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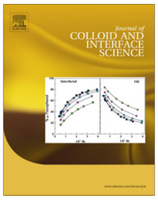

Binding of cationic surfactants to a thermo-sensitive copolymer below and above its cloud point

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ABSTRACT

The binding interactions between cationic surfactants and a statistical thermo-sensitive copolymer based on oligo(ethylene glycol) methacrylates were studied by isothermal titration calorimetry (ITC), surfactant selective electrode (SSE) and dynamic light scattering (DLS). Strong binding interactions were observed between this copolymer and cationic surfactants. The binding is driven by the hydrophobic effect, occurring on the hydrophobic backbone instead of the ethylene–glycol side chains. The surfactant saturation concentration C_2 depended on the polymer concentration, but was not affected by temperature. Three types of cationic alkyltrimethylammonium bromide surfactants (RTAB with R equal to C_{12}, C_{14}, and C_{16}), namely, dodecyltrimethylammonium bromide (DoTAB), tetradecyltrimethylammonium bromide (TTAB), and cetyltrimethylammonium bromide (CTAB), were examined, and the results confirmed that the binding affinity followed the sequence: CTAB > TTAB > DoTAB.

1. Introduction

The interactions between surfactants and water-soluble polymers have been extensively studied due to their wide applications, such as in detergents, cosmetic and pharmaceutical products. Mixing surfactants and polymers can generate many interesting functional polymorphic micro- or nano-structures, such as micelles, complexes, vesicles, precipitates, liquid crystals, and gels, which have a direct impact on the phase behavior, rheological and interfacial properties [1–4]. Thus, knowledge on the physical properties of mixtures of surfactants and polymers will guide formulators in optimizing the formulation of personal care products. Due to the absence of strong electrostatic forces, the binding interaction between ionic surfactants and nonionic water-soluble polymers displays a much simpler behavior than ionic surfactant/opposite charged polymer systems. In these systems, hydrophobic effects play a significant role as an attractive force producing surfactant micelles that bind to the polymers below their critical micelle concentration (CMC) [5]. In general, the binding interactions between cationic surfactants and neutral polymers are much weaker than the corresponding interactions between similar polymers and anionic surfactants [6–11]. For example, an anionic surfactant such as sodium dodecylsulfate (SDS) displays strong cooperative binding interaction with a diverse range of neutral water-soluble polymers, such as poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), and poly(vinylpyrrolidone) (PVP), while a cationic surfactant such as tetradecyltrimethylammonium bromide (TTAB) is more selective and only binds to those polymers with specific hydrophobic groups, such as hydrophobically modified water-soluble polymers [10,11]. The binding isotherms and resulting mechanisms for ionic surfactant/neutral polymer systems are also dependent on polymer molecular weight, electrolytes, temperature, and solvent types.

Among these neutral water-soluble polymer/surfactant systems, temperature can play an important role in the binding interactions, particularly for thermo-sensitive polymers that exhibit a lower critical solution temperature (LCST) in aqueous solutions. Poly(*N*-isopropylacrylamide) (PNIPAM) is a thermo-sensitive polymer that undergoes chain conformation transition from an extended coil to a compact globule near the LCST, which is also referred to as the cloud point (T_c). The impact of ionic surfactants on the phase transition and chain conformation below and above the cloud point has received increasing attention [12–15]. Swanson et al. [12] investigated the interactions between SDS and PNIPAM in aqueous solution using anisotropic time-resolved fluorescence measurements, and they found that below the LCST, PNIPAM chains transformed from an expanded chain conformation to a swollen surfactant–polymer complex with reduced mobility due to the repulsion between the ionic groups of the polymer-bound surfactants. Above the LCST, the addition of SDS transformed the collapsed globule into an expanded surfactant swollen polymer coil. Similar results were observed by Yang and co-workers using nuclear magnetic resonance (NMR), and the effect of surfactant

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concentration was also studied in details [13,14]. The interactions of PNIPAM with cationic surfactants were examined by Loh et al. [15], using isothermal titration calorimetry, where the interactions were significantly affected by temperature due to changes in the hydration of polymer chains near the LCST. The binding interactions between ionic surfactants and thermo-sensitive Pluronic triblock copolymers such as PPO-PEO-PPO [5] and PEO-PPO-PEO [11,16] were also reported. Mixed micelles of Pluronic copolymer and surfactant were produced in aqueous solution, and the percolation transition temperature of the mixture was found to decrease with the volume fraction of surfactants [16].

In this contribution, the binding interactions between cationic surfactants and a thermo-responsive statistical copolymer based on oligo(ethylene glycol) methacrylates (OEGMA) were studied by several techniques, such as isothermal titration calorimetry (ITC), surfactant selective electrode (SSE) and dynamic light scattering (DLS). The copolymer possesses a brush-like structure with a relatively hydrophobic methacrylate and hydrophilic ethylene glycol segments, and as reported, poly(OEGMA) is touted to be an excellent alternative to PNIPAM due to its biocompatible properties [17]. Three types of cationic surfactants, namely, DoTAB, TTAB, and CTAB, were studied, where the effect of surfactant hydrophobicity on the binding interactions was elucidated. The different binding processes below and above the cloud point were examined by analyzing the calorimetric titration and electromotive force (EMF) data, while the size of microstructure during the binding process was monitored by DLS.

2. Experimental

2.1. Materials

The well-defined brush-like statistical copolymer containing 2-(2-methoxyethoxy) ethyl methacrylate (MEO_2MA, M_n = 188 g/mol) and poly (ethylene glycol) methyl ether methacrylate (PEGMA, M_n = 2080 g/mol) (poly(MEO_2MA-*co*-$PEGMA_{2080}$)) was prepared via the atom transfer radical polymerization (ATRP) to yield a copolymer with M_n = 17,300 g/mol and a polydispersity index (PDI) of 1.61. The copolymer possessed a cloud point of 27 °C in aqueous solution. The details of synthetic procedures and characterizations of the copolymer were reported previously [18]. Cationic surfactants, such as DoTAB, TTAB, and CTAB of high purity were purchased from Sigma–Aldrich, and used without further purification. The water used was obtained from the Millipore-Q water purification system, which has a resistivity of 18.2 MΩ·cm. The chemical structure of the copolymer is shown as below in Fig. 1.

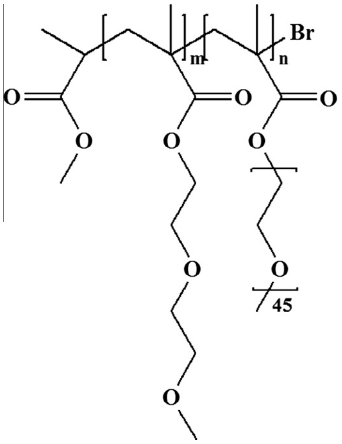

Fig. 1. Chemical structure of statistical copolymer with monomer ratio 99–1 (m:n).

2.2. Isothermal titration calorimetry (ITC)

The calorimetric data on the binding interactions between cationic surfactants and copolymer poly(MEO_2MA-*co*-$PEGMA_{2080}$) were obtained using a Microcal VP-ITC calorimeter (Northampton, MA). The stock solutions with different concentrations, i.e. CTAB (20 mM), TTAB (100 mM), and DoTAB (200 mM), were selected for each cationic surfactant by considering their different CMCs. The titrations of 0.05, 0.1, and 0.2 wt% copolymer solutions were conducted at both 25.0 and 30.0 °C, which were below and above the cloud point of the copolymer (27.0 °C). A detailed description on this power compensated differential calorimetric instrument was previously described by Wiseman and co-workers [19]. The microcalorimeter consists of a reference cell and a sample cell of approximately 1.451 mL in volume, and surfactant solution was injected from an injection syringe into the sample cell filled with either water or copolymer solutions. The syringe is tailor-made such that the tip acts as a blade-type stirrer to ensure an efficient mixing at 307 rpm. In this study, we utilized identical injection protocol and same time interval between successive injections for all ITC measurements.

2.3. Surfactant selective electrode (SSE)

An ionic surfactant electrode (Metrohm 6.0507.120) was used to monitor the binding interactions by measuring changes in the electromotive force (EMF) attributed to changes in the free surfactant concentration. The EMF was measured and recorded on a Metrohm 809 Titrando system equipped with a surfactant selective electrode and a double junction Ag/AgCl reference electrode (Metrohm 6.0750.100). The EMF measurements were designed to complement the ITC experiments using similar copolymer and surfactant concentrations performed at both 25.0 and 30.0 °C. For example, a 20 mM CTAB stock solution was added dropwise to a rapidly stirred 20 mL 0.05, 0.1 and 0.2 wt% copolymer solutions at 25.0 and 30.0 °C. The EMF values were recorded when the equilibrium was achieved after each injection of the surfactant solution. The resulting experimental data were plotted with EMF (mV) versus CTAB concentration, and the critical points for the binding interactions were determined.

2.4. Dynamic light scattering (DLS)

Dynamic light scattering measurements were performed on a Brookhaven BI-200SM goniometer system equipped with a PolyScience water-bath. All the samples were filtered through a 0.45 μm filter to remove dust prior to the measurements. For a DLS measurement, the time correlation function of the scattering intensity $G_2(t)$ is defined as $G_2(t) = I(t)\ I(t+\Delta t)$, where $I(t)$ is the intensity at time t and Δt is the lag time, and the inverse Laplace transform of REPES in the Gendist software package was used to analyze time correlation functions. Thus, the translational diffusion coefficient D of the particle can be determined from the slope of Γ versus q^2, and the apparent hydrodynamic radius R_h was then determined from the Stokes–Einstein equation:

$$R_h = \frac{kT}{6\pi\eta D} = \frac{kTq^2}{6\pi\eta\Gamma} \tag{1}$$

where k is the Boltzmann constant, η is the solvent viscosity, D is the translational diffusion coefficient, Γ is the decay rate, and q is the scattering vector ($q = 4\pi n \sin(\theta/2)/\lambda$, where n is the refractive index of solvent, θ is the scattering angle, and λ is the wavelength of the incident laser light in vacuum).