On the Adsorption of Merocyanine Dyes to Silver Bromide

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Abstract

Molecular structures and electronic states of merocyanine dyes adsorbed on AgBr grains have been examined on the basis of their visible and infrared spectra. The conclusion is that the contribution of the ionic form to the resonance structure of a merocyanine dye molecule is greater on the surface of AgBr than in its simple crystal and in organic solvents used in this work. The fact is well explained by the interaction of anionic oxygen and cationic nitrogen atoms in the dye molecule with Ag⁺ and Br⁻ on the surface of AgBr grains, respectively. No evidence has been obtained for the presence of the strong interaction between C=S in the dye molecule and Ag⁺ on the surface of AgBr crystals.

§ 1. Introduction

During the course of the investigation of spectral sensitization of the photographic process¹, it is thought desirable to obtain the knowledge about the nature of the adsorption of photographic dyes to silver halides. In the paper previously reported³, the authors have studied the nature of the adsorption of basic dyes which involve many typical sensitizers and desensitizers to silver halides by means of spectroscopic devices.

The nature of the adsorption of photographic dyes to silver halides depends upon their electric charge⁴. Merocyanine dyes are typical photographic sensitizing dyes whose molecules are electrically neutral. However, the nature of the adsorption of merocyanine dyes to silver halides is not clear at the present. In this paper, the nature of the adsorption of merocyanine dyes has been examined by means of spectroscopic devices according to the procedure used in the paper previously reported.

§ 2. Materials and Experiments

Merocyanine dyes studied in this paper which are represented below, were supplied by Japanese Research Institute for Photosensitive Dyes Co.

\[
\text{\(n=0\), \(2\text{-}(3\text{-ethyl-benzothiazole})\)}
\]
\[
\text{\(5\text{-}(3\text{-ethylrhodanine})\)}
\]
merocyanine (I)

\[
\text{\(n=1\), \(2\text{-}(3\text{-ethyl-benzothiazole})\)}
\]
\[
\text{\(5\text{-}(3\text{-ethylrhodanine})\)}
\]
dimethine merocyanine (II)

\[
\text{\(n=2\), \(2\text{-}(3\text{-ethyl-benzothiazole})\)}
\]
\[
\text{\(5\text{-}(3\text{-ethylrhodanine})\)}
\]
tetramethine merocyanine (III)

Silver bromide powder was prepared as follows: one liter of 1N silver nitrate aqueous...
solution was put drop by drop into 1.1/l potassium bromide aqueous solution at 25°C. After being washed to remove small particles, the precipitate deposited at the bottom of a vessel was gathered, dried and used for experiments. Water and nitrate ion were ascertained to be eliminated by measuring infrared spectra of the sample.

Dyes were adsorbed to the silver halide powder as follows: one gram of the silver halide powder and 30 ml of aqueous dye solution of the already-known concentration were put into an air-tight vessel, which is shaked for more than 10 hours at 30°C. Then, the solution was centrifuged to separate the powder from it. The dyed powder was dried and submitted to the measurement of visible and infrared adsorption spectra.

Measurements of visible spectra of adsorbed dyes on the silver halide powder, and quantitative measurements of dye concentration were made by Shimazu Recording Spectrophotometer MPS-50. Infrared spectra of dye crystals and adsorbed dyes were measured by Infrared Spectrophotometer Model DS-301 made by Japan Spectroscopic Co..

§3. Infrared Spectra of Merocyanine Dyes

Infrared spectra of Merocyanine Dyes I, II, and III adsorbed to silver bromide are shown in Figs. 1, 2 and 3, being compared with those of the dye crystals.

As is seen in these figures, the absorption peak due to C=O stretching vibration which is observed at about 1680 cm⁻¹ of the spectra of the crystals of dye II and of dye III al-
most disappears in the spectra of dye II and III adsorbed to silver bromide. Moreover, the absorption spectra of the dye II and III adsorbed to silver bromide which appear from 1200 to 1600 cm\(^{-1}\) are different from those of the crystals of these dyes.

§ 4. Visible Absorption Spectra of Merocyanine Dyes

The influence of the adsorption of dyes to silver halides on the electronic structure of the dyes can be examined by the shift of the wavelength of the adsorption peak \(\lambda_{\text{max}}\) of the adsorbed dyes on the silver halides, on the basis of the solvent effect of the electronic absorption spectra of organic molecules\(^{3}\). According to the theory of the solvent effect, \(\lambda_{\text{max}}\) of organic molecules depends upon the squared refractive index \(n^2\) and electrostatic dielectric constant \(D\) of solvents\(^{3}\).

The observed values of \(\lambda_{\text{max}}\) and \(\tilde{\nu}_{\text{max}}\) of dye II and III are shown in Table 1, being compared with the values of \(n^2\) and \(D\) of the solvents and adsorbent used in the experiment. As is seen in this figure, the value of \(\lambda_{\text{max}}\) increases with increasing the value of \(n^2\) and \(D\) of solvents. This phenomenon is qualitatively consistent with the theory of the solvent effect of electronic spectra of organic molecules. However, in the case of dye III adsorbed to silver bromide, the shift of \(\lambda_{\text{max}}\) to longer wavelength is extremely larger than is expected by the theory of the solvent effect\(^{4, 5}\). This fact suggests that the electronic structure of dye III is disturbed by its adsorption by silver bromide.

Table 1. Solvent effect of electronic spectra of merocyanine dyes

<table>
<thead>
<tr>
<th>Solvent or adsorvent</th>
<th>(n^2)</th>
<th>(D)</th>
<th>Dye II</th>
<th>Dye III</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)OH</td>
<td>1.77</td>
<td>33.2</td>
<td>528</td>
<td>613</td>
</tr>
<tr>
<td>C(_2)H(_5)OH</td>
<td>1.85</td>
<td>25.8</td>
<td>526</td>
<td>605</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>2.10</td>
<td>5.05</td>
<td>525</td>
<td>597</td>
</tr>
<tr>
<td>C(_2)H(_5)N</td>
<td>2.28</td>
<td>12.4</td>
<td>531</td>
<td>614</td>
</tr>
<tr>
<td>C(_2)H(_5)Cl</td>
<td>2.34</td>
<td>5.9</td>
<td>521</td>
<td>594</td>
</tr>
<tr>
<td>C(_2)H(_5)Br</td>
<td>2.44</td>
<td>5.4</td>
<td>519</td>
<td>591</td>
</tr>
<tr>
<td>C(_2)H(_5)Cl</td>
<td>2.67</td>
<td>5.04</td>
<td>530</td>
<td>613</td>
</tr>
<tr>
<td>AgBr+air</td>
<td>2.84*</td>
<td>7.1*</td>
<td>552</td>
<td>677</td>
</tr>
</tbody>
</table>

* The arithmetical mean of the values between silver bromide and air (Ref. 1)

§ 5. Discussion on the Adsorption Condition of Merocyanine Dyes

As is seen in 3 and 4, the molecular and electronic structures of merocyanine dyes adsorbed to silver bromide are not identical to those of the merocyanine dye crystals. Discussions on these facts are thought to lead to the clarification of the nature of the adsorption of the merocyanine dyes by silver bromide.

Merocyanine dyes have the following resonance structures in common\(^{5}\).
The value of the wavenumber of the absorption peak due to the C=O stretching vibration $\nu_{C=O}$ (~1680 cm$^{-1}$) indicates that the double bonding character of C=O of the dyes in crystal and in solutions is still large and that the contribution of the neutral form to the resonance structure is larger than that of the ionic form. Usually, the magnitude of the contribution of these forms depends on solvents and adsorbents. When the contribution of the ionic form increases to become equal to that of the neutral form, the longest wavelength is expected to be observed in the case of these dyes.

Based on the discussion mentioned above, the results obtained in 3 and 4 are thought to arise from the fact that the contribution of the ionic form to the resonance structure of the merocyanine dyes increases remarkably by their adsorption to silver bromide. Namely, the increase of the contribution of the ionic form to the resonance structure of the dyes is thought to result in the decrease of the wavenumber of $\nu_{C=O}$ and, therefore, in the change of the absorption spectra of these dyes which are observed from 1600-1200 cm$^{-1}$.

While, the decrease of the difference of the contribution between the neutral form and the ionic one to the resonance structure is thought to result in the large shift of the absorption peak to the longer wavelength.

As is indicated in 3 and 4, the longer the methine chain length of the dyes is, the larger is the increase of the contribution of the ionic form. It is thought to arise from the fact that the dye with the long poly-methine chain obtains larger stabilization energy due to the resonance by the increase of the contribution of the ionic form to the resonance structure than the dye with the short poly-methine chain does.

From 1200-650 cm$^{-1}$, no significant change is observed between the infrared spectra of the dyes crystals and those of the dye adsorbed to silver bromide. Therefore, it is not supported that the special interaction exists between C=S group of these merocyanine dyes and the silver ions at the surface of silver bromide grains.

References

8) T. Tani, Kogyo Kagaku Zasshi, in press.