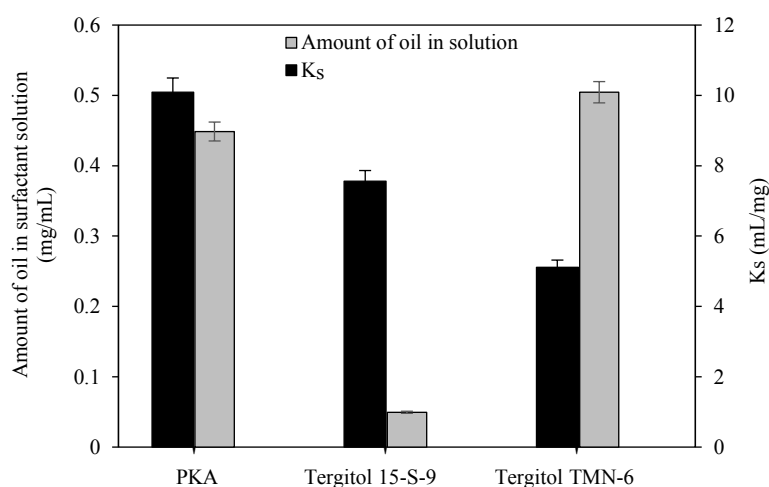
Surfactant	CMC (mmol/L)		K_s (mL/mg)
	without salt	0.1 mol/L NaCl	
PKA	0.23	0.19	10.33
CTAB	1	0.27	7.94
SDS	8.2	2.6	6.90

At controlled salinity, the results in Table 6 reveal that K_s has the rank order PKA>CTAB>SDS. This trend is reversed from the order of CMC for these surfactants. Theoretically, a nonionic surfactant has greater solubilizing performance than cationic or anionic surfactants, due to its lower CMC. Additionally, the greater solubilization of cationic over anionic might be due to looser packing of surfactant aggregation in micelles (Rosen, 1989). Thus, PKA has the lowest CMC and the highest K_s indicating the highest crude oil accessibility to the micellar core.

3.3 Comparison of PKA performance with commercial nonionic surfactants adsorption on silica and crude oil solubilization

The behaviors of PKA adsorption on silica surface and crude oil solubilization were compared with the secondary alcohol ethoxylates Tergitol 15-S-9 and Tergitol TMN-6. Both are widely considered good candidate nonionic surfactants in EOR studies (Bera et al., 2017; Shaw, 1984; Worthen et al., 2012). These surfactants are remarkably stable in high salinity or elevated temperature and show good oil recovery performance (Sharma and Mohanty, 2013; Mohan, 2009; Mandal et al., 2012). The results of

surfactant adsorption and crude oil solubilization are shown in Figures 5 and 6, respectively. Figure 5 reveals that Tergitol 15-S-9 is adsorbed on silica better than Tergitol TMN-6 or PKA. The van der Waals interactions dominate in the adsorption of a nonionic surfactant on silica surfaces, and these forces increase with molecular mass of the surfactant (Paria and Khilar, 2004). Tergitol 15-S-9 has the highest molecular weight (see Table 1), resulting in the highest adsorption among these three surfactants.

**Figure 5.** Amounts of nonionic surfactants adsorbed on silica at 1 CMC and 30°C.**Figure 6.** Amount of crude oil partitioning into nonionic surfactant solution and the K_s values in 0.1 mol/L NaCl solution at 1 CMC, 50°C.

Moreover, Figure 6 reveals that crude oil partitioning into surfactant solutions had the rank order Tergitol TMN-6>PKA>Tergitol 15-S-9. This is consistent with the rank order of CMC. As Tergitol TMN-6 has the highest CMC, its amount as monomer in bulk solution is greater than those of PKA or Tergitol 15-S-9. This leads to the most surfactant molecules available at crude oil/surfactant solution interfaces, giving the highest crude oil partitioning in the surfactant solution (Rosen, 1989).

Additionally, the results in Figure 6 show that K_s had the rank order PKA>Tergitol 15-S-9>Tergitol TMN-6. Theoretically, this trend is consistent with micelle size. From the data listed in Table 1, Tergitol TMN-6 has a higher CMC than Tergitol 15-S-9, indicating smaller micellar size. Additionally, Tergitol 15-S-9 has similar hydrocarbon chain length as PKA, but its hydrophilic moiety is larger (Parnthong et al., 2018; Wetchakul, 2013). This causes greater repulsion between Tergitol 15-S-9 head groups and decreases aggregation number as well as size of micelles. As a result, less crude oil could be encapsulated in Tergitol 15-S-9 micelles than with PKA surfactant. Thus, it could be possible that the size of micelles for selected surfactants had the rank order PKA>Tergitol 15-S-9>Tergitol TMN-6. PKA possibly has the largest micelles and illustrates the most crude oil solubilization among the three nonionic surfactants (Rosen, 1989).

From the results above on surfactant adsorption and crude oil solubilization, it can be seen that PKA shows good potential for use in EOR when compared with these commercial surfactants. Typically, the natural surfactant loss due to adsorption in reservoir rocks has been reported as 3-15 mg/g (Seethapalli et al., 2014; Ahmadi et al., 2012; Ahmadi and Shadizadeh, 2015). In this work, the adsorption of PKA at initial concentration of 1 CMC was found to be around 4.4 mg/g, which is within the common range. Additionally, PKA shows good crude oil solubilization performance similar to the commercial surfactants tested. Thus, PKA is an interesting nonionic surfactant in terms of its potential for EOR, and is a promising natural product.

4. CONCLUSION

Based on our studies, palm kernel derivative surfactant PKA shows the lowest adsorption on silica among the tested surfactants, suggesting low surfactant losses in reservoirs. Additionally, the adsorption of PKA on silica is insignificantly affected

by added salt or increased temperature. The adsorption kinetics of PKA follows pseudo-second order kinetics and Langmuir adsorption isotherm, indicating chemical adsorption and monolayer formation on silica surfaces. The thermodynamic parameters reveal that the surfactant adsorption on silica surface occurs simultaneously and uniformly on the water/silica interfaces. The adsorption process for PKA, SDS, and CTAB is exothermic. Moreover, PKA shows high performance in crude oil solubilization in comparison to the tested commercial ionic and nonionic surfactants.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial assistance provided by Faculty of Engineering's Graduate Study Scholarship, the Graduate school of Prince of Songkla University (PSU), and for facility support from the Department of Chemical Engineering, Faculty of Engineering, PSU. In addition, we would like to thank Assoc. Prof. Dr. Seppo Karrila for reviewing the draft manuscript.

REFERENCES

- Ahmadi MA, Shadizadeh SR. Experimental investigation of a natural surfactant adsorption on shale-sandstone reservoir rocks: Static and dynamic conditions. *Fuel* 2015;159:15-26.
- Ahmadi MA, Zendehboudi S, Shafiei A, James L. Nonionic surfactant for enhanced oil recovery from carbonates: Adsorption kinetics and equilibrium. *Industrial and Engineering Chemistry Research* 2012;51(29):9894-905.
- Arabloo M, Ghazanfari MH, Rashtchian D. Spotlight on kinetic and equilibrium adsorption of a new surfactant onto sandstone minerals: A comparative study. *Journal of the Taiwan Institute of Chemical Engineers* 2015;50:12-23.
- Atia AA, Radwan NRE. Adsorption of different surfactants on kaolinite. *Adsorption Science and Technology* 1997;15(8): 619-26.
- Atkin R, Craig VSJ, Wanless EJ, Biggs S. Mechanism of cationic surfactant adsorption at the solid-aqueous interface. *Advances in Colloid and Interface Science* 2003;103(3):219-304.
- Barati-Harooni A, Najafi-Marghmaleki A, Tatar A, Mohammadi AH. Experimental and modeling studies on adsorption of a nonionic surfactant on sandstone minerals in enhanced oil recovery process with surfactant flooding. *Journal of Molecular Liquids* 2016;220:1022-32.
- Belhaj AF, Elraies KA, Alnarabiji MS, Shuhli JABM, Mahmood SM, Ern LW. Experimental investigation of surfactant partitioning in Pre-CMC and Post-CMC regimes for enhanced oil recovery application. *Energies* 2019;12(12):1-15.
- Belhaj AF, Elraies KA, Mahmood SM, Zulkifli NN, Akbari S, Hussien OS. The effect of surfactant concentration, salinity, temperature, and pH on surfactant adsorption for chemical enhanced oil recovery: A review. *Journal of Petroleum Exploration and Production Technology* 2020;10(1):125-37.
- Bera A, Kumar T, Ojha K, Mandal A. Adsorption of surfactants

- on sand surface in enhanced oil recovery: Isotherms, kinetics and thermodynamic studies. *Applied Surface Science* 2013;284:87-99.
- Bera A, Mandal A, Belhaj H, Kumar T. Enhanced oil recovery by nonionic surfactants considering micellization, surface, and foaming properties. *Petroleum Science* 2017;14(2):362-71.
- Dutkiewicz E, Jakubowska A. Effect of electrolytes on the physicochemical behaviour of sodium dodecyl sulphate micelles. *Colloid and Polymer Science* 2002;280(11):1009-14.
- Emadi S, Shadizadeh SR, Manshad AK, Rahimi AM, Mohammadi AH. Effect of nano silica particles on Interfacial Tension (IFT) and mobility control of natural surfactant (Cedr Extraction) solution in enhanced oil recovery process with nano-surfactant flooding. *Journal of Molecular Liquids* 2017;248:163-7.
- Eriksson T, Börjesson J, Tjerneld F. Mechanism of surfactant effect in enzymatic hydrolysis of lignocellulose. *Enzyme and Microbial Technology* 2002;31(3):353-64.
- Iglauer S, Wu Y, Shuler P, Tang Y, Goddard WA. New surfactant classes for enhanced oil recovery and their tertiary oil recovery potential. *Journal of Petroleum Science and Engineering* 2010;71(1-2):23-9.
- Ijagbemi CO, Baek MH, Kim DS. Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions. *Journal of Hazardous Materials* 2009;166(1):538-46.
- Juang LC, Wang CC, Lee CK. Adsorption of basic dyes onto MCM-41. *Chemosphere* 2006;64(11):1920-8.
- Karnanda W, Benzagouta MS, AlQuraishi A, Amro MM. Effect of temperature, pressure, salinity, and surfactant concentration on IFT for surfactant flooding optimization. *Arabian Journal of Geosciences* 2013;6(9):3535-44.
- Lee SH, Roichman Y, Yi GR, Kim SH, Yang SM, Van Blaaderen A, Van Oostrum P, Grier DG. Characterizing and tracking single colloidal particles with video holographic microscopy. *Optics Express* 2007;15(26):18275-82.
- Liu Y. New insights into pseudo-second-order kinetic equation for adsorption. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2008;320(1-3):275-8.
- Mandal A, Bera A, Ojha K, Kumar T. Characterization of surfactant stabilized nanoemulsion and its use in enhanced oil recovery. *Proceedings of the 1st Society of Petroleum Engineers International Oilfield Nanotechnology Conference and Exhibition*; 2012 Jun 12-14; Palace Hotel, Noordwijk: Netherlands; 2012.
- Markandeya, Shukla SP, Dhiman N. Characterization and adsorption of disperse dyes from wastewater onto cenospheres activated carbon composites. *Environmental Earth Sciences* 2017;76(20):1-12.
- Mi X, Li G, Zhu W, Liu L. Enhanced adsorption of orange II using cationic surfactant modified biochar pyrolyzed from cornstalk. *Journal of Chemistry* 2016;2016:1-7.
- Mohan K. Alkaline surfactant flooding for tight carbonate reservoirs. *Proceedings of the 1st Society of Petroleum Engineers Annual Technical Conference and Exhibition*; 2009 Oct 4-7; New Orleans Ernest N. Morial Convention Center, Louisiana: USA; 2009.
- Mukherjee I, Sovacool BK. Palm oil-based biofuels and sustainability in southeast Asia: A review of Indonesia, Malaysia, and Thailand. *Renewable and Sustainable Energy Reviews* 2014;37:1-12.
- National Center for Biotechnology Information (NCBI). PubChem Compound Database; CID= 3423265 [Internet]. 2005 [cite 2020 Jan 13]. Available from: <https://pubchem.ncbi.nlm.nih.gov/compound/3423265>.
- National Center for Biotechnology Information (NCBI). PubChem Compound Database; CID=5974 [Internet]. 2004 [cite 2020 Jan 13]. Available from: <https://pubchem.ncbi.nlm.nih.gov/compound/5974>.
- Negin C, Ali S, Xie Q. Most common surfactants employed in chemical enhanced oil recovery. *Petroleum* 2017;3(2):197-211.
- Paria S, Khilar KC. A review on experimental studies of surfactant adsorption at the hydrophilic solid-water interface. *Advances in Colloid and Interface Science* 2004;110(3):75-95.
- Park S, Lee ES, Sulaiman WRW. Adsorption behaviors of surfactants for chemical flooding in enhanced oil recovery. *Journal of Industrial and Engineering Chemistry* 2015;21:1239-45.
- Parnthong J, Kungsanant S, Chavadej S. The influence of nonionic surfactant adsorption on enzymatic hydrolysis of oil palm fruit bunch. *Applied Biochemistry and Biotechnology* 2018;186(4):895-908.
- Qazi MJ, Lieferink RW, Schlegel SJ, Backus EH, Bonn D, Shahidzadeh N. Influence of surfactants on sodium chloride crystallization in confinement. *Langmuir* 2017;33(17):4260-8.
- Rabiu AM, Elias S, Oyekola O. Evaluation of surfactant synthesized from waste vegetable oil to enhance oil recovery from petroleum reservoirs. *Energy Procedia* 2016;100:188-92.
- Rosen MJ. *Surfactants and Interfacial Phenomena*. New York, USA: Wiley; 1989.
- Rostami P, Mehraban MF, Sharifi M, Dejam M, Ayatollahi S. Effect of water salinity on oil/ brine interfacial behaviour during low salinity waterflooding: A mechanistic study. *Petroleum* 2019;5(4):367-74.
- Seethapalli A, Adibhatla B, Mohanty KK. Physicochemical interactions during surfactant flooding of fractured carbonate reservoirs. *Society of Petroleum Engineers* 2004;9(4):411-8.
- Sharma G, Mohanty K. Wettability alteration in high-temperature and high-salinity carbonate reservoirs. *Society of Petroleum Engineers* 2013;18(4):646-55.
- Shaw JE. Carboxylate surfactant systems exhibiting phase behavior suitable for enhanced oil recovery. *Journal of the American Oil Chemists' Society* 1984;61(8):1395-9.
- Siddiqui MA, Kungsanant S, Chairapat S. Oil solubilization using surfactant for biohydrogen production. *Advanced Materials Research* 2014;931:183-7.
- Somasundaran P, Healy TW, Fuerstenau DW. Surfactant adsorption at the solid- liquid interface - Dependence of mechanism on chain length. *Journal of Physical Chemistry* 1964;68(12):3562-6.
- Spildo K, Sun L, Djurhuus K, Skauge A. A strategy for low cost, effective surfactant injection. *Journal of Petroleum Science and Engineering* 2014;117:8-14.
- Tehrani-Bagha AR, Holmberg K. Solubilization of hydrophobic dyes in surfactant solutions. *Materials* 2013;6(2):580-608.
- Wetchakul W. Production of Palm Kernel-Diethanolamide in a Stirred- tank Reactor [dissertation]. Songkhla, Prince of Songkla University; 2013.
- Wiśniewska M. The temperature effect on the adsorption mechanism of polyacrylamide on the silica surface and its stability. *Applied Surface Science* 2012;258(7):3094-101.

Worthen A, Bagaria H, Chen Y, Bryant SL, Huh C, Johnston KP.
Nanoparticle stabilized carbon dioxide in water foams for
enhanced oil recovery. Proceedings of the 18th Society of

Petroleum Engineers SPE Improved Oil Recovery
Symposium; 2012 Apr 14-18; Cox Business Convention
Center, Oklahoma: USA; 2012.