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# Effect of $Cl^-$ and $Br^-$ Ions and pH on the Flatband Potentials of Silver Halide Sheet Crystal Electrodes

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Flatband potential ($E_{fb}$), which coincides with the Fermi level in energy, was determined for AgCl and AgBr electrodes by electrochemical measurement of the capacitance of the space charge layer of a semiconductor in contact with a solution. The values of $E_{fb}$ for both AgCl and AgBr electrodes in an electrolyte solution were $-4.8$ V *vs.* vacuum. The energy levels of the electrodes could be determined from this value. The behavior of the AgCl electrode is somewhat like an n-type semiconductor, and that of the AgBr electrode very much like an intrinsic semiconductor. The $E_{fb}$ values for the AgCl and AgBr electrodes change cathodically in electrolyte solutions with $Cl^-$ and $Br^-$ ions, respectively, but not with $H^+$ or $OH^-$ ions. This seems to be associated with the $Ag^+$ ion effect in spectral sensitization. It is concluded that the $Ag^+$ ion effect arises from a downward shift of the band edge of silver halides.

Studies are in progress on silver halides (AgX), major constituents of photographic emulsions, with respect to such problems as the number of silver atoms needed to form the minimum latent image,1) and whether the ionic2) or the electronic process3) comes first in latent image formation. Positions of the conduction and valence bands are important for semiconductors, but, the data given by investigators for AgX differ as much as 0.1 V.4–7)

Only a few papers have appeared on the Fermi energy level of AgX. Williams *et al.*8) analyzed ultraviolet photoemission and reported energy differences between the Fermi energy level and the top of the valence band, 1.7 eV for AgCl, 1.2 eV for AgBr, and 1.1 eV for AgI. They determined the energy differences but not the positions of the Fermi energy levels of AgX *vs.* a reference electrode. In this study, the positions of the Fermi energy level for Ag/AgX/solution electrodes (X=Cl and Br) were determined *vs.* a saturated caromel electrode (SCE) as the flatband potential ($E_{fb}$) by electrochemical measurement of the capacitance of the space charge layer of a semiconductor in contact with a solution. The positions thus obtained seem to be useful for the electrochemical study of AgX.

Wagner9) and Matejec10) investigated the conductance of AgX (X=Cl, Br, and I) under various halogen pressures and found that there are many more electrons than holes for AgCl and somewhat more for AgBr in contact with silver at room temperature. Other investigators11–13) reported that silver halides are n-type or p-type semiconductors. However, from the results of $E_{fb}$ measurements, we have found the properties of AgCl and AgBr electrodes to be n-type and intrinsic semiconductors, respectively.

The spectral sensitivity of a photographic emulsion increases as the pAg (pAg$=-\log[Ag^+]$) decreases. The $Ag^+$ ion effect was explained by Gilman,5) and Collier and Gilman14) in terms of subconduction band event, $Ag^+$ ions on the AgX surface acting as an electron trap. Iwasaki *et al.*15) found that the sensitized photocurrent due to the electron injection from a photoexcited sensitizing dye increases with lowering of the pAg of the electrolyte solution. They concluded that the $Ag^+$ ion effect results from the anodic band edge shift of the AgCl electrode. Thus, the band edge shift due to $Ag^+$ ions seems to be important for clarifying the mechanism of the $Ag^+$ ion effect. The band edge shift of AgX could be determined by measuring $E_{fb}$. The $Ag^+$ ion effect was also investigated from the result of $E_{fb}$ measurement.

## Basic Principle

In the electrochemistry of semiconductors, the $E_{fb}$ value is important for determining their energy levels and studying their electrode reactions. The relation between the capacitance of the space charge layer ($C_s$) and the surface potential ($\Delta\Phi_s$) is as follows.16,17)

$$C_s = \frac{\varepsilon\cdot\varepsilon_0}{L}\,\frac{|y(e^{-V_s}-1)-y^{-1}(e^{+V_s}-1)|}{[y(e^{-V_s}-1)+y^{-1}(e^{+V_s}-1)+(y-y^{-1})V_s]^{1/2}} \quad (1)$$

where

$$y=\left(\frac{P_0}{N_0}\right)^{1/2},\ V_s=\frac{e_0\cdot\Delta\Phi_s}{k\cdot T},\ L=\left(\frac{\varepsilon\cdot\varepsilon_0\cdot k\cdot T}{2\cdot N_i\cdot e_0{}^2}\right)^{1/2},$$
$$\Delta\Phi_s=\Phi_s-\Phi_i,$$

and $\varepsilon$=dimensionless dielectric constant of semiconductor, $\varepsilon_0$=dielectric constant of the vacuum, $P_0,N_0$= equilibrium concentration of holes and electrons in bulk of semiconductor, $k$=Boltzmann constant, $T$=absolute temperature, $e_0$=elementary charge, $N_i=\sqrt{P_0\cdot N_0}$, $\Phi_s$=potential of semiconductor surface, and $\Phi_i$= potential of semiconductor bulk. When $\Delta\Phi_s$ and $1/C_s^2$ are represented by abscissa and ordinate, respectively, curves can be obtained depending on the values of $y$, $\varepsilon$, and $N_i$. The potential at which $\Delta\Phi_s$ becomes zero is $E_{fb}$. The value of $\Delta\Phi_s$ shows the potential difference between the bulk and the surface of a semiconductor, not directly showing the potential *vs.* reference electrode. This can be altered by changing the potential of a semiconductor bulk which can be changed by the electrode potentials ($E$) *vs.* reference electrode. The value of $E_{fb}$ can be determined from the shape of the $1/C_s^2-E$ curve with respect to a reference electrode.

Equation 1 can be applied to n-type, intrinsic, and p-type semiconductors. However, it is so complicated that it is not generally used for n- or p-types. In the case of a highly doped n-type (or p-type) semiconductor, Eq. 1 can be simplified to the Mott-Schottky relationship:

$$\frac{1}{C_s^2} = \frac{2}{\varepsilon\cdot\varepsilon_0\cdot e_0\cdot C_D}\left(\Delta\Phi_s - \frac{k\cdot T}{e_0}\right), \qquad (2)$$

where $C_D$ = the donor concentration of an n-type semiconductor or the acceptor concentration of a p-type. It is significant that the plots of $1/C_s^2$ *vs.* $\Delta\Phi_s$ or ($E$) derived from Eq. 2 are linear. The donor (acceptor) concentration can be calculated from the slope, giving the concentration of impurity added to the semiconductor. The potential where $1/C_s^2$ nearly approaches zero is $E_{fb}$ in Eq. 2, the slope of the $1/C_s^2-E$ curve being upward for an n-type semiconductor and downward to the right for a p-type.

## Experimental

The methods of crystal preparation were the same as before,[18] except that the melting temperature was 455 °C for the AgBr crystal.

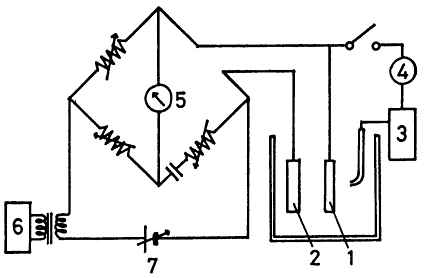

Fig. 1. Capacitance bridge circuit.
1: AgX electrode, 2: Pt counter-electrode, 3: SCE, 4: Voltmeter, 5: Null detector, 6: Oscillator (1 kHz), 7: Dry cells.

One side of the sheet crystals (diameter: 10 mm) was fastened to a lead wire with silver paste and to a glass spatula with epoxy resin, the electrodes prepared being left to stand overnight. The other surface was then etched with 1 M (1 M= 1 mol dm$^{-3}$) KCN for 5 min and washed thoroughly with distilled water. The AgX electrodes were immersed in electrolyte solutions of various compositions, $C_S$ being measured by means of the capacitance bridge circuit shown in Fig. 1. The electrode potential *vs.* SCE was controlled by dry cells. During the course of measurements, contact to the voltmeter was cut to exclude extraneous capacitances. All experiments were carried out in a darkroom at room temperature. The electrolyte solutions were not deoxygenated. In addition to $C_S$, electrochemical cells also have counter electrode capacitance and Helmholtz layer capacitance, but they can be disregarded.

## Results and Discussion

*AgCl Electrode.* $1/C_s^2$ is plotted against the electrode potential *vs.* SCE for the AgCl electrode in 0.1 M KCl aqueous solution (Fig. 2). The linearity of the plots shows that the Mott-Schottky relationship (Eq. 2) holds for AgCl. The $E_{fb}$, the potential where $1/C_s^2$ is close to zero, was 0.0 V *vs.* SCE, the value showing the position of the Fermi energy level of the AgCl electrode in 0.1 M KCl aqueous solution. The value of $kT/e_0$ in Eq. 2 is about 26 mV at room temperature, not being considered significant in comparison with the data of other investigators. Since the $1/C_s^2$ value increases with anodic polarization, the AgCl electrode can be considered as an n-type semiconductor. Assuming that $\varepsilon$ of AgCl is 11.2[19] and the roughness factor of the electrode surface is 1, the donor concentration ($C_D$ in Eq. 2) can be calculated from the slope to be $1.7\times10^{13}$, much smaller than the values for other perfectly n-type semiconductors (*e.g.*, $10^{16}$—$10^{17}$ for ZnO[20]). Though reproducibility was poor for the slope, it was good for $E_{fb}$. It seems that the $C_D$ of the AgCl electrode shows either the concentration of interstitial silver ions or of divalent cation impurities.

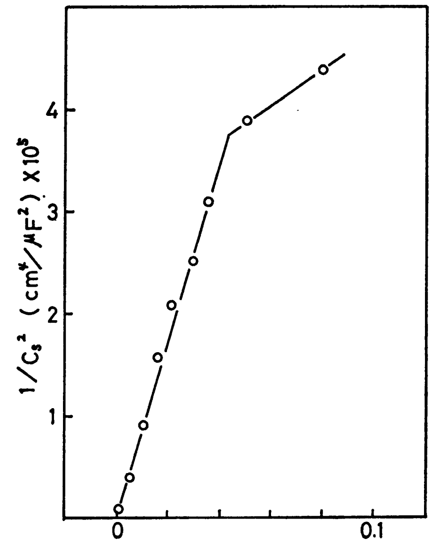

Fig. 2. Mott-Schottky plot for the AgCl electrode in 0.1 M KCl aqueous solution.

The energy level of AgCl obtained from $E_{fb}$ is shown in Fig. 3. The Fermi energy level *vs.* vacuum was determined in this work to be −4.8 eV. It should be noted that an energy of −4.5 eV vacuum is found to be equivalent to 0.0 eV *vs.* a standard hydrogen electrode.[21] The energy difference of 1.7 eV between the valence band and the Fermi energy level reported by Williams *et al.*[8] gives the position of the valence band. The band gap of 3.1 eV was determined from the average values of other investigators,[4-7] giving the position of the conduction band. Despite the simplicity of the method the energy levels we obtained coincide approximately with those of the other investigators.

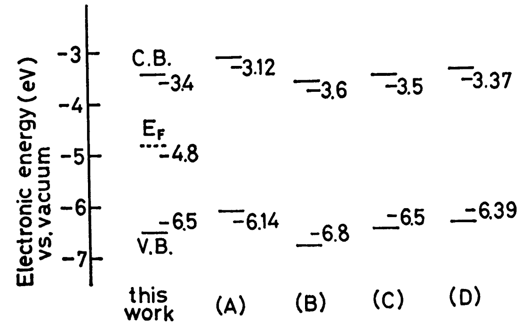

Fig. 3. Energy level of the AgCl electrode obtained from the flatband potential, C.B.: conduction band, V.B.: valence band, $E_F$: Fermi energy level, (A): Berry,[7] (B): Brown,[4] (C): Peterson,[6] (D): Gilman.[5]

The position of the Fermi energy level is slightly higher than the mid-point between the conduction and the valence bands (Fig. 3). In the case of a highly doped n-type semiconductor, the position of the Fermi energy level is almost identical to that of conduction band. We see that the AgCl electrode behaves like an n-type semiconductor. This coincides qualitatively with Wagner's findings that electrons are majority carriers for AgCl in contact with silver at room temperature.[9,10] Thus the conclusion that AgCl behaves like an n-type semiconductor was derived by studies of an Ag/AgCl/solution electrode, the AgCl crystals contained in photographic emulsions not being an n-type but an intrinsic semiconductor.

The position of the conduction band obtained (Fig. 3) seems to be of great importance for studies of the spectral sensitization by electrochemical methods. The relation between sensitized photocurrents and the lowest vacant levels of sensitizing dyes was also investigated electrochemically.[18] The position of the AgCl conduction band at −3.4 eV *vs.* vacuum is also supported by the result that the sensitization of AgCl was initiated by the sensitizing dye having the lowest vacant level from −3.52 to −3.61 eV *vs.* vacuum.

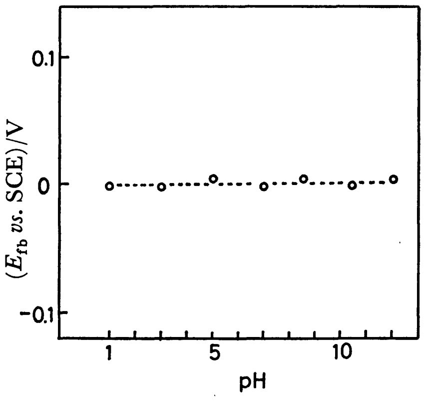

Fig. 4. pH dependence of the flatband potential ($E_{fb}$) of AgCl in 0.1 M KCl aqueous solution, pH control using HCl or KOH.

The $E_{fb}$ of AgCl was measured in 0.1 M KCl aqueous solutions having different pH adjusted by the addition of HCl or KOH. As shown in Fig. 4, neither $H^+$ nor $OH^-$ ions affect the $E_{fb}$, indicating that the band edeg of AgCl does not change with $H^+$ or $OH^-$ ions, and that the photocurrent sensitized by a sensitizing dye is not dependent on the pH of electrolyte solution.[15]

$E_{fb}$ was also measured with various concentrations of $Cl^-$ ion (Fig. 5), and was found to shift cathodically with an increase in $Cl^-$ ions. In order to make a comparison with the $Cl^-$ ion effect on $E_{fb}$, current-potential curves were measured at various concentrations of $Cl^-$ ion, and the relation between zero-current potential ($E_z$) and the concentration of $Cl^-$ ion was plotted (Fig. 6). Measurements of photocurrent were carried out under illumination from a 500 W Xe lamp without filter. The photocurrent was measured while increase in current occurring when the AgCl electrode was exposed to the light. The photocurrent was about one-tenth of the dark current. The $E_z$ value coincided well with the $E_{fb}$ measured in 0.1 M KCl.

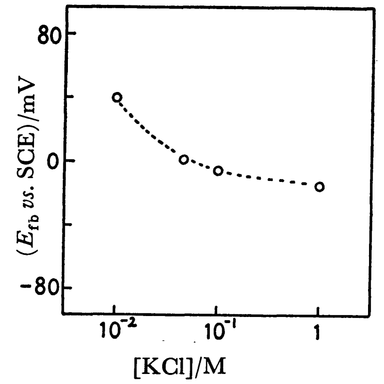

Fig. 5. $Cl^-$ ion dependence of the flatband potential ($E_{fb}$) of AgCl.

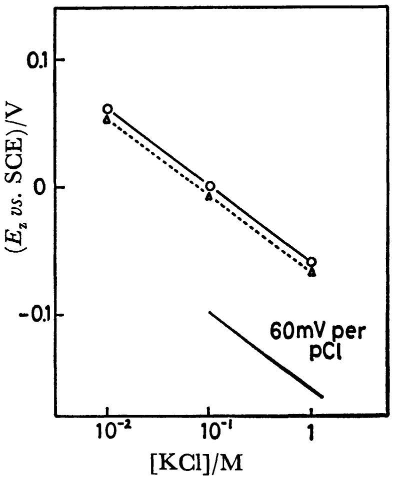

Fig. 6. $Cl^-$ ion dependence of the zero-current potential ($E_z$) of AgCl, —○—: dark current, ···▲···: photocurrent.

Thus taking into consideration the following electrochemical reactions of $Ag/AgCl/Cl^-$

$$AgCl(s) \rightleftarrows Ag^+ + Cl^- \tag{3}$$

$$Ag^+ + e \rightleftarrows Ag(s) + Cl^- \tag{4}$$

$$AgCl(s) + e \rightleftarrows Ag(s) + Cl^- \tag{5}$$

and making use of the Nernst equation, we have for the shift of electrode potential $\Delta E$,

$$\Delta E = \text{const} + \frac{RT}{F}\ln\frac{a(Ag(s))}{a(AgCl(s))} + \frac{2.3RT}{F}\text{pCl} \tag{6}$$

where AgCl(s) = solid AgCl, Ag(s) = solid Ag, e = electron, $R$ = gas constant, $F$ = Faraday constant, $a$( ) = activity, and pCl = −log [$Cl^-$]. Equation 6 suggests that an electrode potential shift of *ca.* 60 mV (2.3 $RT/F$) per unit on the pCl scale should be detected. Though the shift per pCl is *ca.* 60 mV for $E_z$ (Fig. 6), it is about 30 mV for $E_{fb}$ (Fig. 5). Mobile interstitial $Ag^+$ ions seem to be associated with the difference in the shifts in $E_{fb}$ and $E_z$. The band edge of AgCl shifts cathodically with an increase in the concentration of $Cl^-$ ion.

The $Cl^-$ ion effect on the band edge of AgCl can be considered as a reverse effect of the $Ag^+$ ion effect on the band edge of AgCl. However, the effect could not be measured directly since the $Ag^+$ ions in the electrolyte solution were deposited as silver on the surface of the AgCl electrode when concentrated $AgNO_3$ solution was added to the solution. Iwasaki *et al.*[15] reported that with increase in $Ag^+$ and $Cl^-$ ions, the equilibrium potential of the AgCl electrode shifts anodically and cathodically, respectively. Minoura *et al.*[22] reported that with an increase in $S^{2-}$ and $Cd^{2+}$ ions, the $E_{fb}$ of CdS shifts cathodically and anodically, respectively. Since the constituent ions of AgCl are $Ag^+$ and $Cl^-$, we might presume that $E_{fb}$ of the AgCl electrode also shifts cathodically and anodically with the addition of $Cl^-$ and $Ag^+$ ions, respectively. The anodic shift of the band edge gives rise to an increase in electron injection from excited sensitizing dyes,[15,18] the cathodic shift decreasing. The $Ag^+$ ion effect on spectral sensitization (Fig. 7) can be explained in terms of a band edge shift of the AgCl electrode.[15,18]

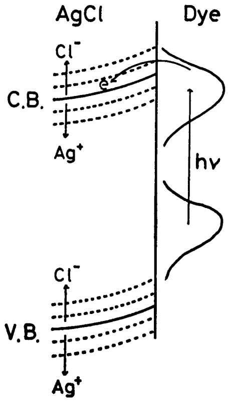

Fig. 7. Scheme of the $Ag^+$ and $Cl^-$ ion effect in spectral sensitization, C.B.: conduction band, V.B.: valence band, e: electron.

Watanabe *et al.*[23] found a phenomenon similar to the $Ag^+$ ion effect, using $TiO_2$ electrode and electrochemical techniques. The sensitized photocurrent increased with decrease in the pH of the electrolyte solution. This was attributed to the shift in the $E_{fb}$ of $TiO_2$ due to $H^+$ ions in the electrolyte solution.

*AgBr Electrode.* The capacitance of the space charge layer of AgBr electrodes was measured by the same procedure as for the AgCl electrode. Since the $1/C_s^2-E$ plots for AgBr were not linear, Eq. 1, which can be adapted to intrinsic semiconductors, was used instead of Eq. 2. The value of $y$ in Eq. 1 was varied from $10^{-10}$ to $10^{10}$ and the theoretical $1/C_s^2-E$ curves were calculated. The capacitances were calculated on the assumption that $\varepsilon\cdot\varepsilon_0/L$ equals 1, because the $N_i$ of the AgBr used was unknown and the value of $\varepsilon\cdot\varepsilon_0/L$ does not change the shape of $1/C_s^2-E$ curve. Equation 1 can be considered to be adapted to AgBr, if the shape of the theoretical curve resembles that of the experimental one.

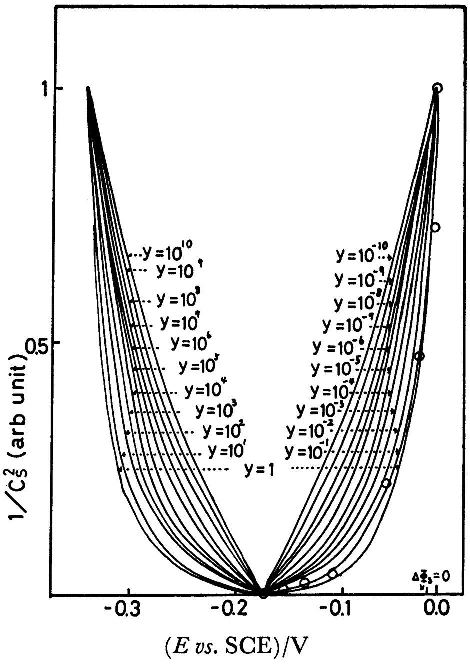

Fig. 8. $1/C_s^2-E$ plot for the AgBr electrode in 0.1 M KBr aqueous solution, ——: theoretical curve, ○: measured values.

Figure 8 shows the theoretical $1/C_s^2-E$ curves ($y=10^{-10}$—$10^{10}$) and the experimental values measured in 0.1 M KBr aqueous solution. Since the potential at which $1/C_s^2$ is closest to zero is $-0.17$ V *vs.* SCE by measurement, the theoretical curve at which $1/C_s^2$ is closest to zero was based at $-0.17$ V. The $1/C_s^2$ of both theoretical and measured values were normalized to 1 at 0.00 V *vs.* SCE when $y<1$, and at $-0.34$ V when $y>1$, since the change in $C_s$ was found only at potential more negative than 0.00 V *vs.* SCE. The experimental values coincide with the curve of $y=10^{-1}$ (Fig. 8). Not all AgBr electrodes, however, agree with the theoretical curve. More precise value than $y=10^{-1}$ could not be determined. The $E_{fb}$ value of the $y=10^{-1}$ curve, $\Delta\Phi_s=0$, was $-0.01$ V *vs.* SCE, and not $-0.17$ V. The $E_{fb}$ of the AgBr electrode was concluded to be 0.0 V *vs.* SCE. The value for $y=10^{-1}$ coincides with that reported by Wagner[9] and others,[10] who suggested that the number of electrons is $10^1$—$10^2$ times the number of holes when AgBr is brought into contact with silver at room temperature.

Figure 9 shows the energy level of the AgBr electrode

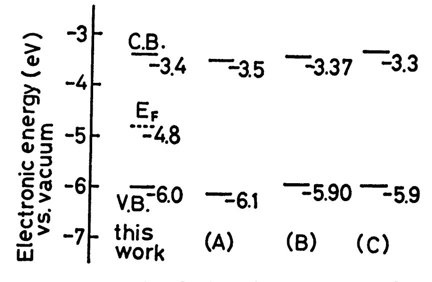

Fig. 9. Energy level of the AgBr electrode obtained from the flatband potential, C.B.: conduction band, V.B.: valence band, $E_F$: Fermi energy level, (A): Brown,[4] (B): Gilman,[5] (C): Berry.[7]

obtained from $E_{fb}$. The potential *vs.* vacuum was determined by Lohmann's value[21] as AgCl electrode. An energy difference 1.2 eV between the Fermi energy level and the valence band of AgBr was reported by Williams *et al.*,[8] giving the position of the valence band. The band gap, 2.6 eV, was determined by averaging the values of the other investigators,[4,5,7] giving the position of the conduction band. The positions of the conduction and valence bands we obtained coincide with those of other investigators.

AgBr electrode behaves almost like an intrinsic semiconductor, since the Mott-Schottky relationship could not be used for AgBr, the Fermi energy level being almost midpoint between the conduction and valence bands.

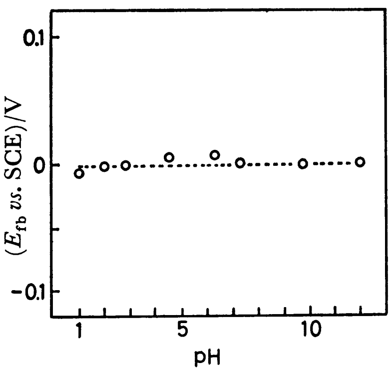

Fig. 10. pH dependence of the flatband potential ($E_{fb}$) of AgBr in 0.1 M KBr aqueous solution, pH control using HBr or KOH.

The $E_{fb}$ value of the AgBr electrode, like that of the AgCl electrode, was not affected by $H^+$ or $OH^-$ ions (Fig. 10). The sensitized photocurrent is expected to remain unchanged by $H^+$ or $OH^-$ ions in electrolyte solution.

Figure 11 shows the $Br^-$ ion dependence of $E_{fb}$. The $E_{fb}$ shifts cathodically with an increase in $Br^-$ ions, the slope being *ca.* 20 mV per pBr. The relation of $E_z$ to $Br^-$ ion concentration is shown in Fig. 12. The potentials of both photocurrents and dark currents shift cathodically with falling pAg. The photocurrents were measured as the increase in current during the course of illumination. The potential difference between dark and photocurrents at a given concentration of $Cl^-$ ion was based on the Dember effect, both slopes being *ca.* 60 mV per pBr. These phenomena can be explained by means of an equation similar to (6). The $Br^-$ ion effect on the potentials suggest that sensitized photocurrent would decrease with falling pBr.

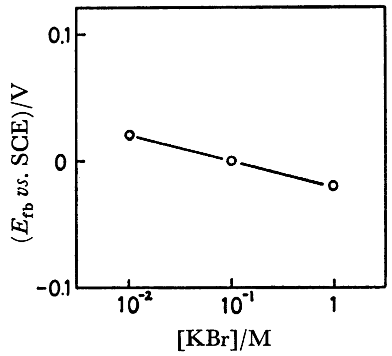

Fig. 11. $Br^-$ ion dependence of the flatband potential ($E_{fb}$) of AgBr.

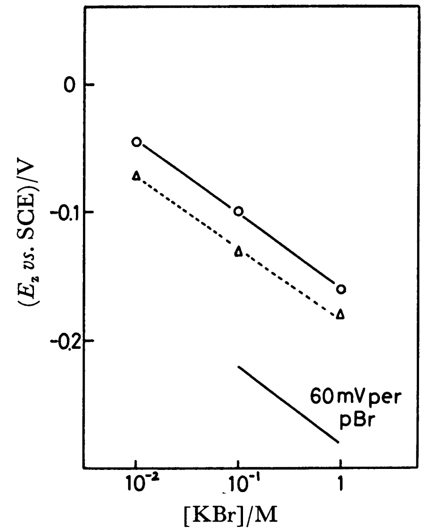

Fig. 12. $Br^-$ ion dependence of the zero-current potential ($E_z$) of AgBr, —○—: dark current, ···△···: photocurrent.

The $Ag^+$ ion effect in spectral sensitization is due to the anodic shift of the AgBr band edge as in the case of AgCl, since the sensitized photocurrent increases with decreasing pAg and decreases with decreasing pBr.

## Conclusion

1. The flatband potentials of both AgCl (in 0.1 M KCl) and AgBr (in 0.1 M KBr) are 0.0 V *vs.* SCE, and the AgCl electrode behaves somewhat like an n-type semiconductor, while the AgBr electrode behaves almost like an intrinsic semiconductor.
2. The flatband potentials of AgCl and AgBr are affected by $Cl^-$ and $Br^-$ ions, respectively, in electrolyte solution. In both cases, the flatband potentials shift cathodically with an increase in halide ion concentration.
3. The effects of $Cl^-$ ion and $Br^-$ ion can be considered as a reverse effect of the $Ag^+$ ion. The $Ag^+$ ion effect in spectral sensitization is due to the anodic shift of the AgX band edge.

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