COLLOID JOURNAL, 2025, Vol. 87, No. 1, pp. 22–31

SPHERICAL POLYMER GELS CONTAINING SULFONATE GROUPS: SYNTHESIS AND ADSORPTION PROPERTIES

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Received September 02, 2024
Revised September 19, 2024
Accepted September 22, 2024

Abstract. Porous cross-linked polyelectrolyte microspheres with diameter from 1 to 5 μm based on para-styrene sulfonate or copolymer of para-styrene sulfonate with vinyl acetate were synthesized. The content of sulfonate groups in the obtained polyelectrolyte microspheres is more than 2 mmol/g. It was shown that introduction of hydrophobic comonomer significantly increased the degree of swelling of polyelectrolyte microspheres. It was found that the value of adsorption of model compounds (fuchsin, methylene blue) significantly exceed the concentration of sulfonate groups. Morphology, structure of the surface layer of polyelectrolyte matrices were studied by optical and scanning electron microscopy, FTIR spectroscopy, specific surface by the BET method.

Keywords: *polyelectrolyte microspheres, hydrogels, adsorption of drugs*

DOI: 10.31857/S00232912250103e3

INTRODUCTION

Modern medicine and pharmacology are dynamically developing fields aimed at introducing innovative technologies and improving diagnostic and treatment methods. One of the key challenges in these areas is targeted/targeted delivery of drug substances (DS) preferentially to areas of inflammation, resulting in a significant reduction of adverse reactions of the body to the used drugs and their dosage. In addition, such delivery systems can gradually release the active substance, which reduces the frequency of drug administration and increases the effectiveness of treatment [1]. The most promising materials for the development of drug delivery systems are polymers, which can be presented in the form of particles [2–4], capsules [5], hydrogels [6], dendrimers [7] and others. At the same time, it is hydrogels that are of particular interest to researchers involved in the development of drug delivery systems. They are characterized by high water content, biocompatibility and required mechanical properties. In addition, current knowledge allows the synthesis of hydrogels at macro-, micro- and nano-scale. According to the literature, it is micro- and nanogels that have the greatest potential for the development of drug delivery systems [8–10].

Polymeric drug delivery systems can be divided into two broad groups: bio- and non-biodegradable compositions, the choice between which depends on the specific clinical requirements and the type of drug. Non-biodegradable systems are often used in the field of radiosurgery as embolizates [6], in dentistry as dental restorative materials [4] or universal implantable DS delivery systems [11]. Common polymers for non-biodegradable drug delivery systems are polymethyl methacrylate [12, 13], polyethylene vinyl acetate [14], polyvinyl alcohol [15], and copolymers based on them. Recently, in addition to the previously mentioned polymers, polyelectrolytes have also become the object of active research in the field of targeted DS delivery [5, 16]. This is due to their unique properties: high adsorption capacity and ion exchange ability [17]. This is particularly interesting for extended-release formulations, where DS diffusion is limited by ion exchange between drugs with ionic groups and polyelectrolytes.

Polyanions contain negatively charged ionogenic groups, SO_3^- (COO^-). They demonstrate their effectiveness in the delivery of cationic DS, which is confirmed by a number of examples: polystyrene sulfonate for the delivery of ligustrazine phosphate for the treatment of various eye diseases [3] or $CaCO_3$ particles coated with polyvinyl sulfonate or dextransulfonate for the delivery of doxorubicin

hydrochloride for cancer therapy [18]. It appeared that modification of $CaCO_3$ particles with dextransulfonate was the most optimal for subsequent in-vivo studies of such particles. In addition, polyanions can be used for the delivery of hormones such as insulin [2].

Nevertheless, the synthesis of polyelectrolyte-based microspheres is not a simple task. Most published articles use sulfation of polystyrene particles [19, 20] to form sulfonate groups in their structure, but the morphology, electrical surface properties, or swelling of such microspheres in solvents differ significantly compared to microspheres obtained using para-styrene sulfonate as a functional monomer. Another common method for the preparation of microspheres with sulfonate groups is multistep synthesis, which includes protection of sulfonate groups, synthesis of hydrophobic microspheres, and removal of protection [21, 22]. Despite the high content of sulfonate groups in the final microspheres, this method is rather complicated, and some steps are characterized by low yields or the formation of unstable compounds. Therefore, the most promising method is the synthesis of microspheres based on commercially available monomers with sulfonate groups in the reverse emulsion polymerization process.

Thus, cross-linked systems based on polyanions may be promising as non-biodegradable DS delivery systems. In this regard, it is necessary to study the mechanisms of sorption and desorption of drugs on polyelectrolyte microspheres. In the present work we synthesized cross-linked hydrogel microspheres based on polystyrene sulfonate and its copolymer with vinyl acetate in order to study their ability to sorb cationic forms of drugs on the example of fuchsin and methylene blue. The optimal conditions for the preparation of polymeric microspheres by reverse emulsion polymerization were determined and the effect of vinyl acetate co-monomer on the sorption ability of the synthesized particles was studied. The structural characteristics of all polymeric microspheres were investigated using IR spectroscopy, optical and scanning electron microscopy, and BET method. The results showed that the synthesized microspheres have a developed specific surface area and a high content of sulfonate groups (more than 2 mmol/g), most of which are localized in the volume of microspheres. These values are an order of magnitude higher than the concentration of surface sulfonate groups for polystyrene microspheres (obtained after their sulfation). At the same time, the introduction of vinyl acetate as co-monomer reduces the content of sulfonate groups, which, in turn, worsens their sorption properties with respect to fuchsin and methylene blue.

EXPERIMENTAL PART

Materials

Particles were synthesized using the following reagents: sodium styrene sulfonate (SSS) (Sigma Aldrich, Germany), *N,N'*-methylene-bis-acrylamide (MBA) (Vecton LLC, Russia), vinyl acetate (Vecton LLC, Russia), potassium persulfate ($K_2S_2O_8$) (Vecton LLC, Russia), Span 80 (Sigma Aldrich, Germany), Tween 80 (Sigma Aldrich, Germany). Vinyl acetate was purified by vacuum distillation according to standard methods, potassium persulfate was purified by recrystallization from water. Other monomers and emulsifiers were used without prior purification. NaCl, HCl, NaOH, ethanol (Vekton LLC, Russia), cyclohexane (LenReactiv JSC, Russia) without preliminary purification were used for particle studies. Fuchsin (Vekton LLC, Russia) and methylene blue (Vekton LLC, Russia) were used without preliminary purification.

Synthesis of polystyrene sulfonate particles

Synthesis of polymer particles was carried out in a three-neck flask equipped with a top-driven stirrer and a reflux condenser. First, the emulsifier Span 80 was dissolved in 12 ml of cyclohexane at 50° C in the flask. In parallel, a solution of the reagents in water was prepared by successively dissolving Tween 80, SSS (1.98 g), vinyl acetate (0–10 wt% of SSS-Na), MBA (50 wt% of total monomer content) and $K_2S_2O_8$ (3 wt% of total monomer content) on an ultrasonic bath at 50°C. The amount of emulsifiers was 5 wt% of the total emulsion content (monomers and solvents), and the Tween 80/Span 80 ratio was 16/84. Immediately after dissolution of $K_2S_2O_8$, the prepared solution was introduced into a three-neck flask. The resulting emulsion was stirred for 30 minutes at 600 rpm at 50°C for 30 minutes to reach equilibrium. The temperature was then raised to 70°C and the reaction was continued for 4 hours with constant stirring. The unreacted monomers, emulsifier and cyclohexane were removed by centrifugation for 30 minutes at 10,000 rpm (Centrifuge 5804, Eppendorf, Germany), redispersing the precipitated particles in the water-alcohol mixture.

Determination of particle size and shape

The size and shape of particles were determined by optical and scanning electron microscopy (SEM). Optical microscopy was performed using an optical microscope (MIKMED-5, Russia) equipped with lenses with magnification ×100 and ×40. For the study, a dispersion of particles in water was prepared, after which it was applied to a slide and the particles were photographed in the swollen state. SEM was performed on a SUPRA 55 VP scanning electron microscope (Germany). For SEM, dried samples were applied on glass substrates and then coated with Au/Pd. The diameter of microspheres was calculated using the Image J software.

Determination of the content of sulfonate groups

The content of sulfonate groups was determined by conductometric titration and by measuring the ion exchange

capacity. Measurement of ion exchange capacity was carried out according to the standard method, for this purpose 0.3 g of particles were dispersed in 10 ml of HCl (0.5 n.) and incubated for 24 hours, after which the particles were washed (excess acid was removed by centrifugation) and dried by lyophilic drying. The particles were then dispersed in a 20% aqueous solution of NaCl and incubated for 24 hours. The acid released as a result of ion exchange under argon current was titrated with aqueous NaOH solution (0.01 n.) in the presence of phenolphthalein indicator.

Conductometric titration was carried out in argon current using 0.1% wt. dispersion of particles. For this purpose, a known excess of HCl (0.01 n.) was introduced into the dispersion, after which the introduced HCl and sulfonate groups were titrated with an aqueous solution of NaOH (0.01 n.), taking values of the electrical conductivity of the dispersion using a SevenMulti conductometer (MetlerToledo, Switzerland).

Determination of specific surface area of particles

The specific surface area of particles was measured using a NOVA 1200e surface analyzer (Quantachrome, USA). Prior to measurements, the sample was degassed in a nitrogen current at reduced pressure.

FTIR spectroscopy

The spectral characteristics of the synthesized samples were studied by FTIR spectroscopy of disturbed total internal reflection. FTIR spectra were taken on an FTIR spectrometer FTIR-Affinity-1S (Shimadzu, Japan) with a diamond prism. All spectra represent the average of 32 scans taken in the wave number range of 20,000–600 cm^{-1}.

Determination of sorption of fuchsin and methylene blue

Determination of sorption ability of synthesized microspheres with respect to fuchsin and methylene blue (MB) was carried out by spectrophotometric method. For this purpose, 1.1–4.3 mg of synthesized particles were incubated in an aqueous solution of fuchsin or methylene blue with a concentration of $4.8 \cdot 10^{-5}$ to $1.45 \cdot 10^{-3}$ mol/L for 1.5 hours. The particles were then precipitated by centrifugation and the supernatant solutions with unsorbed fuchsin/MB were studied by optical spectroscopy in the visible region ($\lambda = 542$ nm and $\lambda = 662$ nm for fuchsin and MB). The concentration of fuchsin and MB was determined using a previously constructed calibration line.

The experimental data on the sorption capacity with respect to hydrocarbons were analyzed using the Langmuir and Freundlich models. For this purpose, linear isotherms were constructed and parameters were calculated according to formulas (1) and (2) for the Langmuir and Freundlich models, respectively.

$$\frac{1}{q} = \frac{1}{C_e \cdot K_L} \cdot \frac{1}{q_{max}} + \frac{1}{q_{max}}, \quad (1)$$

where q is the adsorption value, mol/g; q_{max} is the maximum adsorption value, mol/g; K_L is the Langmuir constant, g/mmol; C_e is the equilibrium concentration, mol/g.

$$\ln q = \ln K_F + \frac{1}{n} \ln C_e, \quad (2)$$

where q – adsorption value, mol/g; K_F – Freundlich constant (at $C = 1$ mol/L K_F is equal to q_{max}); $1/n$ – constant (adsorption index depending on temperature and nature of adsorbent).

In addition, the parameter R_L, the partition coefficient (equilibrium parameter), was calculated for the Langmuir model using formula (3).

$$R_L = \frac{1}{1 + K_L \cdot C_0}, \quad (3)$$

where C_0 – initial concentration of absorbate, mol/g.

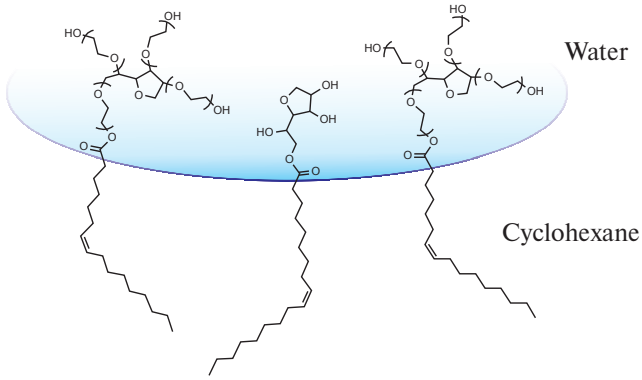

Fig. 1. Schematic arrangement of emulsifiers at the water–cyclohexane interface.

Table 1. Composition of the monomer mixture

N	Concent. mon, mol/L	SSS-Na: MBA, mol. %	Vinyl acetate, wt%	Emulsifier		
				Tween 80/ Span 80	Content, wt%	HLB
PSS	2	60:40	–	16/84	5	6
P(SSS-VA)	2	60:40	10	16/84	5	6

The applicability of the theoretical model of adsorption isotherms to the obtained experimental data was evaluated based on the coefficient of determination (R^2) calculated in Origin 2019 software.

RESULTS AND DISCUSSION

Synthesis of microspheres

Polyelectrolyte particles promising for drug sorption were synthesized in this work. The aim of this work was to investigate the sorption properties of microspheres based on cross-linked polystyrene sulfonate with respect to cationic drugs. Polyelectrolyte particles were synthesized by reverse emulsion copolymerization of SSS-Na and MBA, and copolymerization of SSS-Na, MBA and vinyl acetate P(SSS-VA) (Table 1). Polystyrene sulfonate (PSS) is a biocompatible polymer that is used for the treatment of hyperkalemia. The introduction of the crosslinking agent MBA into the reaction system was necessary to form crosslinked polymer chains to prevent their solubility in the aqueous phase. Vinyl acetate was used in order to form hydrophobic sites in the polymer chain structure, which can improve the interaction of microspheres with water-insoluble DS. In addition, vinyl acetate will allow the formation of polyvinyl alcohol links in the polymer structure (due to further hydrolysis of polyvinyl acetate links). Polyvinyl alcohol links contribute to the improvement of mucoadhesive properties of polymer microspheres, which is important when microspheres are used as embolizers or universal implantable DS delivery systems. Cyclohexane was chosen as

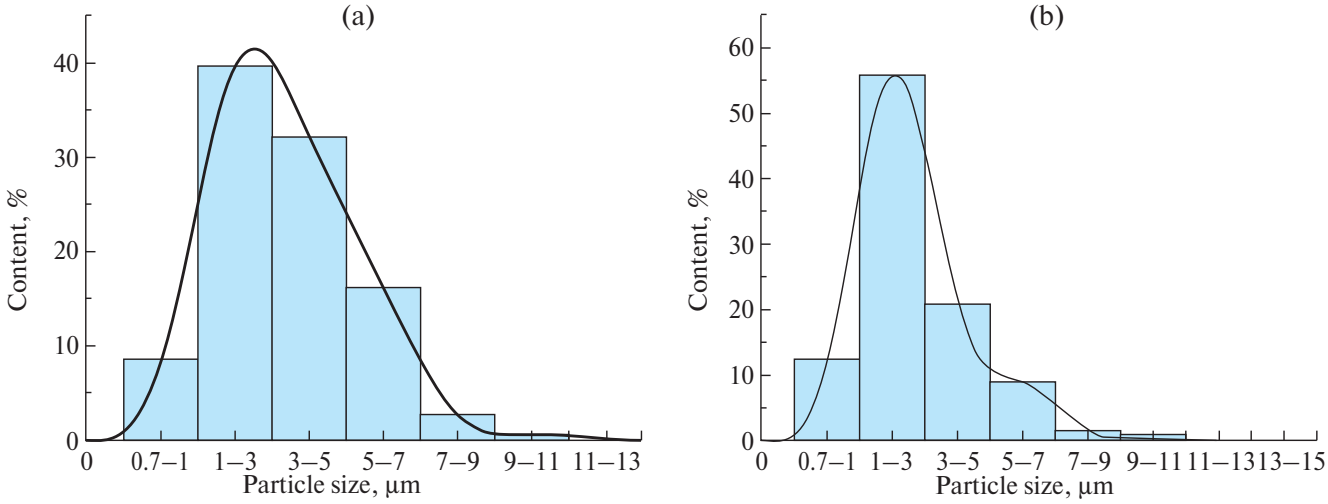

Fig. 2. Particle size distribution for PSS particles (a) and P(SSS-VA) copolymer (b).

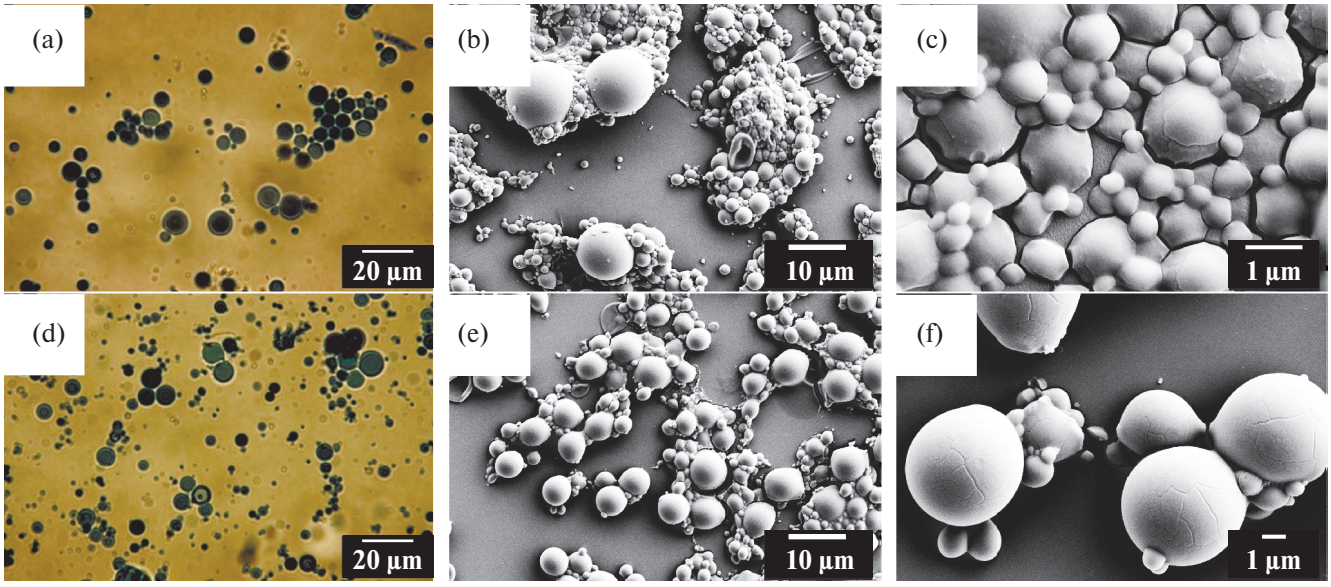

Fig. 3. Optical microscopy micrographs of PSS (a) and P(SSS-VA) particles (d); SEM micrographs of PSS particles (b, c) and P(SSS-VA) copolymer particles (e, f).

the dispersion medium. The stability of the resulting emulsion is important in the reaction. Therefore, Span 80 and Tween 80 emulsifiers were chosen as the emulsifying system. Span 80 has a low hydrophilic-lipophilic balance (HLB) value (4.3), which effectively stabilizes the monomer droplets in the oil phase. The auxiliary emulsifier Tween 80 with a HLB value of 15 provided uniform distribution of polar substances in the aqueous phase and improved the stability of emulsions by reducing droplet coalescence. In addition, the hydrophobic tails of these emulsifiers are identical and the hydrophilic head differs greatly in size (Fig. 1), resulting in maximum synergistic effect [23]. In addition, according to the study [24], the most effective stabilization of emulsions is observed when emulsifiers are introduced into different phases (lipophilic – into oil phase, hydrophilic – into water phase). In this case, after mixing the phases, there is no diffusion of surfactant (surfactant) into the aqueous phase, on the contrary, surfactant molecules are immediately oriented at the interface in the desired direction, which provides the formation of a denser layer at the interface. Therefore, in this work, surfactants were introduced into different phases and after mixing were kept for 30 min to establish equilibrium.

The emulsions formed were white colored colloidal systems. After equilibrium was established, the temperature was increased to 70°C to start the reaction polymerization. After two hours of the reaction, a sharp increase in the viscosity of the system was observed, which is probably due to the high content of the polymer swollen in water relative to the volume of the aqueous phase. The synthesis resulted in the formation of hydrogel spherical microspheres with a diameter of 1–5 μm in the swollen state (Fig. 2), as evidenced by optical microscopy photographs (Fig. 3a, d). The introduction of vinyl acetate promoted the formation of particles with a narrower particle size distribution, which may be due to a slight increase in the amount of emulsifiers in the system, dependent on the mass of the introduced co-monomers. In addition, the synthesized microspheres had a large specific surface area, the value of specific surface area for PSS and P(SSS-VA) microspheres was 2.09 and 2.23 m^2/g, respectively. However, it is worth noting that this size of microspheres is not suitable for all drug delivery routes. It is known that when polystyrene sulfonate particles are used orally, particles smaller than 5 μm can be absorbed through the mucosa and deposited in the tissues of the mononuclear phagocyte system.

The size and shape of polymer particles based on PSS and copolymer P(SSS-VA) were also investigated by scanning electron microscopy. It can be seen from the photographs that all particles have a spherical shape. At the same time, the size of particles in SEM (dry form) and optical microscopy (swollen form) photographs are different, which confirms their gel-like structure. In addition, the swelling degree of the particles based on cross-linked PSS and P(SSS-VA) copolymer, were ~20% and 95%, respectively. The swelling degree of P(SSS-VA) is higher compared to that of PSS despite the fact that the MBA content in the conditions for synthesizing P(SSS-VA) microspheres is higher by 10 wt%. The introduction of VA may have affected the phase homogeneity at the water–cyclohexane interface, which affected how the MBA was arranged in the polymer mesh structure. The IR spectroscopy results (Fig. 4) showed that the vinyl groups of MBA were present in the polymer structure and were not involved in the polymerization reaction. Taking this into account, it can be assumed that the crosslinking agent is incorporated into the polymer chain by only one vinyl group.

FTIR spectroscopy

The chemical composition of the obtained particles was analyzed by FTIR spectroscopy of disturbed total internal reflection. The obtained FTIR spectra for the samples of PSS and copolymer P(SSS-VA) are presented in Fig. 4. The polystyrene sulfonate structure in the particles is indicated by the transmission bands at 673 cm^{-1}, which corresponds to C–S and C–H bonds in the sulfonate group

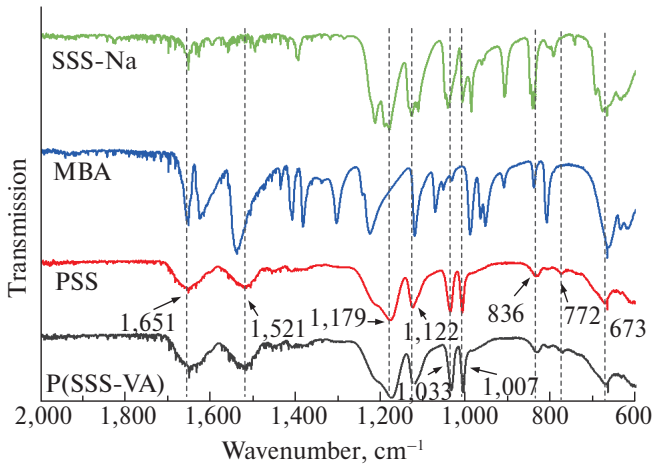

Fig. 4. FTIR spectra of SSS-Na (green), MBA (blue) and synthesized particles PSS (red) and P(SSS-VA) (black).

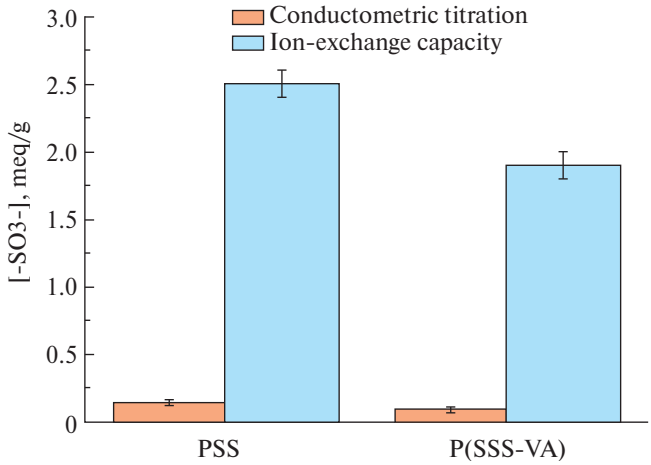

Fig. 5. Content of sulfonate groups in the synthesized particles determined by conductometric titration (orange) and ion exchange capacity measurement (blue).

attached to the aromatic ring. The valence asymmetric vibrations at 1,179 cm^{-1} and valence symmetric vibrations at 1,033 cm^{-1} also indicate the presence of the group SO_3^-, substituted in the para-position in the structure, which is confirmed by the planar vibrations at 1,122 cm^{-1} and 1,007 cm^{-1}. The transmission bands at 836 cm^{-1} and 772 cm^{-1} correspond to δ(C–H) deformation vibrations of the aromatic ring. The bandwidth at 1,651 cm^{-1} is much broader relative to the starting monomers. This may be due to the simultaneous overlap of the ν(C=C) valence vibrations of the aromatic ring of PSS and the ν(C–O) valence vibrations belonging to the MBA structure with the ν(C=C) valence vibrations of the vinyl group of MBA (bandwidth at 1,620 cm^{-1}). The content of MBA particles is also indicated by a band at 1,521 cm^{-1} corresponding to δ(N–H) strain vibrations [25]. However, the IR spectra of P(SSS-VA) particles lack the characteristic transmission bands at 1,018 cm^{-1}, 1,206 cm^{-1} and 1,755 cm^{-1} corresponding to C–O, O–C=O and C=O vibrations in the VA structure. This may indicate that the vinyl acetate content in the copolymer structure is below the sensitivity threshold of the method.

Sulfonate group content

The content of sulfonate groups in the synthesized microspheres was studied by 2 methods: conductometric titration and measurement of ion exchange capacity. As can be seen from Fig. 5, the results for the two methods are very different. The hydrogel/solvent-permeable structure of the microspheres contributed to the fact that sulfonate groups located both on the surface and in the entire volume of the particles participated in ion exchange. Probably due to diffusion limitations, only sulfonate groups localized in the surface layer of the microspheres could be titrated by conductometric titration. Whereas the measurement of ion exchange capacity implied a prolonged incubation of particles in aqueous solutions of HCl and NaOH, which made it possible to exclude diffusion limitations and measure the total content of sulfonate groups available for ion exchange. The introduction of VA into the composition of microspheres led to a decrease in the content of sulfonate groups by 33 and 24% for conductometric titration and measurement of ion exchange capacity, respectively, which can serve as an indirect confirmation of the presence of VA in the copolymer structure.

Adsorption of fuchsin and methylene blue

Two drugs were chosen to study the sorption properties of the synthesized microspheres: methylene blue (MB) and fuchsin. Methylene blue is a multifunctional drug with antimicrobial properties and is used for the treatment of

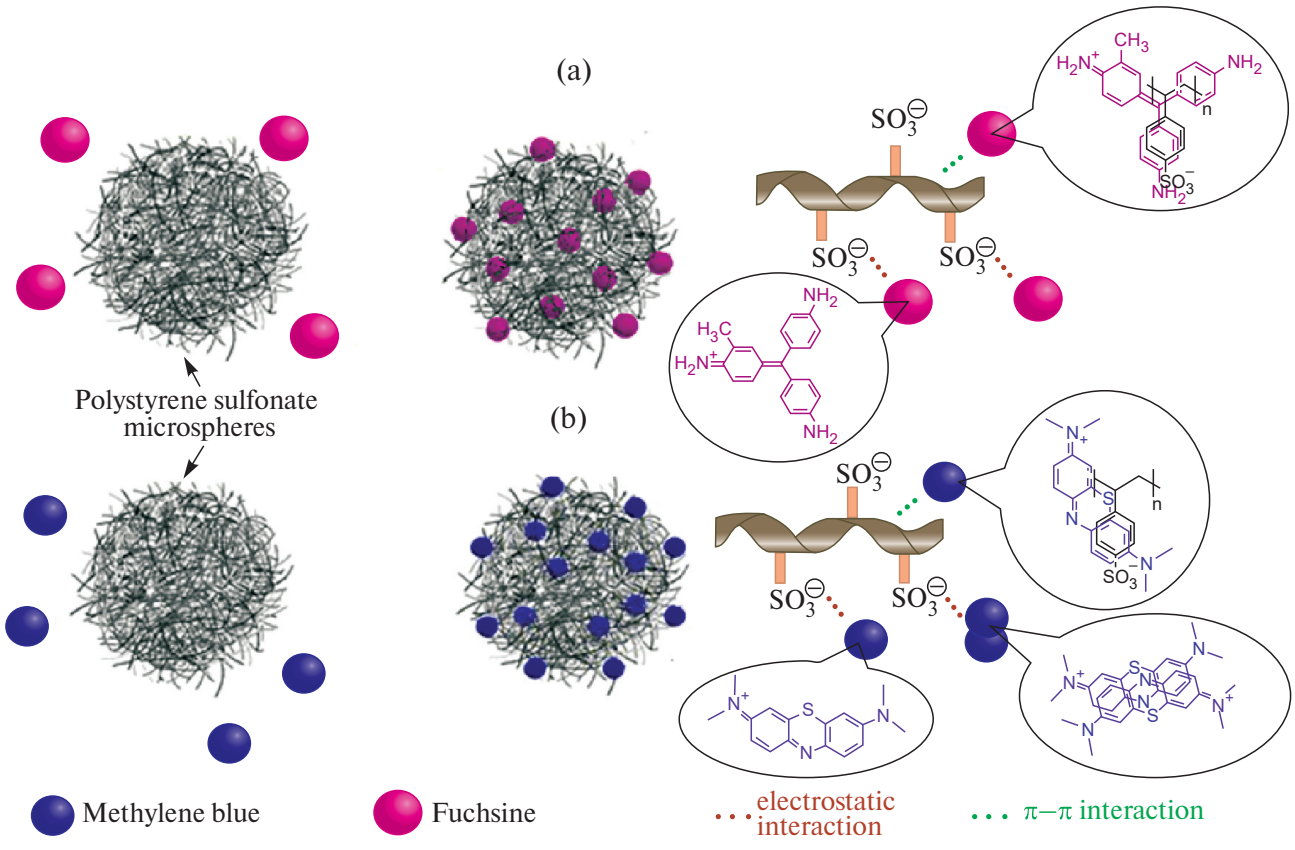

Fig. 6. Scheme of interaction of microspheres with fuchsin (a) and methylene blue (b).

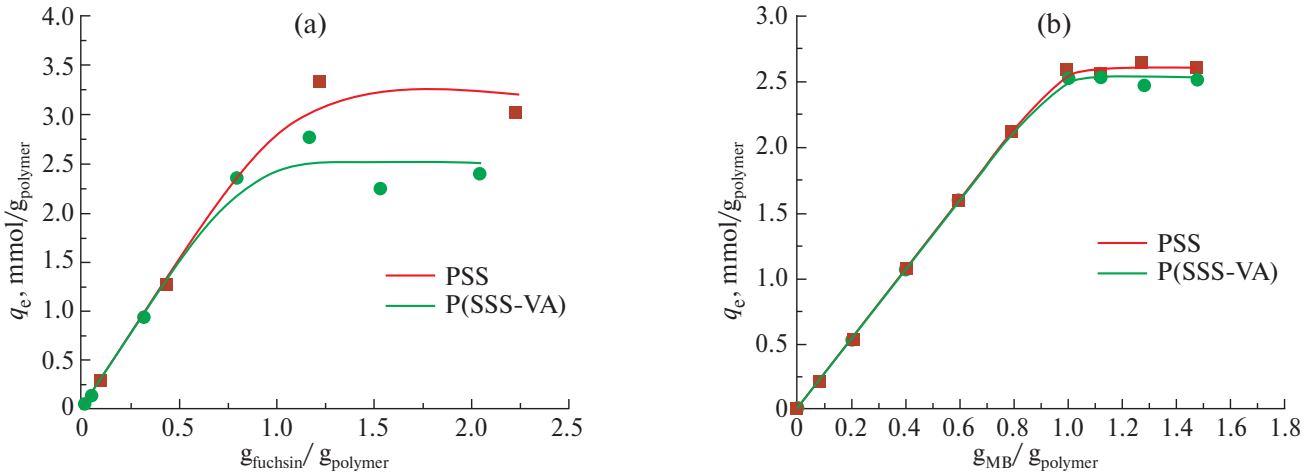

Fig. 7. Adsorption isotherms of fuchsin (a) and methylene blue (b) on the synthesized microspheres.

Table 2. Main parameters of models of fuchsin and MB adsorption isotherms on PSS and P(SSS-VA) microspheres

Model	Model parameters	Fuchsin		Methylene blue	
		PSS	P(SSS-VA)	PSS	P(SSS-VA)
Langmuir	q_{exp}, mmol/g	3.3	2.3	2.7	2.5
	$q_{max\ theor}$, mmol/g	5.2	4.6	10.1	7.6
	$K_L \cdot 10^{-3}$	0.83	0.78	0.29	0.41
	R_L (at 0.25)	0.83	0.84	0.93	0.91
	R^2	0.83	0.86	0.64	0.63
Freundlich	$1/n$	0.86	0.81	0.91	0.88
	K_F, mmol/g	2.48	2.02	2.33	1.09
	R^2	0.97	0.95	0.98	0.97

urinary tract diseases, methemoglobinemia, and as a dye in various medical manipulations. Fuchsin also exhibits antimicrobial properties and can be used as an antiseptic for the treatment of wounds and other surfaces. These compounds were chosen as model samples because of their positively charged cationic structure, which is able to interact with the sulfonate groups in the structure of the synthesized microspheres. The interaction of MB and fuchsin with the particles was carried out due to ion–ion interaction (Fig. 6), as well as due to other types of bonding (hydrogen, π–π interaction, etc.).

The sorption properties of the synthesized particles with respect to MB and fuchsin were studied by spectrophotometry. Fig. 7 shows the adsorption isotherms of fuchsin and MB from aqueous solutions onto the synthesized PSS microspheres and copolymer P(SSS-VA). The figure shows that all isotherms belong to class L according to the Charles Giles classification. They are characterized by an increase in adsorption with rising equilibrium concentration of adsorbate and its gradual approach to the maximum value of sorption capacity. According to the data obtained, the maximum values of fuchsin sorption after 2 hours are 3.3 and 2.3 mmol/g for PSS and P(SSS-VA), respectively. For MB, the maximum sorption capacity after 2 hours was 2.7 and 2.5 mmol/g for PSS and P(SSS-VA), respectively. It is worth noting that the obtained values exceed the content of sulfonate groups available for ion–ion interaction. In this connection, it can be assumed that multilayer adsorption of fuchsin and MB onto the synthesized particles occurs.

The adsorbent-adsorbate interactions were investigated by analyzing the linear adsorption isotherms using the Langmuir (equation (1)) and Freundlich (equation (2)) models. The linear correlations of the Langmuir and Freundlich isotherms are shown in Fig. 8. The calculated constants corresponding to each model, as well as the coefficient of determination, showing the convergence of theoretical and experimental data, are presented in Table 2.

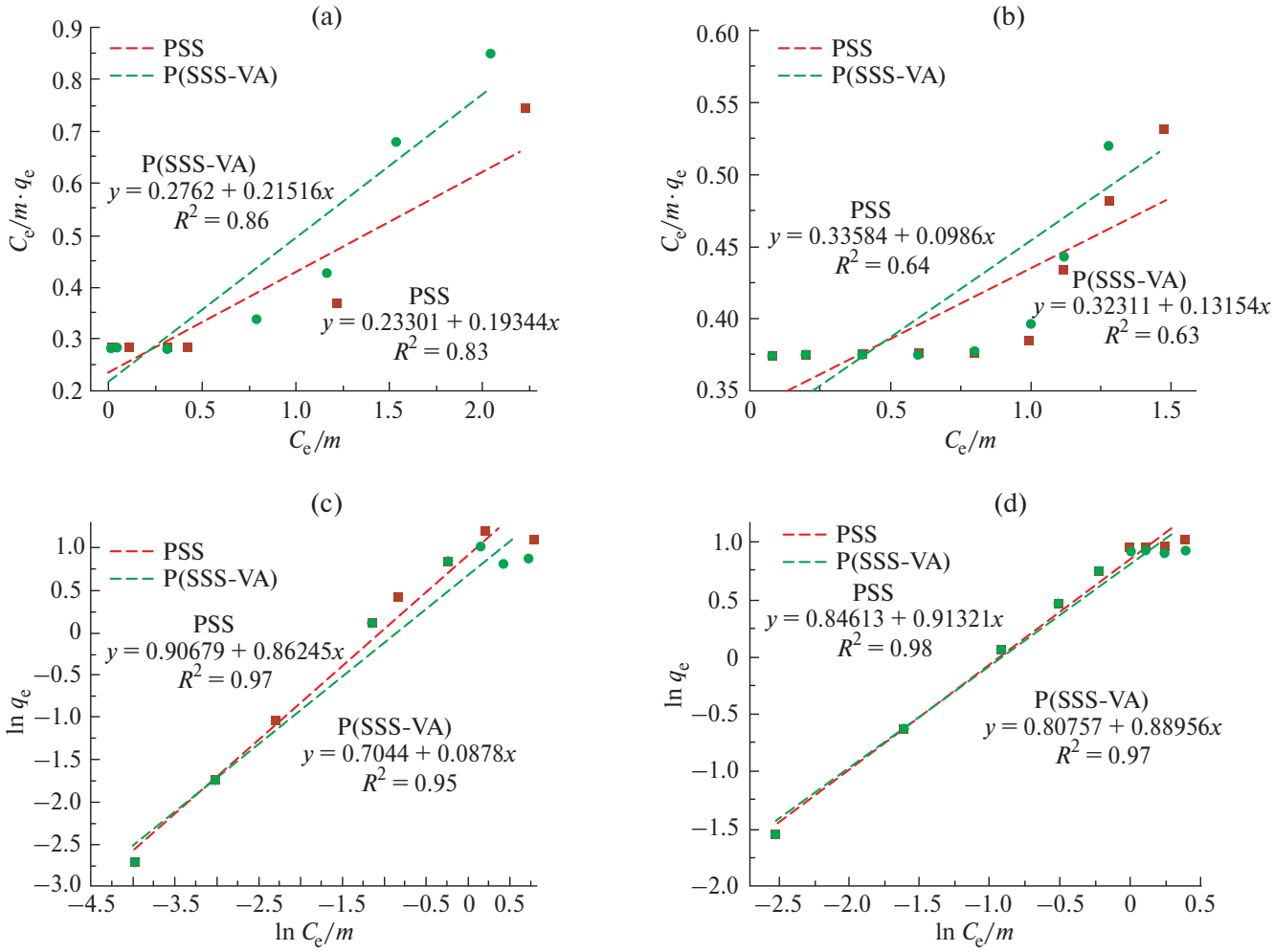

Fig. 8. Linear correlations of Langmuir isotherms for fuchsin (a) and methylene blue (b); linear correlations of Freundlich isotherms for fuchsin (c) and methylene blue (d).

The Langmuir model implies the formation of a monolayer of adsorbate molecules due to their adsorption on a homogeneous solid surface containing a finite number of active centers with equal energy. The Freundlich model describes multilayer adsorption of adsorbate on a homogeneous solid surface with active centers having different adsorption energies. The obtained coefficients of determination for the Langmuir model showed low values (0.63–0.86) for all investigated microspheres for both adsorption towards fuchsin and MB. This indicates the low applicability of this theory to the processes occurring during adsorption. The Freundlich model (R^2 = 0.95–0.98) was found to be the best fitting model for all microspheres. This indicates the formation of several layers of fuchsin and MB molecules both on the surface and in the volume of the polymer microspheres. In addition, in the Freundlich model, the parameter $1/n$ is a power-law parameter and shows the nature of adsorption proceeding. At $1/n = 1$, the distribution of adsorbed molecules between the two phases is independent of concentration; at $1/n$ equal to 0, adsorption is irreversible; at $1/n < 1$ adsorption is favorable, and at $1/n > 1$ adsorption is unfavorable. For this work, the $1/n$ was in the range of 0.81–0.91 in all cases, indicating favorable adsorption of fuchsin and MB onto the synthesized particles.

Taking into account the use of the Freundlich multilayer adsorption model and the increased value of the maximum sorption capacity relative to the content of sulfonate groups in the synthesized microspheres, it can be assumed that the adsorption of fuchsin and MB occurs not only due to ion–ion interaction. It is possible that other interactions, such as hydrogen bonds [26] or π–π stacking between the aromatic rings of DS and the aromatic ring in the PSS structure, are also important in adsorption. In addition, it is known that MB is prone to self-association and formation of dimers and trimers [27], so it can be assumed that not only monomeric MB molecules, but also dimers and trimers are involved in adsorption, which may be the reason for such a high sorption capacity.

CONCLUSION

Cross-linked polystyrene sulfonate microspheres were synthesized by reverse emulsion polymerization with and without the use of VA monomer. It was shown that this method formed microspheres with a high content of sulfonate groups, which were localized both in the surface layer and in the volume of the microspheres. Such localization of sulfonate groups influences the sorption properties of microspheres with respect to model cationic chromophores – fuchsin and methylene blue. The obtained polyelectrolyte microspheres possess developed specific surface area, which was confirmed by BET method. The obtained results indicate that the polyelectrolyte microspheres obtained are promising for their further study as carriers of hydrocarbons.

FUNDING

The work was performed within the framework of the state assignment (No. 124013000730-3).

ETHICS DECLARATION

There are no human or animal studies in this paper.

CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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