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ABSORPTION OF IONIC AMPHIPHILS BY OPPOSITELY CHARGED POLYELECTROLYTE GELS.

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Abstract: Slightly cross-linked polyelectrolytes absorb oppositely charged surfactants in aqueous media. Transfer of amphiphilic ions from solution into the swollen network proceeds as a frontal heterogeneous cooperative reaction causing a collapse of the original polyelectrolyte gel. Small and wide angle X-ray diffraction data show that electrostatic complex formed as a result of the reaction consists of lamellar type surfactant micelles embedded in a polyelectrolyte network. It is also shown that such complexes contain equimolar amount of surfactant ions and ionized polyelectrolyte units paired with amphiphil head groups. In other words a charged network is not able to bind surplus oppositely charged surfactant ions. However, it is still able to solubilize a substantial amount of a nonionized surfactant. Chemical structure of surfactants strongly affect internal structure of lamellae and stability of the complexes.

INTRODUCTION

Active transport of linear polyions into oppositely charged gels was observed in the end of 80's (Refs. 1, 2). It was established that a gel sample brought in contact with aqueous solution of a linear polyelectrolyte can absorb linear polyions due to cooperative electrostatic coupling to form interpolyelectrolyte complexes (IPECs). It has been shown that the reaction causes a sharp decrease of the volume of a reacted gel

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(about three order of magnitude). In course of the reaction a distinctly differentiated weakly swollen IPEC shell coexists with highly swollen original polyelectrolyte core. In fact a collapse of the gel network is closely interrelated with macroscopic phase separation within the reacting gel sample. Recently we revealed quite similar peculiarities studying interaction between slightly cross-linked polyelectrolyte gels and oppositely charged surfactants (Ref. 3) not taken into account in earlier workers (Refs. 4-8) describing collapse phenomena in similar systems. We suppose that such studies are also worth to enlarge our knowledge on self assembly phenomena in complex macromolecular systems and to design functional polymer-micellar constructs. This paper is devoted to elucidate a character of complexation between swollen polyelectrolyte network and oppositely charged amphiphilic ions as well as the structure and some properties of cross-linked polyelectrolyte-surfactant complexes (#-PESC) formed.

EXPERIMENTAL PART

Acrylic acid (AA) and N,N'-dimethylaminoethylmetacrylate (DMAEM) were purified by distillation. N,N'-dimethyl-N-ethylaminoethylmetacrylate bromide (DMAEM•EtBr) was synthesized by alkylation of DMAEM with ethyl bromide (EtBr): DMAEM was added dropwise to 5-fold excess of EtBr on stirring and ice-cooling. DMAEM•EtBr formed as a white precipitate was washed by ethyl ether and dried in vacuum.

The cross-linked polyelectrolytes - poly(acrylic acid) (#-PAA), poly(N,N'-dimethylaminoethylmetacrylate) (#-PDMAEM) and poly(N,N'-dimethyl-N-ethylaminoethylmetacrylate bromide) (#-PDMAEM•EtBr) were prepared by radical copolymerization of AA and DMAEM in 10 wt.% and DMAEM•EtBr in 20 wt.% aqueous solution respectively with 1 mol.% of N,N'-methylenebisacrylamide as a cross-linker initiated by ammonium persulfate/sodium methabisulfite redox system (0.2 % of monomer mass) and performed at 40°C for twenty four hours under argon atmosphere (Refs. 1, 2). The #-PAA was completely neutralized by NaOH before use. #-PDMAEM was prepared in salt form (#-PDMAEM•HCl) by adding equivalent amount of HCl to the reaction mixture. Concentration of the monomer units in equilibrium-swollen gels was about 0.1 base mol/l.

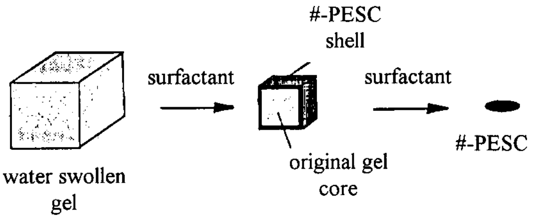
The following cationic surfactants were used: dodecylpyridinium chloride (DPC), cetylpyridinium bromide (CPB), dodecyltrimethylammonium bromide (DTMAB), tetradecyltrimethylammonium bromide (TTMAB), cetyltrimethylammonium bromide (CTMAB), eicosyltrimethylammonium bromide (ETMAB), cetylamine hydrochloride (CA HCl). Caprylic ($C_7H_{15}COOH$), caprynic ($C_9H_{19}COOH$), myristinic ($C_{13}H_{27}COOH$) and palmitinic ($C_{14}H_{29}COOH$) acids, sodium tetradecylsulfonate (STDS), sodium dodecylbenzosulfonate (SDBS), sodium octadecylsulfonate (SODS) and sodium dodecylsulfate (SDS) were used as anionic surfactants. All surfactants were purchased from "Serva" and purified by repeated precipitation from ethanol before use. All alkylcarboxylic acids were transformed into potassium salt by neutralization with KOH.

Absorption of the surfactants by the polyelectrolyte networks was measured as follows. First the gel sample was controlled thermostatically at 20°C and equilibrated in aqueous solution. Similar to be used in the further experiment, but with no surfactant. Then a piece of the gel was immersed in the reaction solution containing certain amount of the dissolved surfactant at the same temperature. Composition of reaction mixtures, Z, was expressed as the ratio of a total mole amount of added surfactant to a overall mole amount of the repeating monomer units in the gel sample used. The extent of absorption was monitored measuring surfactant concentration in the surrounding reaction solution and characterized as a mole fraction, F, of polyelectrolyte repeating units in the whole reacting sample paired with surfactant ions at given conditions. Concentration of surfactants absorbing UV - light was measured spectrophotometrically: DPC and CPB at λ=259 nm (ε=4100), SDBS at λ=260 nm (ε=420). Spectrophotometric measurements were carried out by the "Hitachi 150-20" (Japan) spectrophotometer. Concentration of alkylcarboxylates was measured by means of potentiometric titration with HCl using "Radiometer pHM-83" (Denmark) pH-meter.

Wide-angle X-ray scattering (WAXS) measurements were carried out by the X-ray device URS-55 (CuK_α radiation with Ni filter). The operating voltage and current were 40 kW and 20 mA, respectively. Small-angle X-ray scattering (SAXS) measurements were performed by the diffractometer "AMUR-K" equipped with the linear position sensitive detector (Ref. 9). The range of scattering vectors was 1.1.10 <Q<4.2.10 Å, the wavelength of incident beam was 1.54 Å (CuK_α). In some experiments the automatic diffractometer with two-dimensional high resolution detector "ARD-1M" was also used (Ref. 10). DSC traces were obtained using the "Mettler TA 4000" thermal analyzer at the heating rate of 10 degree/min. Elemental analysis of PESC were carried out by CHNS-analyzer "Carbo Erba 1106" (Italy).

RESULTS AND DISCUSSION

Slightly cross-linked highly swollen polyelectrolyte gels immersed in aqueous solution of an oppositely charged surfactant absorb the amphiphilic ions so that their solution concentration gradually decreases. Correspondingly the equivalent amount of the small counter-ions releases from the original gel. Importantly that the whole process represents a frontal heterogeneous reaction. At the early stage a thin iridescent layer of #-PESC forms on the gel surface. Then this layer progressively increases in thickness and becomes turbid. At the same time the volume of the gel sample drastically decreases. Finally the original highly swollen piece of gel transforms into a compact opaque #-PESC species. Such transformation represented in the scheme I is typical for all studied systems.



(I)

The partially converted sample consists of a slightly swollen #-PESC shell containing practically all absorbed surfactant ions and an inner transparent core of the original gel. It is worth mentioning that the shell-core boundary remains rather sharp as the process goes on. Moreover, this sharp boundary does not diffuse if the partially converted gel is transferred from the surfactant solution into the limited volume of pure water and kept there for a long period of time. At the same time addition of new portions of the surfactant into the bulk solution is again accompanied by advance of the sharp boundary inside the gel; so that increase of the outer layer thickness is followed by consequent decrease of the weight fraction of the inner core. The degree of swelling of #-PESC in water $H=(m_s-m_d)/m_d$ is usually close to 1 (m_s and m_d are the masses of swollen and dry samples, correspondingly). This is by two or three orders of magnitude less than H-value of the original gels we used. In other words formation of #-PESC inside of a polyelectrolyte network is followed by a sharp collapse of the gel.

The typical binding isotherms of DPC (1) and CPB (2) by #-PANa and SDBS (3) by #-PDMAEM·HCl are shown in Fig. 1.

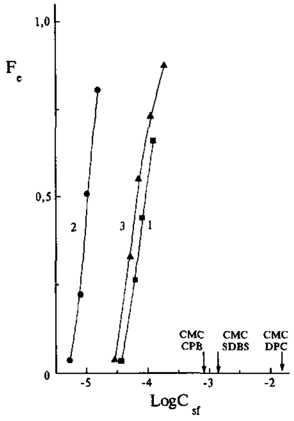


Fig. 1. Binding isotherms of DPC (1) and CPB (2) by #-PANa; and DBS (3) by #-PDMAEM·HCl in salt free solutions. The samples of the initial gel were prepared in the form of cubes with mass about 3g. Curves (1) and (3) were obtained at 20°C; curve (2) - at 40°C, F_e=F at equilibrium.

One can see that binding of the surfactant ions by the gels occurs at surfactant concentrations two-three orders of magnitude lower than CMC values of the corresponding surfactants. It is important that the isotherms are rather steep. This indicates the cooperative character of interaction between a polyelectrolyte network and oppositely charged surfactant ions similar to well known for linear polyelectrolytes (Ref. 11). Compositions of #-PESC, φ, expressed as mole fractions of polyelectrolyte repeating units in #-PESC phase paired with surfactant ions were determined measuring decrease of surfactant concentration in surrounding solution. In the cases of SDS and STDS φ was determined by elemental analysis of #-PESC formed. The φ values obtained for different Z are listed in Tab. 1.

Tab. 1. Compositions of #-PESC (φ) obtained at different compositions (Z) of the reaction mixtures. Salt free aqueous solution. 20°C. pH=8

SYSTEM	Z	φ
#-PANa-DPC	1.0	0.92±0.05
	2.0	0.93±0.05
	4.0	0.95±0.05
#-PANa-CPB	1.0	0.95±0.05
	2.0	0.98±0.05
	4.0	1.0±0.05
#-PDMAEM·EtBr-$C_7H_{15}CO_2K$	1.0	1.0±0.1
	2.0	1.0±0.1
#-PDMAEM·EtBr-$C_9H_{19}CO_2K$	1.0	1.0±0.1
	5.0	1.0±0.1
#-PDMAEM·EtBr-SDS	1.0	1.0±0.05
	2.0	1.0±0.05
	6.0	1.0±0.05
#-PDMAEM·EtBr-STDS	1.0	1.0±0.05
	2.0	1.0±0.05
#-PDMAEM·EtBr-SDBS	1.0	1.0±0.05
	2.0	1.0±0.05

One can see that #-PESCs contain equimolar amounts of the surfactant ions and charged polyelectrolyte units. Addition of excess amount of ionic surfactant to the reaction mixture ($Z>1$) does not change #-PESC composition indicating that its stoichiometry is determined by electrostatic interaction. The data represented in Tab. 1 correspond to the case when polyelectrolyte repeating units and surfactant molecules are fully ionized, so that $\varphi=1$. A decrease in ionization degree, α, of a weak polyelectrolyte network caused by pH change results in a corresponding decrease of #-PESC composition (Tab. 2). However, φ values still correspond to equimolar ratio of surfactant ions and ionized groups of the gel. In other words the number of absorbed surfactant ions is limited by the number of oppositely charged units of the network.

Tab. 2. Dependence of #-PESC compositions (φ) on ionization degree (α) original networks.

SYSTEM	IONIZATION DEGREE, α	φ
#-PDMAEM-SDS	1.0	1.0±0.05
	0.6	0.6±0.05
	0.3	0.3±0.05
#-PAA-DPC	1.0	0.9±0.1
	0.7	0.7±0.1
	0.5	0.5±0.1
	0.3	0.3±0.1

This differs polyelectrolyte networks from linear polyelectrolytes, which are able to bind a significant excess of ionized surfactant and form water soluble nonstoichiometric PESC (Ref. 11). Such difference is of an entropy nature. Indeed, pairing of surfactant ions with ionized groups of the gel network is followed by release of small counterions in solution resulting in compensation of entropy loss. On the contrary incorporation of surplus surfactant ions would require also immobilization of small counterions in #-PESC phase, i.e. noncompensated entropy decrease.Quit different behavior was observed for the systems containing a mixture of ionized and neutral surfactant species. Interaction of partially dissociated alkylcarboxylic acids (about 50% at pH=4.5-5.0) with fully ionized #-PDMAEM·EtBr is accompanied by considerable extra sorption of neutral surfactant molecules. It is seen from the data of Tab. 3 where #-PESC composition are represented as a total number, N_S, of surfactant species (charged and non-charged) per one repeating unit of a fully charged network. It is also seen that N_S increases with Z, followed with 3-4 times expansion of the samples volume comparing to equimolar #-PESC. More studied are required to describe the extra sorption phenomenon quantitatively. However it is very likely that it is due to solubilization of poor water–soluble fatty carboxylic acids in hydrophobic domains of firstly formed electrostatic #-PESC. The latter assumption is supported by the fact that the original gel does not absorb the studied carboxylic surfactants at pH<4 when they are fully protonated, so that electrostatic interaction of the components is depressed. The similar behavior was observed when completely ionized #-PANa gel interacted with partially (≅50%) ionized cetylamine at pH=8 absorbing 1.5-fold excess of the surfactant at Z=2.

Tab. 3. Compositions of #-PESC (N_S) formed in lightly acids media (pH=4.5-5.0) obtained at different compositions (Z) of the reaction mixture. Salt free aqueous solution. 20°C.

SYSTEM	Z	N_S
#-PDMAEM·HCl-$C_7H_{15}CO_2H$	13.6	6.8
#-PDMAEM·HCl-$C_9H_{19}CO_2H$	2.5	2.2
	3.5	2.7
	4.0	3.7
#-PDMAEM·EtBr-$C_9H_{19}CO_2H$	1.5	1.1
	3.6	3.0
	5.0	4.2

Electrostatic and hydrophobic interactions are both necessary to form #-PESCs. Elimination of any of these two factors leads to destabilization of the complexes (Ref. 12). Therefore #-PESC containing a weak polyelectrolyte network or (and) weak ionic amphiphils can be destroyed when at least one of the components is deionized by changing of pH. #-PESC can also be destroyed by addition of simple salts shielding polyelectrolyte/surfactant ion pairs. Dramatic uncoupling of #-PESC ion pairs proceeds in narrow range of a simple salt concentration indicating a cooperative character of the process. The values of NaCl concentration, $[NaCl]_c$, sufficient to destroy #-PESC depend on chemical nature of ionic groups of interacting PESC components, but do not depend on the length of surfactant aliphatic radical (see Tab. 4)

Tab. 4. The values of NaCl concentration sufficient to destroy #-PESCs.

Stoichiometric #-PESCs	$[NaCl]_c$, mol/l
#-PA - DTMA	0.45
#-PA - CTMA	0.45
#-PA - ETMA	0.45
#-PDMAEM·Et - $C_7H_{15}CO_2$	0.45
#-PDMAEM·Et - $C_9H_{19}CO_2$	0.45
#-PDMAEM·Et - $C_{13}H_{27}CO_2$	0.45
#-PDMAEM·Et - $C_{14}H_{29}CO_2$	0.45
#-PA - CA·H	1.50
#-PDMAEM· Et - DS	1.7
#-PDMAEM·Et - TDS	1.7
#-PDMAEM·Et - ODS	1.7

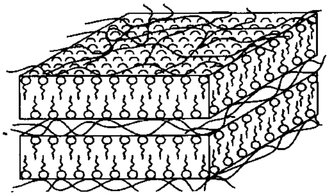
#-PESC can also be destroyed in water-alcohol mixed solvents at alcohol concentration sufficient to eliminate hydrophobic interaction between aliphatic radicals of ionic amphiphils (Ref. 12).

The structure of #-PESC recently became a subject of a considerable interest of the researches (Refs. 8, 13-16). We studied the structure of some above mentioned #-PESCs in the dry and water-swollen states (Refs. 13, 14). In this paper we concentrate on the data related to the dry #-PESCs. The data obtained using SAXS technique show well pronounced small-angle periodicity for all studied systems. The scattering curves contain two or in some cases three maxima. The interplanar distances for various #-PESC are represented in Tab. 5. Bragg parameters, d, were calculated using the common equations $d=2\pi/Q$, where $Q=(4\pi/\lambda)\times\sin\Theta$ is the scattering vector, Θ is the scattering angle, $\lambda=1,54$ Å is the wavelength of the incident beam. One can see that the ratio of the corresponding values of d_1/d_2 is equal to 2 and d_1/d_3 is equal to 3, allowing to conclude that lamellar structure is characteristic for all #-PESC studied.

Tab. 5. The values of Bragg parameters (Å) for various PESCs in dry state estimated from SAXS data at 20°C.

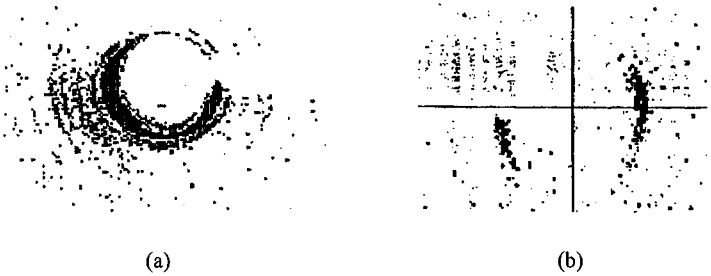
Stoichiometric #-PESCs	d_1	d_2	d_3
#-PA - DTMA	34.0	17.1	
#-PA - CTMA	32.8	16.2	
#-PA - ETMA	44.3	21.8	
#-PA - CA·H	28.2	14.0	9.3
#-PDMAEM·Et - $C_7H_{15}CO_2$	25.3		
#-PDMAEM·Et - $C_9H_{19}CO_2$	29.2		
#-PDMAEM·Et - $C_{13}H_{27}CO_2$	42.1	21.1	13.6
#-PDMAEM·H - DS	37.0		
#-PDMAEM·Et - TDS	34.7	17.3	
#-PDMAEM·H - TDS	36.8		
#-PDMAEM·H - ODS	42.1		
linear PA - CTMA	32.9	16.3	
linear PDMAEM·H - $C_9H_{19}CO_2$	27.0	13.5	9.0

The Tab. 5 demonstrates that the lamellar thickness increases with increase of the length of a hydrocarbon chain in surfactants homologues. SAXS diffraction data allow to represent the #-PESC structure as a system of surfactant lamellae inserted into oppositely charged network as it is shown on Scheme II.



(II)

It is worth to note that directional growth of surfactant lamellae within the oppositely charged swollen polyelectrolyte gel may result in their spontaneous macroscopic orientation in the #-PESC layer as it follows from textured SAXS patterns represented in Fig. 2.



(a) (b)

Fig. 2. Small-angle X-ray scattering patterns of outer layers of #-PESC (#-PA-CTMA) (a) and #-PESC (#-PDMAEM·H-ODS) (b). Data obtained using the automatic diffractometer with two-dimensional high resolution detector "ARD-1M".

The inner structure of #-PESC lamellae was determined by means of WAXS (Refs. 13, 14). We found that #-PESCs formed by #-PANa and surfactant homologous with the number (n) of C-atoms in the aliphatic chain equal or exceeding 16 and #-PESCs composed of polyamine network and anionic surfactants with n ≥ 14 have crystalline structure in a dry state at room temperature. The typical WAXS pattern reveal a single reflection corresponding to the Bragg parameter d=4,2 Å. Therefore one can assume that hydrocarbon fragments of surfactant ions in such complexes are packed in hexagonal lattice. Formation of crystalline hexagonal packing is proved by existence of corresponding texture on X-ray diffraction pattern of uniaxially oriented samples which contains six spot reflections (Fig. 3).

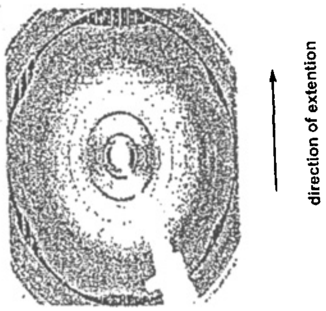


Fig. 3. X-ray scattering pattern of uniaxially oriented #-PESC (#-PANa - CTMAB). T=20°C. Data obtained using the automatic diffractometer with two-dimensional high resolution detector "ARD-1M".

Importantly that internal lamellar structure of #-PESCs is substantially different from crystalline structures of the corresponding surfactants. DSC thermograms of crystalline #-PESCs reveal well-pronounced melting peaks, which can be attributed to melting of hexagonal packed aliphatic chains of surfactants. At the same time melting peaks of pure surfactants are not revealed on #-PESCs thermograms. As an example the DSC-thermogram of #-PESC (#-PDMAEM·H - ODS) is shown in Fig. 4. The data on melting point (T_m) and melting heat (ΔH_m) for various #-PESCs are summarized in Tab. 6.

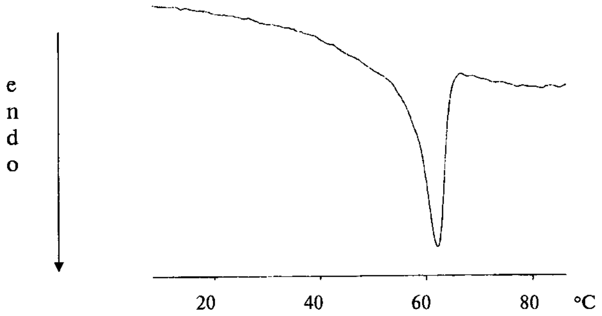
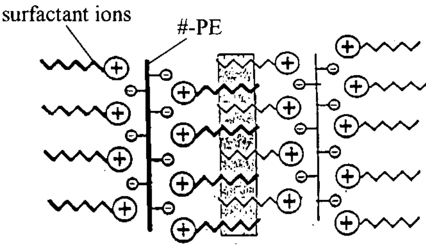


Fig. 4. DSC thermograms of dry #-PESC (#-PDMAEM·H - ODS).
Heating rate 10 K/min.

Tab. 6. The melting points (T°_m) and melting heats (ΔH_m) of dry equimolar PESCs and surfactants.

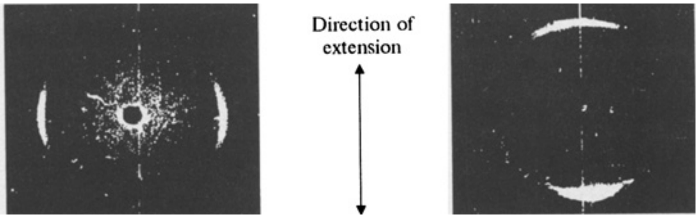
Samples	T°_m (± 3°)	ΔH_m, J/g (± 5 J/g)
Stoichiometric #-PESCs:		
#-PA - CTMA	43	40
#-PA - CP	43	40
#-PA - ETMA	65	60
#-PA - CA·H	59	50
#-PDMAEM·Et - $C_{14}H_{29}CO_2$	40	49
#-PDMAEM·Et - TDS	39	35
#-PDMAEM·Et - ODS	62	46
#-PDMAEM·H - ODS	62	45
linear PESC (PA - CTMA)	43	45
Surfactants:		
CTMAB	110	150
CPB	66	150
ETMAB	94	115
$C_{13}H_{27}CO_2H$	57	179
$C_{14}H_{29}CO_2H$	54	
SDS	206	

As can be seen T_m and ΔH_m values for the #-PESCs studied are lower than those of the related surfactants. Comparison of ΔH_m values of #-PESCs with those of the comb-like polyalkylacrylates with hexagonal packing (Ref. 17) allowed us to conclude that crystallinity of #-PESCs is 25-35%. This means that only small fraction of surfactant methylene groups is included into the crystalline lattice. The substitution of bulky trimethylammonium group of CTMA with protonated primary amino group of CA·H results in increase of lamellae crystallinity. It can be seen from the comparison of T_m and ΔH_m values of #-PESCs, which include CTMAB and CA·HCl. It is worth to note that the period of lamellar structure, d_l, is noticeably higher than the calculated length L of the fragment $-\overset{|}{\underset{|}{C}}H\text{-}COO^{-}\,{}^{+}N(CH_3)_3C_nH_{2n+1}$, L=20, 25 and 30 Å for DTMAB CTMAB and ETMAB, respectively (in cases #-PESC on the base of #-PANa). At the same time d_l is smaller than 2L. The same situation is realized for #-PESCs including polyamine network and anionic surfactant. These speculations suggest that the #-PESCs structure shows neither the bilayer packing characteristic of side hydrocarbon chains of comb-like poly(alkyl acrylates) nor monolayer packing. We believe that there is overlapping of surfactant aliphatic radicals within lamellae as it is shown in Scheme III. Boldprint fragments are located in the plane of the picture, the thin ones are above or bellow the plane of the picture.



(III)

Perpendicular orientation of surfactant aliphatic chains to polyion fragments is proved by existence of equatorial SAXS and meredional WAXS textures on the patterns of uniaxially oriented #-PESC samples (Fig. 5).



(a) (b)

Fig. 5. Small-angle (a) and wide-angle (b) X-ray scattering patterns of uniaxially oriented #-PESC (#-PA - CTMA). T=20°C.

Upon swelling of #-PESC in water, crystalline hexagonal packing of aliphatic chains of surfactant vanishes, and the period d_l increases (Ref. 13, 14).

Finally, we would like to emphasize a certain similarity between the structure of the #-PESC and stoichiometric polycomplexes composed of linear polyelectrolytes, in particular, of those with surfactant ions. As can be seen from the data represented in Tab. 5 and Tab. 6 the structural parameters of linear and network analogs are virtually the same, i.e., at low cross-linking density (one cross-link per 100 units), the network structure of PESC is not associated with noticeable distortions in the structure of polymer-surfactant complex.

As it was mentioned above interaction between fully ionized polyelectrolyte network and partially dissociated ionic amphiphils leads to formation of #-PESCs containing in addition to surfactant ions surplus neutral surfactant molecules. Importantly that SAXS patterns of such complexes (namely, #-PESC (#-PDMAEM·Et - $C_9H_{19}CO_2$), #-PESC (#-PDMAEM·Et - $C_{13}H_{27}CO_2$) and PESC (#-PDMAEM·Et - $C_{14}H_{29}CO_2$)) indicate only one type of lamellar structure with no microphase separation in equilibrium water-swollen state.

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