

Study on the influence of surfactants on the adsorption and electrokinetic properties of the system: Cationic starch/alumina



Elżbieta Grządka*

Faculty of Radiochemistry and Chemistry of Colloids, Department of Chemistry, Maria Curie-Skłodowska University, M. Skłodowskiej–Curie 3 Sq., 20-031 Lublin, Poland

ARTICLE INFO

Article history:

Received 10 December 2014
Received in revised form 7 May 2015
Accepted 10 May 2015
Available online 14 May 2015

Keywords:

Cationic starch
Alumina
Surfactants
Interface

ABSTRACT

The aim of this paper was to investigate the influence of some surfactants of different chemical character (SDS, CTAB, TX-100 or their equimolar mixtures) on the adsorption and electrokinetic properties of the cationic starch (CS)/alumina system. The obtained results show that CS creates multilayer complexes with SDS, TX-100 and their mixture, but does not interact with CTAB. The reason for that is connected with chemical character of the polyelectrolyte and the above-mentioned surface active agents. Formation of complexes was confirmed by the surface tension measurements and by the measurements of surfactants adsorption at the alumina surface in the presence and absence of CS. The crucial information about both the electrokinetic properties of the system and the structure of the adsorption layer was obtained from the surface charge density and zeta potential measurements. The obtained data showed the specific structure of the adsorption layer polymer/surfactant/metal oxide. According to the results the polymer is directly bonded to the surface whereas the surfactants are present in the upper parts of the electrical double layer.

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1. Introduction

Water-soluble polymers play a crucial role as additives in many technological processes where they are used as adhesives, demulsifiers, dispersants, binders, thickeners, stabilizers and film formers [1]. Cationized polysaccharides are non-toxic, relatively cheap and easily biodegradable. They find applications as effective flocculants over a wide range of pH [2,3], in the paper making industry as a cellulose adhesive [4] and also as hairstyling and conditioning products [5] as well as to treat organic and inorganic matter in wastewater carrying negative charges [2]. Cationic starch (CS) is a cationic polyelectrolyte produced by chemical reaction of starch with various reagents possessing positively charged groups (amino, ammonium, imino, sulphonium, phosphonium). Introducing a positively charged group to starch provides good mineral binding properties which is required for anchoring the mineral to the fibers [6]. Starch, a natural, non-ionic polysaccharide is a mixture of low-molecule weight amylose (MW: from 10^5 to 7×10^5 g/mol) which is mostly linear and a high-molecule-weight amylopectin (MW: from 10^6 to 10^8 g/mol) which is a highly branched globular macromolecule [7]. The amylose/amylopectin

weight ratio in starch is typically 1:3. Many commercial products widely used in different fields contain cationic starch. Among them, the most important are papermaking chemicals, drug delivery systems, daily chemicals and petroleum as well as products used in spinning and weaving, drilling, water treatment and flotation [8–12]. The cationic character of modified starch offers adsorption abilities in anionic materials, which can be exploited in practical applications [13]. The adsorption of mixtures of CS with surfactants on solid surface is of considerable practical interest because mixed cationic polymer/anionic surfactant systems are used in formulations of many personal care products especially in hair shampoos [14]. In such a situation the surface of the metal oxide can be considered as the hydrophobic hair surface (untreated hair) or hydrophilic one (hair treated with permanent color products) [15]. However, there is no information concerning the adsorption of CS in the presence of cationic and non-ionic surfactants as well as the mixtures of the surface active agents at the solid surface. Taking into account the fact that personal care products rarely contain only one type of surfactant, this paper presents new data, which might be of great practical importance.

As far as the adsorption of cationic starch is concerned, Nyström et al. [3] investigated the interactions between highly cationic starch and likewise cationic calcite by determining the adsorption isotherms and the flocculation of calcite at different concentrations of starch and also at three different temperatures. They found out

* Tel.: +48 81 537 56 02; fax: +48 81 533 28 11.
E-mail address: egrzadka@wp.pl (E. Grządka).

that the entropy and low solubility of starch were expected to be the dominant driving forces for adsorption. However, the adsorption of CS on the calcite surface increases with the increase of NaCl concentrations, as did the degree of flocculation, which was the effect of screening repulsion forces between the adsorbent and the adsorbate by anions of electrolyte. Chen et al. [16] studied the kinetics of CS adsorption and flocculation in the kaolin suspension. According to their results, the electrostatic adsorption of CS on the kaolin surface is spontaneous and endothermic process followed the Langmuir isotherm. Li et al. [17] investigated the adsorption of CS on the aluminium magnesium hydroxalcalite-like compound. They found out that CS can adsorb on the external surface of positively structurally charged aluminium magnesium hydroxalcalite-like compound, which is an entropic driving process. The adsorption isotherms are low-affinity Langmuir type, and the adsorption kinetic shows an overshoot, which is the effect of the CS clustering process. The addition of NaCl and AlCl_3 to the adsorption system may increase the adsorption as well as the increase of pH and temperature. The results obtained by Guan et al. [18] showed that the main driving force of the adsorption of cationic starch on the cellulose fibers is electrostatic interaction, dependent on the temperature, pH, ionic strength and charge density. According to Petersen et al. [11] CS and synthetic polycations compete against each other during adsorption on fibers. The higher the cationic charge of the synthetic polycation was, the lower cationic starch adsorption occurred. Han et al. [13] studied the adsorption of alkyl cationic modified starches on the SiO_2 surface. They investigated the adsorption behaviour of CS and the effects of cationic alkyl (C_{12-18}) substitutions. It was proved that the amount of adsorption increased relative to that of a cationic surfactant, and the gap in the amount of adsorption between the adsorption and desorption steps was remarkably small. For the cationic alkyl (C_{12-18}) substituted starches, the hydrophobic interaction among the polymers contributed to the typical characteristics of a polyelectrolyte due to the presence of both the starch polymer backbone and long alkyl chains, what demonstrated that the adsorption layer became much more rigid.

It is known that polymers and surfactants can interact which often leads to formation of complexes of specific structure and characteristics. The systems with polymers and surfactants pose unique properties completely different from those of individual components. This is why mixtures of polymers and surfactants are used together in many industrial processes such as flotation, enhanced oil recovery, and detergency as well as in food products, pharmaceutical formulations, paints, cosmetics and pesticides [19,20] where they provide colloidal stability, enhancement of viscosity, solubilization, phase separation, gel formation and emulsification [21,22]. There are two main mechanisms of polymer–surfactant interactions electrostatic and hydrophobic, depending on the polymeric molecule (backbone, pendant groups, hydrophobic moieties, chain stiffness), on the surfactant type (cationic, anionic, zwitterionic and non-ionic) and on their relative concentration [23]. A literature survey on the adsorption of cationic polymer at the solid surface in the presence of anionic [19,22,24–28], cationic [11,19] or non-ionic [19,29] surfactants revealed that the mechanism of polymer–surfactant interaction is an area of continuous debate. It is well known from the surface tension measurements that the addition of an anionic surface active agent to the system containing a cationic polymer causes strong interactions between them far below the critical micelle concentration (cmc) of the surfactant (Fig. 1) because the cationic polymer screens repulsion between the anionic head groups of the surfactants. Moreover, in the mixture of the surfactant and the polymer some transition points can be found [30] There are T_1, T_2 , and T_2' . T_1 refers to the initiation of interactions between the surfactant and the polymer and very often is interpreted as the

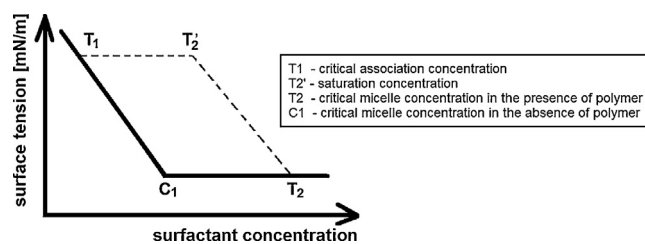


Fig. 1. Theoretical representation of the surface tension against surfactants concentration in the absence of polymer (dashed line) and in the presence of polymer (solid line).

critical association concentration (cac) whereas T_2 is the saturation point beyond which further addition of a surfactant leads to the increasing formation of regular surfactant micelles. Point T_2' refers to the saturation of the polymer with the surfactant. However, it was proven that for the systems containing an oppositely charged ionic surfactant and a polyelectrolyte, the strong electrostatic interaction may lead to the non-cooperative binding of surfactant molecules to the polyions far below the cac point [31]. Moreover, according to Lange [32] under the concentrations of surfactant lower than T_1 , the surface tension might be below that of the surfactant solution by itself, implying that an interacting polymer is surface active in its own right. It also should be mentioned that in systems containing polyelectrolyte and oppositely charged surfactant, the profile of surface tension versus surfactant concentration could show more than three above-mentioned transition points [33]. The main driving forces for this association between a polymer and a surfactant are electrostatic, dipole–dipole, hydrophobic, and even hydrogen bonding between the macromolecules and surfactants.

As one can see, there is little information about the influence of different types of surfactants on the adsorption of cationic starch on the surface of the solid, especially those of cationic and non-ionic character. Due to this fact, a comparative study of adsorption in such systems is of considerable practical interest concerning personal care products such as shampoos and hair conditioners. Moreover, fundamental understanding of these phenomena is strongly required for the increase of the effectiveness of such products. Because of that, the aim of this work was to investigate the effect of the surface active compounds of different chemical character (anionic, cationic, non-ionic) as well as their mixtures on the adsorption and electrokinetic properties of the cationic starch/alumina system. It should be emphasized that the adsorption in the systems containing CS and cationic and non-ionic surfactants as well as mixtures of the surface active agents has not been studied before, which limits their new possible applications. Another advantage and the novelty of this study is to present the structure of the electrical double layer in the polymer/surfactant/adsorbent system.

2. Experimental

2.1. Materials

Alumina (Al_2O_3) of analytical grade was procured from Merck. The specific surface area of this adsorbent estimated using the BET method was $107 \text{ m}^2 \text{ g}^{-1}$ whereas the mean pore diameter equalled 7.2 nm which excludes the adsorption of the polymer in the pores. The particle size distribution of alumina was measured using Mastersizer 2000. The obtained data were as follows: $d(0.1)$ (10% of the distribution is below this value) was $47.8 \mu\text{m}$; $d(0.5)$ (the median diameter where 50% of the distribution is above and 50% is below this value) was $71.6 \mu\text{m}$; $d(0.9)$ (90% of the distribution is below this value) was $96.4 \mu\text{m}$. The adsorbent was washed with

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