Adsorption of Poly(N-ethyl-4-vinyl pyridinium bromide) onto Langmuir-Blodgett Films Built up from Amphiphilic Polymers

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SUMMARY: The interaction of a strong cationic polyelectrolyte, poly(N-ethyl-4-vinyl pyridinium bromide), with Langmuir-Blodgett (LB) films built up from four monolayers of amphiphilic derivatives of the alternating copolymers of maleic acid and alkenes (one of the monolayers was formed by the amphiphilic copolymer containing pyrenyl groups as fluorescent labels) was examined. Transformations of absorbance spectra and quenching of fluorescence of the LB films were detected after their contact with aqueous solutions of the cationic polyelectrolyte. These changes were attributed to the adsorption of poly(N-ethyl-4-vinyl pyridinium bromide) onto such films. The efficiency of this process was found to be rather sensitive to the variations in pH of the surrounding medium: adsorption of the cationic polyelectrolyte onto the LB films was pronounced in basic media while it became rather weak in acidic media.

Introduction

Due to numerous important industrial applications of polyelectrolytes (for example, for waste water treatment, paper processing, production of functional polymeric coatings, etc.), considerable attention of scientists during the last years has been focused on adsorption of such polymers at a solid-liquid interface. A deep understanding of this phenomenon is required to control technological processes dealing with a use of polyelectrolytes. The main achievements of both experimental and theoretical investigations related to interface behavior of ionic polymers have been reviewed by Bajpai1).

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The surface characteristics of substrates (sign of surface charge, surface charge density, etc.) play a crucial role in adsorption of polyelectrolytes at a solid-liquid interface$^{2-4)}$. In connection with this, the use of well-defined and characterized surfaces whose properties can be rather easily varied in a relatively large scale opens a possibility to study this process in a systematic manner.

The Langmuir-Blodgett (LB) technique provides an attractive opportunity to construct well-defined surfaces with desired characteristics. In particular, LB films formed by amphiphilic polymers are of especial interest because of their higher stability compared to those built up from low molecular weight amphiphiles. Such polymeric model surfaces have been suggested to be applied for systematic studies on adsorption of polyelectrolytes at a solid-liquid interface$^{5)}$.

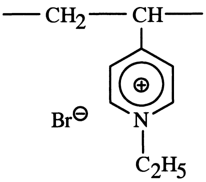
In this paper, we consider the results of our ongoing research focused on the interaction of a cationic polyelectrolyte, poly(N-ethyl-4-vinyl pyridinium bromide), with multilayer films built up by means of the LB technique from amphiphilic derivatives of the alternating copolymers of maleic acid and alkenes.

Experimental

Materials

Poly(N-ethyl-4-vinyl pyridinium bromide) (**1**) was synthesized via exhaustive quaternization of poly(4-vinylpyridine) with weight average molecular mass M_w = 300000 g/mole (Polysciences Inc., USA) by about 10-fold excess of ethyl bromide in methanol at elevated temperature. According to the data of ^{1}H NMR spectroscopy, the molar content of quaternized pyridine units in the resulting polymer was approximately 90%. The chemical structure of the polymer **1** is presented in Fig. 1.

Amphiphilic copolymers, poly(maleic acid hexadecyl monoamide – *alt* – propene) (**2**) and poly(maleic acid octyl / pyrenyl monoamide – *alt* – ethene) (**3**) with the molar content of (maleic acid pyrenyl monoamide – ethene) units of about 5%, were synthesized from the corresponding alternating copolymers of maleic anhydride and propene with M_w = 27000 g/mole (Leuna AG, Germany) or maleic anhydride and ethene with M_w = 166000 g/mole (Polysciences Inc., USA) as described elsewhere[5]. The chemical structures of the copolymers **2** and **3** are shown in Fig. 1.



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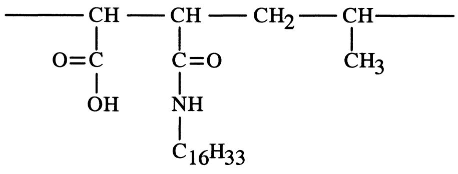

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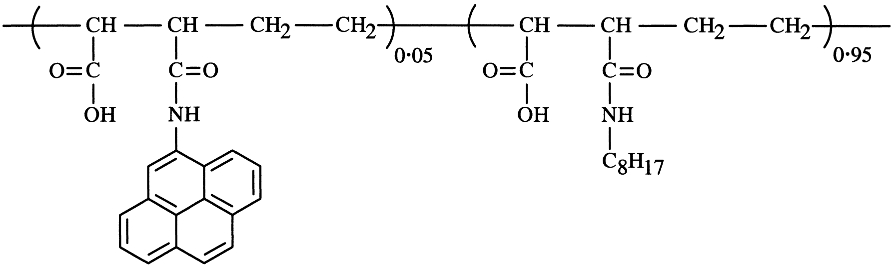

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Fig. 1. Chemical structures of monomer units of the polymers used.

TRIS (2-amino-2-hydroxymethyl-1,3-propanediol) and its hydrochloride were obtained from Fluka and used without further purification to prepare buffer solutions with pH ranged from 5.5 up to 10. Water purified and deionized (reverse osmosis followed by ion exchange and filtration) by means of Milli-RO 5Plus and Milli-Q Plus systems (Millipore GmbH, Germany) was used as a solvent.

Preparation of LB films

The LB films were prepared to contain four monolayers of the amphiphilic copolymers: 1st, 2nd, and 4th monolayers were built up from the copolymer **2** while 3rd monolayer was formed by the copolymer **3**. The schematic representation of the structure of the LB films used is given in Fig. 2.

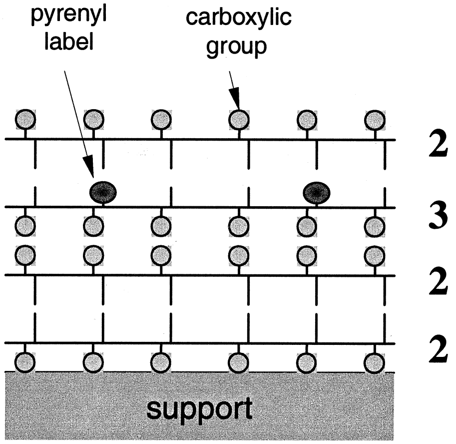

Fig. 2. Schematic representation of the LB films used.

Quartz plates Spektrosil B (Thermal Quartz-Schmelze GmbH, Germany) with the size of 75 mm x 25 mm were used as the supports for the LB films. The plates were thoroughly cleaned by a mixture of sulfuric acid with potassium dichromate at 80°C for about 2 hours in an ultrasonic bath prior the deposition of such films.

For some experiments (surface plasmon resonance), high refractive index glass slides SF10 (Hellma Optic GmbH, Germany) covered by a thin evaporated gold layer with the thickness of 50 nm were used as the supports for the LB films.

Ultrapure water with specific resistance of 18.2 MΩ·cm was used as a subphase. The solutions of the copolymer **2** in trichloromethane and the copolymer **3** in a mixture of trichloromethane and dimethylsulfoxide with the concentrations of 1 mg/ml were prepared to be spread by a microsyringe onto the subphase.

A deposition of the polymeric monolayers was performed with a KSV 3000 device (KSV Instruments, Finland). The compression speed of monolayers was approximately 1 cm/min. A monolayer transfer was carried out with the speed of about 1 mm/min at the constant pressure of 30 mN/m^2 for the copolymer **2** or 25 mN/m^2 for the copolymer **3**. The monolayer transfer ratios measured were always close to 1.

Methods

Absorbance Spectroscopy

Absorbance spectra of the dried LB films were measured by means of a Lambda 800 UV/VIS spectrometer (Perkin Elmer Ltd., USA).

Fluorescence Spectroscopy

Steady-state fluorescence spectra of the dried LB films were recorded by means of a LS 50 luminescence spectrometer (Perkin Elmer Ltd., UK) at the excitation wavelength of 341 nm. The incident angle of the excitation beam was 45°, the excitation and emission slit widths were chosen to be 15 and 5 nm respectively.

Electrokinetic Measurements

Electrokinetic measurements for the LB films were carried out by means of an Electrokinetic Analyzer device (A. Paar KG, Austria). The values of ζ-potential were calculated according to the formula:

$$\zeta = \frac{\eta}{\varepsilon_0 \varepsilon_r} \cdot \frac{\Delta U}{\Delta p} \cdot \kappa \qquad (1) \quad ,$$

where ΔU is streaming potential measured between two Ag/AgCl electrodes located at the opposite ends of the substrates, η, ε_r, κ are dynamic viscosity, relative dielectric permittivity, and conductivity of the flowing electrolyte solution (0.001 M KCl) respectively, ε_0 is dielectric permittivity of vacuum, and Δp is the pressure applied (150 mbar). The 0.1 M solutions of NaOH and HCl were used to change pH of the flowing electrolyte solution in the range from 10 to 3.

Surface Plasmon Resonance

Surface plasmon resonance data for the LB films were obtained by means of the equipment consisting of a He-Ne laser with λ = 632.8 nm (Uniphase, USA), a semi-cylinder made of SF10 glass, a liquid flow cell with the volume of 2.5 ml, and a E10V large area silicon photodiode detector with an integral preamplifier (Linus GmbH, Germany). The laser emitted polarized light (polarization ratio was 500:1) with power of 3 mW onto a semi-cylinder whose plane face was coupled, via index matching fluid, to the substrate examined (SF10 glass slide covered by the gold layer and then by the LB film). The liquid flow cell was attached to the other side of the substrate and sealed with a rubber O-ring. The light was reflected onto the gold layer to excite surface plasmons. The intensity of the reflected light was measured by the photodiode. Both the semi-cylinder and the detector were mounted in an in-house $\theta/2\theta$ goniometer in such a way that the laser beam was incident on the detector at any angle of incidence. The goniometer and the photodiode were interfaced (MotionMaster 3000, Newport Corp., USA) to a personal computer. An in-house 32-bit software package was used for goniometer control, data acquisition, curve modeling, and curve fitting. For scans over a certain range of incidence angles, a step width of 0.1° was used. The curves obtained were fitted according to Fresnel equations for a four-layer model (glass / metal / dielectric / surrounding medium).

All measurements were made at room temperature.

Results and Discussion

Whereas the charge of the polymer **1** is pH-independent, the surface charge of the LB films due to the presence of carboxylic groups can be controlled by variations in pH of the surrounding medium. The results of electrokinetic measurements show that isoelectric point of such films is close to 4 (Fig. 3). This fact implies that at pH > 4 surfaces of the LB films bear negative charge and macromolecules of the cationic polyelectrolyte are naturally expected to adsorb onto such films because of electrostatic attraction.

To demonstrate this, the support covered by the LB film was immersed in a glass beaker containing 100 ml of a continuously stirred solution of the polymer **1** in 0.01 M TRIS buffer. The initial concentration c_0 of the cationic polyelectrolyte in the solution was 1×10^{-5} base-mole/l, the value of pH of the solution was about 10, temperature of the solution was kept constant at 23°C. After 1 hour had been elapsed, the support was thoroughly washed with ultrapure water for 5 min, dried at room temperature in air atmosphere, and then analyzed by means of the spectroscopic methods.

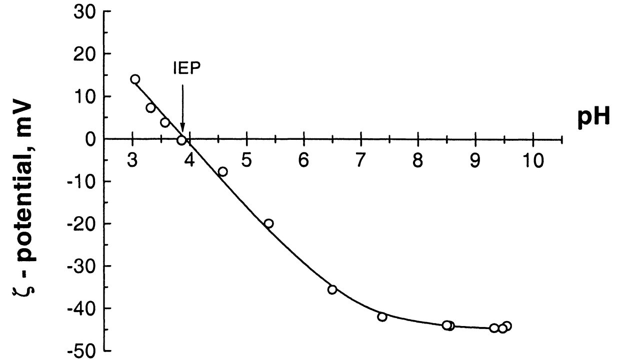

Fig. 3. The pH-dependence of ζ–potential of the LB film.

Fig. 4a illustrates the absorbance spectra of the LB film before and after the contact with the solution of the polymer **1**. A considerable difference between these spectra is observed: an appearance of new absorption bands can be clearly detected at $\lambda < 300$ nm. A comparison of the absorbance spectrum of the LB film after the contact with the solution of the cationic polyelectrolyte (Fig. 4a, solid line) with the absorbance spectrum of this solution (Fig. 4b) provides evidence that these new absorption bands appeared as a consequence of adsorption of macromolecules of the polymer **1** onto the LB film.

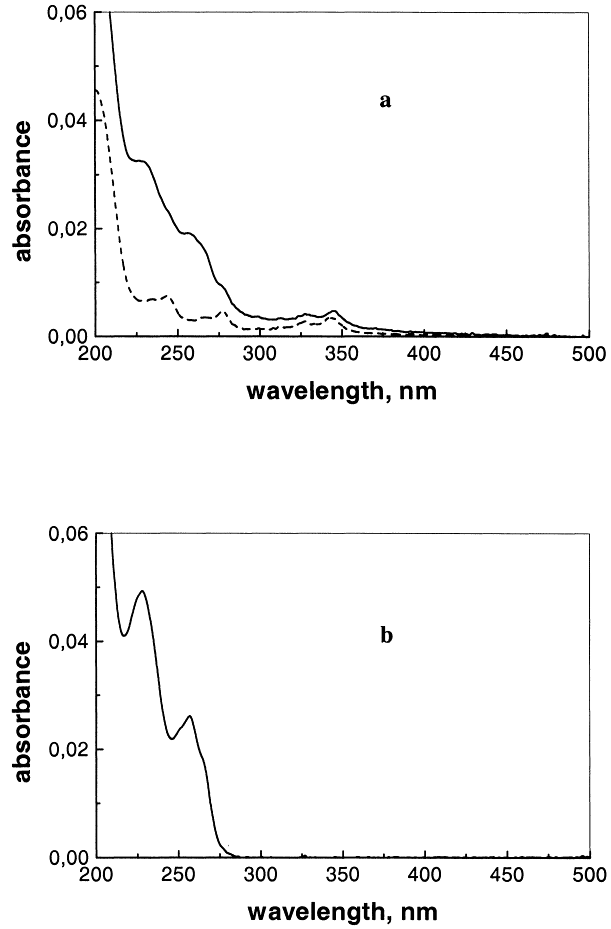

Fig. 4. (**a**) The absorbance spectra of the LB films before (dashed line) and after (solid line) the contact with the solution of the polymer **1** at pH 10 for 1 hour; (**b**) the absorbance spectrum of the solution of the polymer **1** measured before the adsorption procedure.

Due to the presence of pyrenyl groups in the LB film, adsorption of macromolecules of the polymer **1** onto this film can also be detected by means of fluorescence spectroscopy. Fig. 5 shows that a pronounced decrease of fluorescence intensity of the LB film is observed after the contact of this film with the solution of the cationic polyelectrolyte. This effect is attributed to a quenching of fluorescence of pyrenyl groups by macromolecules of the polymer **1** adsorbed onto the LB film since the copolymer **3** remains in the multilayer structure after adsorption as it follows from the absorbance spectra given in Fig. 4a: absorbance around 341 nm results from pyrenyl groups in the LB film. A possible reason for such a fluorescence quenching could be an energy transfer from excited pyrenyl groups of the copolymer **3** to pyridinium units of the cationic polyelectrolyte.

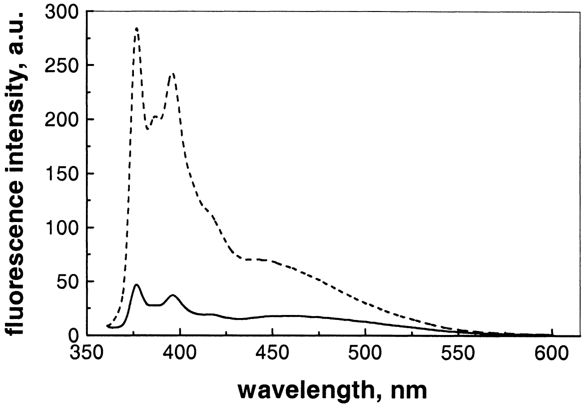

Fig. 5. The fluorescence spectra of the LB films before (dashed line) and after (solid line) the contact with the solution of the polymer **1** at pH 10 for 1 hour.

It is important to note that reference measurements carried out for the similar LB film which was in the contact for 1 hour with 0.01 M TRIS buffer indicated only minor changes in absorbance and fluorescence spectra of this film.

Absorbance and fluorescence spectra of the LB film covered by the polymer **1** demonstrated no transformations when this film was kept in ultrapure water for about a week. This result indicates that cationic macromolecules adsorbed do not desorb from the multilayer structure. Such a behavior suggests that adsorption of the polymer **1** onto the LB film can be considered as an irreversible process.

On the assumption that the extinction coefficient ε_λ of the polymer **1** adsorbed onto the LB film is equal to that obtained for its dilute solution at the same wavelength λ, the amount n of the cationic polyelectrolyte covering this film can be evaluated from the data presented in Fig. 4a according to the formula:

$$n = \frac{\Delta OD_\lambda}{\varepsilon_\lambda} \cdot S \qquad (2) \quad ,$$

where ΔOD_λ is the difference between the values of optical density measured at the wavelength λ for the LB film before and after the contact with the solution of the polymer **1**, S ($S = 7.5$ cm^2) is the surface area of the LB film covering one side of the support (the LB film was deposited onto both sides of the support, therefore, the total surface area of the LB film was 15 cm^2). The calculation made for $\lambda = 257$ nm ($\varepsilon_{257} = 2.6\times10^6$ cm^2/mole), which corresponds to one of the characteristic absorption bands of the solution of the cationic polyelectrolyte (Fig. 4b), yields $n \approx 4.5\times10^{-8}$ basemole.

The π-A isotherm obtained for the copolymer **2**[5)] provides evidence that one carboxylic group of this copolymer occupies a surface area of about 25 Å^2. On the basis of this fact, the total amount of carboxylic groups on the surface of the LB film was determined to be 1×10^{-8} mole approximately. Thus, the monomer units of the cationic polyelectrolyte adsorbed were found to be in about 4.5-fold excess compared to carboxylic groups located on the surface of the LB film.

The average thickness of the layer of the cationic polyelectrolyte adsorbed onto the LB film was evaluated by means of surface plasmon resonance. In this case, the LB film was deposited onto the SF10 glass slide covered by the thin gold layer. At first, the angular dependence of reflectivity was obtained for the original film that was brought in contact with 100 ml of 0.01 M TRIS buffer (pH 10) continuously circulated at the speed of 10 ml/min through the liquid flow cell by a peristaltic pump. Then, the pure buffer was changed for 100 ml of the solution of the polymer **1** in this buffer ($c_0 = 1\times10^{-5}$ basemole/l). After 1 hour had been elapsed, the angular dependence of reflectivity was measured again.

Fig. 6 presents the angular dependencies of reflectivity obtained. It is seen, the minimum of reflectivity shifts towards higher angles after the contact of the LB film with the solution of the cationic polyelectrolyte. This shift is supposed to be induced by adsorption of macromolecules of the polymer **1** onto the LB film. On the assumption that the value of refractive index of the adsorbed polymeric layer is 1.5, which is the typical value for organic compounds, the average thickness of this layer was evaluated to be about 2 nm.

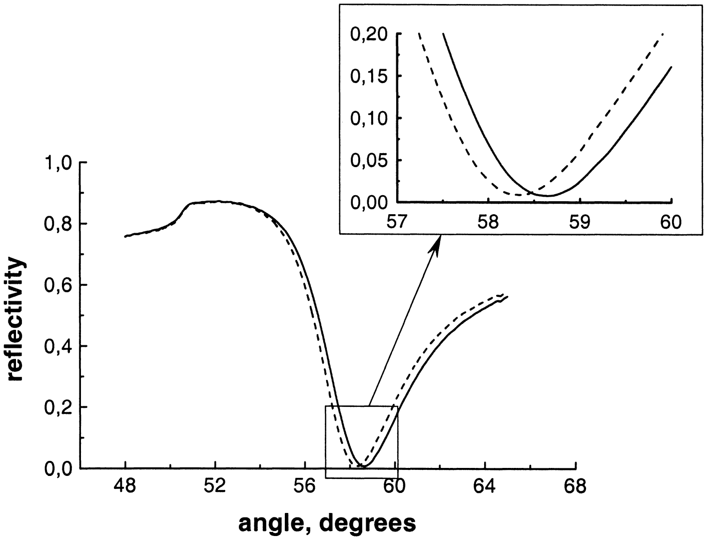

Fig. 6. The angular dependencies of reflectivity obtained for the LB films before (dashed line) and after (solid line) the contact with the solution of the polymer **1** at pH 10 for 1 hour.

It is interesting to make a semi-quantitative comparison of the data obtained by means of absorbance spectroscopy and surface plasmon resonance. Taking into account the determined average thickness of the adsorbed polymeric layer and on the assumption that density of this layer is about $1 g/cm^3$, we roughly determined the amount of the polymer **1** covering $1 cm^2$ of the LB film to be 2×10^{-7} g. On the other hand, the amount of the cationic polyelectrolyte adsorbed onto $1 cm^2$ of the LB film can be evaluated from the data of absorbance spectroscopy given in Fig. 4a: this amount was found to be within 4.0 … 6.4×10^{-7} g, the exact value being dependent on the fraction of the monomer units of the adsorbed macromolecules which retain their counterions. As is seen, these values are in the same order of magnitude. Thus, this semi-quantitative comparison shows that the results obtained by the different techniques applied are in a relatively good agreement.

Adsorption of macromolecules of the polymer **1** onto the LB films was found to be rather sensitive to the variations in pH of the surrounding medium. As for the other experiments considered above, c_0 was 1×10^{-5} basemole/l while pH of the solutions ranged from 5.5 up to 10. To characterize the efficiency of adsorption of the cationic polyelectrolyte at different pH, the difference ΔOD_{257} in the values of optical density measured at 257 nm before and after the contact of the LB films with the solution of the polymer **1** (Fig. 4a) and the relative fluorescence intensity $(I/I_0)_{396}$ where I_0 and I are fluorescence intensities measured at 396 nm before and after the contact of the LB films with the solution of the polymer **1** (Fig. 5) were used.

The pH-dependencies of ΔOD_{257} and $(I/I_0)_{396}$ obtained for the LB films that were brought in contact with the solution of the cationic polyelectrolyte for 1 hour are presented in Fig. 7. As is seen, both dependencies are in a fair agreement with each other: adsorption of macromolecules of the polymer **1** is pronounced in basic media but it becomes rather weak in acidic media, the drastic changes in the amount of the cationic polyelectrolyte adsorbed being clearly detected for pH varying from 6 up to 7.

It is remarkable that at pH > 7, where adsorption is effective, the LB films bear considerable negative charge (the values of ζ-potential are less than – 40 mV) whereas a steep increase of ζ-potential of these films with decreasing pH is observed at pH < 7 (Fig. 3). Thus, efficiency of adsorption of macromolecules of the polymer **1** onto the LB films correlates rather well with surface charge of such multilayer structures. This finding manifests a significant role of the electrostatic contribution in the interaction between the cationic polyelectrolyte and the LB films examined.

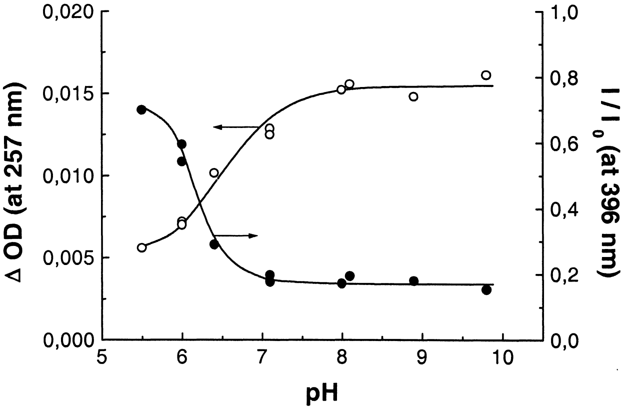

Fig. 7. The pH-dependencies of ΔOD_{257} (open circles) and $(I/I_0)_{396}$ (solid circles) obtained for the LB films that were brought in contact with the solution of the polymer **1** for 1 hour.

Concluding Remarks

It has been shown that the interaction of poly(N-ethyl-4-vinyl pyridinium bromide) with polymeric model surfaces formed by the LB films built up from amphiphilic derivatives of the alternating copolymers of maleic acid and alkenes leads to adsorption of macromolecules of this cationic polyelectrolyte onto such films, this process is irreversible. The efficiency of adsorption was found to be rather sensitive to the variations in pH of the surrounding medium: adsorption of poly(N-ethyl-4-vinyl pyridinium bromide) onto the LB films was pronounced in basic media while it became rather weak in acidic media. This fact manifests a significant role of the electrostatic contribution in the interaction of the cationic polyelectrolyte used with the LB films examined.

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