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EFFECT OF WATER STRUCTURE ON POLY-ε-BENZYLOXYCARBONYL-L-LYSINE MONOLAYERS

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In relation to the structure of water at the interfacial region, the effects of monovalent anions on the surface pressure-area curves of poly-ε-benzyloxycarbonyl-L-lysine were investigated. The effects of anions on increasing the surface pressure were in the order of $SCN^- > Br^- > Cl^- > F^-$ in accordance with that of these anions as breakers of water structure.

It is currently believed that the structure of water at biosurface is significantly influenced and ordered by constituent macromolecules.[1)] In other words, water is considered to affect the properties and structure of biopolymers at the interfaces. Recent evidence suggests that the water adjacent to interfaces significantly differs from bulk water.[2)] In this connection, we report here the effects of various anions on the poly-ε-benzyloxycarbonyl-L-lysine(PLL(Z)) monolayers.

PLL(Z) (mol wt = 4.7×10^5) was prepared by the NCA method. The IR spectrum exhibited the characteristic amide I and II bands assignable to the α-helical conformation. A spreading solution was made by dissolving the polymer(ca. 4 mg) in 9:1(v/v) mixture of methylene dichloride and DMF(10 cm^3). By using a micrometer syringe, the spreading solution was deposited onto the surface of aqueous solution containing KF, KCl, KBr or KSCN. The trough(65 x 15 x 1 cm) and compressing barriers were made of Teflon. The initial spreading area was 50 $Å^2$/residue. After standing for 15 min, the film was compressed at a rate of 1 $Å^2$/residue/min. The surface pressure was measured by the Wilhelmy method at 25 °C.

Figure 1 shows the surface pressure-area(π-A) curves for PLL(Z) spread on 2 M various salt solutions. There exists a plateau in each curve. The plateau was found for a number of synthetic polypeptide monolayers, and ascribed to the transition from a two-dimensional ordered state to a three-dimensional disordered state.[3)] It is noticeable that the film transition pressure is much higher on the subsolution containing KSCN than on distilled water.

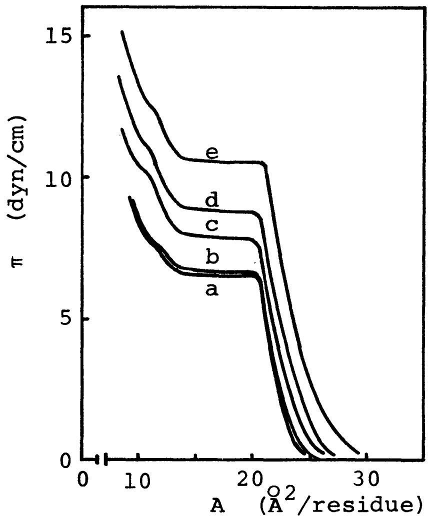

Fig. 1 π-A curves for PLL(Z) spread on 2 M various salt solutions. a, KF; b, distilled water; c, KCl; d, KBr; e, KSCN
1 dyn = 10^{-5}N, 1 Å = 0.1 nm.

In Fig. 2 are shown the π-A curves for PLL(Z) spread on various concentrations of KSCN. With the increasing concentration of KSCN, the film expansion becomes remarkable and the transition pressure increases. On the other hand, in the presence of various concentrations of KF, the effect on surface areas was quite small.

Figure 3 shows the film transition pressures as a function of salt concentration for PLL(Z) spread on various potassium salts. It can be seen that, with the exception of KF, the transition pressure increases with salt concentration. The effect of anions is in the order of $SCN^- > Br^- > Cl^- > F^-$ in accordance with that of anions as breakers of water structure.[4,5] This order also agrees with the effect of these anions on macromolecular systems.[4,5]

It has been reported that PLL(Z) spread on 0.01 M HCl is in the α-helical conformation.[6] As a result of breaking of water structure adjacent to the surface, chaotropic ions such as SCN^- may cause either conformational change or increase in side chain solubility of the polymer. In that event, the increase in hydrophilic character of the polymer is expected, and the transition pressure will increase with salt concentration.

In the case of F^-, the situation is different from other ions. This ion has been known as a maker of water structure.[4,5] In the presence of F^-, the hydrated structure built up around the hydrocarbon moieties of polymer may be reinforced. As a result, the hydrophobicity of the polymer increases. On this basis, the transition pressure decreases with KF concentration.

From the present study on PLL(Z) as a protein model, we conclude that the structure of water at the interfacial region is important for biopolymers at the interface.

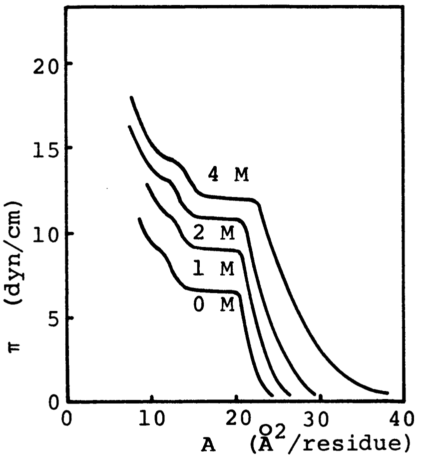

Fig. 2 π-A curves for PLL(Z) on distilled water and KSCN.

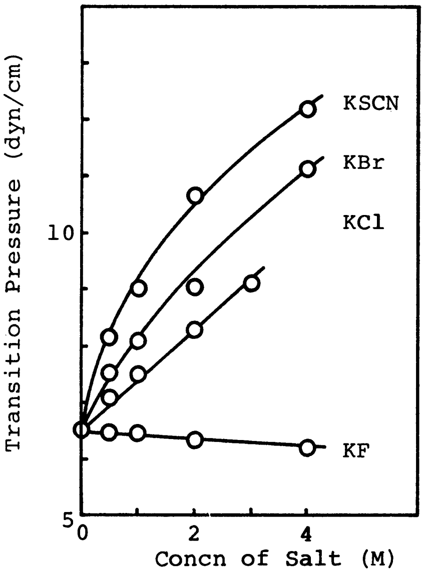

Fig. 3 Plots of transition pressure as a function of salt concentration.

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