

Organosoluble Polyelectrolyte-Surfactant Complexes

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Summary: Organosoluble polyelectrolyte-surfactant complexes (PSCs) based on cationic polymer – JR-400 and anionic surfactant – sodium salt of dodecylbenzenesulfonate (SDDBS) were isolated as a precipitate from polyelectrolyte/surfactant aqueous mixture. The reduced viscosity of JR-400/SDDBS in ethanol showed polyelectrolyte anomaly that was suppressed upon addition of 0.05N and 0.1N KBr. Light scattering measurements of JR-400/SDDBS in ethanol showed 4 peaks belonging to non-aggregated and aggregated polycomplex particles. The elemental composition and morphology of thin layers of polyelectrolyte-surfactant complexes deposited on SiO₂ surface were evaluated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The height of PSC aggregates evaluated using AFM and Surface Enhanced Ellipsometry Contrast (SEEC) microscopy data is in good agreement and range within 10–50 nm. The XRD analysis revealed that PSCs have amorphous structure with a broad halo near 20°. The contact angle measurements were used to demonstrate the hydrophobization of glass surface after the deposition of PSCs.

Keywords: anionic surfactant; cationic polyelectrolyte; mixing; nanoparticles; polycomplexes; solution properties; thin films; viscosity

Introduction

Polyelectrolyte-surfactant complexes (PSCs) have attracted much attention of researchers both from fundamental and practical 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 the interaction of polyelectrolytes and surfac-

tants leads to the formation of insoluble stoichiometric polycomplexes that limits the possibility of their characterization and processing in solutions. However, the discovery of PSCs which are soluble in organic solvents considerably intensified interest in this area.^[4] In low-polarity organic solvents, hydrophobic interactions can be suppressed, and thus, essentially only electrostatic interactions play a role in the complexation process. These electrostatic interactions are naturally expected to be very strong in low permittivity media, thereby leading to non-equilibrium (“frozen”) macromolecular co-assemblies. Moreover organosoluble PSCs as model systems will allow for a better understanding of physical behavior of polyelectrolytes in general and colloidal interactions in nonaqueous media in particular.

The authors^[5] reported organosoluble, in particular in chloroform, PSCs assembled from DNA-cationic surfactant pairs, poly-(L-lysine)-anionic surfactant^[6] and cationic polyelectrolyte-anionic surfactant.^[7] These

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complexes were studied in chloroform by viscometry, turbidimetry, ^1H NMR, isothermal diffusion, flow birefringence, and dynamic light scattering techniques^[8,9]. The solubility of these PSCs in low-polarity solvents increased in the following order: chloroform > chlorobenzene > benzene. Only few reports are available from literature on organosoluble PSCs, inverted micelles, formed from poly-(amidoamine) dendrimers^[10] and hyper-branched 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 these complexes^[12]. The PSCs formed between N,N,N-trimethylammonium derivatized hydroxyethyl cellulose JR-400 and anionic surfactants are known to show a tendency to adsorb on solid surfaces^[13]. This unique behaviour of organosoluble PSCs may open up the possibility to vary solvent polarity in a rather broad range, which may lead to the development of some novel nano-architectures^[8]. For example, the mixed Langmuir-Blodgett monolayers consisting of organosoluble PSCs and fluorescent dyes may have a high fluorescence quantum yield in the visible region of spectrum

and to prepare specific nanostructures with predictable optical properties. Moreover, PSCs prepared in organic media are substantially water-free and can be further processed to design separation membranes, oil-soluble drag reducers, pour point depressants and antifogging materials.

The present paper reports the preparation of ethanol-soluble polyelectrolyte-surfactant complexes derived from cationic polyelectrolyte JR-400 and anionic surfactant – sodium dodecylbenzenesulfonate, focusing on their behaviour in organic solutions and solid state; fabrication and deposition of nanosized thin films on solid substrate as well as evaluation of thin films morphology and wettability.

Experimental Part

Materials

Polymer JR-400–N,N,N-trimethylammonium derivatized hydroxyethyl cellulose – with molecular weight $M = 1 \cdot 10^5$ – $3 \cdot 10^6$ and sodium dodecylbenzenesulfonate (SDDBS) purchased from Polysciences Inc. (USA) were used without additional purification (Figure 1). Ethanol and organic solvents (>99.5%, Fluka) were used as received. Distilled, bidistilled and deionized water was used for preparation of aqueous solutions of JR-400 and SDDBS as well as for washing the precipitate and decantation.

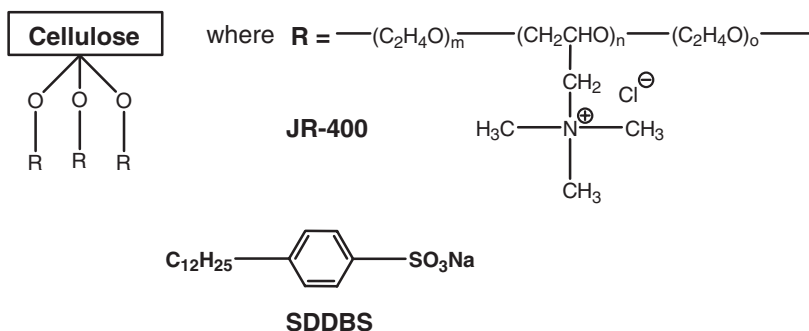


Figure 1.

Structures of JR-400 and SDDBS.

Preparation of PSCs

Due to the difficulties in identification of repeating monomer units for JR-400 the mass ratio of $[m_{\text{SDDBS}}]/[m_{\text{JR-400}}]$ was used in PSCs preparation protocol. For this 40 mg of JR-400 was dissolved in 100 mL of distilled water. 10 mL aliquot was titrated by aqueous solution of 1 mM SDDBS. The inflection point on the conductimetric titration curve that corresponded to 11 mL was taken as the optimal amount of SDDBS necessary for formation of stoichiometric complex and full precipitation of JR-400 (Figure 2). It was found that 40 mg of JR-400 precipitates by 68 mg of SDDBS. It corresponds to the mass ratio of $[m_{\text{SDDBS}}]/[m_{\text{JR-400}}] \approx 5/3$. Additional turbidimetric experiments were also carried out (Figure 3). The maximal turbidity of the mixture of JR-400 and SDDBS ($V_{\text{total}} = 3 \text{ mL}$) was found to correspond to $V_{\text{JR-400}}/V_{\text{SDDBS}} = 1.8/1.2 \text{ mL/mL}$ solution ratio that also is in agreement with $[m_{\text{SDDBS}}]/[m_{\text{JR-400}}] \approx 5/3$ mass ratio.

For quantitative preparation of PSCs as the precipitate, 90 mg of SDDBS dissolved in 25 mL of deionized water was added drop-wise to 150 mg of JR-400 dissolved in 25 mL of deionized water with continuous stirring during 2 h. Then the precipitate was decanted by deionized water several times and finally centrifuged at 10^4 rpm . White precipitate was then dried in air at room temperature and finally in vacuum oven at 40°C until constant mass was reached. The

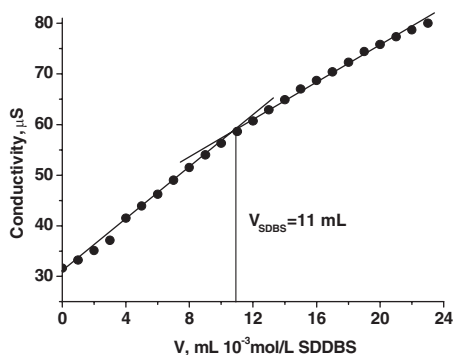


Figure 2.

Conductimetric titration curve of aqueous solution of JR-400 by aqueous solution of SDDBS.

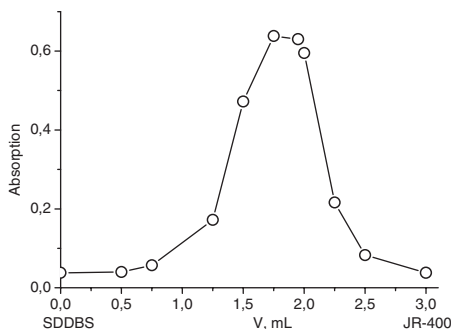


Figure 3.

Turbidimetric titration curve of aqueous solution of JR-400 by aqueous solution of SDDBS from which the optimal volume ratio of $V_{\text{JR-400}}/V_{\text{SDDBS}} = 1.8/1.2 \text{ mL/mL}$ was found.

yield of PSCs glass powder was equal to 66.7%.

DLS Measurement

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 $\lambda = 633 \text{ nm}$ in quartz cells (Hellma, Germany). These measurements were carried out at 90° with an ALV6000 multibit autocorrelator. 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 the 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 conducted for each sample to ensure repeatability. The experimental error of the R_h determination was typically 2.5% for all measurements. The sample with the concentration of $5 \text{ mg} \cdot \text{mL}^{-1}$ was filtered through $0.45 \mu\text{m}$ filter (Millex, Millipore) before use. In the course of DLS measurements the ethanol solution of PSCs was transparent (not turbid) and stable without any phase separation observed.

SEEC Microscopy

Real-time visualization and topographic characterization of polyelectrolyte complexes were performed using an innovative quantitative optical imaging technique called Surface Enhanced Ellipsometry Contrast (SEEC) Microscopy^[15]. This technique is based on the use of a new generation of microscope slides (called Surfs) for the characterization of nanometric samples with a conventional optical microscope. The study was implemented in a Sarfus Mapping Air apparatus (Nanolane, France) based on a verified upright optical microscope for 3D measurements, a high resolution video camera and Sarfusoftware 2.4 3D Premiun software. The PSCs patterns were deposited by microsyringe on untreated SiO₂ top layer Surfs (Nanolane, France).

Contact Angle Measurements

The determination of contact angles was performed using “Dataphysics” Contact Angle System OCA (Germany) equipped with SCA20 software. The PSCs solutions of three different concentrations (1; 5 and 10 mg · mL⁻¹) prepared in ethanol were deposited on glass substrate that was fixed in the metal mold on a flat surface. 1 and 3 μ L of PSC solutions with 13.5 μ L · sec⁻¹ drop rate were placed on the glass edge then the solution was evenly distributed on the surface with the second metal part of the mold to obtain a 0.2 mm thin film. The samples were dried in air for 20 minutes, and then the contact angles were measured at 24.5 °C. The average error of contact angle measurements was in the range of 1.2–6.5%.

Methods

Conductimetric titration was carried out using the pH/conductivity meter “Mettler Toledo MPC 227” (Switzerland) at room temperature. Viscosity of PSCs in ethanol was measured using Ubbelohde viscometer at 25 ± 0.1 °C. SEM micrographs were recorded using scanning electron microscope JEOL, JSM5800 (Japan). FTIR

spectra were recorded using Alpha-P spectrometer (Burker). AFM measurements were conducted with the help of NT-MDT (Russia). 5 or 10 mg · mL⁻¹ ethanol solution of PSCs was deposited onto silicon surface SURF by microsyringe and the morphology of PSCs was studied. The XRD spectra of PSCs were recorded using X’Pert MPD PRO (PANalytical). The separation of PSCs precipitate from supernatant was carried out with the help of the preparative centrifuge “Eppendorf” (Germany) at 10⁴ rpm and room temperature. The amount of sodium and chloride ions in the supernatant was determined with the help of ion-plasma coupled emission spectrometer “Optima 5100 DV” (Perkin Elmer, USA) and by applying the method used for determination of chloride ions in drinking water as described in^[16].

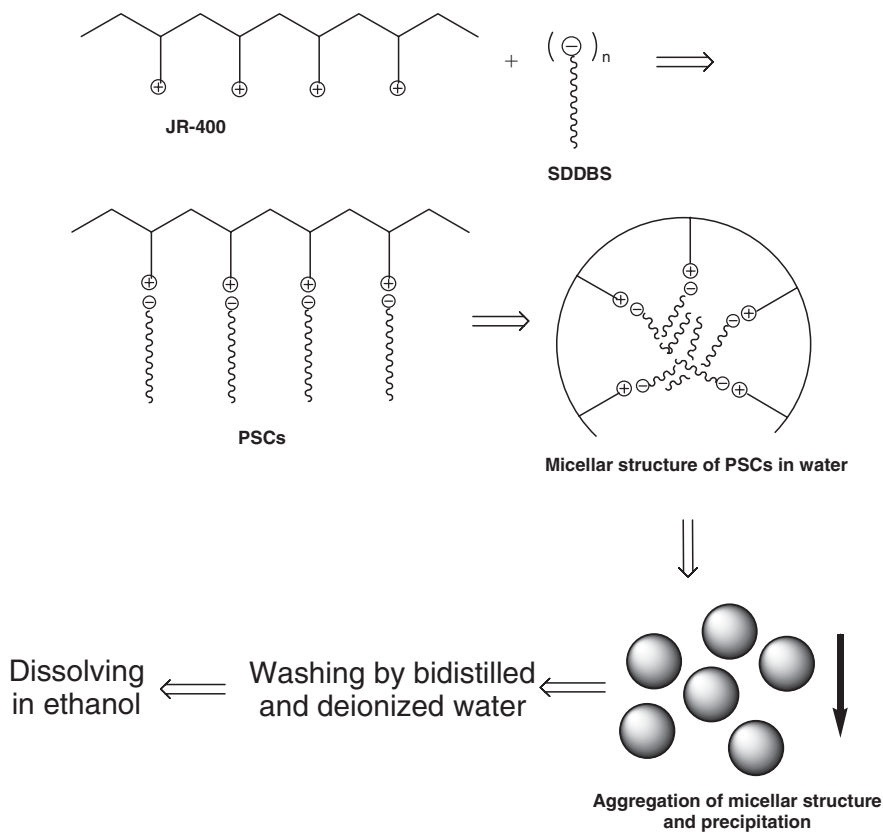
Results and Discussion

Formation and Behavior of PSCs in

Solution

The PSCs preparation protocol is shown in Figure 4. It 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 their precipitation; 4) thorough wash of the precipitate by distilled and deionized water; 5) drying of precipitate and 6) dissolution of PSCs in ethanol. Taking into account that the complexation process is an ion-exchange reaction driven by electrostatic attraction between the JR-400 and SDDBS that is accompanied by precipitation of PSCs and that the amount of discharged NaCl reflects the yield and stoichiometry of PSCs we have determined the amount of Na⁺ and Cl⁻ in aqueous solutions of initial components and in the supernatant (Table 1).

As seen from Table 1 the content of Na⁺ and Cl⁻ ions in the supernatant is equal to 67.2% and 68.5%, respectively. The percentage ratio of [Cl⁻]/[Na⁺] is close to 1 indicating that the composition of the

**Figure 4.**

Protocol used for PSCs preparation.

polycomplex is stoichiometric with respect to the ratio of dodecylbenzenesulfonate to quaternary nitrogen atoms of JR-400.

The solubility of PSCs was checked in various organic solvents and the results are summarized in Table 2. Ethanol solution of PSCs used for further experiments was transparent and stable in time.

Figure 5 shows the dependence of the reduced viscosity on PSCs concentration in ethanol. It is seen that in pure ethanol PSCs exhibits a polyelectrolyte character, e.g. the

reduced viscosity increases upon dilution. This may be due to the partial dissociation of PSCs in ethanol resulting in polyelectrolyte behavior. In the presence of 0.05 or 0.1 N KBr the polyelectrolyte effect disappears and PSCs solution behave like a nonionic polymer. Earlier^[9,17] the polyelectrolyte character of PSCs was also observed in various polar organic solvents.

Dynamic light scattering (DLS) results show an appearance of 4 peaks that correspond to 2 nm (1%), 29 nm (1%), 417 nm (7%) and 2600 nm (91%) (Figure 6). Auto-correlation functions measured at 90° are represented in Figure 7.

However DLS data do not provide a solid confidence that diffusion modes obtained under polyelectrolyte behavior conditions (without added KBr) correspond to translational diffusion of scatter-

Table 1.

Elemental analysis of aqueous solutions of JR-400, SDDBS and the supernatant.

	JR-400	SDDBS	Supernatant
[Na ⁺], mg · L ⁻¹	–	23.2	15.6
[Cl ⁻], mg · L ⁻¹	302.1	–	207.1

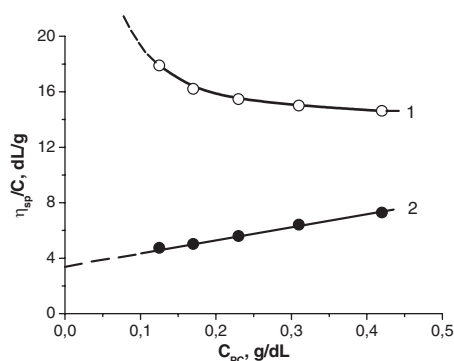
Table 2.

Solubility of JR400/DDBSNa in various organic solvents.

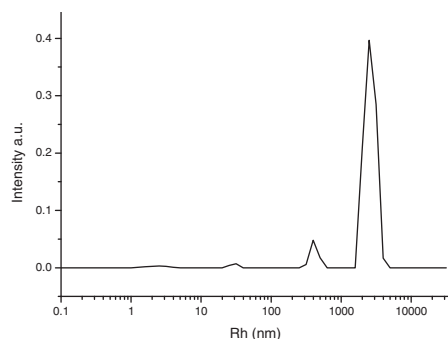
Solvent	Acetone	DMF	DMSO	Ethanol	Toluene	Ethanol:Toluene (3:1 vol/vol)
Solubility*	–	+	+	+	–	+

*+ soluble, – insoluble.

ing particles due to absence of DLS measurements at different scattering angles (60° and 120°). In spite of this fact one can suppose that the smallest peak probably belongs to free SDDBS micelles because the calculated length of extended SDDBS molecules is approximately 2 nm; the species of 29 nm may be considered as non-

**Figure 5.**

Dependence of the reduced viscosity of JR-400/DDBSNa on its concentration in ethanol (1) and in ethanol solution containing 0.05N KBr (2).

**Figure 6.**

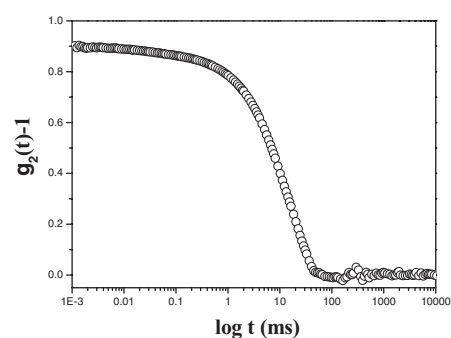
Light scattering results of PSCs in ethanol. $C_{PSCs} = 1 \text{ mg} \cdot \text{mL}^{-1}$.

aggregated PSCs particles. The peak 3 (417 nm) may represent some aggregates of PSCs. However the biggest peak at 2600 nm is not representative and can not be taken into account because the laser wavelength (633 nm) is much lower than that of big particles. It should be mentioned that PSCs solution was filtrated through a filter with 450 nm pores and the DLS still shows the presence of 2600 nm aggregates, which is likely related to their flexible nature and capability to deform and pass through smaller-size pores. Alternatively, the aggregation of PSCs particles may take place after filtration.

Structure and Morphology of Solid PSCs

Ethanol solution of PSCs with concentrations of 5 or $10 \text{ mg} \cdot \text{mL}^{-1}$ was deposited onto SURF surface and the elemental composition of thin films was evaluated by SEM-EDX (Figure 8).

Pure SURF contains only Si and O originating from SiO_2 . Masking of Si and appearance of S and C and increasing of the amount of O confirms deposition of PSCs on SiO_2 surface. FTIR spectra of PSCs also

**Figure 7.**

Autocorrelation functions $g_2(t)$ measured at scattering angle 90° .

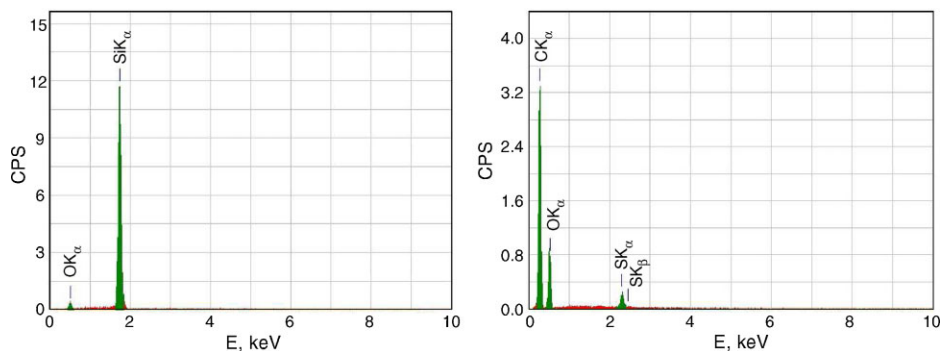


Figure 8.

Elemental composition of pure SURF (a) and 5 times deposited PSCs onto SURF. $C_{\text{PSCs}} = 10 \text{ mg} \cdot \text{mL}^{-1}$.

contain the characteristic bands of SO_2 scissoring, symmetric stretching vibrations of $\text{O}=\text{S}=\text{O}$ and $\text{S}=\text{O}$ at $\nu = 578$, 1031, and 1061 cm^{-1} together with functional groups of JR-400 and SDDBS (Figure 9). XRD pattern of PSCs shows a broad halo at $\Theta = 20^\circ$ that is typical for amorphous materials (Figure 10). This suggests that the polyelectrolyte chains impose restrictions on surfactant chain packing and decrease the tendency of short chains of

SDDBS consisting of 12–14 carbon atoms to form ordered structures^[4].

The morphology of thin layers of PSCs deposited on SiO_2 surface was evaluated by AFM and SEEC microscopy (high-resolution optical microscope) (Figure 11 and 12). The data on the dimensions of PSCs aggregates produced by two microscopic techniques are in good agreement for AFM and SEEC microscopy and indicate the presence of particles whose size ranges within 10–50 nm.

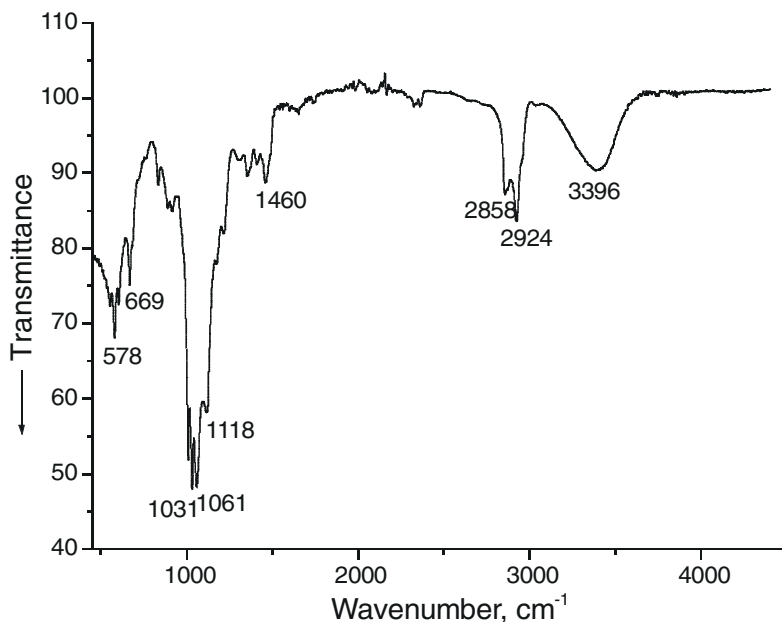


Figure 9.

FTIR spectra of solid PSCs derived from JR-400 and SDDBS.

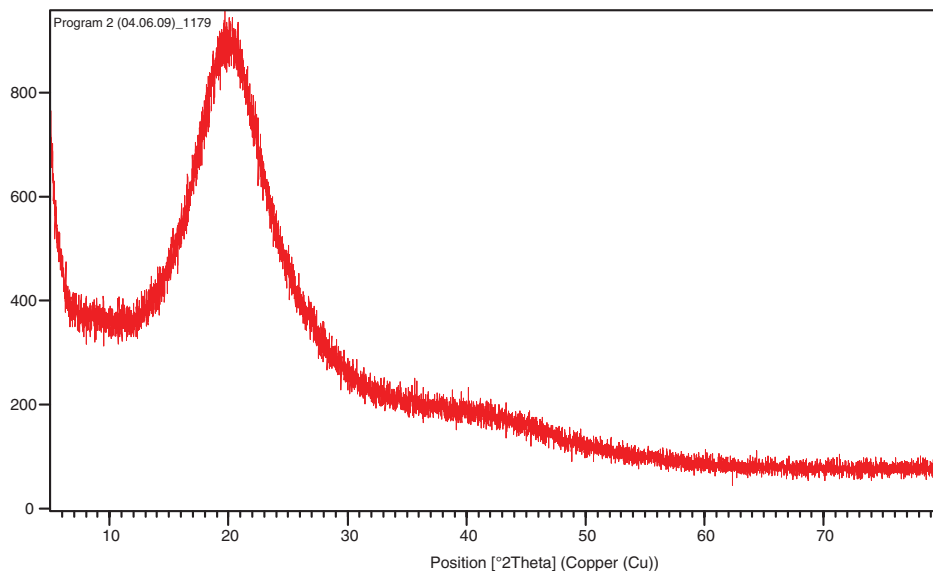


Figure 10.

X-ray spectrum of solid complex JR-400/SDDBS.

The equivalent diameter distribution of PSCs particles derived from SEEC microscopy is shown in Figure 13.

Taking into account the results of the authors^[13] on the adsorption behaviour of JR-400 at silica surface one can suppose that the major driving force for the

adsorption is electrostatic interaction. The uncompensated by SDDBS cationic groups of JR-400 are probably adsorbed on the negatively charged surface of SiO₂ while the PSCs are replaced out-of-plane position. The adsorption of aggregated PSCs particles on SiO₂ surface can generate

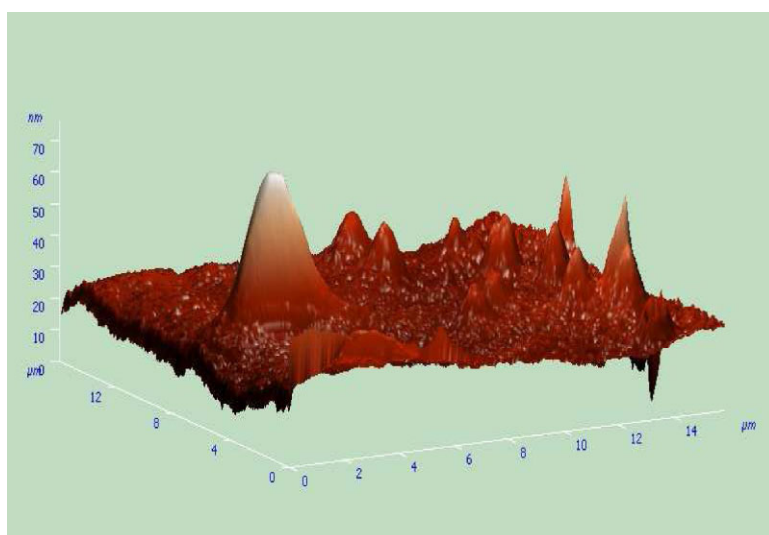


Figure 11.

AFM image of PSCs deposited on SiO₂ surface.

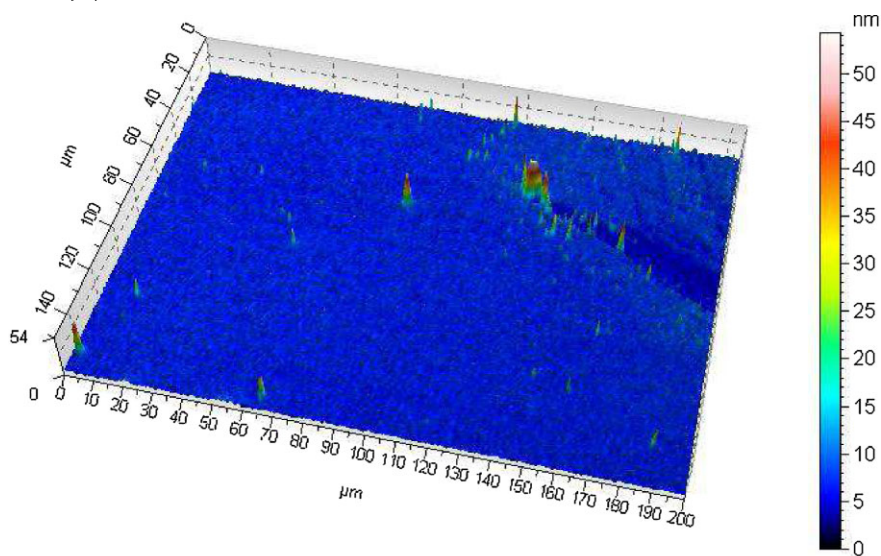


Figure 12.

SEEC Microscopy image of PSCs deposited on SiO₂ surface.

the smooth morphology and larger, elongated interconnected patches. Their dimensions as shown from the AFM and SEEC line profiles are several ten nanometers. Analogous results were reported by Kundu^[18] who studied the morphology of DNA-DTAB and CMC-DTAB complexes deposited on solid surface.

Hydrophobicity of the PSCs

The surface properties of glass surface before and after the treatment with PSCs was also evaluated. The dependence of

contact angle on the concentration of covered film for different drop volumes (1 and 3 μ L) is shown in Figure 14. This graph demonstrates that increasing of the solution concentration leads to an increase in the contact angle values, which, in turn, indicates the enhancement of hydrophobic surface properties.

Photos of water drop on the clean glass surface and the surface coated with PSCs films are shown in Figure 15a-d.

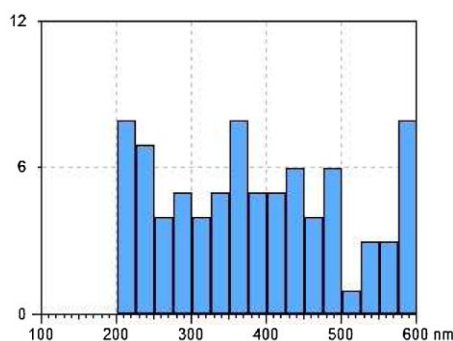


Figure 13.

Diameter distribution of 78 particles of PSCs deposited on solid surface.

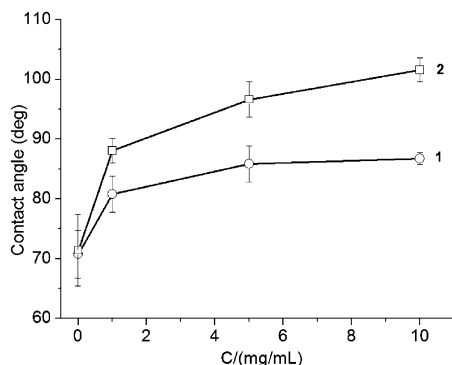


Figure 14.

Dependence of contact angle on the concentration of covered film for drop volumes of 3 (curve 1) and 1 μ L (curve 2).

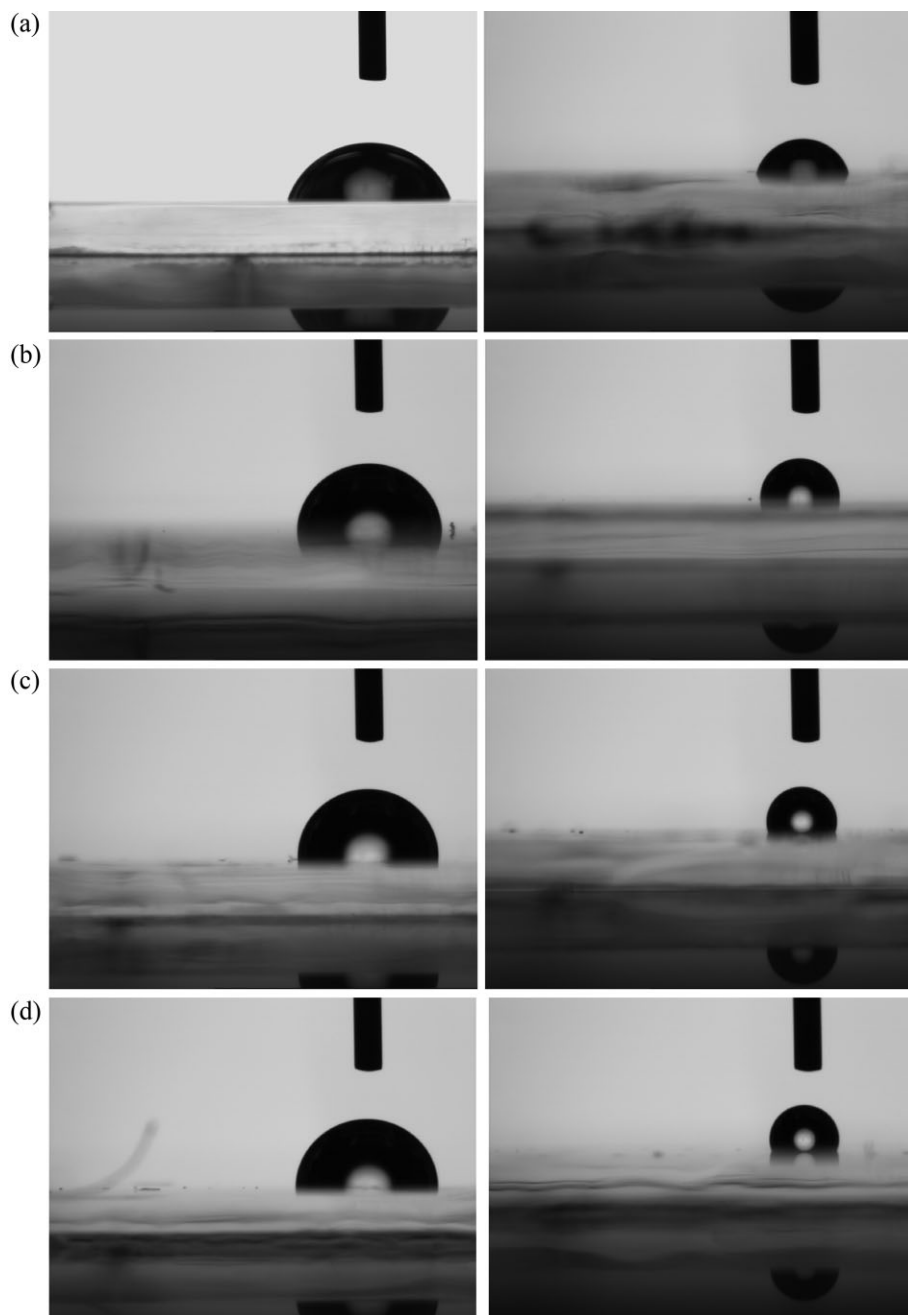


Figure 15.

a) Drop of water on the surface of the clean glass. b) Drop of water on the glass surface, covered with a polycomplex film (concentration of the initial solution is $1 \text{ mg} \cdot \text{mL}^{-1}$). c) Drop of water on the glass surface, covered by polycomplex film (concentration of the initial solution is $5 \text{ mg} \cdot \text{mL}^{-1}$). d) Drop of water on the glass surface, covered with a polycomplex film (concentration of the initial solution is $10 \text{ mg} \cdot \text{mL}^{-1}$).

As seen from Figure 15a–d, the glass surface treated with PSCs solutions is more hydrophobic than that of the untreated ones suggesting the potential applicability of PSCs as antifogging coating. Upon increasing of the PSCs concentration the contact angle increases. It should be noted that the smaller drops of water correspond to higher contact angles.

Conclusion

Polyelectrolyte-surfactant complexes (PSCs) based on cationic polyelectrolyte and anionic surfactant were isolated as a precipitate from aqueous solution. Then they were dissolved in ethanol. It was shown that PSCs in ethanol exhibits polyelectrolyte anomaly that disappears upon addition of KBr. The dynamic light scattering results reveal that PSCs particles in ethanol solution can exist in non-aggregated ($R_h = 29.3$ nm) and aggregated ($R_h = 417$ nm) forms. The deposition of ethanol solution of PSCs on SiO_2 surface leads to the formation of thin films with the thickness of 10–50 nm. Increasing of the PSCs concentration deposited on glass surface increases the contact angle values; the smaller drops of water correspond to higher contact angles indicating the enhancement of hydrophobic surface properties.

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