Alternate Intercalation of Fluoran Dye and Tetra-n-decylammonium Ion Induced by Electrolysis in Acetone-Clay Suspension

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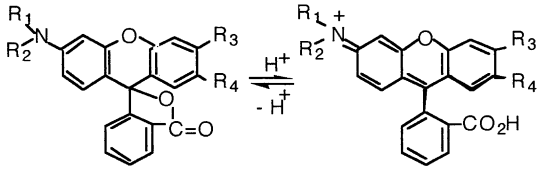
Electrochemically induced acid and base promoted the alternate intercalation of fluoran dye and tetra-n-decylammonium ion and the reversible color change of the dye in the acetone-clay suspension, and the procedure was applied to rewritable recording media by changing the polarity of the voltage.

Fluoran dye is well known as one of leuco dyes or colored cationic dyes (color former, CF51, Hodogaya chemical, Tokyo) for thermal copy paper. Acid-activated montmorillonite clay (H^+/Clay) is often used as color developer of the dye. Scheme 1 shows the acid-base equilibrium of the dye. Recently, we have confirmed that the cationic dye (Dye^+) is intercalated onto the clay, which is suspended in non aqueous medium and even in polymer matrix.[1,2] The driving force of the dye fixation inside the clay is the formation of the thermodynamically stable clay-dye complex, based on the ion exchange reaction between the cationic dye and previously incorporated hydrophobic alkylammonium ion. The equilibrium (K=1520, 25 ℃, acetone) of the ion exchange reaction between cationic fluoran dye and bulky tetra-n-decylammonium ion intercalated into the clay ($(C_{10}H_{21})_4N^+$/Clay) is compared with that for Na^+/montmorillonite (K=0.179, acetone) (Scheme 2).[3] The high stability of fluoran dye intercalated into the clay makes it possible to provide a good fixing performance, that is comparable to the traditional photography.[2]



Colorless Colored

Scheme 1. Acid-base equilibrium of fluoran dye.

$$(C_{10}H_{21})_4N^+/Clay + Dye^+ \underset{Acetone}{\overset{K}{\rightleftharpoons}} Dye^+/Clay + (C_{10}N_{21})_4N^+$$

Scheme 2. Equilibrium of cationic dye and alkylammonium ion in the clay suspension.

As fluoran dye has also electrochromic property, many attempts have been made to control colorization or decolorization of the dye in the field of the electrolytic recording. Thus, the combination of electrochemically induced color change and the dye-clay intercalation will bring about a new technology for the rewritable recording media. Herein, we wish to report the alternate intercalation of the dye and alkylammonium ion and the simultaneous color change in the clay suspension, controlled by an electrochemical stimulus.

Acetone suspension comprising leuco fluoran dye and H^+/Clay exhibited dark greenish color as the result of the dye-clay interaction. However, in place of H^+/Clay, the modified clay ($(C_{10}H_{21})_4N^+$/Clay) substituted beforehand with tetra-n-decylammonium ion gave no color appearance of the leuco dye. This means that there are no acidic centers on the clay or even if present, acids make it hard to approach to a leuco dye molecule owing to sterically crowded alkylammonium ion.

Oxidization potential of the dye was evaluated about 0.85 V by CV in CH_3CN. The oxidized dye (Dye^+) gave an intensive visible absorption with greenish black color and it was restored to the colorless solution by electrochemical reduction. This electrochemical reaction proved to be reversible in the solution. When the acetone suspension, composed of leuco fluoran dye, the modified clay and tetra-n-decylammonium perchlorate was oxidized with 2 V of anodic potential in a H-type cell, black particles effectively appeared. The contraction of the interlayer distance of the clay was observed through the electrochemical reaction, i.e., the spacing of the modified clay was 27.7Å before electrolysis and lessened to 23.2Å after oxidation process. Simultaneously, IR signals of alkylammonium ion (2900 cm^{-1}) disappeared and carbonyl signal (1770 cm^{-1}) appeared. The electrochemical oxidation of the suspension brings about the production of the cationic dye and makes it intercalate onto the clay. When the polarity of the applied voltage was reversed to the cathode, the black colored suspension gradually faded with applying the voltage and finally became entirely white one. The isolated clay gave just the similar IR chart and basal spacing (27.3 Å) to those of the initial modified clay. This electrochemical reduction induced re-adsorption of alkylammonium ion onto the clay layer and at the same time reproduction and desorption of the original leuco dye.

When the acetone suspension of H^+/Clay and alkylammonium perchlorate was electrochemically treated in the cathode compartment in the absence of the dye, the spacing gradually increased and the increment was ca.10Å (Figure 1). There was no expansion of the spacing unless adding the voltage. Collected precipitates revealed new methylene peaks at around 2900 cm^{-1}. Such a remarkable expansion of the space began to occur at below -1.5 V, owing to the intercalation of bulky alkylammonium ion accompanying the increasing electric current with applying the voltage (Figure 1). When either of the H^+/Clay or Na^+/Clay was added into the acetone solution of tetra-n-decylammonium perchlorate, which had been electrochemically treated beforehand, the basal spacings similarly increased. These results imply that alkylammonium ion dissolved in acetone as electrolyte is intercalated into the clay layer by applying the cathodic voltage. A diluted aqueous solution showed a drastic pH change (pH9 and 3-4 for the cathodic and anodic sides, respectively). Applying the cathodic voltage turned to the basic surroundings and on the contrary the anode compartment became acidic. Although the basic and acidic components are not identified yet, their active species seem to induce both of chromism and intercalation of the dye if the dye is present. Acetone molecule is easily reduced by electron transfer to form ketyl (radical anion), which dimerizes reversibly. As might be expected, ketyl operates as strong base. This species may be an important candidate to bleach the cationic dye trapped into the clay and also to promote the adsorption of alkylammonium ion on the clay. This finding that electrochemical reactions might produce basic and acidic species from acetone-electrolyte solution can provide a novel procedure alternately to intercalate cationic dye and bulky alkylammonium ion into the clay.

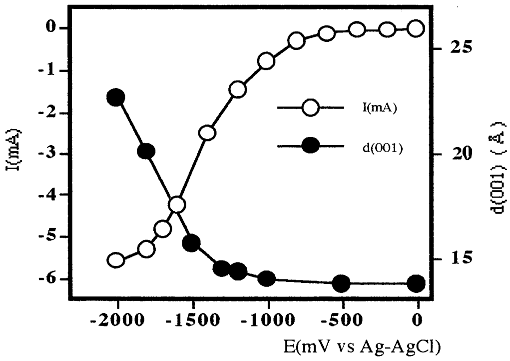
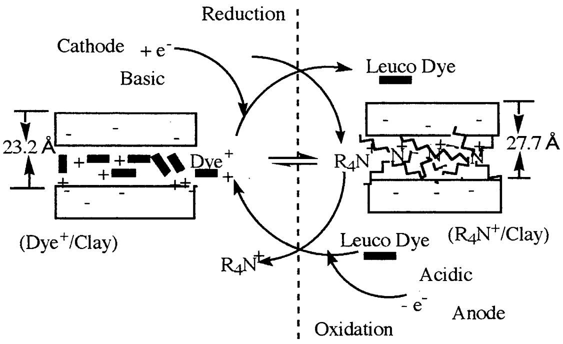


Figure 1. Changes of electrolytic current (mA) and basal spacing (d_{001}) of H^+/Clay with applied potential.

These results so far can present an overall reaction scheme for an electrochromic intercalation behavior of fluoran dye as shown in Scheme 3. The reversible color change of fluoran dye is not owed to the direct electrochromic reaction but the acid-base equilibrium induced by electrolysis. Acetone suspension of the leuco fluoran dye and the modified clay (($(C_{10}H_{21})_4N^+$/Clay) becomes acidic on applying the controlled anodic voltage, followed by the color appearance owing to the cationic fluoran dye formed by acid. Simultaneously, the colored dye (Dye^+) is inserted into the clay by exchanging with alkylammonium ion and permanently fixed because of the thermodynamically stable clay-dye complex.[3] On the contrary, by changing the polarity of the electrode the colored suspension becomes basic and finally turns to the colorless. Basic species generated in the cathodic compartment attack the dye chromophore to produce the nonionic leuco dye. The colorless dye is no more capable of forming ionic bonding to the negative clay and then released, so that free alkylammonium ion is inserted to compensate the lack of the positive charge, in place of the cationic dye. As far as mass balance is maintained, the reactions are repeatable. In fact, at least ten times of dye adsorption and desorption cycles (at the same time, colored and colorless cycles) were done in the suspension by alternately changing the plus and minus electrodes. Although the electrical reduction and oxidation of the dye may readily occur in the solution, the applied potential will be too high to reduce the dye intercalated into the clay.



Scheme 3. Plausible mechanism of alternate intercalation of the dye and decylammonium ion (R_4N^+).

For practical electrochromic printing,[4] the rewritable papar was prepared by being dipped into the acetone solution containing electrolyte (5 wt%) and ethylene carbonate (10 wt%), and further by coating the acetone suspension composed of the modified clay (8 wt%), fluoran dye (1 wt%), electrolyte (3 wt%), ethylene carbonate (15 wt%), and polyester resin (5 wt%) on one side of the paper. These reagents used here were the same as those in the H-type cell except ethylene carbonate. Electrolytic recording was carried out by running a copper head on the paper (working voltage: 60 V, head speed: 10mm/sec, head temperature: 100 ℃). The paper in a fused state above 60 ℃ had the proper conductivity. Reflective optical density of an image was variable with the applied voltage between a head and a roller and reached 1.5 at 60 V, which was sufficient to recognize the image in practical use. The rewritable paper exhibited a good fixation of the cationic dye in humidity and plasticizer, which was compared with that of current thermal copy paper. Drastic color change occurred on the surface of recording layer when the positive or negative potential was applied on the printing head. These behaviors showed good similarity with the experimental results in the H type-cell. The recorded image was erased at least once by changing of polarity of the applied voltage. However, the pale yellowish brown color remained on the sheet with repeated cycles, depending upon the contact time and/or the applied voltage. The residual image may be due to decomposed products because of considerably high energy. To improve repeatability in practical printing, it would be necessary to design more electrochemically sensitive recording layer and/or to suppress the decomposition of its components.

References and Notes

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