

# Adsorption behavior and conformational changes of acrylpimamic acid polyglycol esters at the air-water interface



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## ABSTRACT

Three acrylpimamic acid polyglycol esters (APAPG) with different molecular weight were successfully prepared. The surface properties of three esters were investigated by surface tension and fluorescence techniques. The critical micelle concentrations (CMC) were detected. Reorientation theory was proposed to describe the adsorption behavior and the conformational changes of these surfactant molecules at the air-water interface. With increasing ester concentration the molar fraction of solvent decreased and that of surfactant molecules increased. The adsorption amount of state 1 presented unimodal shape and adsorption amount of state 2 presented sigmoid with the growth of  $\Gamma$ . The free energy of adsorption is more negative than that of micellization, thus the surfactant molecules adsorb on the surface firstly and then form micelles after saturation adsorption.

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## 1. Introduction

Surfactants are amphipathic molecules with both hydrophilic and hydrophobic moieties. They play an important role in many chemical industries, including detergents, emulsions, paints, foaming agents, cosmetics and pharmaceuticals etc. [1–7]. With increasing concern for the need to develop sustainably and protect the environment, renewable resources are crucial areas in the research for alternatives to fossil-based raw materials. Renewable sources of the hydrophobic moiety are steroids, monoterpenes, rosin acids and long chain alkyl groups as well as aromatic compounds [8–12]. Rosin is a kind of natural material that possesses hydrophobic groups with a tricyclic hydrophenanthrene structure and the synthesis and application of rosin-based surfactants have attracted great attention. So far, a variety of rosin-based surfactants such as N,N,N',N'-tetramethyl-N,N'-diethanolamine dehydroabietate butyldiamine dibromide, quaternary amine of diethylaminoethyl rosin ester, bisquaternary ammonium salt of rosinat,

dehydroabietic acid (2-Acryloyloxy) ethyl ester and rosin-based betaine zwitterionic surfactant have been prepared [9,13–16].

Polyethylene glycol is an important water-soluble polymer. Its non-toxic, biocompatible and excellent reactivity due to the two equivalent hydroxyl groups make it a promising candidate in many applications, such as controlled and targeted drug delivery systems, cell hybridization technology and biotechnology. Polyethylene glycol also has been used most widely for surface modification because of its unique hydrophilicity, flexibility and high exclusion volume properties in water. Moreover, modification of polyethylene glycol has been extensively studied. Polyethylene glycol ethers, polyethylene glycol esters, polyethylene glycol amides, polyethylene glycol amines, polyethylene glycol aldehydes and other derivatives have been synthesized and proved valuable applications [17]. Among them, amphipathic PEGylated rosin derivatives including Poly (oxyethylene) dehydroabietates, rosin-maleic anhydride-polyethylene glycol copolymer were studied and were used successfully as surfactant and microencapsulating material respectively [18,19]. In the meantime, many studies have been carried out regarding the surface properties of polyoxyethylene surfactants [20].

It is important to understand the underlying principle governing

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interfacial properties of a given surfactant and to design the system or the molecular structure of surfactants for the purpose of optimizing the performance like surface activity, micellar and self-assembly properties. Many adsorption models have been developed to further describe the equilibrium adsorption of surfactants at the air-water interface. In particular, many efforts were made to investigate the effect of molecular conformation and intermolecular interaction on the adsorption properties of surfactants [21–29]. However, to the best of our knowledge, there has little systematic study investigating the effect of molecular weight of surfactant molecules on the adsorption process and interfacial properties of the air-water interface [30].

In this paper, the equilibrium surfactant tensions and the critical micelle concentrations (CMC) of three acrylicpimaric acid polyglycol esters (APAPG) were detected. In the meanwhile, reorientation theory was proposed to describe the adsorption states, adsorption process and the conformational changes of these surfactant molecules at the air-water interface.

## 2. Experimental

### 2.1. Materials

Acrylicpimaric acid was prepared in our laboratory. Trichloromethane ( $\text{CH}_2\text{Cl}_2$ , Admmas-beta, AR) were refluxed for 12 h with calcium hydride and stored in glass bottles with molecular sieves (Kayou Type 4A). 1-Ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDCI, Kayou, China, 98%), 4-dimethylaminopyridine (DMAP, Admmas-beta, 99%), Polyethylene glycol (average  $M_n = 1000, 1500$  and  $2000$ ) and pyrene (AR, 99%) were used as received. Doubly distilled deionized water was used for all sample preparations and dilution.

### 2.2. Characterization

The surface tensions of the solutions were measured. All solutions of different concentrations were prepared and stored in closed bottles for 24 h before measurement. Surface tensions were measured with a tensiometer BZY-2 (Shanghai, China). The platinum plate was always cleaned and heated to a red/orange color with a Bunsen burner before use. The aging time was at least 20 min. All experiments were recorded at least three times to ensure perfect duplication.

$6 \text{ mg L}^{-1}$  pyrene solution was prepared by adding a known weight of pyrene in methanol.  $0.1 \text{ mL}$  pyrene solution was added to  $100 \text{ mL}$  different concentration APAPG aqueous solutions. The mixture was sonicated to yield a clear solution and keep at room temperature for 24 h before experiments. Fluorescence measurements were taken on a LS-55 Fluorescence Spectrophotometer (Perkin Elmer, America), using  $10 \text{ mm}$  path length quartz cuvette. Excitation was done at  $331.5 \text{ nm}$  and emissions were recorded in

the  $340\text{--}450 \text{ nm}$  wavelength range. Excitation and emission slits with a bandpass of  $2.5 \text{ nm}$  were used for all measurements. All measurements were taken at  $25 \text{ }^\circ\text{C}$ .

For transmission electron microscope (TEM) measurement,  $0.05 \text{ g L}^{-1}$  low molecular weight APAPG,  $0.1 \text{ g L}^{-1}$  medium molecular weight APAPG and  $1 \text{ g L}^{-1}$  high molecular weight APAPG were drop casted onto a carbon-coated copper grid followed by drying in air for 2 days under ambient condition. The images were then recorded on a Tecnai F30 transmission electron microscopy and the samples were operated at an accelerating voltage of  $120 \text{ kV}$ .

The dynamic light scattering (DLS) experiments were carried out in Malvern Instruments Zetasizer Nano ZS instruments attached with a He-Ne gas laser.  $0.05 \text{ g L}^{-1}$  low molecular weight APAPG,  $0.1 \text{ g L}^{-1}$  medium molecular weight APAPG and  $1 \text{ g L}^{-1}$  high molecular weight APAPG were used and the solutions were then filtered through membrane filter paper (pore diameter =  $0.22 \text{ }\mu\text{m}$ ). DLS measurements of the filtered solutions were then carried out at  $25 \text{ }^\circ\text{C}$ .

### 2.3. Synthesis of APAPGs

Three APAPGs nonionic surfactants with different molecular weights have been prepared. They have the same phenanthrene structure but different in the number of oxyethylene groups. Acrylicpimaric acid ( $3.741 \text{ g}$ ,  $10 \text{ mmol}$ ) and 4-dimethylaminopyridine (DMAP) ( $6.1 \text{ mg}$ ,  $50 \text{ mmol}$ ) were dissolved in  $30 \text{ mL}$  trichloromethane ( $\text{CHCl}_3$ ). The reaction mixture was cooled to  $0 \text{ }^\circ\text{C}$  and then 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDCI) ( $5.748 \text{ g}$ ,  $30 \text{ mmol}$ ) was added. The mixture was allowed to slowly warm to RT for 4 h. Subsequently, polyglycol solutions containing  $11 \text{ mmol}$  polyglycol in  $20 \text{ mL}$   $\text{CHCl}_3$  was added into the above mixture respectively. The mixtures were stirred at  $50 \text{ }^\circ\text{C}$  for 48 h under the protection of nitrogen. The crude products were separated by the Weibull Method [31]. The procedure and the characterization have been described in detail in our previous paper [32].

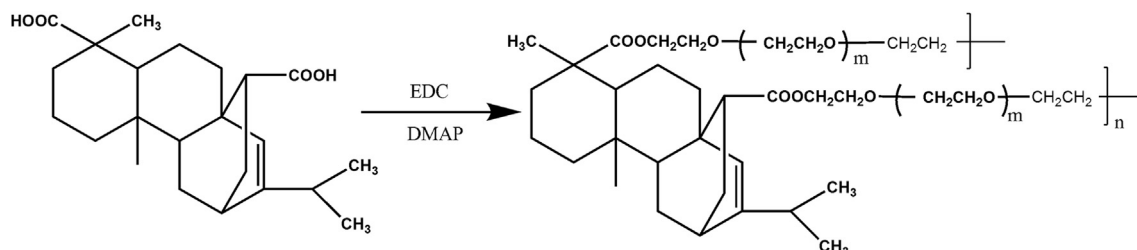
The preparation process of APAPGs can be expressed in Scheme 1.

Three polymers were synthesized with different molecular weight grades polyglycol and were referred to as LMW, MMW and HMW APAPGs respectively. The yields of HMW, MMW and LMW-APAPG are 52%, 50% and 47% respectively. The  $M_n$ s of LMW, MMW and HMW APAPGs are  $4240, 4710$  and  $7181 \text{ g/mol}$  and the PDI are about 1.2, 1.36 and 1.14 respectively.

## 3. Results and discussion

### 3.1. Equilibrium surfactant tension

The CMC values were obtained from surface tension ( $\gamma$ ) measurements of the micellar solutions. For LMW-APAPG, as the



Scheme 1. Diagram of synthesis process for acrylicpimaric acid polyglycol esters.

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