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EFFECT OF pH ON SPECTRAL SENSITIZATION OF SILVER CHLORIDE

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The effect of pH on the spectral sensitization of silver chloride was studied electrochemically. The sensitized photocurrent by rhodamine B decreased with lowering pH of the electrolyte solution, whereas in the case of 1,1'-diethyl-2,2'-quinocyanine chloride, the increase in the sensitized photocurrent was observed. The above fact suggests that H^+ existing in the vicinity of the silver chloride surface plays an important role in increasing the sensitized photocurrent.

It is known that the absorbance and fluorescence of dye often decrease with lowering pH of a dye solution.1) This tendency will bring about the decrease in the sensitized photocurrent with lowering pH. From the above standpoint, we investigated the effect of pH of the electrolyte solution containing dye on the spectral sensitization of a silver chloride membrane electrode.

The preparation of silver chloride crystals and the experimental setup are the same as those reported previously.2,3) The electrochemical cell was constructed as follows: Pt(I)/electrolyte(I),dye/ AgCl/electrolyte(II)/Pt(II). In order to control the pH of the electrolyte solution, nitric acid or hydrochloric acid was used.

Since the absorbance of 1,1'-diethyl-2,2'-quinocyanine chloride in the visible region decreases with lowering pH of the dye solution,1) the sensitized photocurrent by the dye is expected to decrease with lowering pH. However, it was observed that the sensitized photocurrent increased with lowering pH as shown in Fig.1. This fact suggests that other factors contributing to the increase in the sensitized photocurrent are predominant in the range of pH region between 4 and 7. The decrease in the sensitized photocurrent in the very low pH region will be interpreted in terms of protonation of the dye. A pK_a value (K_a: dissociation constant) of 1,1'-diethyl-2,2'-quinocyanine chloride is reported to be about 4.0[1]. Therefore, remarkable protonation of the dye is expected to occur in the range of pH region lower than 4, causing the decrease in the dye concentration at the silver chloride crystal surface, and consequently resulting in the decrease in the sensitized photocurrent. The relation between the sensitized photocurrent and pH was also studied for various kinds of electrolyte and acid which was used to control the pH of the electrolyte solution (I). The degree of the increase in the sensitized photocurrent with pH was found to be the lowest in the case of $AgNO_3$ electrolyte solution.

We could not investigate the effect of pH on the intrinsic photocurrent, because it was not induced in reproducible magnitude by the intrinsic excitation of silver chloride probably owing to producing lots of print-out silver atoms. However, we observed the pH-dependency of the background photocurrent in the visible region which flowed even in the absence of a sensitizing dye. This observation suggests that the increase in the sensitized photocurrent is not due to the change in the silver chloride crystal.

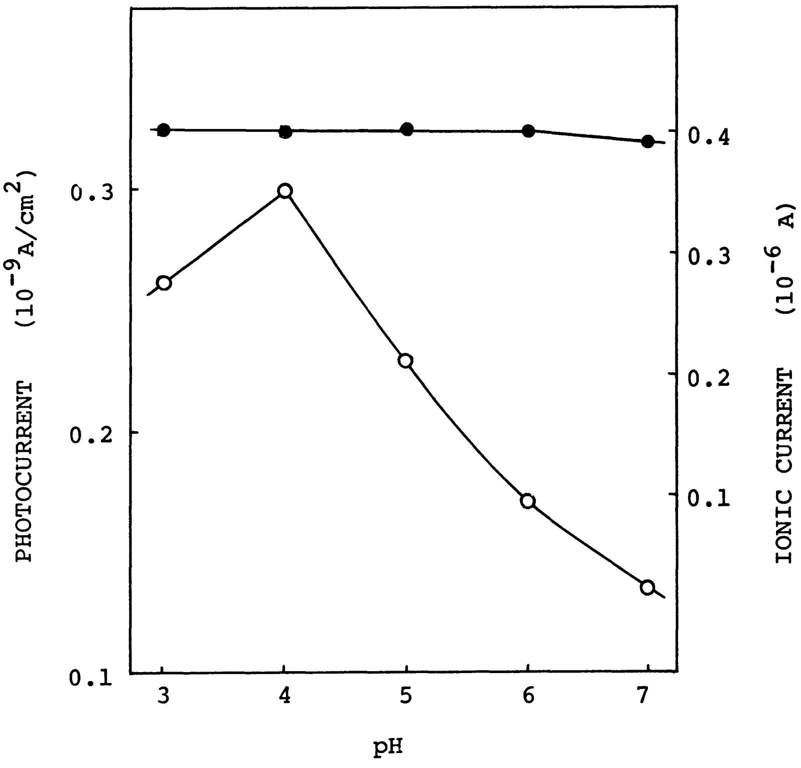

Fig.1. Effect of pH on the sensitized photocurrent by 1,1'-diethyl-2,2'-quinocyanine chloride (1×10^{-4} mol/l) in KCl electrolyte solution.

—○— : Sensitized photocurrent at 570 nm,

—●— : Ionic current.

The ionic current was hardly affected by changing pH as shown in Fig.1. This fact indicates that the change in the sensitized photocurrent with pH is not based on the change in the structure of the electric double layer at the silver chloride-electrolyte solution interface.

Watanabe et al.4) found that the dye-sensitized photocurrent at TiO_2 electrode increased with lowering pH of the electrolyte solution containing dye. They interpreted their results in terms of the pH-dependence of the flat-band potential of TiO_2. Assuming a dissociation equilibrium between $Ti\text{-}O^{2-}$ and $Ti\text{-}OH^-$ on the TiO_2 crystal surface, they obtained the linear relation between logarithmic photocurrent and pH of the electrolyte solution. However, the above discussion cannot be extended to the present case, because the complex formation of silver chloride with proton is not found here. In fact, we did not found the linear relation between logarithmic dye-sensitized photocurrent and pH.

According to Tani,5) the polarographic half-wave potentials of 2,2'-cyanine dyes are not affected by the change in pH, indicating that the electrochemical properties of the dyes do not depend on the pH of the electrolyte solution.

In the case of rhodamine B as a spectral sensitizer, the decrease in the sensitized photocurrent was observed in the range of pH region between 3 and 7 as shown in Fig.2. Since the absorbance of rhodamine B decreases more markedly with lowering pH than that of 2,2'-cyanine, it is expected that rhodamine B has larger pK_a value than 2,2'-cyanine. Probably, the protonation of rhodamine B will predominantly bring about the decrease in the sensitized photocurrent in the above pH region.

At the present stage, we can only suggest that H^+ existing in the vicinity of the silver chloride surface might play a role in getting rid of hindrances which interrupt the spectral sensitization process.

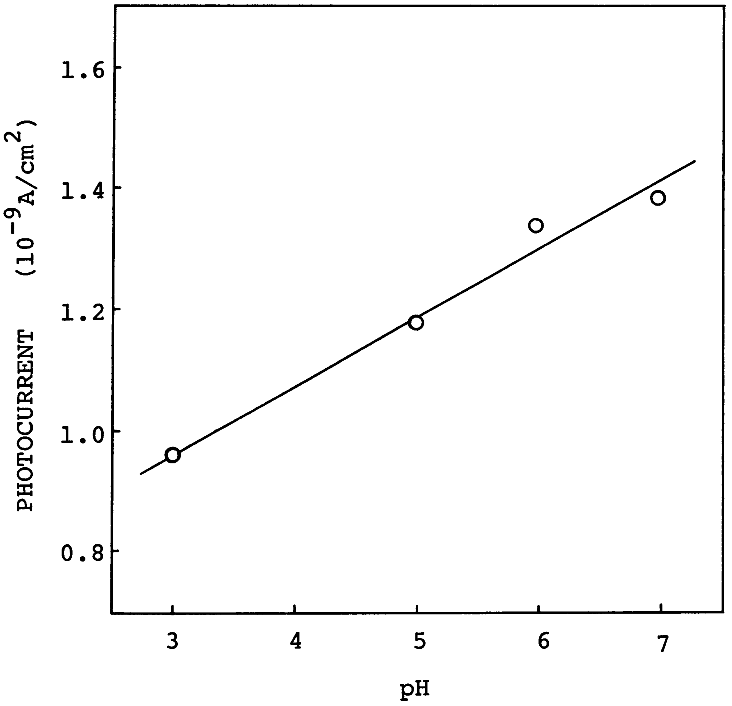

Fig.2. Effect of pH on the sensitized photocurrent at 570 nm by rhodamine B ($1x10^{-4}$mol/l) in $AgNO_3$ electrolyte solution.

If the positive charge of H^+ is very important, the increase in the sensitized photocurrent with lowering pH will be remarkable in the case of KCl electrolyte solution rather than $AgNO_3$. The observation on the kinds of electrolyte as described above supports this supposition. In the very low pH region, the protonation of sensitizing dye becomes remarkable resulting in the decrease in the sensitized photocurrent. More experimental results should be required to interpret clearer the pH-dependence of the sensitized photocurrent.

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