



## Performance of palmitoyl diglycol amide and its anionic and nonionic derivatives in reducing crude oil/water interfacial tension in absence of alkali



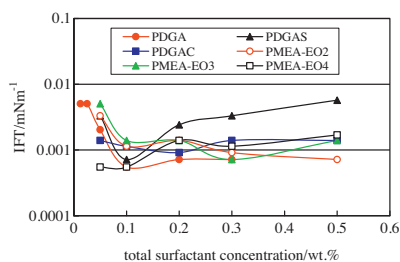
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### HIGHLIGHTS

- Palmitoyl diglycol amide (PDGA) was synthesized and characterized.
- Anionic and nonionic derivatives of PDGA were synthesized and characterized.
- IFT behavior of these products for surfactant–polymer flooding was evaluated.
- Performance is found to correlate with their cross section area at interface.
- Those with small cross section area at interface give better performance.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Palmitoyl diglycol amide (PDGA) and its anionic derivatives, palmitoyl diglycol amide sulfate (PDGAS), palmitoyl diglycol amide carbonate (PDGAC), and nonionic derivatives, palmitoyl monoethanol amide ethoxylates (PMEA-EO<sub>n</sub>,  $n = 2, 3, 4$ ), were synthesized, characterized and incorporated into surfactant formulations for reducing Daqing crude oil/connate water IFT by mixing with a lipophilic surfactant, didodecylmethylcarboxyl betaine (diC<sub>12</sub>B), and a hydrophilic surfactant, cetyldimethylcarboxyl betaine (C<sub>16</sub>B), in absence of alkali. Suffering from solubility limit PDGA can be incorporated into the formulation at a molar fraction of 0.5 and ultra low IFT can be attained in a total surfactant concentration range, 0.01–0.3 wt.%. The nonionic derivatives, PME-A-EO<sub>n</sub> ( $n = 2, 3, 4$ ), with improved solubility in water, can be incorporated into the formulation at a higher molar fraction, 0.6, and ultra low IFT can be attained in a wide total surfactant concentration range, 0.05–0.5 wt.%. The increase of EO number in PME-A-EO<sub>n</sub> can be compensated by increasing/decreasing the molar fraction of diC<sub>12</sub>B/C<sub>16</sub>B in the mixture. The anionic derivatives, PDGAS and PDGAC, however, can be incorporated into the formulations at a much lower molar fraction, 0.25 and 0.29, respectively. Although the increased hydrophilicity of the anionic derivatives can be compensated by increasing the molar fraction of diC<sub>12</sub>B in the mixtures, and ultra low IFT can be achieved in the same total surfactant concentration range, the overall IFT behavior is not so good as systems containing the nonionic derivatives. It seems that the IFT behavior of these systems correlates well with the cross section area,  $a^\infty$ , of PDGA and its derivatives, those with smaller  $a^\infty$ , give in general better IFT behavior, showing that the cross section area of a surfactant at interface is crucial for selecting surfactants for surfactant–polymer flooding free of alkali.

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## 1. Introduction

It has been well known that after first and secondary (water flooding) recoveries there are still 60–70% original oil in place (OOIP) remained underground [1,2], mostly as droplets trapped in porous locks due to capillary action [3,4]. The early researches have revealed that if the interfacial tension (IFT) between crude oil and connate water can be reduced to ultra low, or  $<10^{-2}$  mN/m, for example, by using surfactants, the capillary force can then be overcome and the oil droplets can be mobilized to flow to production wells under water flooding pressure [5,6]. This had resulted in the appearance of a new type of tertiary oil recovery technique, surfactant flooding, since 1970s [7].

In a surfactant–oil–water (SOW) system, the oil/water IFT usually decreases with increasing surfactant concentration, but the achieving of an ultra-low IFT depends not only on the structure and concentration of surfactants, but also on the property of crude oil and connate water, as well as temperature and additives such as co-surfactants and electrolytes [8–10]. Researches have indicated that for suitable surfactant systems ultra low IFT can usually be attained in two surfactant concentration ranges, typically 2–10 wt.% (concentrated) and 0.05–0.5 wt.% (dilute) in water [8,11]. The concentrated systems involve usually formation of middle phase (Winsor III) microemulsions [8–10], whereas the dilute systems concern simply adsorption of surfactant molecules at oil/water interface [8]. As a result two type of surfactant flooding techniques, concentrated microemulsion flooding [12] and dilute surfactant flooding [8], have been developed and extensively studied in the past half century. Compared with concentrated surfactant flooding techniques, which ensures theoretically high recovery due to solubilization of the microemulsion to oil, dilute surfactant flooding techniques give relatively low recovery, but are economically more attractive and has been paid more attention during the past decades [13,14].

A typical dilute surfactant flooding technique is alkali–surfactant–polymer (ASP) flooding [13,15], where the alkali added into the aqueous phase significantly improves the recovery by reacting with the active components, such as long chain hydrophobic acids and esters in the crude oil, to form soap type surfactants in situ, which together with the added surfactants makes it easier to achieve an ultra-low oil/water IFT [13], whereas the hydrophilic polymers like polyacrylamides (PAM) are responsible for increasing the sweep efficiency of injected fluids by increasing the viscosity of the solutions. This protocol has been proved to be efficient for most of the oilfields in China [16] and a series of inexpensive anionic surfactants, such as petroleum sulfonates, alkylarylsulfonates, petroleum carbonates, etc., have been developed and tested in China in the past decades [17]. However, the pilots carried out recently indicates that the use of alkali may also result in some side effects, such as plugging of porous structure and formation of deposits on apparatus and pipelines, due to the production of water insoluble compounds by reaction of alkali with ions from connate water and sandstones [18–22]. Improved protocols, such as ASP flooding using weak alkali and surfactant–polymer (SP) flooding free of alkali, are therefore currently more fascinating [18].

The mechanism of achieving an ultra low oil/water IFT in microemulsion systems has been well understood. It is typically a concomitant of middle-phase (Winsor III) microemulsions, and usually a minimum IFT can be attained on the settling of “optimum state” [8]. A series of parameters and criterions have been proposed to define and for looking for this state, such as partition coefficient ( $\rightarrow 1$ ) [4,8,9], Winsor *R* ratio ( $\rightarrow 1$ ) [10], packing parameter ( $\rightarrow 1$ ) [10,23], solubilization parameter ( $\rightarrow$  maximum)

[10], HLB and PIT [24,25] and hydrophilic/lipophilic deviation (HLD) ( $\rightarrow 0$ ) and surfactant affinity difference (SAD) ( $\rightarrow 0$ ), etc. [25–27]. Nevertheless, the key governing the achieving of an ultra-low IFT is that the interactions of the surfactant film with both the oil and water molecules should be as big as possible and balanced [10]. In other word the surfactant molecules adsorbed at the oil/water interface should be composed of both a big hydrophobic tail and a strong hydrophilic headgroup, and have simultaneously a cross section area as low as possible for achieving a maximum adsorption, based on the Winsor *R* ratio principle.

The settling of an ultra low IFT in dilute SOW systems is quite different, where solubilization effect is usually minor [8] and the achieving of an ultra low  $\gamma_{cmc(O/W)}$  relies on only the adsorption of surfactant molecules at oil/water interface. According to the Gibbs adsorption theory and the Langmuir monolayer equation, surfactants which give high adsorption at oil/water interface but have less micellization tendency in bulk solutions are in general superior. In ASP flooding there are synergisms between the surfactants in situ produced and those added, and the excess alkali behaves also as an electrolyte, both are beneficial to the increase of surfactant adsorption onto the crude oil/water interface [13,16]. This advantage, however, disappeared in SP flooding free of alkali, and as a result, surfactants effective in an ASP flooding may be ineffective or less effective in a SP flooding. New surfactants therefore need to be designed and developed [17,18].

Recent studies have shown that for Daqing crude oil/connate water amphiphilic surfactants such as alkyl betaines [28–31] may be good candidates due to their overall electrical neutrality and dense adsorption at oil/water interface. In addition nonionic surfactants with small hydrophilic headgroups, such as alkanolamides [17,32], have been found to be superior to typical ethoxylates with long ethylene oxide (EO) chains, and can be contained into the formulations at a high molar fraction ( $>0.5$ ), which is significant for reducing the cost of the chemicals, since alkanolamides are derived from reproducible materials and are much cheaper than betaines. In this paper we try to further understand the structure factor governing the performance of the alkanolamides so as to obtain optimal surfactants for SP flooding free of alkali. For this purposes palmitic diglycol amide (PDGA) and its anionic and nonionic derivatives were synthesized, characterized, and their performance in reducing Daqing crude oil/connate water IFT were examined. It is found that the performance of PDGA and its anionic and nonionic derivatives correlates with their cross section area,  $a^\infty$ , at saturated adsorption at air/water interface, and the nonionic derivatives, possessing small  $a^\infty$  and reasonable solubility, are in general superior to the anionic derivatives with big  $a^\infty$ .

## 2. Experimental

### 2.1. Materials

Palmitoyl chloride of 98% purity was purchased from Acros Co. Ltd. Diglycolamine (DGA) of  $\geq 98\%$  purity was purchased from Aladdin-reagent (Shanghai). Monoethanol amine, magnesium oxide, tetrahydrofuran (THF), chloroform (all AR grade), and chlorosulfonic acid and 717 anion exchange resin (alkaline polystyrene) of CP grade were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Chloroacetic acid  $\geq 98\%$  purity was provided by Rhodia Feixiang Chemicals Co. Ltd., China. Methyl palmitate of commercial grade was supplied by Jinan Jinlun Chemicals Co. Ltd., China. These chemicals were all used as received. Ultrapure water with a resistance of 18.2 M $\Omega$  cm at 25 °C was purchased from a

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