



Extended surfactants: A well-designed spacer to improve interfacial performance through a gradual polarity transition



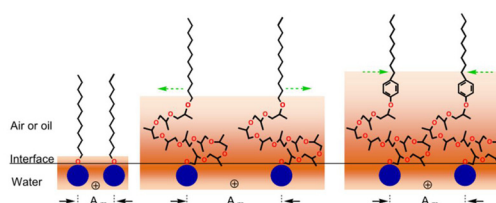
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HIGHLIGHTS

- Novel extended surfactants using a phenyl group as a part of spacer.
- Well-designed spacer provides a more gradual polarity transition intramolecularly.
- The improved spacer promotes various interfacial properties.
- Understanding the effect of spacer structure on the performance of surfactants.

GRAPHICAL ABSTRACT



Spatial configurations of SDS (left), APoS (center) and PPoS (right) in the interfacial layers of air (oil)/water

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ABSTRACT

Four novel alkylaryl sulfate extended surfactants were synthesized by introducing a phenyl group, together with a polypropylene oxide (PPO) chain, as the intermediate polarity spacer in the extended surfactant molecules. Some characteristic properties of the novel extended surfactants were investigated in view of the effect of spacer structure on the performance of the surfactants. It is found that not only the PPO chain but also the phenyl group exerts a strong influence on the performance since these extended surfactants exhibit low *cmc*, great effectiveness and efficiency of surface tension reduction, high electrolyte resistance and ultralow interfacial tension comparing with the phenyl-free counterpart. It is notable that using a polarizable phenyl group as a junction unit in the intermediate polarity spacer may produce two potential effects: one is obviously resulting in a more gradual polarity transition intramolecularly than that of the PPO chain itself as a spacer; and the other is possibly forming a denser molecular packing and a thicker interfacial layer when the novel extended surfactants occupy at air/water (brine) surface or decane/water (brine) interface, which is attributed to a well-designed molecular structure in favor of forming a more gradual polarity transition zone in the interfacial layer.

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1. Introduction

Conventional surfactant molecules generally consist of two parts: a polar hydrophilic head and a nonpolar hydrophobic tail that are directly connected by chemical bond. Introducing a junction unit between hydrophilic head and hydrophobic tail is expected

to improve interfacial performance of surfactants. For example, sodium alkylbenzene sulfonate (SDBS) contains one more phenyl group in the molecule compared with sodium alkyl sulfonate (AS), and exhibits lower Krafft temperature, better foamability and greater detergency than those of AS [1]. Otherwise, inserted with an additional polar PEO chain, sodium alkyl polyoxyethylene sulfate (AES) shows superior aqueous solubility, foamability and electrolyte tolerance to the precursor substance sodium dodecyl sulfate (SDS). Nowadays, an intermediate polarity spacer such as a polypropylene oxide (PPO) or polypropylene–polyethylene oxide

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Glossary

PON	the numbers of propylene oxide groups
cmc	critical micelle concentration
γ_{cmc}	surface tension at cmc
pC_{20}	efficiency in surface tension reduction
a_m	minimum area occupied per surfactant molecule
IFT	interfacial tension
$\Delta G_{ad}^0(PO)$	(in J/mol), the average contributions to free energy of adsorption per PO group

(PPO–PEO) chain has been tried to insert between the hydrophilic head and the hydrophobic tail of the surfactant, then so called “extended” or “extended chain” surfactants are obtained [2,3]. The introduction of PO groups in the hydrophobe of the surfactant molecule helps to extend the tail further into the oil phase without sacrificing water solubility [4] due to the longer tail. On the water side, the interactions with the water phase can be enhanced by inserting EO groups. This arrangement makes membrane of extended surfactants formed at air/water surface or oil/water interface incassated and facilitates smooth change from polar to apolar media because of the occurrence of a PPO chain offering a thick and smooth polarity transition zone between two bulk phases [3,5,6]. This is considered as a key factor for extended surfactants with desirable ultralow interfacial tension (IFT) [7–10] and good solubilization properties, especially for highly hydrophobic oils and vegetable oils [11–13]. In addition, adsorption tests [14] onto kaolinite clay indicated that the loss of these surfactants can be comparable to other types of anionic surfactants. These excellent properties make extended surfactants desirable in numerous applications, including cosmetics, drug delivery systems, cleaning technologies, soil remediation and especially enhanced oil recovery [9,14]. Therefore extended surfactants have received significant attention from both scholars and practitioners in decades.

Although early in 1980s, Exxon Production Research Company [15] initiated alkyl polypropoxylate sulfate surfactants and applied them for enhanced oil recovery, until 1995 Miñana-Perez [2,7] assigned a name “extended” to these surfactants containing an intermediate polarity spacer, such as a PPO chain, in the middle of molecule between hydrophobic tail and hydrophilic head. The term “extended surfactants” refers to the fact that the PPO chain brings a polarity transition zone between the head and the tail of a surfactant molecule, thus “extending” the reach of these groups into oil and aqueous phases. Recent researches have shown that extended surfactant structure works with different head groups such as sulfate, galactose, xylitol, carboxylate and phosphate, with a linear and branched alkyl chain and with a PPO or PPO–PEO chain as a spacer [2,16–20]. They also found that the nature of the head groups, the numbers of PO groups (PON), the numbers of EO groups (EON) and the sequence of PO and EO groups in an extended surfactant molecule play an important role in properties such as aggregation, adsorption, microemulsion and interfacial tension, etc. Although an extended surfactant involving a phenyl group has once been mentioned in 1990 [21], it is noticed that the work was only focused on the effect of the alkyl chain lengths and the PON on the surface activity and wetting ability. It is conceivable that the introduction of an easily polarizable phenyl group together with a PPO chain as the intermediate polarity spacer would make the extended surfactant underwent a more gradual transition from nonpolar to polar intramolecularly. Additionally phenyl group having a better compatibility with polar oil, long chain alkane and crude oil, it is expected that the extended surfactant with a phenyl group would stretch out further into two bulk phases, and result in a smoother and thicker transition zone on the interface. This should

bring a greater reduction of interfacial tension and create a more suitable environment for solubilizing lipophilic molecules.

To date, extended surfactants have been a foremost candidate for producing ultralow IFT for microemulsion and enhanced oil recovery (EOR). However, since extended surfactants are a relatively new class of surfactants, the understanding of their fundamental properties is still quite limited. In this paper, a fine-tuned structure of extended surfactant is designed through a gradual polarity transition intramolecularly to improve interfacial performance, and then sodium nonylphenoxy polypropyleneoxide sulfates, a series of novel extended surfactants, were prepared by combining the phenyl group and the PPO chain together as the intermediate polarity spacer. This study provides an insight into the role of the phenyl group and the PPO chain inserted into extended surfactant molecules, especially the PON on performance of the surfactants, such as surface activity, micellization, electrolyte resistance, and IFT. The goal of this paper is that these remarks and the corresponding understanding will bring us a step closer to fully exploiting the exciting potential of extended surfactants.

2. Experimental

2.1. Materials

Propylene oxide (PO, analytical grade), N,N-dimethylformamide (DMF, analytical grade), chlorosulfonic acid (chemical grade), and the other reagents (analytical grade), were purchased from the Sinopharm Chemical Reagent Company (Shanghai, China) and used as received without further purification. Nonylphenol (NP, industrial grade), was purchased from Dyestuff Chemical Factory (Changzhou, China). *n*-decane (min. 99.0%), was purchased from TCI (Japan).

2.2. Synthesis of sodium nonylphenoxy polypropyleneoxide sulfates

Scheme 1 shows the synthetic route of the intermediates nonylphenoxy polypropyleneoxide ethers (PP_n) and the target extended surfactants sodium nonylphenoxy polypropyleneoxide sulfates (PP_nS), where n indicates the average PON .

Nonylphenol was firstly propoxylated according to a conventional synthesis method [20,22] to get the intermediates nonylphenoxy polypropyleneoxides (PP_n). Four kinds of PP_n with different n of 3, 6, 9 and 12 were labeled as PP_3 , PP_6 , PP_9 and PP_{12} , respectively.

Taking synthesis of nonylphenoxy tripropyleneoxide sulfate (PP_3S) as an example, PP_3 (10 mmol, 9.85 g) was dissolved in DMF (30 mL), and HSO_3Cl in DMF (10 g, contain 28 mmol SO_3) was added dropwise as the mixture stirred at 0 °C. The post-sulfonation reaction was held for another 15 min after finishing feeding; after that the reaction mixture was neutralized with a 25% aqueous sodium hydroxide solution. Solvents were then evaporated under reduced pressure and crude PP_3S product was obtained. Purified PP_3S product was obtained (11.9 g, 93% yield) on treatment over a silica-gel column with elution using ethyl acetate/methanol (90:10, v/v). The other three products PP_6S , PP_9S and $PP_{12}S$ were obtained using the similar procedure and the yields were 92, 92 and 90%, respectively.

2.3. Measurements

2.3.1. Krafft point (T_K)

The Krafft temperatures (T_K) were determined by heating 1.0 wt% of the surfactant solution until a clear solution was obtained [1,23], or by cooling the 1.0 wt% surfactant solution to cloudy state

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