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Electrochemical Study of Spectral Sensitization Using AgCl Sheet Crystal as a Window. Ag$^+$ Ion Effect

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With use of AgCl sheet crystal as a window, sensitized photocurrent was measured in an electrochemical cell with a lock-in amplifier. With five sensitizing dyes having different lowest vacant levels, it was found that the higher the level of the dye, the larger the sensitized photocurrent, the sensitized photocurrent increasing with decreasing pAg of the dye-bearing solution. The Ag$^+$ ion effect can be explained by a band edge shift of the AgCl electrode, which also explains the blue desensitization recovery by Ag$^+$ ions.

Recent studies on spectral sensitization have made it clear that the electron transfer mechanism is dominant.[1–3] On the basis of electron transfer, three processes of donation or acceptance between the dye and silver halide (AgX) can be considered (Fig. 1): (1) spectral sensitization, *i.e.*, electron transfer from excited dye to the conduction band of the AgX (Fig. 1a), (2) desensitization, *i.e.*, the transfer generated in AgX by intrinsic light absorption to the dye (Fig. 1b), (3) hole injection, *i.e.*, the transfer from the AgX valence band to oxidized dye (Fig. 1c). Ag$^+$ ion is known to influence these processes.

As regards (1), Gilman *et al.*[1,4] found that spectral sensitivity increases with decreasing pAg (pAg$=-$log [Ag$^+$]) of photographic emulsions and explained this by a subconduction band event, a process in which Ag$^+$ ions at the AgX surface accept electrons from excited dyes to form silver atoms, with the result that the surface sensitivity of the photographic emulsion increases. Silver atoms are unstable, decomposing by thermal energy to Ag$^+$ ions and electrons, and the electrons go up the conduction band of the AgX. Iwasaki *et al.*[5] have utilized electrochemical techniques using AgCl sheet crystal as a membrane. They found that sensitized photocurrent (SPC) increases with decrease in the pAg of the solution containing dye, and explained the phenomenon by a band edge shift of AgCl.

As regards (2), Collier and Gilman[6] found the recovery of blue desensitization by Ag$^+$ ions in emulsion systems, and explained this by a subconduction band event.

As regards (3), Berriman and Gilman[7] reported a restraining action by Ag$^+$ ions in photographic emulsion systems, and explained it by change in the oxidation potential of silver by Ag$^+$ ions.

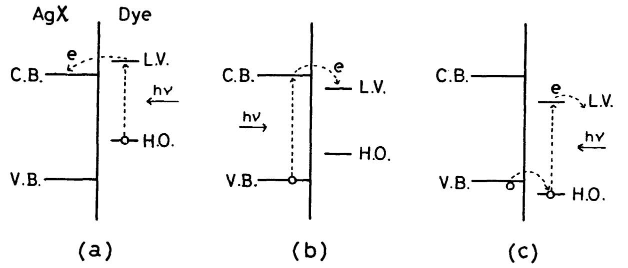

Fig. 1. A scheme of electorn transfer.
C.B.: Conduction band, V.B.: valence band, L.V.: lowest vacant level, H.O.: highest occupied level, e: electron, o: hole, a): spectral sensitization, b): desensitization, c): hole injection.

In connection with AgX/dye electron donation/acceptance, it is of great interest that Ag$^+$ ions can influence these three processes. In our experiment on the Ag$^+$ ion effect using electrochemical techniques, five sensitizing dyes were used, each having different lowest vacant levels. Constitutional formulas of the dyes and their energy levels[1] are shown in Figs. 2 and 3, respectively. Using these dyes, we measured SPC based on electron transfer from excited dyes to the AgCl conduction band[5,8] by an electrochemical method with use of a lock-in amplifier, AgCl sheet crystal being used as an electrochemical cell window.

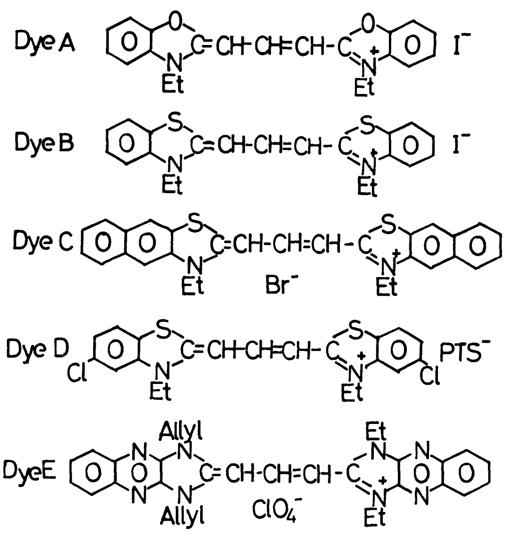

Fig. 2. Constitutional formula of sensitizing dyes.

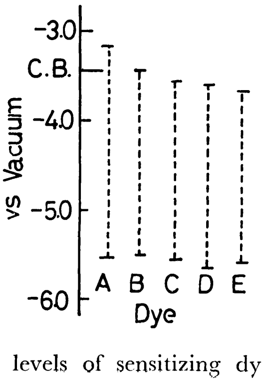

Fig. 3. Energy levels of sensitizing dyes reported by Gilman.[1]

Experimental

Preparation of AgCl Sheet Crystal. 2 M (1 M=1 mol dm^{-3}) $AgNO_3$ (Kojima Chemical Co., Ltd., reagent grade) and 5 M HCl (Sankyo Chemical Co., Ltd., reagent grade) were mixed, and the resulting precipitate was washed with distilled water and ground to powder in a mortar. The powder was packed into a quartz tube, and melted at 465 °C in a vacuum. When all the AgCl powder was melted, zone melting was carried out at a velocity of 1 cm/h. The upper (less pure) half of the transparent crystal produced was used in dye-adsorption experiments. The lower half was used to measure SPC. Cutting was done by a slicer (Maruto Co., Ltd.) to make crystals 0.5 mm thick, and the crystal surface was treated with 1 M KCN and polished with silk cloth to make it 80% transparent. All the crystals showed nearly the same behavior toward blank photocurrent which is due to intrinsic light absorption, as well as dark current which is based on interstitial silver ion.

Apparatus for Measurement. The apparatus is shown in Fig. 4. The exciting light from a 500 W Xe lamp (Ushio Electric Co.) illuminated the AgCl-dye interface through a light chopper, an interference filter (10 nm half-width), and transparent AgCl. AgCl electrode potential was adjusted to 0.4 V *vs.* a saturated calomel electrode (SCE) with dry cells. SPC was measured with a lock-in amplifier having a frequency of 125 Hz. During measurement, contact to the voltmeter was broken to exclude noise.

Measurement of Sensitized Photocurrent. The AgCl sheet crystal was held in contact with an electrochemical cell with epoxy resin. After *ca.* 10 h the crystal face not in contact with the electrolyte solution was attached to a lead wire with silver paste, while the opposite face was etched with 1 M KCN for 15 min and washed with distilled water. Dye solutions A, B, C, D, and E were prepared, methanol content being 5 vol % for A and B, 15% for C, 35% for D, and 25% for E. A dye solution with 0.04 M KNO_3 was put into the cell. SPC measurement was started 30 min after the addition of dye solution, and repeated every 10 min to check changes due to dye adsorption. If no change was observed, $AgNO_3$ solution was added to control pAg, SPC being measured after 5 min. After SPC measurement at pAg 1, dark currents were again measured to confirm that no large change have occurred in comparison with solutions without dye. All experiments were carried out at room temperature in a dark room, the solution used not being deoxidized. The photon distribution of the light source was measured with a thermocouple.

Adsorption Experiments. The AgCl sheet crystal was immersed for 30 min in dye solutions of the same composition as those used in the SPC measurement (in this case dye adsorbed to both faces of AgCl crystal), and washed with hexane. The absorbance of this dyed crystal was measured as a reference of AgCl without dye using Shimadzu Model MPS-5000 recording spectrometer, after which the crystal was again immersed for 10 min in the same solution to check changes due to dye adsorption. The duration of immersion increased when such a change was found. The pAg of the dye solution was controlled by addition of $AgNO_3$ solution. The crystal was immersed in the solution for 5 min and washed with hexane, and its absorbance was measured. All the experiments were carried out at room temperature in a dark room.

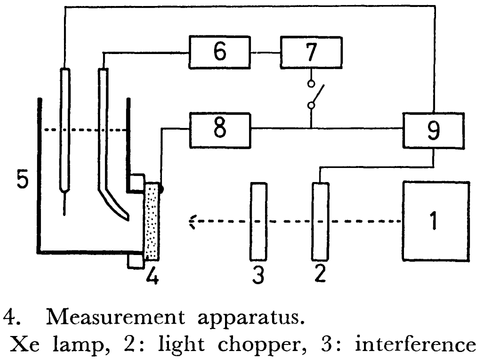

Fig. 4. Measurement apparatus.
1: Xe lamp, 2: light chopper, 3: interference filter, 4: AgCl, 5: Pt counter electrode, 6: SCE, 7: voltmeter, 8: dry cell, 9: lock-in amplifier.

Results

The characteristics of dye A are shown in Fig. 5. The insets in Fig. 5 a) and b) show the dependence of values of solid curve peaks on pAg. The adsorption of dye A decreases with the addition of Ag^+ ions, the absorption peak of the dye solution remaining unchanged. The dye solutions are diluted slightly by the addition of $AgNO_3$ solution. It was found that the 500 nm peak in the SPC action spectra is based on a dye monomer, and the 465 nm peak on a dimer. In the adsorption of dye A, the absorption peaks shifted to longer wavelength by an approximately 20 nm than that for the solution itself by stabilization, its SPC action spectra coinciding with its absorption spectrum when dye was adsorbed. The SPC increased, despite the decrease in adsorption of dye A with lowering pAg. The pAg ∞ shows the case without addition of $AgNO_3$.

The characteristics of dye B are shown in Fig. 6 a) and b). Adsorption was not influenced by Ag^+ ions, while SPC increased with lowering in pAg. The peak at 585 nm arose from a dye monomer, and the SPC of dimer could not be detected clearly.

Figure 7 shows the characteristics of dye C. Adsorption was not influenced by Ag^+ ions. No SPC could be detected at pAg 4 and above, but at 3 and below, SPC increased with fall in pAg. A 600 nm absorption peak arose from a dye monomer and 560 nm peak from a dimer. We could detect only the monomer peak in SPC. It is very interesting that SPC could be detected only at pAg 3 and below for dye C.

Figure 8 shows the characteristics of dye D. Adsorption was not influenced by Ag^+ ions, SPC increasing with decreasing pAg. An SPC peak was detected at 585 nm based on a monomer, but there was no clear peak on a dimer.

For dye E, no SPC could be detected down to pAg 1.

Though the methanol content of the various dye solutions was changed from 5% to 35%, the change in reference electrode (SCE) potential was less than 20 mV,[9] negligibly small. The redox potential of halide ions, which can act as electron donors,[15] shifted due to the change in methanol content. However, the amount contained as a counter ion to the cation dyes was very small, so that this effect can also be neglected. The NO_3^- ions contained in the 0.04 M electrolyte solution did not behave as electron donors.[15] The changes in methanol content influenced dye ad-

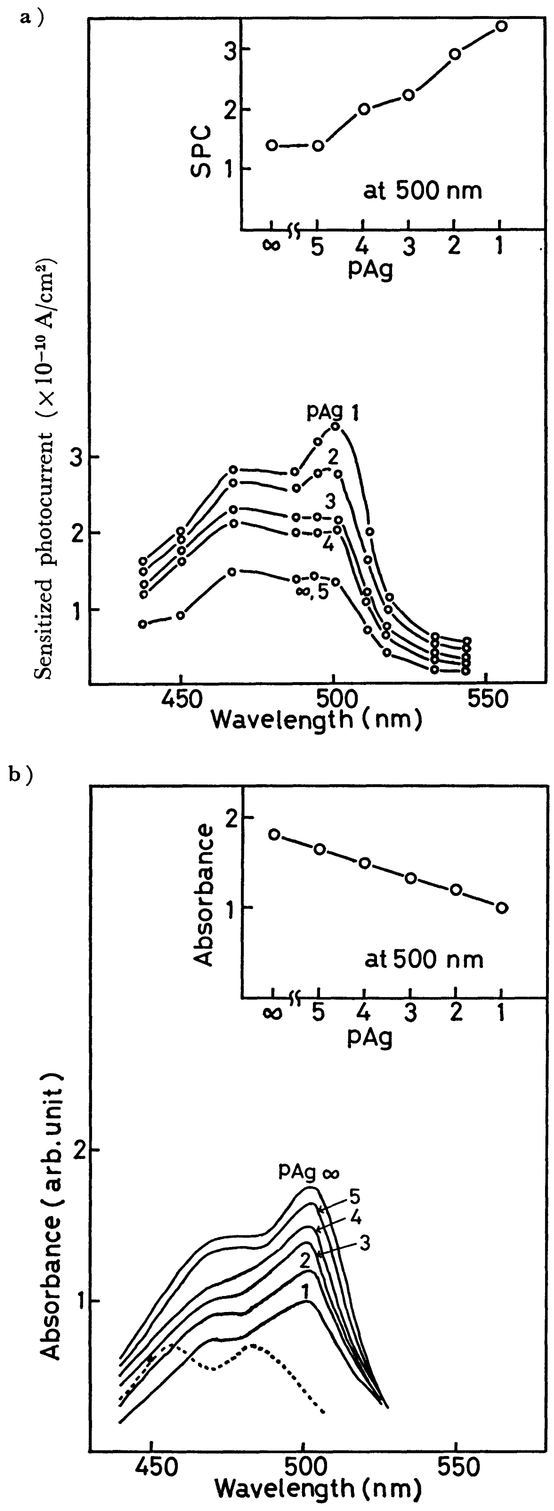

Fig. 5. Dye A characteristics (10^{-4} M dye in 0.04 M KNO_3 aqueous solution containing 5% methanol). a): pAg dependence of SPC, b): pAg dependence of absorption spectra, ——: adsorption to AgCl, ----: solution only.

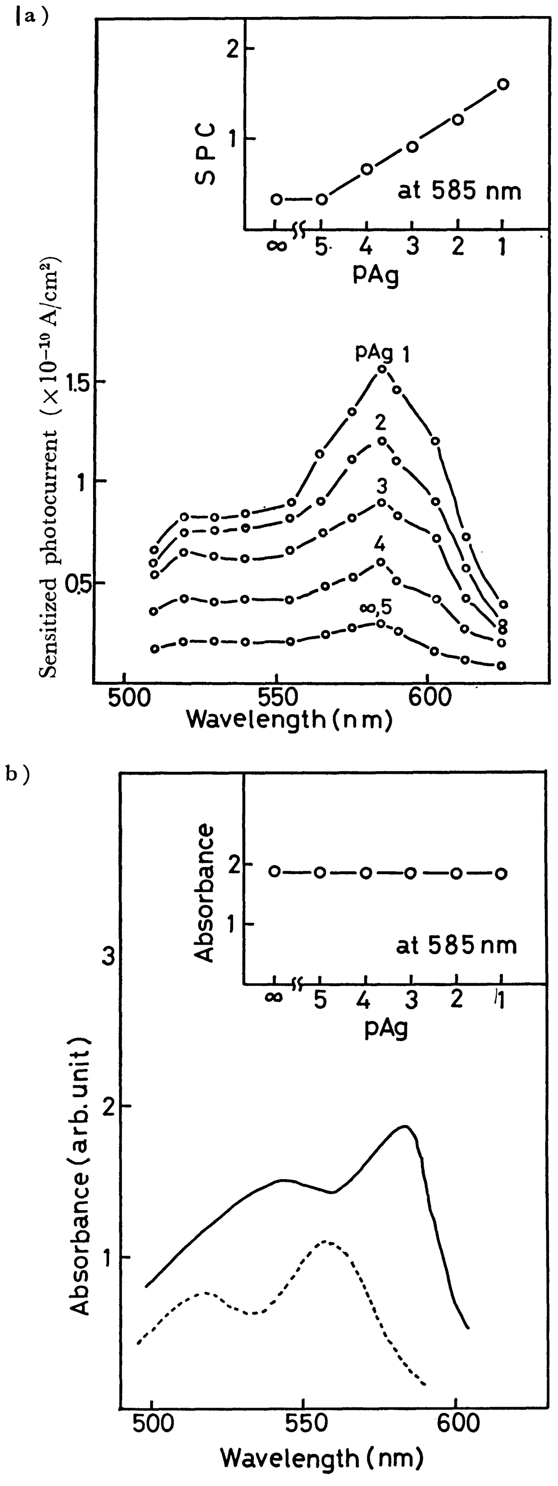

Fig. 6. Dye B characteristics (10^{-4} M dye in 0.04 M KNO_3 aqueous solution containing 5% methanol). a): pAg dependnence of SPC, b): pAg dependence of absorption spectra, ——: adsorption to AgCl, ----: solution only.

sorption only.

Levy[10] found that if AgX is brought into contact with silver, a print-out effect occurs, producing small silver specks absorbing light of *ca.* 585 nm wavelength. In our experiments, blank photocurrents were measured for 3 h, but almost no effect was detected at wavelengths of 500—700 nm. Thus it is concluded that the print-out effect due to silver paste does not influence SPC. The actual duration of SPC measurement including all processes was *ca.* 2 h.

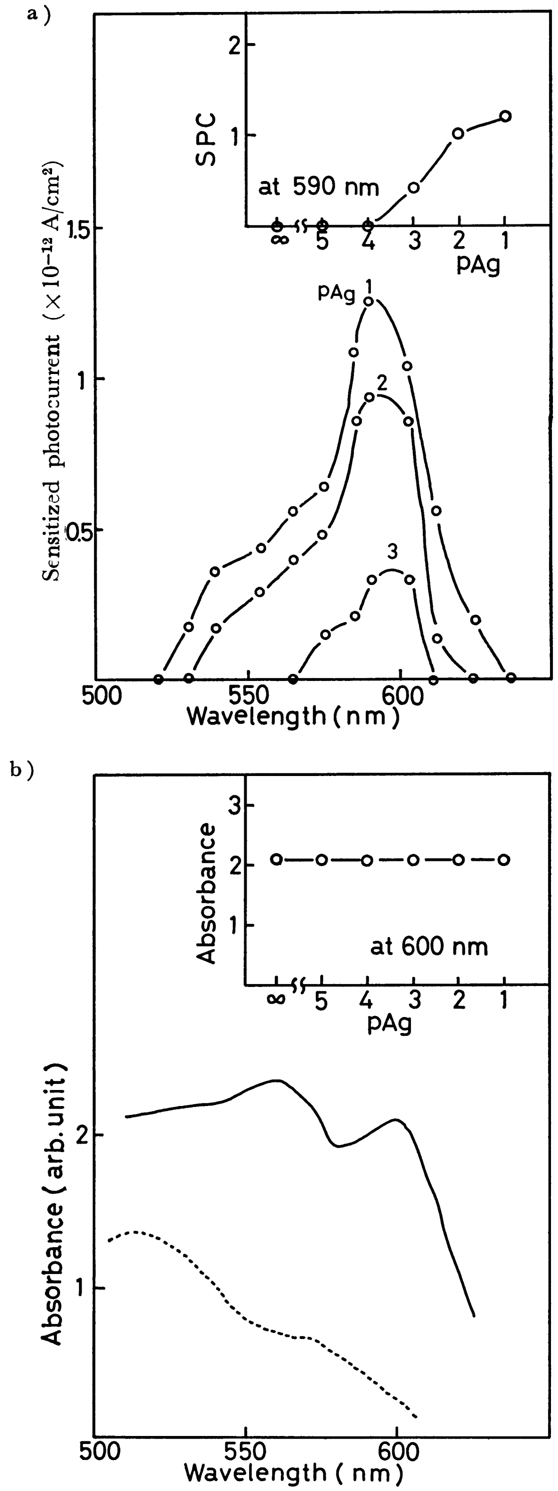

Fig. 7. Dye C characteristics (10^{-4} M dye in 0.04 M KNO_3 aqueous solution containing 15% methanol). a): pAg dependence of SPC, b): pAg dependence of absorption spectra ——: adsorption to AgCl, ----: solution only.

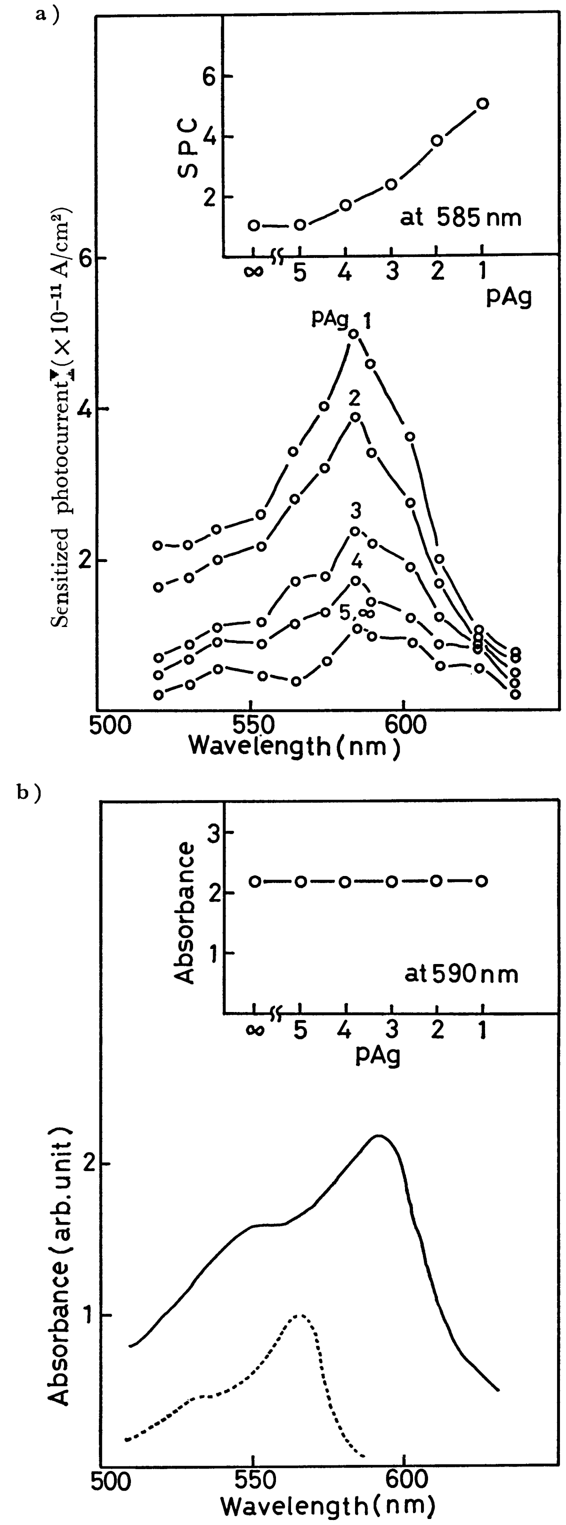

Fig. 8. Dye D characteristics (10^{-4} M dye in 0.04 M KNO_3 aqueous solution containing 35% methanol). a): pAg dependence of SPC, b): pAg dependence of absorption spectra ——: adsorption to AgCl, ----: solution only

Discussion

As shown in Figs. 5—8, the absorption spectra of dyes adsorbed to AgCl coincide with the SPC action spectra detected by the lock-in amplifier, showing that SPC indicates electron transfer from excited dyes to the conduction band of AgCl.[5,8] No dark currents based on interstitial Ag^+ ions could be detected with the lock-in amplifier at a light chopper frequency of 125 Hz.

However, in electrochemical studies using other semi-

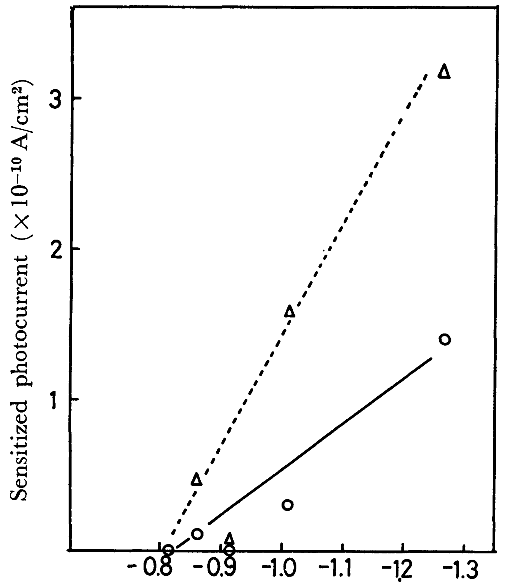

Fig. 9. Relation between SPC and reduction potential of sensitizing dyes.
----: at pAg 1, ——: at pAg ∞.

conductors such as ZnO,2) and TiO_2,3) SPC values exceeded 10^3 times of our values. This indicates that difficulty of movement of electrons from the excited dyes is due to resistance and electron traps in the AgCl. It is evident that this trait makes AgX most sensitive to light.

Since dye adsorption was restrained or not influenced by Ag$^+$ ions (Figs. 5—8) and the absorption peaks of adsorbed dyes did not change with lower pAg, the interaction between the dyes and Ag$^+$ ions can be neglected.5) Ag$^+$ ions and NO_3^- ions can not donate electrons to oxidized dyes because of their redox potentials.15) Therefore, the increase in SPC with lower pAg indicates a higher probability of electron transfer from excited dyes to the AgCl conduction band. Our results coincide qualitatively with those of the experiments of Gilman1) on emulsion systems.

Increase in the spectral sensitivity of dye A was reported to be only slightly dependent on Ag$^+$ ions.1) However, in our experiments, the SPC of dye A was greatly influenced by Ag$^+$ ions. Since the adsorption of dye A was reduced by Ag$^+$ ions even 5 min (Fig. 5b), it seems that the adsorption is reduced more in emulsion than in the electrochemical system so that the spectral sensitivity of the emulsion did not change.

Figure 9 shows the relationship between SPC and the reduction potential of sensitizing dyes;1) the higher the reduction potential, the larger the SPC. This finding indicates that the electron transfer mechanism is dominant in this system. Adsorption experiments, however, showed that there is not much difference among dyes in terms of absorbance; we suppose that the quantum efficiency in spectral sensitization is proportional to the SPC.

We measured the current due to electrons going through the conduction band of the AgCl. If Ag$^+$ ions at the surface of AgCl trap the electrons, and the electrons are excited to the conduction band by thermal energy, SPC should increase as pAg falls. At room temperature, however, thermal excitation energy is 20—30 mV, so we can neglect this thermal process. Since high-level electrons such as those in dye A can transfer smoothly to the conduction band, even temporary traps by Ag$^+$ ions bring about a decrease in SPC. Explanation of the Ag$^+$ ion effect by means of a subconduction band event does not seem feasible.

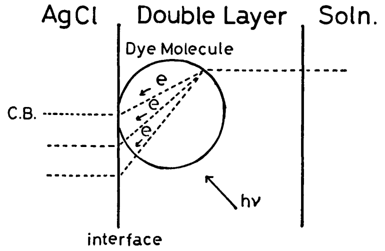

Fig. 10. Mechanism of Ag$^+$ ion effect.

Yaenicke,11) Leubner,12) and Berriman and Gilman7) considered that the Ag$^+$ ion effect arises from the potential shift of AgX. From the relationship between a potential shift of AgCl and SPC, Iwasaki *et al.*5) postulated that the Ag$^+$ ion effect is due to a band edge shift of AgCl. Usually a potential shift of a semiconductor is measured by the flatband potential using the Mott-Schottky relationship, but if the present experiment is conducted using an AgCl electrode, Ag$^+$ ions in electrolyte solution are deposited as silver at the AgCl surface, making quantitative measurement impossible. However, this effect can also be measured by adding Cl$^-$ ions.14)

The flatband potential of AgCl was found to shift cathodically with an increase in Cl$^-$ ions in the electrolyte solution. If Ag$^+$ ions were added, the flatband potential would shift anodically in contrast to Cl$^-$ ions. Since potential distribution through the dye molecules becomes steeper with lower pAg, the rate of electron transfer from the excited dye increase, the probability of the transfer becoming higher (Fig. 10).

This provides a particularly satisfactory explanation in the case of dye C (Fig. 7a). There is no overlap between the excited level of this dye and the AgCl conduction band at pAg 4 and above. At pAg 3 and below, overlap begins to occur due to the anodic potential shift, SPC becoming detectable.

Studies on the SPC change in TiO_2–pH3) and ZnO–pH2) systems by a potential shift of a semiconductor show that SPC increases by several powers of ten with lower pH. In our experiments, however, the increase was only a few times. This can be attributed to the small shift of potential of AgCl. In a CdS–S^{2-}, Cd^{2+} system,13) flatband potential shift differs according to the face index. However, since we have used no AgCl single crystal, it was impossible to determine its face index.

The recovery of blue desensitization6) by Ag$^+$ ions can also be explained by the potential shift. It was deduced that the electron transfer from the conduction band of the AgX to the dyes occurs with lower probability as a result of band edge shift.

Conclusion

1. The use of AgCl sheet crystal as a window of an electrochemical cell is very effective in the study of spectral sensitization. 2. The Ag$^+$ ion effect arises from the potential shift of AgX. 3. The electron transfer is the dominant mechanism in AgX spectral sensitization.

We would like to thank Dr. Paul B. Gilman, Jr., the Kodak Research Laboratory, for valuable dyes, and Dr. Tamotsu Iwasaki and Dr. Kiminori Itoh of our laboratory for their useful suggestions.

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