

Preparation and Characterization of Thin Films Derived from Polyelectrolyte-Surfactant Complexes based on Cationic Polymer – JR-400 and Anionic Surfactant – Sodium Dodecylbenzenesulfonate

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ABSTRACT

Thin films derived from polyelectrolyte-surfactant complexes on the basis of cationic polymer – JR-400 and anionic surfactant – sodium salt of dodecylbenzenesulfonate (SDDBS) were isolated from the equimolar mixture of aqueous solutions of polyelectrolyte and surfactant. Characteristic bands of functional groups of JR-400 and SDDBS involved into complexation reaction were identified from FTIR spectra. Elemental composition and morphology of thin layers of polyelectrolyte-surfactant complexes deposited on SiO₂ surface were evaluated by SEM and AFM. The height of polyelectrolyte-surfactant complexes evaluated from AFM and SURFUS data is in good agreement and arranged between 10 and 50 nm. The XRD analysis of thin films revealed that polyelectrolyte-surfactant complexes have amorphous structure with a broad halo near 20°. Contact angle measurements show that the glass surface treated by polyelectrolyte-surfactant complexes is more hydrophobic than that of untreated glass surface due to replacement of surfactant brushes on air. Thin films of polyelectrolyte-surfactant complexes may be perspective materials as antifogging materials.

Key words: cationic polyelectrolyte, anionic surfactant, polycomplexes, solubility, structure, morphology, thin films, coating

INTRODUCTION

Polyelectrolyte-surfactant complexes (PSCs) attract much attention from fundamental and applied points of view. PSCs based on biopolymers – DNA and/or proteins and lipids play a crucial role in biological systems to model the structure and function of biological membranes in living cells [1,2]. Applied aspects of PSCs cover bio-, and nanotechnology, medicine, food science etc. Self-assembled polyelectrolyte-surfactant complexes in the solid state and as nanoparticles have been reviewed by Thunemann [3]. Usually interaction of

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polyelectrolytes and surfactants leads to formation of insoluble stoichiometric polycomplexes that restrict their wide researches in solution. However discovery of PSCs which are soluble in organic solvents considerably intensified interest in this area [4]. Authors [5] reported on organosoluble, in particular in chloroform, PSCs assembled from the pairs DNA-cationic surfactant, poly(L-lysine)-anionic surfactant [6] and cationic polyelectrolyte-anionic surfactant [7]. They were studied in chloroform by viscometry, turbidimetry, ^1H NMR, isothermal diffusion, flow birefringence, and dynamic light scattering techniques [8, 9]. Solubility of the PSCs in low-polarity solvents increased in the order chloroform > chlorobenzene > benzene. Only few reports are available from literature on organosoluble PSCs, inverted micells, formed from poly(amidoamine) dendrimers [10] and hyperbranched poly(ethyleneimine) [11] and fatty acids. It has been reported that stoichiometric polyelectrolyte-surfactant complexes precipitated from aqueous solution can be further dissolved in some organic solvents and form a bottle-brush arrangement where the head groups of amphiphiles are electrostatically attached to the polyelectrolyte backbone and the solvation of the hydrophobic tails contributes to the stability of the complexes [12]. Concerning the PSCs formed between N,N,N-trimethylammonium derivatized hydroxyethyl cellulose JR-400 and anionic surfactants literature survey [13] shows their adsorption onto solid surfaces. Information on isolation of PSCs based on JR-400 and anionic surfactants from aqueous solution and their further dissolution in organic solvents to our knowledge is lacking. The present paper is devoted to ethanol solution behavior and thin films morphology of PSCs derived from cationic polyelectrolyte JR-400 and anionic surfactant – sodium salt of dodecylbenzenesulfonate.

EXPERIMENTAL PART

Materials

Cationic polymer JR-400 – N,N,N-trimethylammonium derivatized hydroxyethyl cellulose – with molecular weight $M=1\cdot 10^5\text{-}3\cdot 10^6$ and anionic surfactant – sodium salt of dodecylbenzenesulfonic acid (SDDBS) purchased from Polysciences.Inc. were used without additional purification.

PREPARATION OF PSCs

40 mg of JR-400 dissolved in 100 mL of distilled water. 10 mL aliquot was titrated by aqueous solution of SDDBS with concentration 1 mM. Inflection point of conductimetric titration curve that is equal to 11 mL was taken as optimal amount of SDDBS that is necessary for full precipitation of JR-400. Thus it was found that to precipitate 40 mg of JR-400 it is needed 68 mg of SDDBS. Due to difficulties in selection of repeating monomer unit for JR-400 in further experiments the mass ratio of $[m_{\text{SDDBS}}]/[m_{\text{JR-400}}] = 5/3$ was used for PSCs preparation protocol.

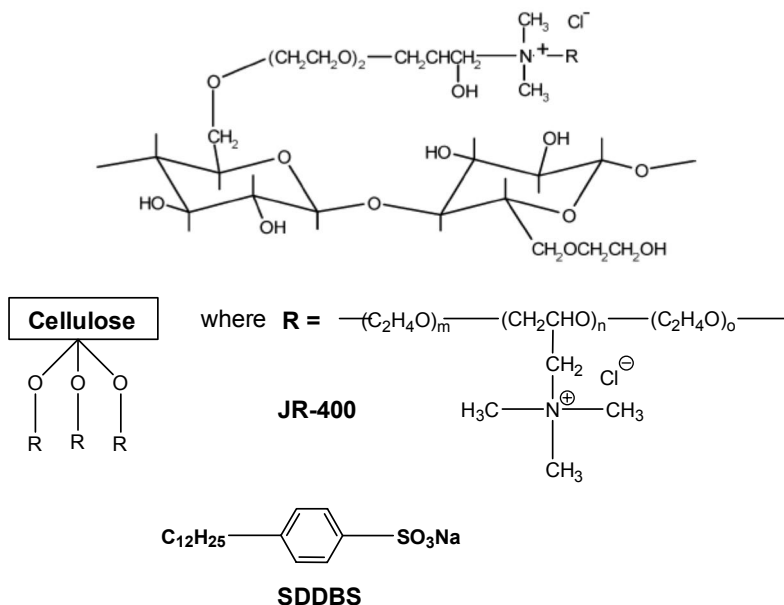


Fig. 1 – Structural unit and formula of JR-400 and SDDBS

For preparation of PSCs as precipitate an aqueous solution of SDDBS was dropwisely added to aqueous solution of JR-400 during 2 h under stirring. After, the precipitate was decanted by distilled and deionized water several times and finally it centrifuged at 10^4 rpm.

White precipitate was then dried in air at room temperature and in vacuum oven at $40\text{ }^\circ\text{C}$ till the constant mass. The yield of PSCs glass powder was equal to 66,7%. The chemical composition of solid sample performed by energy dispersive X-ray (EDX) attached to SEM indicated on the absence of counterions (Na^+ and Cl^-) that release into aqueous solution in the course of complexation reaction. Additionally the absence of chloride ions in supernatant was confirmed by titration with $AgNO_3$. The solubility of PSCs was checked in various organic solvents (Table 1).

Methods

Viscosity of PSCs in ethanol was measured on Ubbelohde viscometer at $25\pm 0,1\text{ }^\circ\text{C}$. The dynamic light scattering (DLS) measurements were performed on a commercial goniometer equipped with a ALV 6000 correlator (ALV, Langen, Germany) with a He-Ne laser (Polytech, Waldbronn, Germany) at a wavelength of $\lambda=633\text{ nm}$ in quartz cells (Hellma, Germany). DLS measurements were performed in the angle of 90° with an ALV6000 multibit autocorrelator.

Table 1 – Solubility of JR400/DDBSNa in various organic solvents

| Solvent | Solubility* |
|-------------------------------|-------------|
| Acetone | – |
| Ethanol | + |
| DMF | + |
| DMSO | + |
| Toluene | – |
| Ethanol:Toluene (3:1 vol/vol) | + |
| Ethanol:Toluene (1:1 vol/vol) | + |
| Ethanol:Toluene (1:3 vol/vol) | emulsion |
| Ethanol:Water (1:4 vol/vol) | + |

*) + soluble; – insoluble

The inverse Laplace transformation using the REPES method [14] of constrained regularization (a part of the GENDIST program), which is similar in many respects to the inversion routine CONTIN, was used for analysis of time autocorrelation functions. The average hydrodynamic radius R_h was calculated from the diffusion coefficient D using the Stokes-Einstein equation. At least 10 measurements were made of the sample to check repeatability. The experimental error of the R_h determination was typically 2.5% for all measurements. The sample with concentration $5 \text{ mg}\cdot\text{mL}^{-1}$ was filtered by $0.45 \mu\text{m}$ filter (Millex, Millipore) before use.

SEM measurements were carried out on scanning electron microscope JEOL, JSM5800 (Japan). FTIR spectra were recorded on a Alpha-P (Burker). AFM measurements were made with the help of NT-MDT (Russia). 5 or $10 \text{ mg}\cdot\text{mL}^{-1}$ ethanol solution of PSCs was deposited onto silicon surface SURF by microsyringe and the morphology of PSCs was studied. XRD spectrum of PSCs was recorded on X'Pert MPD PRO (PANalytical). Conductimetric titration was carried out on the pH/conductivity meter "Mettler Toledo MFC 227" (Switzerland) at room temperature. Separation of PSCs precipitate from solution was carried out on preparative centrifuge "Eppendorf" (Germany) at 10^4 rpm and room temperature.

RESULTS AND DISCUSSION

The PSCs preparation protocol includes the following stages: 1) mixing of aqueous solutions of JR-400 and SDDBS; 2) formation of hydrophobic micellar polyelectrolyte-surfactant complexes (PSCs); 3) aggregation of micelles and precipitation; 4) thoroughly washing of precipitate by distilled and deionized water; 5) drying of precipitate and 6) dissolution of PSCs in ethanol. *Fig.2* shows the dependence of the reduced viscosity on PSCs concentration in ethanol. It is seen that in pure ethanol PSCs behave polyelectrolyte character, e.g. the reduced viscosity increases with dilution. This is probably connected with existing of some uncompensated with SDDBS cationic sites of JR-400. In pure

ethanol PSCs can be represented as expanded chains. In the presence of 0,05 or 0,1 N KBr the polyelectrolyte effect disappears and PSCs solution behave as nonionic polymer. Earlier [15] the polyelectrolyte character of PSCs based on poly-N,N-dimethyl-N-benzyloxyethylmethacryloylammonium chloride and sodium dodecylsulfate (or sodium salts of alkylsulfonic acids RSO_3Na , where $\text{R} = \text{C}_{16}\text{-C}_{18}$) was observed in chloroform and methanol. Dependence of the reduced viscosity of JR-400/DDBSNa on the composition of ethanol-water mixture passes through maximum at ethanol-water mixture 3:2 vol/vol. Appearance of well defined maximum may be explained by expanding of PSCs chains as a result of solvation of hydrophobic groups by ethanol and hydrophilic ones by water. Sharp decrease of the reduced viscosity in enriched by water mixture may be due to poor quality of water with respect to hydrophobic tails of surfactant. Light scattering results show on appearance of 4 peaks that correspond to 2,4 nm (1,2%), 29,3 nm (1,07%), 417 nm (7,13%) and 2600 nm (90,5%) (Fig.3). In our mind the peak 1 is probably responsible for the single PSCs chains; the peak 2 reflects the micelles or PSCs coils. The peaks 3 and 4 may represent big aggregates of PSCs. It should be mentioned that PSCs solution was filtrated through filter with diameter of pores 450 nm while the hydrodynamic radius of agglomerated particles is 2600 nm. It means that aggregation of PSCs particles takes place after filtration. However big particles or aggregates scattering more light are not so representative than that of small particles.

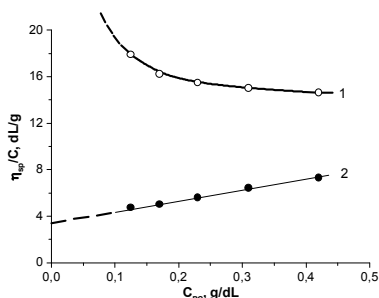


Fig.2 – Dependence of the reduced viscosity of JR-400/DDBSNa on concentration in ethanol (1) and in ethanol solution containing 0,05N KBr (2)

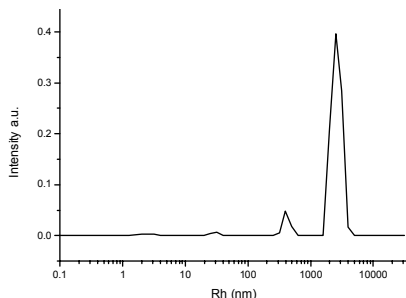


Fig.3 – Light scattering results of PSCs in ethanol. $C_{PSCs} = 1 \text{ mg}\cdot\text{mL}^{-1}$

Ethanol solution of PSCs with concentrations of 5 or 10 $\text{mg}\cdot\text{mL}^{-1}$ was deposited onto SiO_2 surface and the elemental composition of thin films were evaluated by SEM-EDX.

Pure SURF contains Si and O originating from SiO_2 . Appearance of S on the deposited PSCs films confirms the presence of SO_3^- groups in the composition of the PSCs. FTIR spectra of PSCs also contain the characteristic bands of

SO₂ scissoring, symmetric stretching vibrations of O=S=O and S=O at $\nu = 578$, 1031, and 1061 cm⁻¹ together with functional groups of JR-400 and SDDBS.

Morphology of thin layers of PSCs deposited on SiO₂ surface was evaluated by AFM and Sarfus (high-resolution optical microscope) (*Fig.4*). The height of PSCs aggregates evaluated from AFM and Sarfus data is in good agreement and arranged between 10 and 50 nm.

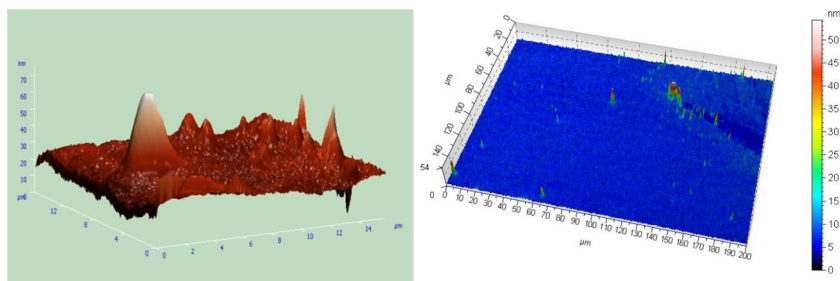


Fig.4 – AFM (left) and Sarfus (right) pictures of PSCs deposited on SiO₂ surface.

Equivalent diameter distribution of PSCs particles derived from Sarfus is depicted on *Fig. 5*.

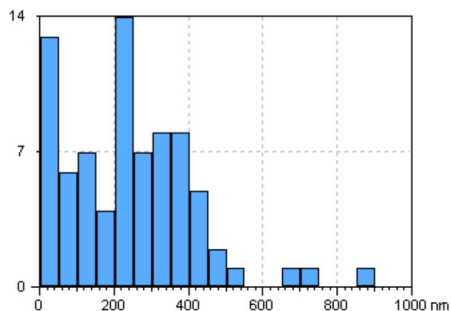


Fig.5 – Diameter distribution of 78 particles of PSCs deposited on solid surface

Mean diameter of PSCs particles is 239 ± 169 nm and is broadly distributed. Approximately 13 particles have average diameter of 30 nm, 14 particles – 230 nm. Mean diameter of 23 particles is about 320 nm. These data are less comparable with light scattering results may be due to adsorption of PSCs particles on charged surface.

XRD pattern of PSCs shows a broad halo at $\Theta = 20^\circ$ that is specific for amorphous structure (*Fig.6*). Analogous XRD picture was also characteristic for hydrophobically modified polyampholytes.

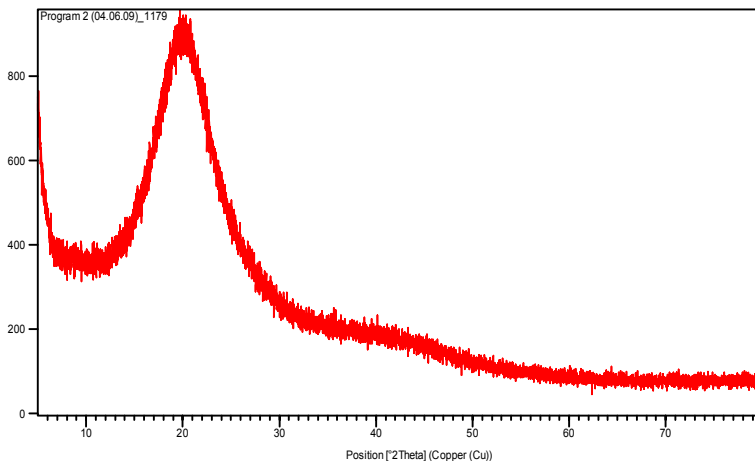


Fig. 6 – X-ray spectrum of solid complex of JR-400/DDBSNa

The wettability of glass surface was also checked. As seen from Table 2, the glass surface treated by 5 and 10 mg·mL⁻¹ PSCs solutions is more hydrophobic than that of untreated ones suggesting the potential applicability of PSCs as antifogging coating. Upon increasing of the PSCs concentration the contact angle increases (*Table 2*).

Table 2 – Contact angle measurements

| No. samples | Concentration of PSCs, mg·mL ⁻¹ | Thickness of film, mm | α , ° |
|-------------|--|-----------------------|--------------|
| 1 | 0 | 0 | 60 |
| 2 | 5 | 0.2 | 83 |
| 3 | <10 | 0.2 | 90 |

CONCLUSIONS

Solid polyelectrolyte-surfactant complexes precipitated from aqueous solution of interacting components were dissolved in ethanol and deposited on solid surface of SiO₂. The height of deposited thin films determined by AFM and SARFUS is in good agreement and arranged between 10 and 50 nm. Contact angle measurements reveal that thin films of polyelectrolyte-surfactant complexes deposited on glass surface may be useful as antifogging coatings.

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