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Polymer–surfactant interactions: Binding mechanism of sodium dodecyl sulfate to poly(diallyldimethylammonium chloride)

Gilat Nizri [a], Serge Lagerge [b], Alexander Kamyshny [a], Dan T. Major [c], Shlomo Magdassi [a,*]

[a] Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel
[b] Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, ESA 5072, Université de Montpellier II, Case 015, 2 Place E. Bataillon, 34095 Montpellier Cedex 05, France
[c] Chemistry Department, Bar-Ilan University, Ramat Gan, 52900, Israel

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Abstract

The binding mechanism of poly(diallyldimethylammonium chloride), PDAC, and sodium dodecyl sulfate, SDS, has been comprehensively studied by combining binding isotherms data with microcalorimetry, zeta potential, and conductivity measurements, as well as *ab initio* quantum mechanical calculations. The obtained results demonstrate that surfactant–polymer interaction is governed by both electrostatic and hydrophobic interactions, and is cooperative in the presence of salt. This binding results in the formation of nanoparticles, which are positively or negatively charged depending on the molar ratio of surfactant to PDAC monomeric units. From microcalorimetry data it was concluded that the exothermic character of the interaction diminishes with the increase in the surfactant/polymer ratio as well as with an increase in electrolyte concentration.

Keywords: Polyelectrolyte–surfactant interaction; Microcalorimetry; Binding isotherms; Cooperative binding; Molar conductivity

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1. Introduction

Mixed solutions of polymers and surfactants are of both scientific and practical interest owing to their increasing applications in the production of paints, coatings, and cosmetic goods, in oil processing, and other industrial fields.

Much attention has been focused on the study of interaction between oppositely charged surfactants and polyelectrolytes [1–11]. It was usually observed that at certain surfactant concentrations such interaction leads to precipitation of a polymer–surfactant complex. This precipitation was characterized for various oppositely charged polyelectrolyte–surfactant systems [12–17]. To prevent or reduce the phase separation in such systems, the addition of a salt is often required [18,19]. Phase separation could also be prevented by addition of more nonionic groups to the polymer or to the surfactant, as reported by Bronich et al. and Dubin et al. [20–22].

Recently we demonstrated that binding of the anionic surfactant sodium dodecyl sulfate (SDS) to cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDAC) results in formation of unique micro- and nanostructures [23]. The complexes and nanoparticles were characterized by light scattering and zeta-potential measurements, and the hexagonal liquid crystalline nature of the complexes was revealed by SAXS and cryo-TEM. The hexagonal structure was also obtained for SDS concentrations below its CMC, and according to these results we have suggested a model for the inner structure of the nanoparticles, in which SDS cylindrical micelles are longitudinally decorated with the polymer chains. In another publication [24], it was found by SANS measurements that the presence of a cationic polyelectrolyte induces the formation of SDS elongated micelles. The formation of cylindrical micelles in the presence of a polycation is explained as a process similar to the effect caused by the addition of high concentration of NaCl to SDS aqueous solutions: formation of elongated structures instead of spherical micelles [25]. It should be noted, that the sphere to rod transition of SDS micelles in the presence of NaCl starts at a relatively high salt concentration, of 0.45 M,

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[*] Corresponding author. Fax: +972 2 658 4350.
E-mail address: magdassi@cc.huji.ac.il (S. Magdassi).

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while the SDS concentration is above CMC [26]. In our system the cylindrical micelles were obtained in the absence of simple electrolyte, and at a very low concentration of the polyelectrolyte, 6.8×10^{-4} M of charge units, which means that, the arrangement of the electrolyte units on a polymer chain amplifies the effect on the SDS micelles shape.

Since the initial step towards formation of the hexagonal nanoparticles is the binding of SDS to the polycations, the present report focuses on the mechanism of binding of SDS to PDAC, which leads to formation of the surfactant cylindrical micelles—polycation complexes. One of the most important thermodynamic aspects of a polyelectrolyte/surfactant system is the binding isotherm, which may provide information on the binding mechanism. A series of investigations have focused on the binding isotherms of polyelectrolyte–surfactant systems [27–34]. Usually, the binding of ionic surfactants to oppositely charged polyelectrolytes has been found to be cooperative, that is, indicative of hydrophobic interactions between bound surfactant molecules [35–37]. Although the system of PDAC–SDS was reported by several authors, there is no detailed study on the mechanism of interactions between the polymer and the surfactant. So far, the binding isotherms for the currently investigated system of SDS and PDAC were evaluated only in one publication [38], that mentioned the binding with relation to solubilization of alkylbenzenes. No thermodynamic parameters were calculated for the binding process itself.

Combining the binding isotherms at various ionic strengths with calorimetry, *ab initio* quantum mechanical calculations and conductivity measurements allowed the understanding of the dominant forces in the SDS–PDAC system, which lead to formation of unusual nanostructures. Therefore, the present report brings for the first time, a comprehensive study on the binding mechanism of the system reported to yield hexagonal inner structure of nanoparticles.

2. Materials and methods

2.1. Materials

PDAC of average M_w 100,000–200,000 (21.8% aqueous solution) purchased from Sigma-Aldrich Co. (Rehovot, Israel), and SDS (minimum 98.5% by GC) purchased from Sigma Co. (St. Louis, MO, USA), were used without additional purification. All other reagents were of analytical grade.

2.2. Zeta potential measurements

The zeta potential was calculated by measuring the electrophoretic mobility, using the Smoluchowsky approximation:

$$U_E = \varepsilon\zeta/\eta, \tag{1}$$

where ζ—zeta potential, U_E—electrophoretic mobility, ε—dielectric constant, η—viscosity.

The ζ potentials were determined without dilution by a Zetasizer 3000 (Malvern Instruments; internal He–Ne laser) and taken as a mean value from 3 to 4 measurements.

2.3. Conductivity measurements

Conductivity measurements were performed by Extech conductivity electrode using titration. A stock solution of SDS containing a low concentration of PDAC ($r > 40$) was pipetted into a PDAC solution at the same concentration as the stock solution (PDAC concentration was kept constant during the SDS addition). The conductivity was recorded continuously. A correction factor for the dilution was taken into consideration (a total of 2.75 ml were added to 100 ml), and the conductivity of the PDAC solution itself ($65.5\ \mu\text{S cm}^{-1}$) was subtracted from the final conductivities measured in SDS–PDAC dispersions at each SDS concentration. The conductivity was recorded also for the SDS solution at the same concentrations but without PDAC addition. Changes in the conductivity of an electrolyte solution become clearer while plotting the molar conductivity as a function of the square root of the concentration, which is usually a linear function according to the Kohlrausch equation:

$$\Lambda_c = \Lambda_\infty - A\sqrt{C_0}, \tag{2}$$

where Λ_c is the molar conductivity, C is the electrolyte (surfactant ion) concentration, Λ_∞ is the molar conductivity at infinite dilution, and A is a constant, which is a function of the valency of the surfactant salt.

2.4. SDS concentration measurement

The SDS concentration was measured with the use of surfactant-ion selective electrode. A surfactant-selective membrane was prepared by a method analogous to that reported by Carlsson and Lindman [33]. Equal volumes of heated aqueous 1% CTAB and 0.8% SDS solutions (molar ratio CTAB:SDS = 1:1) were poured together into a glass container, and the formed complex precipitated. Dried precipitate (10 mg) was mixed with 5 ml of tetrahydrofuran and 2 g of dinonyl phthalate. The slurry was heated at 60 °C while stirring, and then 0.5 g of PVC was gradually added to obtain a clear and viscous solution. To obtain the SDS-selective electrode, the prepared solution was cast on a glass plate, and after slow evaporation of the solvent in dry atmosphere, the resultant gel membrane was cut out, glued on a silicon tube, and annealed at 60 °C under vacuum for 42 h.

The device for SDS concentration measurements was composed of the selective electrode described above, which contains an SDS solution of known concentration (1 mM for measurements in the absence of electrolyte, and 0.1 mM for measurements in the presence of electrolyte), a reference electrode (Ag/AgCl), and the SDS (or SDS/PDAC at various molar charge ratios, r) sample to be tested. The concentration difference between the specific electrode and the tested solution causes a potential difference, E, which is measured by a voltmeter. The free SDS concentration in a sample can be determined from the linear range of the calibration curve, presenting E as a function of the logarithm of SDS concentration.