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Adsorption Behavior of a Cationic Surfactant Derivative of Ferrocene on phthalocyanine Pigment Surface

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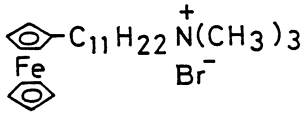
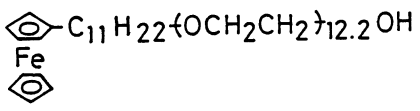
Double adsorption layers of a cationic surfactant derivative of ferrocene were found to be built up on phthalocyanine pigment particles in an aqueous solution, leading to re-dispersion of the particles. Electrochemical oxidation of this dispersion system gave a thin phthalocyanine film on an electrode.

An increasing number of studies have been reported on thin film processing using micellar disruption method.[1,2] By using this method, thin films of azo-dye,[1] viologen,[2] and polymer compounds[3] were prepared on the anode through electrochemical oxidation of a cationic surfactant derivative of ferrocene, (11-ferrocenylundecyl)trimethylammonium bromide (FTMA), which is adsorbed on the surface of film-forming compounds.

Recently, it has been reported that thin films of pigments, phthalocyanine complex,[4] dianthraquinone, etc., were prepared using a nonionic surfactant, (11-ferrocenylundecyl)polyethylene glycol (FPEG), but pigment films could not be formed using the FTMA surfactant. This may suggest that FTMA do not have ability to disperse these pigments.[5] However, it is unlikely that thin films can be formed exclusively using the nonionic FPEG surfactant. In the present study, we have succeeded in dispersing pigment and preparing the pigment film by using the cationic FTMA surfactant.

FTMA  FPEG 

FTMA and FPEG (Dojin Co.) were used as the surfactants for dispersing a metal-free phthalocyanine (PcH_2, Tokyo Kasei Co.). Surfactant solutions were prepared by dissolving FPEG or FTMA in distilled-deionized water, and the

solutions were filtered through a 0.05 μm membrane filter. A PcH_2 pigment was washed with hot distilled water five times for 2 hours. A supporting electrolyte used in this work was LiBr (Wako Pure Chemicals).

The washed PcH_2 (25.7 mg) and LiBr (1.04 g) were added to 100 ml of an aqueous solution containing various concentration of FTMA or FPEG. The mixture was treated with an ultra-sonicater bath for 30 min. Then, this dispersion was stirred for three days and allowed to stand for a day. A supernatant solution was separated by decantation and used for experiments. The dispersion was characterized by UV-vis absorption, mean particle size, and ζ potential measurements. The mean particle size and the ζ potential were determined by ELS-800 (O-otsuka Electric Co.). In electrochemical measurments, an indium tin oxide (abbreviated as ITO, 20 Ω/square) was used as the working electrode. A platinum plate and a saturated calomel electrode (SCE) were used as the counter and the reference electrode, respectively. Controlled-potential electrolysis was conducted by the use of a model HA-501G potentio-galvanostat (Hokuto Denko Co.).

An adsorption behavior of the surfactants was investigated by measuring ζ potential. Figure 1 shows plots of the ζ potential on the PcH_2 surface vs. the concentration of the surfactant, [surfactant], for (A) FTMA and (B) FPEG. As the concentration of FTMA is increased, the ζ potential changed drastically from negative to positive at a concentration of ca. 100 μM. In the vicinity of the neutral point, the particle size of PcH_2 rapidly increased, leading to the precipitation of PcH_2 particles (Fig. 2.). Upon a further addition of FTMA, the PcH_2 particles were re-dispersed.

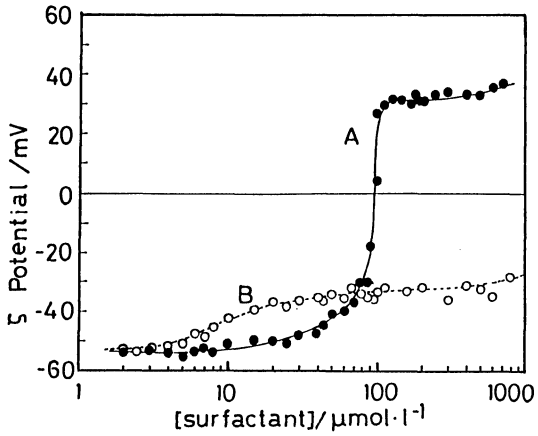


Fig. 1. Change in ζ potential as a function of the concentration of FTMA (A) and FPEG (B).

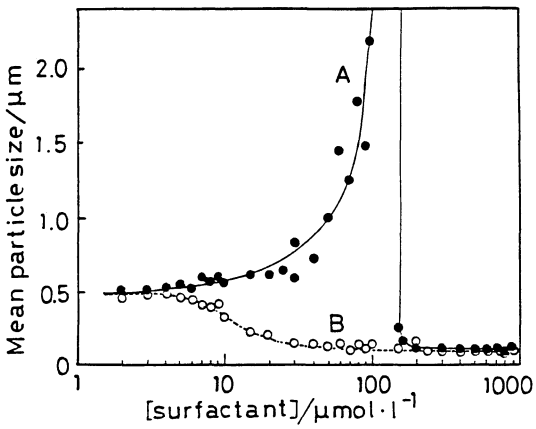


Fig. 2. Change in mean particle size as a function of the concentration of FTMA (A) and FPEG (B).

Figure 3 shows a plot of absorbance at 535 nm (λ_{max}) of the FTMA/PcH_2 dispersion vs. the concentration of the FTMA surfactant, [FTMA]. No adsorption at ca. 100 μM of FTMA and the subsequent rise in absorbance beyond 170 μM of FTMA indicate the precipitation and the re-dispersion of the FTMA/PcH_2 dispersion, respectively.

On the other hand, the values of ζ potential, mean particle size, and absorbance of the dispersion changed only slightly with the concentration in the case of FPEG.

These results for the FTMA/PcH2 dispersion system may be explained by a dispersion-flocculation-re-dispersion process [6] of particles through bilayer adsorption of surfactants. In this model, at first, the ammonium moiety of the FTMA surfactant is adsorbed on the surface of a PcH2. The hydrophobic hydrocarbon chain with ferrocenyl moiety is exposed to the water phase. The first layer adsorption of FTMA is formed through electrostatic attraction between the negatively charged phthalocyanine surface positively charged ammonium moiety of the FTMA. This brings about flocculation of the PcH2 particles, because the PcH2 surface covered with the first layer is hydrophobic.

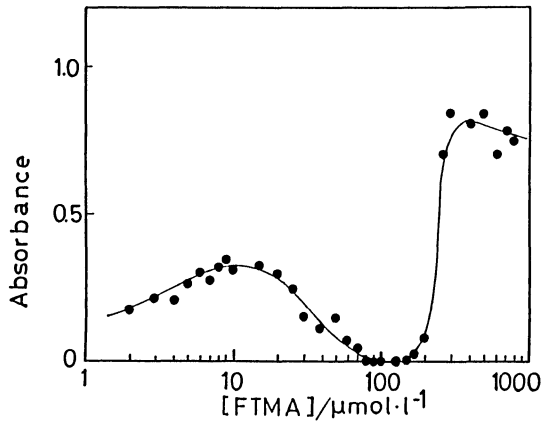


Fig. 3. Change in absorbance as a function of the concentration of FTMA, [FTMA].

The amount of FTMA adsorption at electrically neutral point was determined to be 100 μM per 500 μM-PcH2 (= 0.39 mmol-FTMA/g-PcH2) as shown in Figs. 1-3. When the concentration of FTMA is increased further, the amount of FTMA adsorption saturates on the PcH2 surface (170 μM per 500 μM-PcH2= 0.66 mmol-FTMA /g-PcH2). This saturation value was in good agreement with that determined by Langmuir adsorption isotherm, 0.61 mmol-FTMA/g-PcH2. Upon further addition of FTMA surfactant, the adsorption of second layer of FTMA takes place on the FTMA monolayer-adsorbed PcH2 surface. The second layer is formed by hydrophobic interaction between the hydrocarbon chain of the monolayered FTMA on the PcH2 surface and the newly adsorbed FTMA, which is followed by re-dispersion of the PcH2 particles. This phenomenon is illustrated by a schematic model shown in Fig. 4.

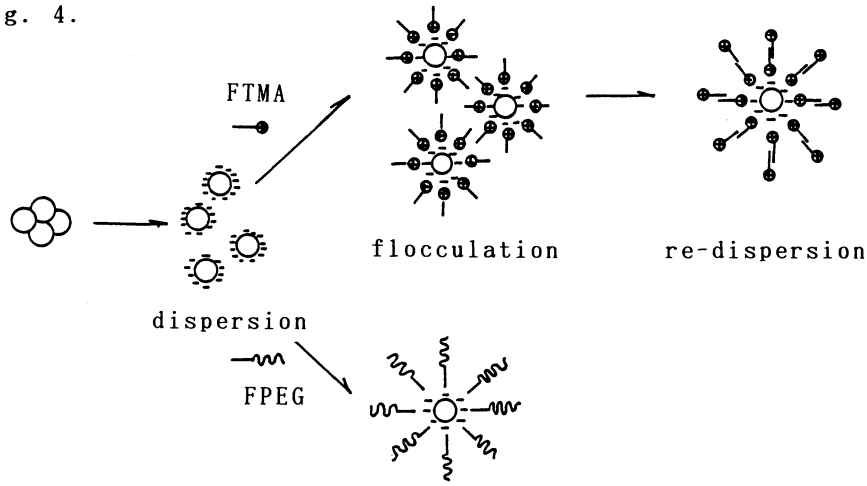


Fig. 4. A dispersion model of the FTMA/PcH2 and the FPEG/PcH2 systems.

Contrary to the case of FTMA, adsorption behavior of FPEG may be explained by the model of Langmuir: the FPEG surfactant is simply adsorbed on the PcH_2 surface, and then the particle is stably dispersed.

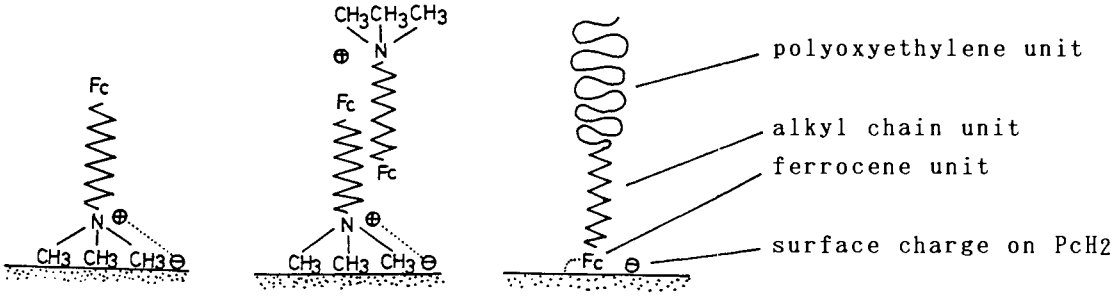


Fig. 5. Model for adsorption of FTMA and FPEG on the PcH_2 surface.

A surface area of PcH_2 measured by N_2-adsorption method was 75 m^2/g. An occupancy area of FTMA was calculated from this value and the amount of the monolayered FTMA. It is determined to be about 0.21 nm^2/molec. This value agrees well with available adsorption area of the ammonium ion moiety of FTMA [7] (0.20 nm^2/ molec.). This agreement indicates that double adsorption layer of FTMA can be formed on the PcH_2 surface (Fig.5). A thin film of PcH_2 could be formed successfully on the ITO electrode by micellar disruption method using FTMA. The value of an applied potential and the amount of electricity passed through the ITO were +0.50 V vs. SCE and 0.15 C/cm^2, respectively. Concentrations of FTMA and PcH_2 were 10 mM and 2 mM, respectively. The SEM image of the film is shown in Fig. 6. There appeared no distinct difference in morphology between the PcH_2 films prepared by FTMA and FPEG.

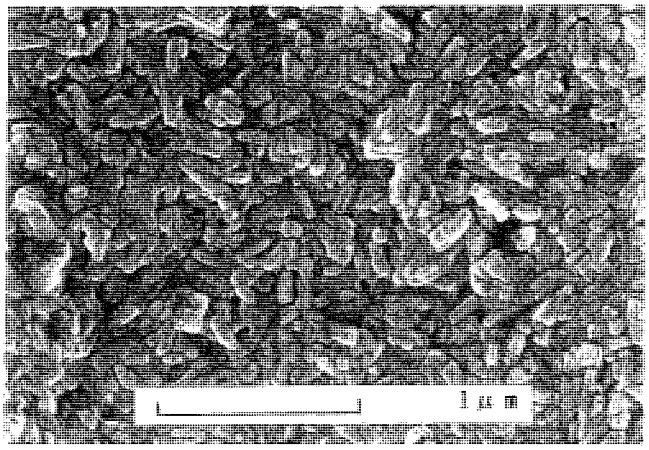


Fig. 6. SEM image of a PcH_2 film prepared by the micellar disruption method using FTMA.

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