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Self-Assembly in Ternary Systems: Cross-Linked Polyelectrolyte, Linear Polyelectrolyte and Surfactant

Alexander B. Zezin, Valentina B. Rogacheva, Olga A. Novoskoltseva,*
Victor A. Kabanov

Faculty of Chemistry, Polymer Department, Lomonosov Moscow State University, Lenin Hills, Moscow 119992, Russia
E-mail: zezin@genebee.msu.su

Summary: The competitive interactions in ternary systems consisting of a slightly cross-linked polyelectrolyte hydrogel and the mixture of linear polyelectrolyte and micelle forming surfactant both oppositely charged relative to the polyelectrolyte network were studied. It was shown that the equilibrium in the competitive reactions depends on the linear polyion charge density and the length of the surfactant aliphatic radical. Dependently on these characteristics the interpolyelectrolyte complex formed by cross-linked and linear polyelectrolytes can uptake surfactant ions from water solution transforming into the cross-linked polyelectrolyte-surfactant complex and releasing the linear polyelectrolyte or vice versa. The ternary systems of this kind are perspective to design the novel family of delivery constructs.

Keywords: competitive sorption; hydrogels; polyelectrolyte; surfactants; self-assembly

Introduction

Sorption of linear polyions,[1-3] proteins[4,5] and micelle forming ionic surfactants[6-11] by oppositely charged slightly cross-linked highly swollen polyelectrolyte hydrogels from water solutions is driven by cooperative electrostatic binding of sorbate species to polyionic fragments of the gel network. As a result cross-linked interpolyelectrolyte complex (#IPEC) or polyelectrolyte-surfactant complex (#PESC) are formed in the gel phase decreasing its volume by more than two orders of magnitude. By and large the process represents a heterogeneous reaction propagating inward the peace of gel. Its mechanism was established in our early

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studies.[1, 3, 6, 10] At the intermediate stage of such a reaction if it proceeds in the absence of an external salt, the sample remains heterogeneous consisting of a newly formed #IPEC or #PESC shell separated by the sharp boundary from the unreacted original gel core. The thickness of the shell can be easily controlled by variation of experimental conditions.[3, 5] It opens the perspective to create novel techniques for constructing either polycomplex layers or multilayers on the hydrogel surface. Moreover, hydrogels loaded with linear polyions, proteins or ionic amphiphils are able to release these constituents at certain conditions into surroundings in a controllable manner. The latter can be used to design novel function-specific complex constructs, in particular for controlled drug release. In contrast to a number of earlier studied binary hydrogel-polyelectrolyte or hydrogel-surfactant systems the ternary systems in which a cross-linked polyelectrolyte hydrogel (#PE) interacts either with linear polyelectrolyte (*l*PE) or an ionic surfactant (Sf) at the same time are still in the opening stage of research.[12-14] A series of such systems is the subject of the present study.

Experimental Part

Materials

Acrylic acid (AA) and N,N-dimethylaminoethylmethacrylate (DMAEM) were purified by vacuum distillation. N,N-dimethyl-N-ethylaminoethylmethacrylate bromide (DMEAEMB) was synthesized by alkylation of DMAEM with ethyl bromide via the dropwise addition of DMAEM to 5-fold excess of ethyl bromide on stirring and ice-cooling. DMEAEMB 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-dimethylaminoethylmethacrylate) (#PDMAEM) and poly(N,N-dimethyl-N-ethylaminoethyl-methacrylate bromide) (#PDMEAEMB) were synthesized by free radical copolymerization of AA with DMAEM in 10 wt.-% and AA with DMEAEMB in 20 wt.-% aqueous solutions with 1 mol-% of N,N-methylenebisacrylamide as a cross-linker. Polymerization was initiated by ammonium persulfate/sodium methabisulfite redox system (0.2% of monomer mass) and performed at 40 °C for 24 hours under argon atmosphere.[6, 10] #PDMAEM was prepared in salt form (#PDMAEM·HCl) by adding equivalent amount of HCl to the reaction mixture.

After polymerization was completed the obtained hydrogels were immersed in a large amount of distilled water to wash out the residual chemicals. The wash water was repeatedly changed every 2-3 days during a month. #PAA hydrogel was transformed into cross-linked poly(sodium acrylate) (#PANa) by complete neutralisation with NaOH (to pH=9). The degree of swelling of equilibrium-water-swollen gels, H=$\frac{m_{sw} - m_{dry}}{m_{dry}}$ (m_{sw} and m_{dry} are the masses of equilibrium swollen and dry samples, correspondingly), was about 600-1000 for different gels.

Linear polyelectrolytes: poly(N-ethyl-4-vinylpyridinium bromide) (PEVPB) of weight-average degree of polymerization $\bar{P}_W$=700 (M_W/M_n=1.2), poly(N,N-dimethylaminoethylmethacrylate) (PDMAEM), $\bar{P}_W$=640, poly(N,N-diallyl-N,N-dimethylammonium chloride) (PDADMAC), $\bar{P}_W$=3000, poly(sodium acrylate) (PANa), $\bar{P}_W$=200, and polyethylenimine (PEI), $\bar{P}_W$=1400, were purchased from "Tokio Kasei" (Japan). Luminescently tagged poly(methacrylic acid) (PMA^t) was prepared by the reaction of pyrenyldiazomethane with poly(methacrylic acid), $\bar{P}_W$=1000 [15].

The cationic surfactants: dodecylpyridinium chloride (DDPyC), cetylpyridinium chloride (CPyC), dodecyltrimethylammonuim bromide (DDTMAB), cetyltrimethylammonuim bromide (CTMAB), cetylamine (CA) and anionic surfactants: caprylic acid ($C_7H_{15}COOH$), caprynic acid ($C_9H_{19}COOH$), sodium dodecylsulfate (SDS) and sodium dodecylbenzosulfonate (SDBS) were purchased from "Serva". Each of them was purified by repeated recrystallization from of ethanol/acetone (15:85 v/v) mixed solvent before use. Caprilic and caprinic acids were transformed into sodium salts by neutralization with NaOH.

Stoichiometric (charge ratio 1:1) #IPECs and #PESCs were prepared at room temperature by immersing equilibrium-swollen hydrogel samples with mass of 2-5g into the aqueous solutions containing two-fold excess of oppositely charged *l*PE or respectively Sf [1,3,6,10]. After a period of time required for completing the interpolyelectrolyte or polyelectrolyte-surfactant reaction, the #IPECs containing equimolar amounts of #PE and *l*PE oppositely charged monomer repeating units or correspondingly #PESCs including equimolar amounts of #PE and Sf oppositely charged ionic fragments were formed. As a result transparent piece of the initial highly swollen hydrogel was transformed into a slightly swollen opaque #IPEC or #PESC peace with mass of 20 - 50 mg. The reactions were accompanied by a decrease in the volume of a reacted gel by more than 2 orders of magnitude.

Measurements

Concentrations of the reagents absorbing UV-light were measured spectrophotometrically in water solutions: DDPyC and CPyC at $\lambda = 259$ nm ($\varepsilon = 4\,100$), SDBS at $\lambda=260$ nm ($\varepsilon = 420$), PEVPB at $\lambda = 257$ nm ($\varepsilon = 2\,700$), PMA^{t} at $\lambda = 342$ nm ($\varepsilon = 50\,000$), PEI in form of tetra-coordinating complex with Cu^{2+} at $\lambda = 630$ nm ($\varepsilon = 200$).[16] Concentration of PDADMAC was estimated by turbidimetric titration with linear poly(sodium styrene sulfonate).[17] Spectrophotometric measurements were carried out by "Hitachi 150-20" (Japan) UV/VIS spectrophotometer.

Concentration of alkylcarboxylates and PANa was measured by potentiometric titration with HCl using "Radiometer pHM-83" (Denmark) pH-meter. The measurement accuracy was ±0.02 pH units. Concentration of SDS was determined either by potentiometric titration of SDS mixture with two-fold excess of linear PDMAEM or using surfactant-selective electrode as described in.[12]

X-ray measurements were performed with an automatic diffractometer equipped with a two-dimensional high-resolution detector (Institute of Crystallography, Russian Academy of Sciences) using monochromatic (1.54 Å) CuK_{α} radiation. The averaging over diffraction cones[18] was used to obtain the dependence of intensity on the scattering angle, θ. Bragg parameters, d, were calculated from measured scattering vectors $Q = (4\pi/\lambda) \times \sin\theta$ where $\lambda = 1{,}54$ Å is the wavelength of the incident beam using the common equation $d = 2\pi/Q$.

Results and Discussion

Generally speaking in a ternary system consisting of #PE immersed in water solution *l*PE and Sf both oppositely charged relative to the #PE, either #IPEC or #PESC can be formed. In other words *l*PE and Sf are in competition for binding to #PE. The systems under study include either the cationic hydrogels (#PDMEAEMB, #PDMAEM·HCl) combined with the anionic *l*PE and Sfs, or the anionic hydrogel (#PANa) combined with the cationic *l*PE and Sfs. To study the competitive interactions in ternary systems the #IPEC sample originally prepared via reaction between #PE and oppositely charged *l*PE as described in the experimental part was placed into the aqueous solution of the Sf. In the preset time intervals the concentration of Sf and *l*PE in the environmental solution as well as the mass of the sample were measured.

It was found that some #IPECs sorb Sf ions charged similarly to the *l*PE incorporated into the original #IPEC if Sf concentration, C_{Sf}, was sufficiently high.[14] Sorption of Sf is accompanied by the release of the originally complexed *l*PE into surroundings and temporal changes in mass of the sample. The experimental data obtained are presented in Table 1 as ultimate extent of Sf sorption $(N_{Sf}/N_{\#PE})_s$ or *l*PE release $(N_{lPE}/N_{\#PE})_r$. N_{Sf} is the maximal mol amount of sorbed Sf estimated by the decrease in its concentration in the solution, $N_{\#PE}$ is the total base mol amount of #PE calculated as $N_{\#PE} = \frac{m_{sw}}{M_o \cdot (H+1)}$, where M_o is the molecular mass of the #PE monomer unit, and N_{lPE} is the maximal base mol amount of *l*PE released determined by the increase in its concentration in the solution. In these experiments initial Sf concentrations were of 2 c.m.c. while initial Sf mol amounts were twice as much as initial base mol amounts of #PE.

Table 1. The data on the Sf sorption by #IPEC and *l*PE release from #IPEC.

№	**SYSTEM**	$\mathbf{(N_{Sf}/N_{\#PE})_s}$	$\mathbf{(N_{lPE}/N_{\#PE})_r}$
1	#IPEC (#PDMEAEM-PMA^t) + sodium caprinate	1.0	1.0
2	#IPEC (#PDMEAEM-PA) + sodium caprilate	1.0	1.0*
3	#IPEC (#PDMEAEM-PA) + sodium caprinate	0.9	1.0*
4	#IPEC (#PDMEAEM-PA) + SDS	0.9	1.0*
5	#IPEC (#PDMEAEM-PA) + SDBS	1.0	1.0*
6	#IPEC (#PA-PEVP) + CA·HCl	1.0*	0.9
7	#IPEC (#PA-PEVP) + CTMAB		0.9
8	#IPEC (#PA-PDADMA) + CPyC	1.0	1.0*

System 1 demonstrates clearly that the processes of Sf sorption and *l*PE release are correlated: the sample of #IPEC (#PDMEAEM-PMA^t) sorbs equimolar amount of sodium caprinate with respect to the base mol amounts of #PE and as a result eliminates the same mol amount of

PMA^t into the surroundings. These data were obtained in the course of continuous measuring of the concentrations of both Sf (by means of potentiometric titration) and tagged PMA^t (by means of UV-spectrophotometry).

The results obtained are evident of quantitative replacement of Sf ions by *l*PE. In other words competitive sorption of Sf ions can be represented as transformation of stoichiometric #IPEC into stoichiometric #PESC as it is sketched by Reaction (1) (simple counter ions are omitted):

$$\mathbf{\#IPEC\ (\#PE\text{-}\mathit{l}PE) + Sf \rightleftarrows \#PESC\ (\#PE\text{-}Sf) + \mathit{l}PE} \qquad \mathbf{(1)}$$

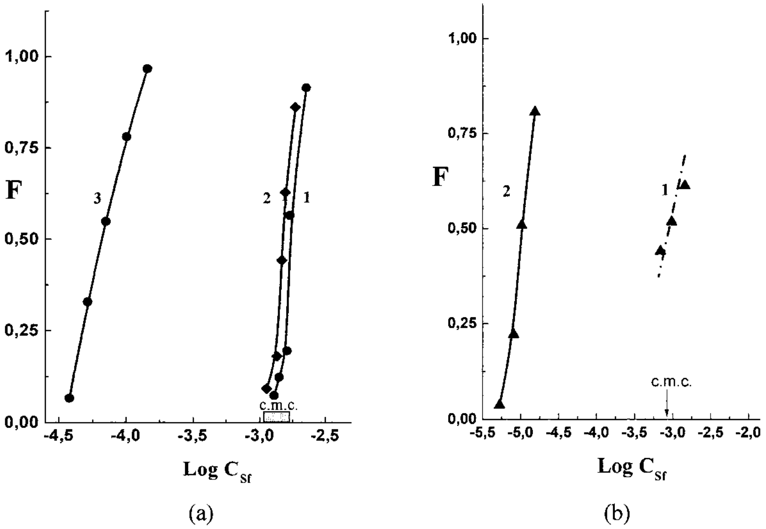
Note, that in other systems listed in Table 1 either the decrease in Sf concentration (lines 2-5, 8) or the increase in *l*PE concentration (lines 6,7) in the solutions was determined experimentally with sufficiently high accuracy. To make sure, that the Sf uptake is accompanied by the *l*PE release and the equilibrium in Reaction (1) is completely shifted to the right we have studied whether the reversed process takes place. In this case the #PESC samples obtained in advance as described in the experimental part and our previous studies[6,10] were put into aqueous solutions of the corresponding *l*PE. During long time (a few months) we could not find any decrease in *l*PE concentration (systems 2-5) or Sf release (system 6, 8) using UV-spectrophotometry and potentiometric tittration as noted in the experimental part. These data are presented in Table 1 as values labelled by asterisk.

The above unambiguously results reveal that actually in the systems listed in Table 1 the Sfs are able to substitute completely *l*PE incorporated in #IPEC. Hand in hand with these systems there are those in which Reaction (1) is reversed, i.e. the #IPEC samples do not sorb Sf ions from aqueous solutions, on the contrary, the samples of the corresponding stoichiometric #PESC obtained in advance[6, 10] uptake *l*PE from aqueous media releasing constituent Sf into the surroundings. The experimental data expressed in terms of ultimate extent of *l*PE sorption $(N_{lPE}/N_{\#PE})_s$ or Sf release $(N_{Sf}/N_{\#PE})_r$ are listed in Table 2. Here we used the same procedures as those for the analyses of the systems shown in Table 1.

Table 2. The data on the *l*PE sorption by #PESC and Sf release from #PESC.

№	**SYSTEM**	$\mathbf{(N_{lPE}/N_{\#PE})_s}$	$\mathbf{(N_{Sf}/N_{\#PE})_r}$
1	#PESC (#PA-DDPy)+PEI·HCl	1.0*	0.9
2	#PESC (#PA-CPy)+PEI·HCl	1.0*	1.0
3	#PESC (#PA-DDTMA)+PEVPB	1.0	

The data presented in Table 2 demonstrate actually that in these systems the equilibrium in Reaction (1) is shifted from right to left, i.e. toward formation of the corresponding #IPECs. Generally the question of the factors controlling the above forward and reverse competitive reactions and position of equilibrium described by Equation (1) is of a crucial importance. To gain a better understanding of the problem we obtained experimentally sorption isotherms for different ternary systems. Some of them are represented in Figure 1 as the dependence of the sorption extent, $F=(N_{Sf}/N_{\#PE})_S$, versus the logarithm of the equilibrium Sf concentration in a solution. The points used to construct the curves were obtained for #IPECs incubated in aqueous solutions of Sf for a month. The amount of Sf sorbed was calculated as the difference between the initial and equilibrium Sf concentration in the solution surrounding #IPEC sample.

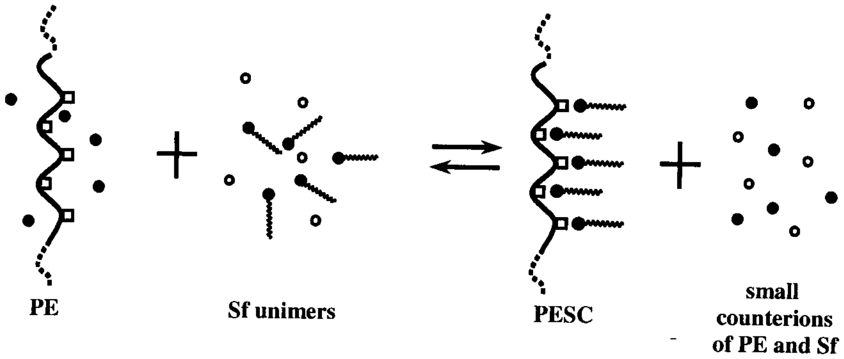


(a) (b)

Figure 1. (a) - Sorption isotherms of SDBS by stoichiometric #IPEC (#PDMEAEM-PA) at 22 °C (1), 45 °C (2) and by #PDMAEM·HCl hydrogel at 20 °C (3);[10] mass of the initial #IPEC sample 0.05 g, mass of the initial hydrogel is 5g.
(b) - Sorption isotherms of CPy cations by stoichiometric #IPEC (#PA-PDADMA) at 22 °C (1), and by #PANa hydrogel at 40 °C (2);[10] mass of the initial #IPEC samples 0.02 g, mass of the initial gel is 2 g.

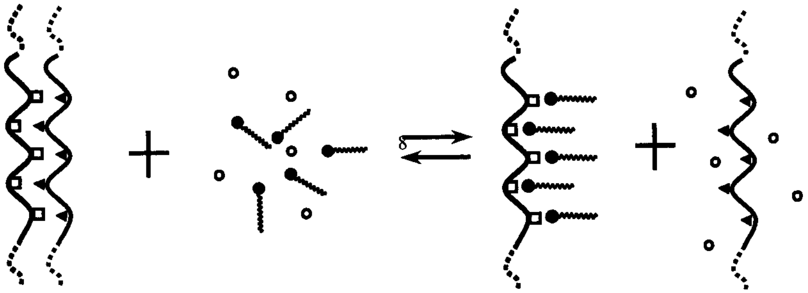
Figure 1a shows that sorption of DBS anions by #IPEC (#PDMEAEM-PA) either at 22 °C (curve 1) or at 45 °C (curve 2) starts at SDBS concentrations located in its c.m.c. region (in literature $(1.2\text{-}1.7)\cdot 10^{-3}$ at 30 °C and $1.7\cdot 10^{-3}$ mol/l at 55 °C[19]). The same is true for sorption of CPy cations (c.m.c. is $9.0\cdot 10^{-4}$ mol/l at 25 °C[20]) by #IPEC (#PA-PDADMA) (Figure 1b, curve 1). It is significant that in contrast to the #IPECs original #PDMEAEM·HCl or #PANa hydrogels start to sorb SDBS (Figure 1a, curve 3) or CPy cations (Figure 1b, curve 2) at Sf concentrations two orders of magnitude below the corresponding c.m.c. values.

The above difference finds a simple qualitative explanation, which involves taking account of translational entropy of low molecular ions in the system. The mere fact that micellization of ionic Sf unimers is induced by oppositely charged linear and cross-linked polyelectrolytes at critical aggregation concentrations much lower than c.m.c. is well known[6, 8, 9, 10, 21] and treated theoretically.[9] Micellization of free ionic Sf is driven by hydrophobic interaction of hydrocarbon tails. At the same time it requires immobilisation of simple counter ions in the vicinity of a micelle surface to neutralize the charge of condensed Sf ionic heads. The latter provides a certain entropy loss. The situation drastically changes if Sf ions are condensed on PE chain so that simple counter ions are replaced and released into environmental solution as it is shown in Scheme 1a. In such case the above entropy loss is nearly prevented. It gives a certain relative gain in free energy, which provides micellization of Sf ions at much lower Sf concentration. Nothing of that kind may happen if ionic Sf interacts with preformed IPEC or #IPEC consisting of high linear charged density polyions.



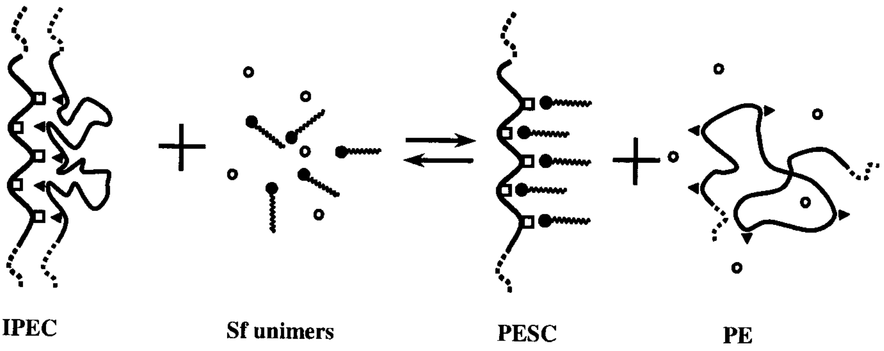
Scheme 1a

Scheme 1b actually illustrates that in such case at $C_{Sf} <$ c.m.c. Sf ions have no reason to form a micellar phase replacing similarly charged polyions from the original IPEC, i.e. to transform IPEC into PESC.



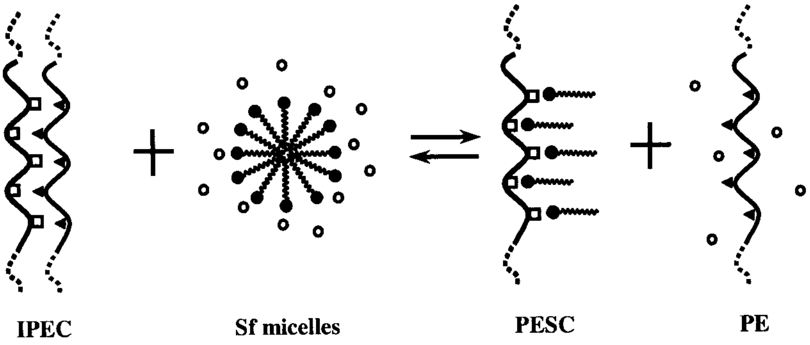
Scheme 1b

Indeed, if it were the case simple counter ions of Sf would become immobilised to neutralize the released polyions. In other words the number of statistically independent species would be diminished decreasing translational entropy, i.e. increasing free energy in the system, while hydrophobic interaction at $C_{Sf} <$ c.m.c. is still not sufficient to drive the process from left to right. In fact experimental data of Figure 1 show that #IPECs does not sorb Sf below c.m.c. However, it must not be ruled out that in some special cases PESCs can be formed even at C_{Sf} somewhat below c.m.c. Hypothetically it may happen e.g. if one of IPEC constituents is of a low linear charge density. Then the original IPEC should contain a number of loops formed by low charge density polyions as shown in Scheme 1c. In such case reaction **1** may be driven from left to right by conformational entropy gain due to untangling the loops when low charge density polyion is released.



Scheme 1c

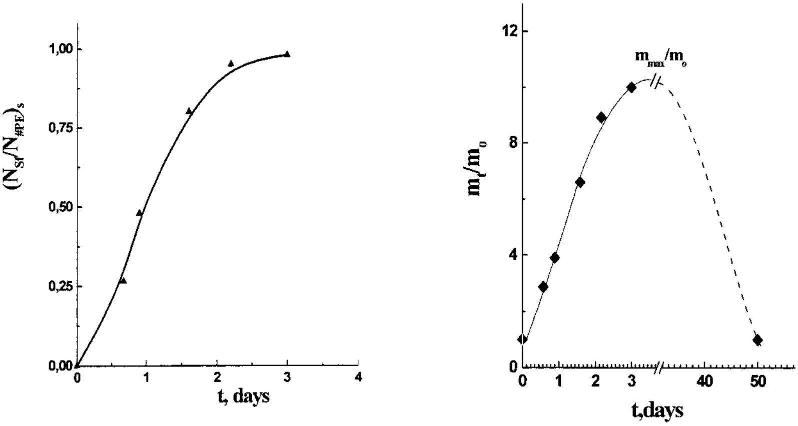
In the ternary systems on study the situation when /PEs and Sf ions may actually compete for binding to #PE on equal terms appears at $C_{Sf} \geq$ c.m.c., i.e. when free Sf micelles are already formed as illustrated by Scheme 1d.



Scheme 1d

In thermodynamic sense this situation resembles the earlier described and considered cases when two similarly charged /PEs[22, 23] or /PE and the vesicle[24] compete for binding to the oppositely charged /PE. In this case if the competitive reaction goes from left to right the counter ions of Sf micelles transfer to the /PE and vice versa. Apparently, the direction of the process therewith is determined by the relative affinity of Sf micellar phase and *l*PE to #PE and the counter ions to Sf micelles and *l*PE. The binding of counter ions by linear polyions predicted by Manning's theory is in a good agreement with the experiments.[25] Comparison of the literature data on the degree of binding of simple counter ions by *l*PE[25] and Sf[26] used in the present study shows that these values are quite congruent. Generally the ability of polyions to be either coupled if oppositely charged, or to bind counter ions increases with an increase in their linear charge density. Indeed, we observed that #IPECs containing PEI as *l*PE don't sorb different Sfs (systems 1-2, Table 2) even at Sf concentrations exceeding c.m.c. It can be referred to high charge density of short-branched PEI chains. On the contrary, PDADMAC polyions of a lower linear charge density in comparison with the fully charged vinyl type polyelectrolytes are not able to replace Sf ions from the studied #PESC (system 8, Table 1). Also note that #IPEC (#PA-PEVP) sorbs CTMAB releasing PEVPB but do not sorb DDTMAB, a lower Sf homologue. In other words equilibrium in Reaction (1) is shifted from left to right in system 7, Table 1 and from right to left in system 3, Table 2. The above difference could be caused by higher affinity of Br^- counter ions to DDTMA micelles as compared with CTMA. However, it was experimentally shown that ability of small ionic Sf micelles to bind counter ions only increases with an increase of Sf homologue number.[26] So the most probable reason is relatively enhanced stabilization of the structure of CTMA phase if reinforced by #PA as compared to DDTMA. The contributions of free *l*PE and Sf micelles in solution free energy should be also taken into account on quantitative treatment.

The kinetics of the above competing reactions in ternary #PE-*l*PE-Sf is of a primary interest. Figure 2a represents a typical kinetic curve of Sf uptake by #IPEC.



(a) (b)

Figure 2. Kinetics of SDBS sorption (a) by the #IPEC (#PDMEAEM-PA) from an aqueous solution and kinetics of change in mass (m_t/m_o) (b) of the swollen stoichiometric #IPEC (#PDMEAEM-PA) sample; mass of the initial #IPEC sample 14 mg. [SDBS] = 0.005 mol/l, pH 8, T = 18 °C.

It is seen that at the given experimental conditions the sorption proceeds monotonously and $N_{Sf}/N_{\#PE}$ approaches unity and levels off for about 2.5 hours. It means that such time is sufficient for transformation of practically all salt bonds between #PE and /PE into the new salt bonds between #PE and Sf ions i.e. formation of stoichiometric #PESC. In other words charged groups of linear chains originally involved in cooperative electrostatic interaction with #PE, now are neutralized by simple counter ions of Sf. It is remarkable that in contrast to monotonous kinetics of Sf uptake the time dependence of mass (degree of swelling) of the reacting sample passes through a maximum. It is seen from Figure 2b that the originally compact #IPEC sample swells progressively when immersed into the Sf salt-free aqueous solution increasing its current mass (m_t) and reaching a maximum mass (m_{max}) one order of magnitude exceeding the mass (m_o) of the initial #IPEC sample. Then the mass gradually decreases and approaches of approximately original value for nearly 50 days.

The explanation is given taking into account that if reaction **1** proceeds from left to right, the influx of Sf unimers trough the surface of the reacting sample is much higher than efflux of *l*PE owing to the significant differences in their internal diffusion coefficients. Therefore by the time formation of #IPES is already completed most of the *l*PE chains still remains in the interior of the piece of the transformed hydrogel. In fact turbidimetric titration of environmental solution with PEVB that is quite sensitive method for detection of dissolved negatively charged polyions [17] showed that a measurable amount of *l*PE was released only in 3 days. However, now the chains temporally trapped in the network of the sample are not bound anymore to ionic groups of #PE, but neutralized by simple counter ions originally belonged to the Sf. These counter ions produce the essential part of additional osmotic pressure responsible for extra swelling of the hydrogel composite. All other systems listed in Table 1 behave in the same fashion, although differ in m_{max}/m_o values (Table 3).

Table 3. ($\mathbf{m_{max}/m_o}$) values of the intermediate products of the interactions between #IPEC and Sf.

№	**SYSTEM**	**C_{Sf}, mol/l**	**m_{max}/m_o**
1	#IPEC (PA – PDADMA) + CPyC	0.006-0.002	40-50
2	#IPEC (PDMEAEM – PA) + SDBS	0.005-0.003	10-20
3	#IPEC (PDMEAEM – PA) + SDS	0.02-0.01	10-20
4	#IPEC (PA – PEVP) + CTMAB	0.10-0.01	5-10

The absolute contribution of *l*PE counter ions in the osmotic pressure depends on their osmotic coefficients, all factors being equal. The osmotic coefficient in its turn is determined by the polyion linear charge density and the ability of a polyion to bind counter ions specifically. Therefore the hydrogel composite containing PDADMA polycation, characterized by a relatively low linear charge density has a highest m_{max}/m_o value. At the same time the lowest m_{max}/m_o value is observed for the hydrogel composite containing PEVP, a polycation of a higher charge density and in addition to that characterised by a certain specific affinity to Br^- ions (Table 3). As the free *l*PE slowly releases from the sample which at m_{max} is nothing but #PESC filled with a swollen *l*PE, the degree of swelling decreases in parallel. Here the release is simply driven by free energy decrease upon mixing *l*PEs with environmental water solution. We believe that ternary hydrogels of this kind approached

$m_t = m_{max}$ may originate a novel perspective family of polymeric constructs applicable for gradual delivery of various polyelectrolytes oppositely charged relative to the #PE, such as proteins or nucleic acids. Earlier it was shown that either proteins[4, 5] or DNA[27] form #IPECs when interact with oppositely charged #PE. Apparently the efflux of releasing macromolecules i.e. the rate of release can be controlled, e.g. by degree of #PE cross-linking.

The kinetic behaviour of the ternary systems listed in Table 2 is entirely different. The equilibrium in competitive Reaction (1) for these systems is shifted from right to left. In other words the preformed #IPECs do not sorb Sfs. However, the preformed corresponding #PESCs immersed in water solutions of /PEs are able to uptake the /PE polyions releasing similarly charged Sf ions in equivalent amount. As an example the kinetics of the release of CPy cations from the stoichiometric #PESC (#PA-CPy) immersed in the solution of PEI·HCl is shown in Figure 3.

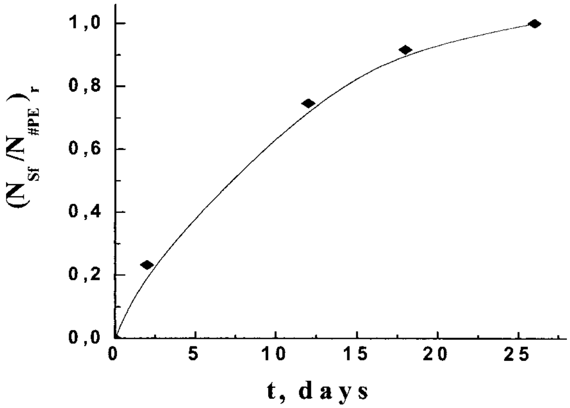


Figure 3. Kinetics of release of the CPy cations from a stoichiometric #PESC (#PA-CPy) sample into an aqueous solution of PEI·HCl; mass of the initial sample 20 mg, [PEI·HCl] = 0.1 mol/l, pH 4.2, T = 45 °C. N_{Sf} – is the mol amount of released Sf, $N_{\#PE}$ – is the total base mol amount of #PE.

It is seen that here the rate of Sf ions release from the reacting sample is much less than their uptake in the reverse Reaction (1) (Figure 2a). No additional swelling similar to that shown in Figure 2b is observed: the reacting sample remains compact through out the whole process of Sf release. The above difference is not surprising and actually means that Sf ions are permitted to release from the reacting sample into surroundings only in response to polyions uptake. So the bottleneck of the process is slow internal diffusion of *l*PE. In so far as the internal diffusion coefficient for Sf unimers is much higher than polyions the release and uptake are synchronized, i.e. the reacting sample does not accumulate Sf at intermediate degrees of conversion in Reaction (1).

#IPECs either synthesized upon direct interaction of #PE hydrogels with water solution of oppositely charged non-stereoregular *l*PE or formed as a result of competitive Reaction (1) exhibit neither wide-angle nor small-angle X-ray ordering. Contrastingly a pronounced ordering is revealed in #PESC samples investigated by small angle X-ray scattering (SAXS). Figure 4 represents a typical SAXS diffractogramm for #PESC prepared via completed Reaction (1) between #IPEC (#PA-PEVP) and CTMAB, which is quite similar to that presented in our earlier paper [7] for the same #PESC obtained directly from #PANa and CTMAB.

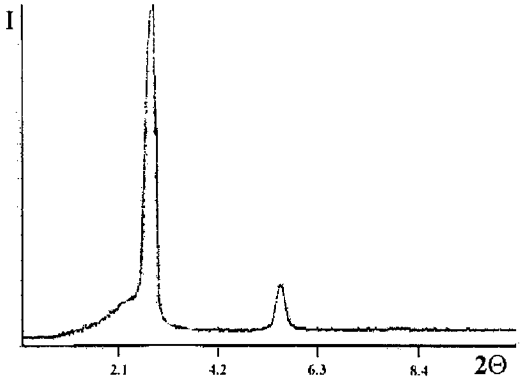


Figure 4. SAXS diffractogramm of the dry #PESC (#PA-CTMA) formed as a result of the complete reaction between #IPEC (#PA-PEVP) and CTMAB. T = 20 °C.

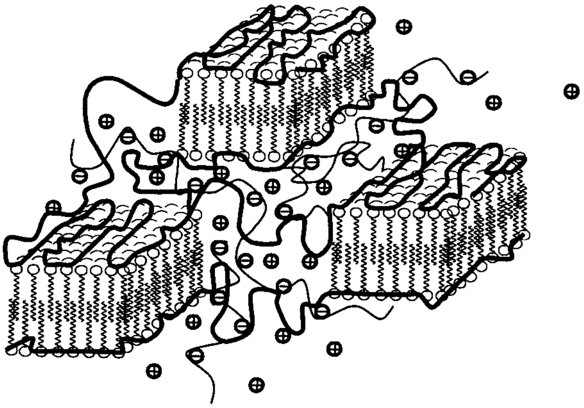
Referring to [7] the two observed peaks should be attributed the first and second order reflections from CTMAB lamellas. Interplanar spacings measured for the dry #PESCs samples prepared either by direct synthesis or via Reaction (1) are shown in Table 4.

Table 4. Interplanar spacings (Å) in dry products of complete reactions between #IPEC and a Sf estimated from SAXS data.

SAMPLES	**d_1**	**d_2**
#PESC (#PA-CTMA)*	32.8	16.2
#PESC (#PA-CTMA)	31.6	16.0
#PESC (#PDMEAEM-DBS)	32.4	16.2
#PESC (#PDMAEM·H-DS)*	36.8	-
#PESC (#PDMEAEM-DS)	35.6	17.8

*#PESC prepared via uptake of the Sf by oppositely charged #PE.

It is seen that the corresponding complexes are characterized by very close spacing values independently on the way they have been prepared. In our previous studies it was found that Sf ions incorporated in directly prepared #PESCs had a lamellar structure.[7] So it is worth to assume that lamellar structure is also typical for dry #PESCs obtained via completed Reaction (1). Having in mind the above considerations it is also worth to assume that swollen intermediate products of competitive Reaction (1) in particular those with a maximum degree of swelling are micro heterogeneous systems consisting of lamellar fragments electrostatically bound to the #PE network and distributed in the continuous phase composed of trapped water swollen /PE as it is shown in Scheme 2.



Scheme 2

Conclusion

The above discussed ternary systems composed of #PE and the mixture of *l*PE and Sf both oppositely charged relative to #PE may be considered as intelligent multicomponent polymeric constructs. They are able to exchange the soluble species such as *l*PE and Sf with surroundings. The polyelectrolyte network is able to release linear polyions into surroundings in respond to uptake of Sf ions. Importantly the base mol amount of *l*PE released equals to the mol amount of sorbed Sf ions. The release rate is determined by characteristics of *l*PE mainly its molecular mass and linear charge density. Sf controlled release of polyelectrolytes from #IPECs may be of a particular interest with respect to proteins, polynucleotides and polysaccharides.

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