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William MacKnight, *University of Massachusetts Amherst*

Ekaterina A. Ponomarenko

David A Tirrell, *California Institute of Technology*

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Water-Insoluble Complexes of Poly(L-Lysine) with Mixed Alkyl Sulfates: Composition-Controlled Solid State Structures

Ekaterina A. Ponomarenko, David A. Tirrell,* and William J. MacKnight

Polymer Science and Engineering Department, University of Massachusetts
Amherst, Massachusetts 01003

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ABSTRACT: Structures of the water-insoluble complexes of poly(L-lysine) with octyl and octadecyl sulfates, and with the mixtures of these surfactants, were examined via X-ray diffraction, infrared spectroscopy, and differential scanning calorimetry. The solid-state structures of the complexes were shown to be governed by their compositions. In the stoichiometric poly(L-lysine) complex with octadecyl sulfate, surfactant chains crystallize on a hexagonal lattice. In the poly(L-lysine)–octyl sulfate complex of nearly stoichiometric composition, the surfactants are arranged on an alkane-type two-dimensional lattice. In the complex with 20 mol % octadecyl sulfate and about 75 mol % octyl sulfate, the longer surfactant chains form hexagonal crystalline blocks, and the shorter chains are arranged on an alkane-type two-dimensional lattice. In the poly(L-lysine) complex with 10 mol % octadecyl sulfate and about 85 mol % octyl sulfate, all surfactant chains are arranged on a two-dimensional alkane-type lattice. All complexes are organized in lamellar structures consisting of layers of poly(L-lysine) chains in β -sheet conformations, separated by layers of surfactants. Complexes with crystalline and partially crystalline surfactants adopt lamellar structures with identical long periods and with interdigitated octadecyl chains. Complexes with two-dimensional order in the surfactant arrangement also adopt lamellar structures with identical long periods and with octyl chains packed tail to tail.

Introduction

Complexes of polyelectrolytes and oppositely charged surfactants form spontaneously if aqueous solutions of the two components are mixed.^{1,2} Complexation is driven by the electrostatic attraction of the oppositely charged polymer chain units and surfactant ions and by the hydrophobic interactions of the surfactant chains in water. If equimolar amounts of charged polymer chain units and surfactant molecules are mixed in water, stoichiometric complexes are formed.³ These complexes are water-insoluble and in the solid state assemble spontaneously into lamellar structures consisting of alternating layers of polymer chains separated by layers of surfactant.^{4–14} The long period of the lamellae is governed by the surfactant chemical structure and the chain length. If the surfactant chains are long enough (typically, 16–18 methylene groups), they can crystallize within the lamellae.^{6,10}

While the stoichiometric polyelectrolyte–surfactant complexes are water-insoluble, they can dissolve in organic solvents of a wide range of polarity.^{9,11,15–18} In the solvents of lower polarity ($\epsilon = 2–10$), the ion pairs in the complexes remain tightly associated, while in solvents of higher polarity ($\epsilon = 10–30$), partial dissociation of the ion pairs is observed.¹⁵ The amphiphilic properties of stoichiometric polyelectrolyte–surfactant complexes make them promising as materials for molecular composites, separation membranes, and compatibilizers.

Stoichiometric polyelectrolyte–surfactant complexes represent a new type of comb-shaped polymers, in which every polymer chain unit has an electrostatically bound “side chain”. Our investigation of stoichiometric polypeptide–surfactant complexes has been aimed at understanding the influence of the electrostatically attached “side chains” on the properties of the polymer chains

and of the effect of the polymer chains on the organization of the complexed surfactant.^{9–11}

In our previous publications, we have reported the properties of the stoichiometric complexes formed by poly(α ,L-glutamate) anions and alkyltrimethylammonium cations^{9,10} and by poly(L-lysine) cations and dodecyl sulfate anions.¹¹ We compared the behavior of these complexes to that of their covalent analogues—alkyl esters of poly(α ,L-glutamic acid) (PALGs) and acyl derivatives of poly(L-lysine). We have shown that the presence of electrostatically bound “side chains” does not preclude ordered secondary structures of the polypeptide chains. Poly(α ,L-glutamate)-based complexes adopt α -helical conformations in the solid state at room temperature, similar to other synthetic polypeptides. A reversible helix-to-coil transition is observed at elevated temperatures. Poly(L-lysine)-based complexes can adopt either α -helical or disordered conformations in chloroform–trifluoroacetic acid solutions, depending on the amount of trifluoroacetic acid present, similar to the analogous poly(L-lysine)s with acyl chains. However, the ordered conformations of the polypeptide chains in the complexes are considerably more susceptible to changes in environment (e.g., temperature, solvent) than those of the covalent analogues, suggesting that dipole–dipole interactions of the “side chains” destabilize the ordered arrangement of the polypeptide chains in the solid state and in organic media.

One of the attractive features of the stoichiometric polyelectrolyte–surfactant complexes is the simplicity of their synthesis, which simplifies the “fine-tuning” of the resulting structures. In this study, we attempt to control the solid-state structures of the polypeptide–surfactant complexes by complexing the polypeptide chains with mixtures of oppositely charged surfactants of different chain lengths. We compare the resulting structures to those of the complexes with each of the

Chart 1. Complexes of Poly(L-lysine) with Mixed Alkyl Sulfates

pure surfactants and to the structures of the covalent analogues of the complexes—copolypeptides with covalently attached side chains. Copolyglutamates are usually synthesized from poly(γ -benzyl α ,L-glutamate) by ester interchange reactions with the corresponding alkyl alcohols^{19–22} or by copolymerization of the *N*-carboxyanhydrides.²³ Both procedures yield copolymers with random distributions of monomer chain units. Polypeptide-surfactant complexes of stoichiometric composition are prepared by mixing equimolar amounts of the two components in water.^{9–11} Hydrophobic self-association of the surfactants in water and the ability of electrostatically attached “side chains” to move along the polypeptide chains may provide a unique way to synthesize “block copolymers” of this type. The goal of this research is to investigate the effects of the content and distribution of electrostatically attached “side chains” on the supramolecular structure of polypeptide-surfactant complexes based on poly(L-lysine) (Chart 1).

For comparison with the complexes with mixed surfactants, we also prepared complexes containing each of the pure surfactants. Choices of surfactant chain lengths and complex compositions were based on the following considerations: (i) the structures of the analogous poly(γ -methyl L-glutamate-co-stearyl L-glutamate)s are well-studied,^{21,24,25} (ii) the minimum octadecyl chain content required for crystallization in poly(γ -methyl L-glutamate-co-octadecyl L-glutamate) is about 35 mol %, ²⁴ and (iii) the octadecyl chains are known to crystallize in the complexes with polypeptides, while the ethyl and octyl chains are expected to be amorphous.¹⁰ Differences in the crystallization behavior of the surfactants of different chain lengths allow us to tailor the molecular organization of the complexes.

Experimental Section

Materials. Poly(L-lysine) hydrobromide (PLys HBr) with viscosity average degree of polymerization (provided by the supplier) of about 1800 was purchased from Sigma Chemical Co. Sodium octadecyl sulfate (ODSNa), sodium octyl sulfate (OSNa) (Research Plus), and sodium ethyl sulfate (ESNa) (Pfaltz and Bauer, Inc.) were used as received. 2-Propanol was purchased from Fisher Chemical Co.

Preparation of Complexes. PL-C₁₈ was prepared by mixing equimolar quantities of a 0.05 M solution of PLys HBr in water and a 0.003 M solution of ODSNa in water containing 35 vol % 2-propanol.²⁶ After the mixture was stirred for 1 h, the resulting white precipitate was isolated by centrifugation, washed 2 times with water, and dried in a vacuum at 45 °C for 36 h. Elemental analysis showed good agreement between the experimental and calculated contents of all elements corresponding to the stoichiometric composition (Table 1).

In an attempt to prepare the complex of poly(L-lysine) containing 20% octadecyl and 80% ethyl “side chains” (PL-C₁₈-

(20)-C₂), a mixture of 0.003 M ODSNa and 0.01 M ESNa solutions in water containing 35 vol % 2-propanol was added to 0.05 M PLys HBr solution in water. The ratio of polypeptide chain units to ODSNa and OSNa in the mixture was 1:0.2:0.8, respectively. After the mixture was stirred for 1 h, the complex was isolated by centrifugation, washed with water, and freeze-dried. Elemental analysis showed that the composition of the complex was essentially the same as that of the PL-C₁₈ complex (Table 1).

PL-C₈ was prepared by mixing equimolar quantities of 0.05 M PLys HBr and 0.1 M OSNa solutions in water. The complex was isolated in the manner described for the PL-C₁₈ complex (vide supra). Elemental analysis showed that about 97% of the polymer chain units were paired with surfactant ions (Table 1).

PL-C₁₈(20)-C₈ was prepared by adding a mixture of 0.003 M ODSNa and 0.01 M OSNa in water containing 35 vol % 2-propanol to a 0.05 M PLys HBr solution in water. The molar ratio of polypeptide chain units to ODSNa and OSNa in the mixture was 1:0.2:0.8, respectively. The complex was isolated in the manner described for the PL-C₁₈ complex (vide supra). Elemental analysis showed that 20% of the polymer chain units were paired with octadecyl sulfate ions and about 75% of the polymer chain units were paired with octyl sulfate ions²⁷ (Table 1).

PL-C₁₈(10)-C₈ was prepared by adding a mixture of 0.003 M ODSNa and 0.02 M OSNa solutions in water containing 35 vol % 2-propanol to a 0.05 M PLys HBr aqueous solution. The molar ratio of polypeptide chain units to ODSNa and OSNa in the mixture was 1:0.1:0.9, respectively. The complex was isolated in the manner described for the PL-C₁₈ complex (vide supra). Elemental analysis showed that 10% of the polymer chain units were paired with octadecyl sulfate ions and 85% of the polymer chain units were paired with octyl sulfate ions²⁷ (Table 1).

Measurements. X-ray diffraction patterns of powder samples were recorded using an evacuated Statton X-ray camera. Ni-filtered Cu K α radiation was used with wavelength $\lambda = 1.5418$ Å. Fourier transform infrared (FTIR) spectra were obtained using an IBM 30 series FTIR spectrometer. Transmission spectra were recorded by coadding 64 scans at 4 cm⁻¹ resolution at room temperature. Samples were analyzed in the form of KBr pellets. DSC experiments were performed on a Perkin-Elmer DSC 7 system at scanning rates of 10 and 20 °C/min. The values of the melting temperatures and enthalpies were independent of the scanning rate. The transitions were reproducible on heating and cooling; the transition temperatures and enthalpies were lower on the second heating but remained constant on the second and third heatings. Transition temperatures and enthalpies were estimated on the basis of the first heating scans.

Results and Discussion

Preparation of Complexes. It is well-known that mixing equimolar amounts of water solutions of polyelectrolyte chain units and surfactants with chain lengths of at least eight carbon atoms results in water insoluble complexes of stoichiometric compositions.^{1,2} In our experiments, mixing equimolar amounts of poly(L-lysine) hydrobromide and octyl or octadecyl sulfates resulted in complexes of essentially stoichiometric compositions, as confirmed by elemental analysis (Table 1). However, mixing poly(L-lysine) hydrobromide with a solution of ethyl and octadecyl sulfates in water containing 35 vol % 2-propanol resulted in the formation of a stoichiometric PL-C₁₈ complex. This indicates that in the PLys HBr-ODSNa-ESNa-water-2-propanol solutions, octadecyl sulfate anions selectively bind poly(L-lysine) chains, forming the water-insoluble stoichiometric complex, while sodium ethyl sulfate and the unreacted polypeptide and/or water-soluble polypeptide-ethyl sulfate complex remain in solution. The

Table 1. Elemental Analysis Results for the Complexes

element	PL-C ₁₈		PL-C ₁₈ (20)-C ₂		PL-C ₈		PL-C ₁₈ (20)-C ₈		PL-C ₁₈ (10)-C ₈	
	theory ^a	exp	theory ^b	exp	theory ^c	exp	theory ^d	exp	theory ^e	exp
C	60.25	59.43	44.94	59.49	49.43	47.9	51.70	51.70	50.69	50.59
H	10.46	10.43	8.16	10.41	8.83	9.00	9.17	9.02	9.01	8.95
N	5.86	5.81	9.36	5.81	8.38	8.05	7.30	7.31	8.10	7.83
S	6.69	6.57	10.70	6.02	9.29	9.12	8.30	8.18	8.80	8.89
Na	0	<0.1	0	<0.1	0	<0.1	0	<0.1	0	<0.1
Br	0	<0.1	0	<0.1	0.72	0.63	1.56	1.60	1.15	1.10

^a [Lys]/[ODS] = 1:1. ^b [Lys]/[ODS]/[ES] = 1:0.2:0.8. ^c [Lys]/[OS] = 1:0.97; for [Lys]/[OS] = 1:1, the expected contents of the elements are C 49.56, H 8.88, N 8.28, S 9.47, Na 0, and Br 0. ^d [Lys]/[ODS]/[OS] = 1:0.2:0.75; for [Lys]/[ODS]/[OS] = 1:0.2:0.8, the expected contents of the elements are C 52.60, H 9.04, N 7.67, S 8.77, Na 0, and Br 0. ^e [Lys]/[ODS]/[OS] = 1:0.1:0.85; for [Lys]/[ODS]/[OS] = 1:0.1:0.9, the expected contents of the elements are C 51.14, H 8.81, N 7.95, S 9.09, Na 0, and Br 0.

Figure 1. Wide-angle X-ray diffraction patterns of PL-C₁₈ (a), PL-C₈ (b), and PL-C₁₈(20)-C₈ (c) complexes at room temperatures.

selective formation of the stoichiometric PL-C₁₈ complex in these mixtures can be explained by differences in the hydrophobic driving forces for complexation with the longer and shorter chain surfactants;²⁸ i.e., the hydrophobic contribution to the binding energy is considerably higher for octadecyl sulfate than for ethyl sulfate. This effect correlates with the differences in the micellization behavior of the homologous surfactants in water, which is also driven by hydrophobic interactions: alkyl sulfates with chains longer than eight methylene groups form micelles, while the lower homologues form considerably smaller aggregates.²⁹

Surfactant Chain Organization at Room Temperature. Information about surfactant chain packing in the complexes is provided by wide-angle X-ray diffraction (WAXD). The WAXD pattern of PL-C₁₈ is characterized by a sharp reflection corresponding to a Bragg spacing of 4.2 Å (Figure 1a) (reflections with larger Bragg spacings on the WAXD patterns will be discussed below).

The sharp reflection indicates that the surfactant chains are organized on a crystal lattice. A spacing of 4.2 Å has been previously assigned to the hexagonal packing of the alkyl chains in complexes of cross-linked polyacrylate anions and hexadecyltrimethylammonium cations,⁶ in complexes of poly(α ,L-glutamate) anions and octadecyl trimethylammonium cations,¹⁰ and in comb-like poly(alkyl methacrylate)s with 12 or more methylene groups in the side chains.³⁰

The WAXD pattern of the PL-C₈ complex is characterized by two reflections with Bragg spacings of 4.6 and 3.7 Å (Figure 1b). These spacings are similar to those of the 010 and 100 reflections (4.3–4.4 and 3.9–4.0 Å, respectively) of the two-dimensional crystal lattices formed by alkane chains of 10 or more methylene groups in PALGs.³¹ These two-dimensional lattices are believed to resemble the subunit cell attained by the projection of the triclinic unit cell in crystals of low molecular weight *n*-alkanes. Reflections of greater breadth but with the same spacings were also observed for the stoichiometric complex of poly(L-lysine) cations and dodecyl sulfate anions and were assigned to short range order in the surfactant chain packing, based on the absence of thermal transitions of the complex observed by DSC.¹⁰

The WAXD pattern of PL-C₁₈(20)-C₈ is characterized by three reflections with Bragg spacings of 3.7, 4.2, and 4.6 Å (Figure 1c). It is reasonable to assume that the 4.2 Å reflection corresponds to the hexagonal crystalline arrangement of the octadecyl chains, similar to that of the PL-C₁₈ complex, and the 3.7 and 4.6 Å reflections arise from a two-dimensional alkane-type arrangement of the octyl chains, similar to that of the PL-C₈ complex.

The WAXD pattern of PL-C₁₈(10)-C₈ is identical to that of the PL-C₈ complex (Figure 1b), suggesting that the packing of both the octadecyl and the octyl chains is similar to that in the PL-C₈ complex.

Thus the WAXD data indicate that the arrangement of surfactant chains depends strongly on the composition of the complex. In the poly(L-lysine) complex with octyl "side chains" only, and in the complex with 10 mol % octadecyl "side chains", surfactant chains are organized on a two-dimensional alkane-type lattice. In the poly(L-lysine) complex with octadecyl "side chains" only, surfactant chains crystallize on a hexagonal lattice. In the complex with 20 mol % of the octadecyl "side chains", both types of the surfactant packing are observed.

Information about the conformational states of the "side chains" can be obtained from FTIR spectra of the complexes. In the PL-C₁₈ complex, the alkyl chains are in the all-trans conformation, as shown by the positions of the asymmetric and symmetric CH₂ stretching vibrations observed at 2919 and 2851 cm⁻¹, respectively³² (Figure 2, curve a).

Figure 2. FTIR spectra of the PL-C₁₈ (a), PL-C₁₈(20)-C₈ (b), PL-C₁₈(10)-C₈ (c), and PL-C₈ (d) complexes.

Figure 3. DSC thermograms of the PL-C₁₈ (a) and PL-C₁₈(20)-C₈ (b) complexes on heating.

Similar positions of the CH₂ vibrational peaks are observed for the PL-C₁₈(20)-C₈ complex (Figure 2, curve b). This indicates that both octadecyl and octyl chains are in all-trans conformations, despite the differences in their packing. In the PL-C₁₈(10)-C₈ and PL-C₈ complexes, the alkyl chains are in disordered conformations (asymmetric and symmetric CH₂ stretching vibrations observed at 2927 and 2856 cm⁻¹, respectively) (Figure 2, curves c and d).

Thermal Transitions. Figure 3 (curve a) shows a DSC thermogram of the PL-C₁₈ complex. The complex undergoes an endothermic first-order transition upon heating at 66 °C. No other transitions were observed in the temperature range 0–150 °C. This transition correlates with the disappearance of the 4.2 Å reflection on the WAXD pattern of the complex and the appearance of two reflections with Bragg spacings of 3.8 and 4.7 Å (pattern not shown), similar to those of the PL-C₈ complex (Figure 1b). These observations allow us to conclude that the transition corresponds to the transformation of hexagonal crystals of the octadecyl chains into a two-dimensional alkane-type arrangement, similar to that in the PL-C₈ complex.

For the PL-C₈ complex, no thermal transitions were observed by DSC in the temperature range 0–100 °C. This correlates with the observation of disordered conformations of the surfactant chains by FTIR. It appears that the octyl “side chains” are too short to crystallize at room temperature. The absence of “side chain” crystallization has been reported previously for complexes of poly(α,L-glutamate) anions with dodecyl and hexadecyltrimethylammonium cations,⁹ as well as for alkyl esters of poly(α,L-glutamic acid) with chains shorter than 10 methylene groups.³¹ The relatively sharp reflections in the WAXD pattern of the complex can be attributed to short-range two-dimensional positional order in the packing of octyl chains.

Figure 3 (curve b) shows a DSC thermogram of the PL-C₁₈(20)-C₈ complex. The complex undergoes an endothermic first-order transition at 49 °C on heating. This transition correlates with the disappearance of the 4.2 Å reflection in the WAXD pattern of the complex and with a slight broadening of the 3.7 and 4.6 Å reflections (pattern not shown). The disappearance of the 4.2 Å reflection upon heating can be attributed to transformation of hexagonal crystals of the octadecyl chains into a two-dimensional alkane-type arrangement, similar to that of the octyl chains in the PL-C₈ complex at room temperature. The two-dimensional order in packing of the octyl chains in the PL-C₁₈(20)-C₈ complex remains essentially unchanged. The fact that crystalline packing of the octadecyl chains in the PL-C₁₈(20)-C₈ complex is identical to that in the PL-C₁₈ complex suggests that the octadecyl chains are arranged in blocks on the polypeptide chains.

PL-C₁₈(10)-C₈ does not undergo any thermal transitions in the temperature range –20 to +100 °C observed by DSC. This is consistent with the observation of disordered conformations of the surfactant chains by FTIR. The fact that the octadecyl sulfate chains do not form hexagonal crystallites in this complex (in contrast to the behavior of the PL-C₁₈ and PL-C₁₈(20)-C₈ complexes), suggests a random distribution of the octyl and octadecyl “side chains” along the polypeptide chains. This conclusion is supported by the observation that the WAXD patterns of the PL-C₁₈(10)-C₈ and PL-C₈ complexes are identical.

The minimum octadecyl chain content required for crystallization in poly(γ-methyl L-glutamate-co-stearyl L-glutamate)s with randomly distributed alkyl chains, determined on the basis of the observation of the crystal melting transitions by DSC for a series of copolymers, is about 35 mol %.²⁴ The considerably lower content of octadecyl chains required for crystallization in the complexes reported here (ca. 20 mol %) indicates the preference of the electrostatically bound “side chains” of different lengths to separate into individual blocks. It is plausible that separation of octadecyl and octyl sulfates into individual blocks occurs in the process of their complexation with the polypeptide in water solutions, considering that no special annealing of the complexes in the solid state has been performed. One of the driving forces for separation is the hydrophobic interaction of alkyl chains in water, which also promotes complexation. Screening of the alkyl chains from water would be more effective if surfactants with similar chain lengths were arranged in blocks. Arrangement of the octadecyl chains into blocks of sufficient size allows their crystallization in the solid state.

Table 2. DSC Data for the Complexes and the Analogous Alkyl Polyglutamates

complex	T_m (°C)	ΔH_m (kcal/mol of $C_{18}H_{37}$)	ΔS_m [cal/(mol of $C_{18}H_{37}$ K)]
PL- C_{18}	66	8.1	24
PL- $C_{18}(20)$ - C_8	49	5.8	19
PG- C_{18} ^a	62 ³⁰	7.3 ³⁰	
PG- $C_{18}(52)$ - C_1 ^b	35 ²⁴		

^a Poly(γ -octadecyl α ,L-glutamate) is abbreviated as PG- C_{18} .

^b Poly(γ -octadecyl α ,L-glutamate-co-methyl L-glutamate) with 52% chain units with octadecyl side chains and 48% chain units with methyl side chains is abbreviated as PG- $C_{18}(52)$ - C_1 .

Table 3. X-ray Diffraction Spacings (Å) Related to the Lamellar Organization of the Complexes^a

PL- C_{18}	PL- $C_{18}(20)$ - C_8	PL- $C_{18}(10)$ - C_8	PL- C_8	hkl
42.0 (vs)	40.0 (vs)	35.0 (vs)	35.0 (vs)	100
		16.8 (vw)	17.3 (vw)	200
14.4 (vw)	14.4 (vw)	12.1 (vw)	11.9 (vw)	300
				400
8.3 (vw)	8.3 (vw)	7.0 (vw)	7.1 (vw)	500
7.0 (vw)	7.0 (vw)			600

^a Visual estimates of intensities are denoted as vs (very strong) and vw (very weak).

Thermal transitions of the PL- C_{18} and PL- $C_{18}(20)$ - C_8 complexes are characterized by relatively small differences in the transition half-width, enthalpy and entropy (Table 2). This allows us to conclude that the crystal sizes of the octadecyl chains in these two complexes are similar.

Indirect information about the relative sizes of the octadecyl chain crystals in the complexes and in their covalent analogues is provided by comparison of their melting temperatures. The melting temperature and enthalpy of the PL- C_{18} crystallites are similar to those of poly(γ -octadecyl α ,L-glutamate) (PG- C_{18}) (Table 2).

However, a decrease in the octadecyl chain content from 100% to about 50% in poly(γ -octadecyl α ,L-glutamate-co-methyl L-glutamate) (PG- $C_{18}(52)$ - C_3) results in a decrease in the melting temperature from 62 to 35 °C. In the complexes studied herein, the 5-fold decrease in the content of crystallizable "side chains" (from PL- C_{18} to PL- $C_{18}(20)$ - C_8) decreases the melting temperature only from 66 to 49 °C.

Supramolecular Structures. The structures of the complexes were investigated by small-angle X-ray diffraction (SAXD). The SAXD patterns of all of the complexes consist of one reflection of high intensity and multiple reflections of low intensity (Table 3).

The ratio of the Bragg spacings of these reflections suggests lamellar structures for all of the complexes. The long periods of the lamellae are independent of temperature in the range 20–100 °C. Lamellar organization has been reported previously for stoichiometric complexes of synthetic polypeptides and oppositely charged surfactants, with lamellae believed to consist of alternating layers of polypeptide chains separated by layers of surfactant molecules.^{9–11}

On the basis of the values of the lamellar long periods, we conclude that two types of lamellar organization are present, depending on the composition of the complex. Lamellae with a long period of 40–42 Å are formed by the complexes with hexagonal crystalline arrangement of the "side chains" (PL- C_{18} and PL- $C_{18}(20)$ - C_8 , respectively), and lamellae with a long period of 35 Å are formed by the complexes with "side chains" in the disordered conformation (PL- $C_{18}(10)$ - C_8 and PL- C_8).

Figure 4. Proposed scheme of the arrangement of the surfactant molecules within the lamellae in the complexes formed by poly(L-lysine) and alkyl sulfates.

Poly(L-lysine) chains in all of the complexes are predominantly in the β -sheet conformation, as shown by the positions of the amide I and amide II vibrations in the FTIR spectra³³ (observed at 1628–1630 and 1532–1534 cm^{-1} , respectively, spectra not shown). The intersheet spacing in poly(L-lysine) hydrochloride crystallized in the β -form is 15 Å,³⁴ and the length of fully extended octadecyl chains is about 21 Å. Thus, the experimental value of the long period of the PL- C_{18} lamellae (42 Å) suggests that the surfactant tails bound to the polypeptide chains lying in adjacent layers should be either interdigitated and perpendicular to the lamellar surface or tilted with respect to the layers without being interdigitated. The fact that the long periods of the PL- C_{18} and PL- $C_{18}(20)$ - C_8 lamellae are nearly identical and the crystalline packing of the octadecyl chains is the same in both complexes suggests that the octadecyl chains in both complexes are interdigitated (Figure 4a,b); tilted octadecyl chains in the PL- $C_{18}(20)$ - C_8 lamellae would result in large unfavorable gaps between the blocks of the longer and shorter chains.

The length of the fully extended octyl chain is about 9 Å. On the basis of the value of the lamellar long period of 35 Å and on the thickness of the poly(L-lysine) layers of about 16 Å,³⁵ we conclude that surfactant chains in the complex are not interdigitated (Figure 4d). The observation that the long periods of the PL- C_8 and PL- $C_{18}(10)$ - C_8 lamellae are identical confirms our conclusion about the random distribution of the octyl and octadecyl chains in the PL- $C_{18}(10)$ - C_8 complex.

Conclusions

We have shown that the solid-state structures of the water-insoluble complexes formed by poly(L-lysine) cations and alkyl sulfate anions can be controlled by altering the composition of the complex.

Organization of the surfactant chains in the complexes is governed by the surfactant chain length and the complex composition. In complexes with a single surfactant, octadecyl chains crystallize on a hexagonal lattice, and octyl chains organize on a two-dimensional alkane-type lattice with short range order. In the complexes with mixed surfactants, incorporation of 20 mol % octadecyl sulfate and about 75 mol % octyl sulfate results in the formation of blocks of the longer chain surfactant with hexagonal crystalline packing in a "sea" of octyl sulfate chains in a two-dimensional alkane-type arrangement. Decreasing the octadecyl sulfate content in the complexes to 10 mol % results in a random distribution of the surfactant chains with short-range two-dimensional ordered packing of both surfactants.

All of the complexes adopt lamellar structures consisting of alternating layers of polypeptide chains in the β -sheet conformation and layers of surfactants. The lamellar structures are governed by the surfactant organization. The complex with the hexagonal crystal-line arrangement of surfactant chains (PL-C₁₈) forms lamellae with interdigitated surfactant chains. The complex with the two-dimensional alkane-type organization of surfactant chains (PL-C₈) forms lamellae with surfactant chains arranged tail to tail. The PL-C₁₈(20)-C₈ complex with the blocky distribution of surfactant chains forms lamellae with interdigitated octadecyl chains and octyl chains arranged tail to tail. The long period of these lamellae is similar to that of the PL-C₁₈ complex. The complex with randomly distributed surfactant chains (PL-C₁₈(10)-C₈) forms lamellae with the long period identical to that of the PL-C₈ complex.

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