

Cationic surfactants/copoly(styrene oxide–ethylene oxide) systems: A physico-chemical investigation

Pablo Taboada *, Emilio Castro, Silvia Barbosa, Víctor Mosquera

*Laboratorio de Física de Coloides y Polímeros, Grupo de Sistemas Complejos, Departamento de Física de la Materia Condensada,
Facultad de Física, Universidad de Santiago de Compostela, Spain*

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Abstract

The interactions between the diblock copolymer $S_{15}E_{63}$ and the surfactants dodecyltrimethylammonium (DoTAB) and hexadecyltrimethylammonium (CTAB) bromides have been investigated by dynamic light scattering, transmission electron microscopy and isothermal titration calorimetry. The surfactants with the same headgroup differentiate in their chain length. At 20 °C, the block copolymer is associated into micelles with a hydrodynamic radius of 11.3 nm, which is composed of a hydrophobic styrene oxide (S) core and a water-swollen oxypolyethylene (PEO) corona. The different copolymer/surfactant systems have been studied at a constant copolymer concentration of 2.5 g dm^{-3} and in a vast range of surfactant concentration, from 5.0×10^{-6} up to 0.1 M. When DoTAB is added to the block copolymer solution, no important variations are observed in the apparent hydrodynamic radius up to a surfactant concentration of $\sim 10^{-2}$ M, for which this magnitude starts decreasing abruptly as a consequence of disruption of the copolymer micelles due to surfactant binding. This phenomenon is also observed for CTAB but at much lower concentrations ($\sim 10^{-5}$ M). This decrease is associated to repulsive electrostatic interactions between surfactant headgroups in the micelle. Complete disruption of the mixed aggregates occurs neither for DoTAB nor CTAB in the measured concentration range. Transmission electron microscopy has confirmed this behaviour. Titration calorimetric data of micellised DoTAB present a plateau region indicating no interaction between the copolymer and the surfactant at low surfactant concentrations, followed by an exothermic decrease as a consequence of starting copolymer micelle disruption. For CTAB, an endothermic maximum points out the existence of interactions between copolymer micelles and this surfactant. This maximum is followed by a steep decrease which reflects the disruption of the mixed surfactant/copolymer micelles up to a very shallow exothermic minimum from which a very slight increase of the heat takes place, indicating that the micelle disruption process has finished.

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1. Introduction

Mixtures of polymers and surfactants are applied in a diverse range of applications using various formulations and colloidal dispersions of industrial importance in modern cosmetics, household products,

paints and so forth [1]. Currently, as a result of their capability to form hydrophobic aggregates, these systems are also attracting great interest as drug delivery systems [2]. Therefore, a great deal of fundamental investigations have been generated to study the interaction between different polymers and surfactants [1,3–6]. Amongst these, interactions between uncharged polymers and surfactants are simpler due to the absence of large electrostatic forces. The binding isotherms and the interaction mechanisms in these

* Corresponding author. Tel.: +34 981563100x14042; fax: +34 981520676.

E-mail address: fmpablo@usc.es (P. Taboada).

systems are dependent on surfactant type, polymer molecular weight, chemical structures of polymer and surfactant, hydrophobic content of the polymer, electrolyte, temperature and solvent quality. The binding interaction between anionic surfactant and uncharged polymer is much larger than between uncharged polymer and non-ionic or cationic surfactants. An anionic surfactant such as sodium dodecyl sulphate (SDS) exhibits large cooperative binding interactions with uncharged water-soluble polymers, such as poly(ethylene oxide) (PEO) or poly(vinylpyrrolidone) (PVP) while a cationic surfactant as dodecyltrimethylammonium bromide (DoTAB) only binds to very hydrophobic polymers [1]. However, recent evidence of interactions between PEO and cationic surfactants, such as dodecylammonium chloride, dodecylammonium bromide and tetradecyltrimethylammonium bromide (TTAB), were reported. This might be due to steric effects since the structure of the positive charge group for the first two surfactants is smaller than DoTAB or due to an increase in the surfactant hydrophobicity as a result of the larger hydrophobic surfactant chain, respectively [1,7].

Non-ionic block copolymers comprising a hydrophilic poly(oxyethylene) block and a second hydrophobic block have focused many attention in recent years [8–10]. The surfactant–copolymer interactions have been mainly studied on mixtures formed by poly(oxyethylene)–polyoxypropylene triblock copolymers and classical anionic, cationic and non-ionic surfactants [11–16], which might have important applications in the preparation of nanostructured materials [17], nanoparticles [18] and control drug delivery systems [19]. It was shown that the mechanism of interaction between the copolymer and surfactant is system specific and strongly dependent on temperature, and binding of surfactants occurs above a critical surfactant concentration, which is lower than the critical micelle concentration (cmc) in aqueous surfactant solutions. However, since the binding interaction between surfactant and polymer is a cooperative process and the driving force for the binding is to minimize the contact area of the hydrophobic segments and water, enhanced hydrophobicity of the polymers will favour the binding process [20–24].

In the present paper we investigate the interactions between the diblock copolymer $S_{15}E_{63}$, where S denotes the styrene oxide as the hydrophobic block ($OCH_2-CH(C_6H_5)$) and E the polyethylene oxide (OCH_2CH_2) as the hydrophilic block, and the cationic surfactants dodecyl- and hexadecyl-trimethylammonium bromides. Solutions and micelle properties of the pure block copolymer were studied previously by light scattering, densimetry and ultrasound velocity measurements [25,26]. On the other hand, it has been demonstrated [27] that the hydrophobicity of the styrene oxide block

based on the molar cmc if compared with those of propylene and butylene oxide blocks is in ratio P:B:S = 1:6:12, so enhanced interactions between the copolymer and the surfactant should occur. To determine the extent of the interactions in these copolymer–surfactant mixtures, a thermodynamic characterization of these systems was carried out through isothermal titration calorimetry (ITC) and density measurements. Dynamic light scattering (DLS) and transmission electron microscopy (TEM) were used to monitor structural changes in the micellar aggregates of the block copolymer.

2. Experimental

2.1. Materials

Dodecyl and hexadecyl trimethylammonium bromides (DoTAB and CTAB, respectively) were purchased from Sigma (stated purity $\geq 99\%$) and used as received without further purification. Water was double distilled and degassed before use. The synthesis of the diblock copolymer $S_{15}E_{63}$, was described in detail by Crothers et al. [25]. Table 1 shows the molecular characteristics of the copolymer. Solutions observed during the tube inversion tests for the copolymer remained clear to the eye throughout the temperature of 20 °C investigated in the present work.

2.2. Dynamic light scattering

Dynamic light scattering measurements were made at 20.0 ± 0.1 °C and at a scattering angle of $\theta = 90^\circ$ to the incident beam, using an ALV 5000 laser light scattering instrument equipped with a 500 mW solid state laser (Coherent Innova) with vertically polarised incident light of wavelength $\lambda = 532$ nm in combination with a ALV SP-86 digital correlator with a sampling time range from 25 ns to 40 ms. All solutions were filtered through a Millipore filter with a 0.22 μm pore size and thermostated the desired temperature for at least 30 min. Experiment duration was in the range of 5–10 min, and each experiment was repeated two or more times.

Table 1
Molecular characteristics of the copolymer

	$M_n/\text{g mol}^{-1}$ (NMR)	wt% S (NMR)	M_w/M_n (GPC)	$M_w/\text{g mol}^{-1}$
$S_{15}E_{63}$	4600	39.7	1.04	4780

Estimated uncertainty: M_n to $\pm 3\%$; wt% S to $\pm 1\%$, M_n/M_w to ± 0.01 . M_w calculated from M_n and M_w/M_n .

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