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Langmuir-Blodgett Films of Ferrocene Sulfide and Sulfone Derivatives with a Long Alkyl Chain

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With ferrocenyl octadecyl sulfide, stable monolayers on water surface can be obtained by mixing with stearic acid or by oxidizing to the sulfone derivative and can be easily deposited on solid supports to form well-organized LB films, as confirmed by polarized IR spectra and X-ray diffraction. The LB films exhibit electrochemical activity.

By introducing ferrocene to amphiphiles and fabricating the monolayer assemblies, we can obtain an electrochemically active thin film as well as an interesting model for the electromagnetic interaction in two-dimensional arrays.[1-6] Previously, for long chain ferrocene and biferrocene derivatives with ester or amide linkage, different orientations of ferrocene nuclei were realized in the Langmuir-Blodgett films, depending on the numbers and the positions of long alkyl substituents.[2,3] In this work, using ferrocene sulfide and sulfone derivatives with a long alkyl chain we investigated the monolayer characteristics and also the molecular orientations together with electrochemical behavior in the LB films.

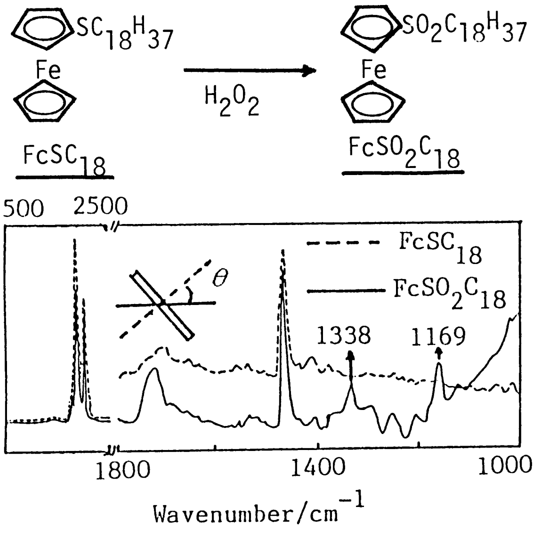


Fig.1. Reaction scheme and FT-IR spectra.

Ferrocenyl octadecyl sulfide($FcSC_{18}$) was newly synthesized[7] and the sulfone derivative($FcSO_2C_{18}$) was obtained by oxidizing $FcSC_{18}$ in benzene solution with H_2O_2 aqueous solution under ultrasonic treatment at 30 °C for more than 1 hr. The reaction scheme and IR spectra are shown in Fig.1. The formation of sulfone derivative was confirmed by the characteristic bands of SO_2 at 1338 and

1169 cm^{-1}. The monolayers were spread from benzene solution onto doubly distilled water and the surface pressure(π)–area(A) isotherms were measured with a Lauda film balance. The multilayers were built up by the LB method on CaF_2 plates for FT-IR measurements, on glass slides for X-ray diffraction and on ITO electrodes for cyclic voltammetry.

Figure 2(A) shows the π–A isotherms for the monolayers of $FcSC_{18}$ and the mixtures with stearic acid($C_{18}A$) in various molar ratios. From the molecular areas in condensed region, it is considered that the $FcSC_{18}$ molecules are incorperated in the mixed monolayers with $C_{18}A$ in the molar ratios of $FcSC_{18}/C_{18}A=0.4$–1.0, although $FcSC_{18}$ alone doesn't spread well enough as a monolayer because of less hydrophilicity of the sulfide linkage. On the other hand, $FcSO_2C_{18}$ forms a stable monolayer on water surface without any matrix amphiphiles as shown in Fig.2 (B). The limiting area ($A_{\pi\to 0}$) is about 26 Å^2/molecule which is similar to the amphiphilic ferrocene amide and ester derivatives with a single alkyl chain, reported previously.$^{2)}$

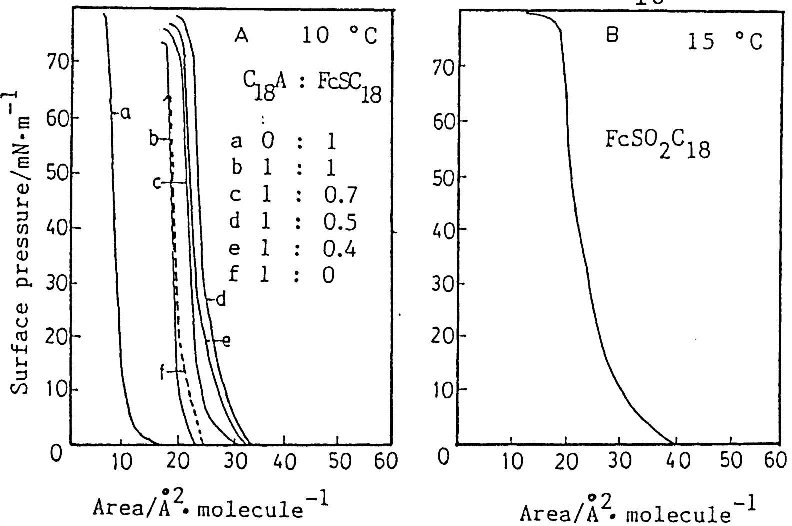
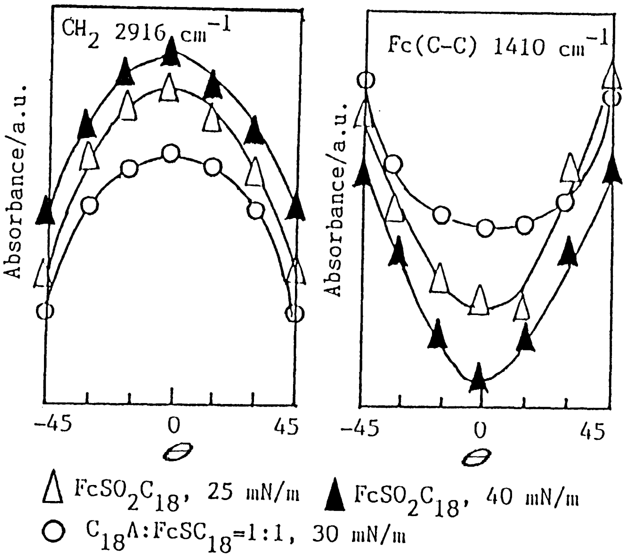


Fig.2. π–A isotherms for mixed monolayers of $FcSC_{18}$ and $C_{18}A$(A), and monolayer of $FcSO_2C_{18}$(B).



△ $FcSO_2C_{18}$, 25 mN/m ▲ $FcSO_2C_{18}$, 40 mN/m
○ $C_{18}A$:$FcSC_{18}$=1:1, 30 mN/m

Fig.3. Plot of the absorbance for CH_2 vibration of alkyl chain and C-C vibration of cyclopentadienyl ring in various LB films as the function of incident angle θ of p-polarized light.

The mixed monolayer of $FcSC_{18}$ and $C_{18}A$(1:1) and the $FcSO_2C_{18}$ monolayer could be deposited with the transfer ratio of almost unity.

Polarized IR spectra for these LB films were measured. In Fig.3, the absorbance of CH_2 stretching band at 2916 cm^{-1} and the C–C stretching of cyclopentadienyl rings at 1410 cm^{-1} are plotted against the incident angle θ of p-polarized light. In all cases the former band shows the maximum at $\theta=0$, while the latter shows the minimum at nearly the same angle. These results indicate that the transition moments for the CH_2 stretching of the chain and the C–C stretching of the rings are nearly parallel and perpendicular to the film plane, respectively. Therefore, it can be concluded that the long alkyl chains and the cyclopentadienyl rings are oriented approximately vertical to the plane of the LB films. The sharpness of these curves suggests more definite orientation of $FcSO_2C_{18}$ molecules than those of $FcSC_{18}$ in the LB films (Fig.3).

Figure 4 shows the X-ray diffraction patterns for the mixed LB films of $FcSC_{18}$ with $C_{18}A$ and for the $FcSO_2C_{18}$ film. The long spacings of double layers for the $FcSC_{18}$ mixed films with $C_{18}A$ in the molar ratio of 1/1 and 1/2 were 55.9 and 52.6 Å, respectively, and those for the $FcSO_2C_{18}$ films deposited at 25 and 40 mN/m were 59.3 and 60.1 Å, respectively. These results indicate that the $FcSO_2C_{18}$ molecules are oriented almost vertically, while $FcSC_{18}$ molecules are somewhat tilted in the LB films.

The electrochemical reaction of these ferrocene derivatives in the LB films deposited on ITO electrodes were investigated in an aqueous solution of KCl(1.3 M). Redox reaction could not be detected for the mixed films of $FcSC_{18}$ and $C_{18}A$ in the molar ratio of 1/1 and 1/2. However, when the mixing ratio of $FcSC_{18}$ is increased up to 5/1, a reversible oxidation–reduction can be observed

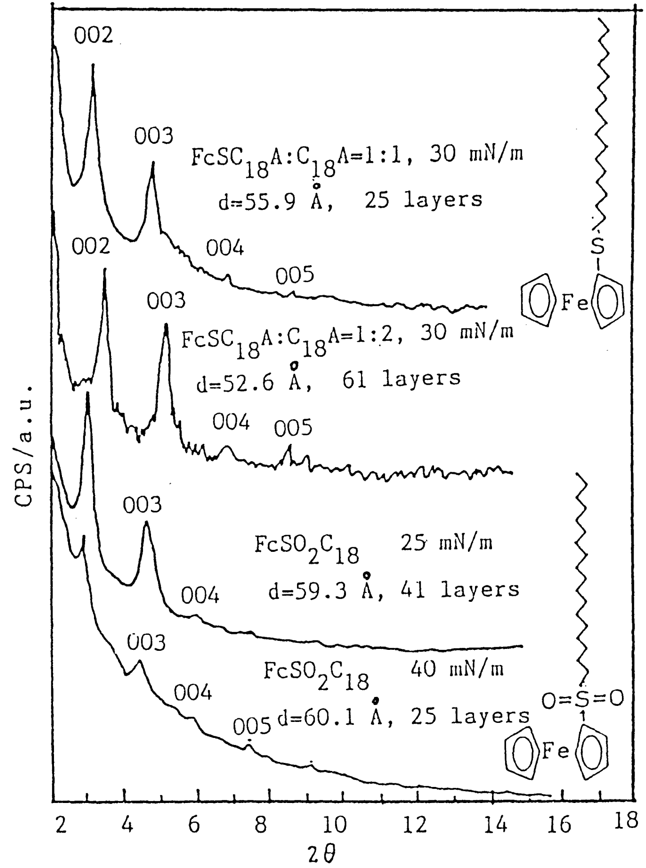


Fig.4. X-Ray diffraction patterns of LB films of ferrocene derivatives.

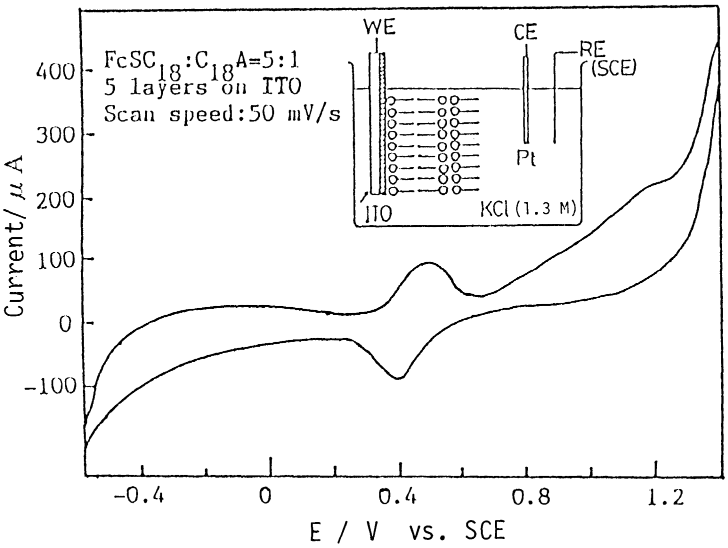


Fig.5. Cyclic voltammogram for mixed LB film of $FcSC_{18}$ and $C_{18}A$ (5:1).

in the cyclic voltammogram as shown in Fig.5, although the $FcSC_{18}$ molecules in this mixed film(5/1) are not necessarily well-organized. On the other hand, the $FcSO_2C_{18}$ film(11 layers deposited at 25 mN/m) can be oxidized at 0.72 V and reduced at −0.12 V vs. Ag/AgCl, as shown in Fig.6(A). In the visible absorption spectra measured simultaneously, an oxidation band due to ferricinium can be observed around 700 nm and a reduction band at 480 nm, as shown in Fig.6(B). However, sufficient reversibility could not be obtained because of peeling off of the film.

Ferrocenyl octadecyl sulfide does not spread well enough as a monolayer on water surface because of less hydrophilicity of the sulfide linkage. However, we can get stable monolayers by mixing it with stearic acid or by oxidizing it to the sulfone derivative. These monolayers can be easily transferred onto solid plates by LB method to give a well-defined layer structure, in which cyclopentadienyl rings together with alkyl chains are oriented nearly perpendicular to the film plane. These films of ferrocene derivatives exhibit electrochemical activity and are expected to have a potential application for modified electrodes.

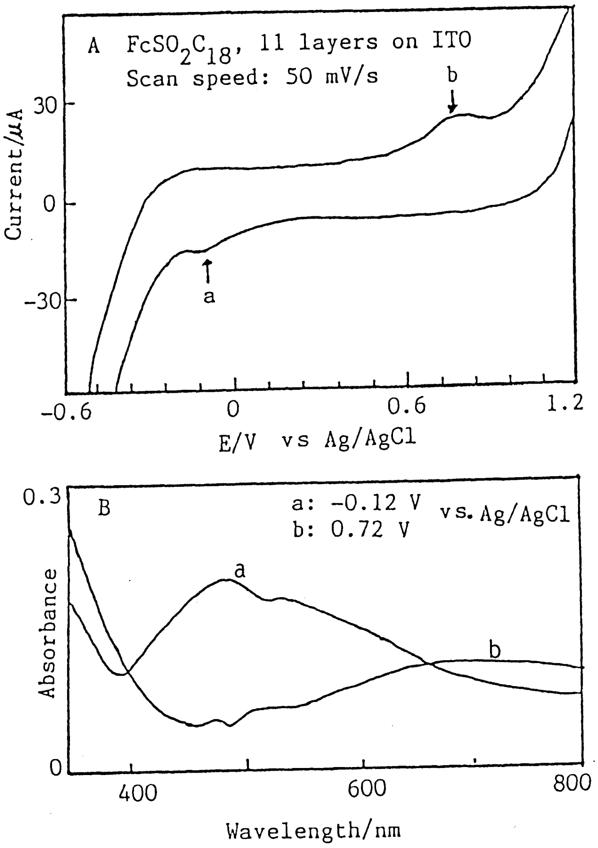


Fig.6. Cyclic voltammogram for $FcSO_2C_{18}$ LB film (A) and UV spectra of the same film under different applied potentials indicated by arrows (B).

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