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Formation of Organized Structures in Systems of Polyelectrolyte-Ionic Surfactants

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Summary

The interaction of polyelectrolytes with ionic surfactants is studied by turbidimetry and electron micrography. The turbidity of the mixed solution of PVS(poly(vinyl sulfate)) and CTAB(cetyltrimethylammonium bromide) showed a sharp maximum at the mole ratio of 1:1, indicating quantitative binding between PVS and CTAB. A multilayer structure was observed on the electron micrograph only at the mole ratio of PVS:CTAB=2:1 with a spacing of about 25A. At the mole ratio of PVS:CTAB=1:1, a single strand structure was observed. The system of ionene polymer(3,4) $(\{\overset{+}{N}(CH_2)_3-\overset{+}{N}(CH_2)_4\}_n)$–SDS(sodium lauryl sulfate) forms a multilayer structure at the equivalent ratio of 1:1 with a spacing of 20A.

Introduction

Micelles of surfactant molecules have extensively been studied as specific reaction sites because of their resemblence in structure and function to enzyme proteins and biomembranes. (FENDLER et al. 1975) Micelles, however, are formed only at above the critical concentration and labile in a sense that micelles are in a dynamic equilibrium with monomeric surfactant molecules in bulk water. In an attempt to stabilize or fix the micell structure on a polymer chain, we have studied the binding of ionic surfactants onto polyelectrolytes.

In this paper, we wish to report the electron-microscopic observation of new types of organized structures formed between polyelectrolytes and ionic surfactants.

Results and Discussion

An aqueous solution of cetyltrimethylammonium bromide(CTAB) (1.00×10^{-3}M) of varying amount from 0.5 to 10 ml was poured at a time into 5 ml of an aqueous solution of potassium poly (vinyl sulfate)(PVS) (1.00×10^{-3} M) at room temperature and absorbance of the solution at 420 nm was measured. The CMC of CTAB is 9×10^{-4} M. As shown in Fig. 1 the absorbance showed a sharp maximum at the mole ratio of 1:1, indicating quantitative binding between PVS and CTAB. The solution showed a slight turbidity. Lower and higher concentrations of CTAB than the equivalent gave clear solutions. On dilution of the mixed solution (1;1) five times, the absorbance decreased to one fifth that of the original mixture.

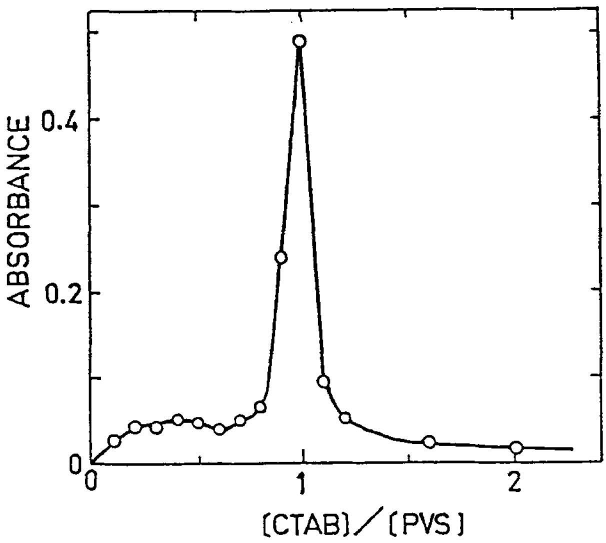

Fig. 1 Absorbance of Mixed Solution of PVS and CTAB

For the preparation of a specimen for electron microscopy a few drops of the solution were mixed with about an equal volume of a 2 % aqueous solution of uranyl acetate. One drop of the stained solution was applied to the 400 mesh copper grid covered with a carbon-coated collodion film, air dried, and subjected to an electron microscopic observation at direct magnification of 60,000. A multilayer structure was observed on the electron micrograph only at the mole ratio of PVS:CTAB=2:1 (Fig.2) The spacing of the layer is about 25 A which is slightly larger than the full length of the surfactant molecule. Diameter of the particle lies in 1000 to 2000 A, roughly corresponding to the stretched length of PVS (average degree of polymerization is 1000).

Particles of various size were observed at the mole ratios of 3:2, 3:1, 5:1 and 10:1, but no inside structure was observed. At the mole ratio of PVS:CTAB=1:1, i.e. at the maximum turbidity, a single strand structure was observed as shown in Fig.2b. The width of the strand is 50-60A which corresponds to the length of two surfactant molecules.

These results led us to the following speculation about the organized structures. Surfactant molecules are tightly bound by the electrostatic force to the polymer chain and the resulting assembly will further aggregate to form the multilayer structure in case a half of the polymer sites is occupied by the surfactant (Fig.3a)

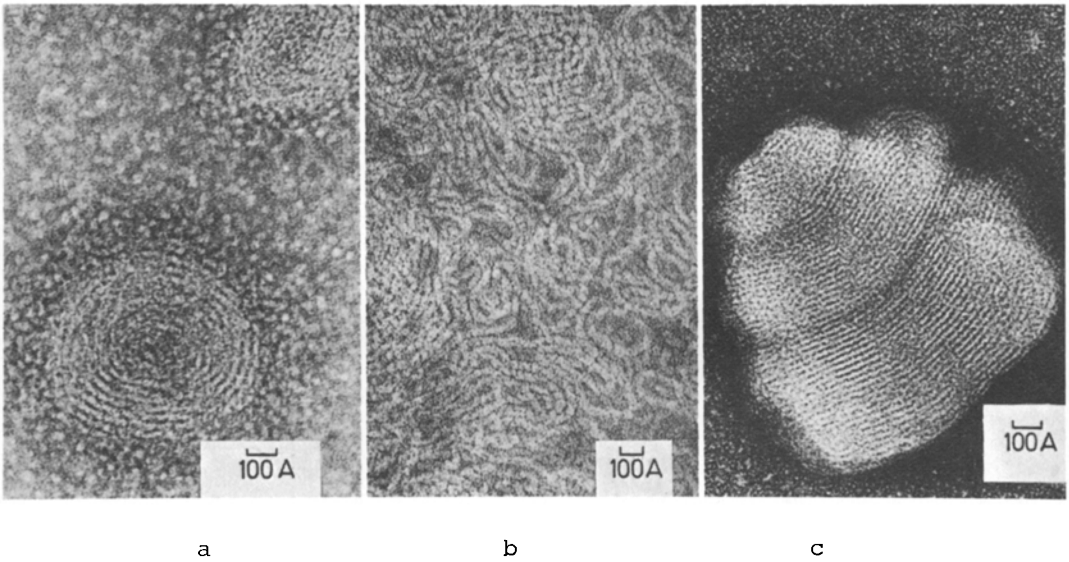

Fig. 2 Electron Micrographs of a) PVS and CTAB (2:1), b) PVS and CTAB (1:1), and c) Ionene polymer (3,4) – SDS (1:1 equivalent)

When the polyelectrolyte sites are completely occupied by the surfanctant molecules, the assembly will result in single strands (Fig.3b). A kind of crystallization of long alkyl chains of the bound surfactants may be responsible for the organization. The schematic arrangements in Fig.3 have the spacing of 5 A between long alkyl chains which is favorable for the crystallization.

Similar observations were made for a number of polyelectrolytes and surfactants. The system of ionene polymer (3,4) -sodium dodecylsulfate(SDS), for example, forms a multilayer structure at the equivalent ratio of 1:1. Spacing of 20 A again corresponds to the length of the SDS molecule. The CMC of SDS is 8×10^{-3}M. In this case the repeating distances between charges along the polymer chain are 5.0 and 6.2 A respectively, instead of 2.5 A for PVS, and hence complete occupancy of the polyelectrolyte sites by surfactant molecules may be necessary for the type of aggregation in Fig.3a to develop. Property of the organized structure is now under investigation.

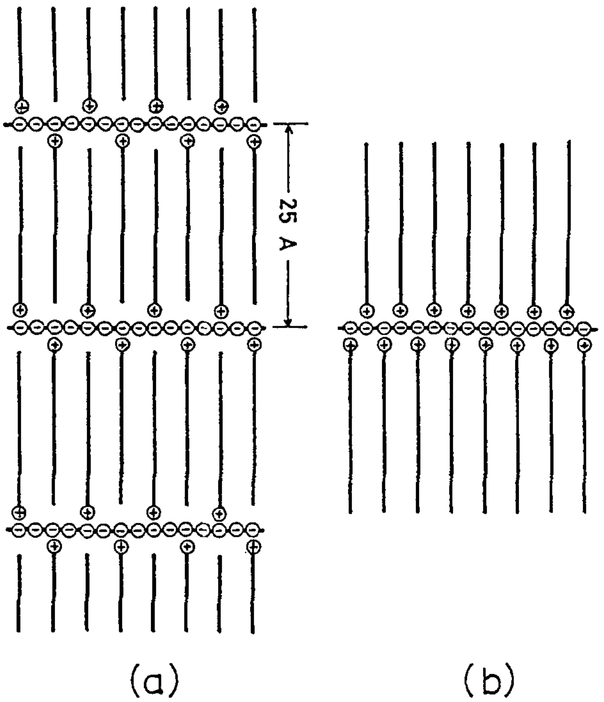

Fig. 3 Schematic Representation of Multilayer Structure (a) and Single Strand Structure (b)

Experimental

The absorbance of the solution was measured with a Hitachi 124 Spectrophotometer. The electron micrographs were obtained by a Hitachi Model HU-11DS at 100 KV.

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Reference

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