

Photoconduction of Alkali-halide Crystals which adsorb Dyes

By

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1. Introduction

It is well known that the adsorption of certain dyes on the surface of silver-halide crystals extends the spectral region of photo-chemical reactions towards the red and even into the infra-red. In practice, this principle has been applied to photographic emulsion and remarkable progress has been made in this field. The fundamental interpretation of this phenomenon was only given on a general idea by R. W. Gurney (1) and others. Recently it has been ascertained experimentally that the maximum of photographic sensitivity of dyed emulsion coincides with that of absorption of those dyes in adsorbed states, and that it moreover coincides with regions of photo-conductive effects of dyed silver-halides (2, 3).

Since all these experiments, spectroscopic or photo-effective, were carried out on powdered sample, the results obtained are not always sufficient for theoretical considerations. Obviously it seems better to carry out these experiments on large single crystals of silver-halide. But, since these were not obtained when our investigations started, artificial single crystals of rock-salt (4) were used in our experiment as the adsorbent, on which effective dyes were adsorbed, and photo-sensitized photoelectric effects appearing from this adsorption were studied. It has been found that all the facts found in silver-halide emulsion occur also in rock-salt. Thus, our interpretation of photo-sensitizing mechanism can stand on more concrete idea.

2. General principle

Dicyanine-A (E. Merck), Kryptocyanine, Phenosafranine (Fuji Photo.) were used as photo-sensitizing dyes. Artificial single crystals of rock-

salt prepared in our laboratory were used as the adsorbent. Absorption spectra of the photo-sensitizing dyes solved in absolute methyl alcohol (E. Merck) and in distilled water were measured and these spectra were compared with those of dyes which were adsorbed on rock-salt. The adsorption was effected by subliming dye molecules upon the surface of a rock-salt plate by means of evaporation in vacuum. It was noticed that the absorption maxima in adsorbed state was shifted towards the long wave-length side. Then the spectral sensitivity of photo-conductive effect of the rock-salt crystal which adsorbed these dyes, was measured. It was found that these photo-conductive regions almost coincide with the shifted absorption maxima of dyes adsorbed on rock-salt crystals (3).

The spectral sensitivity of photo-electric effect of these dyes were measured and the distance of electronic energy levels between stable state and zero-state of those dyes were determined. The photo-electric effects of rock-salt crystals containing F-centers were also measured and rough estimations of differences of electronic energy levels between ground state and zero state of F-centers were made. Thus, correlations of electronic energy levels between rock-salt and these dyes can be obtained.

If use is made of these correlations of electronic energy levels, relations between conduction levels of rock-salt and the lowest excited levels of these dyes can be obtained and mechanism of sensitized photo-conduction may be considered.

3. Experimental results

(1) Absorption of dyes in solution and in adsorbed states.

Absorption spectra of photo-sensitizing dyes solved in methyl alcohol and in water respectively were measured using a monochromator provided with a concave grating of 1 m. focus and a photo-cell (PG-65-G; Mazda) with an amplifier of DuBridge's type (6) using UX-54 tube. A 750 watt tungsten-filament projection lamp was used as a light source. The output of the amplifier was connected to the galvanometer (sensitivity: 10^{-10} Amp.) and its deflection was read by a scale 4 m. apart from the galvanometer. This arrangement can be used for the measurement of currents by about 10^{-14} Amp.

In order to investigate the absorption of these dyes in adsorbed state, dyes were evaporated in thickness of about 500 m μ on a rock-salt plate in vacuum and the absorption was measured.

TABLE 1. Absorption of dyes (Unit: $m\mu$)

| Dyes | Band | in Water | in Alcohol | on Rock-salt | λ |
|-----------------|----------|----------|------------|--------------|-----------|
| Dicyanine-A | α | 650 | 660 | 690 | 30 |
| | β | 580 | 615 | 638 | 23 |
| Krypto-cyanine | α | | 705 | 725 | 20 |
| | β | | | 665 | |
| | γ | | | 601 | |
| Pheno-safranine | α | | 558 | 590 | 32 |
| | β | | 528 | 548 | 20 |

Wave-lengths of maximum absorption are shown in Table 1. Shifts (λ) may be noticed in adsorbed states towards the long wave-length side in comparison with those of solution and their values decrease gradually as the thickness of dyes increases larger than 1μ .

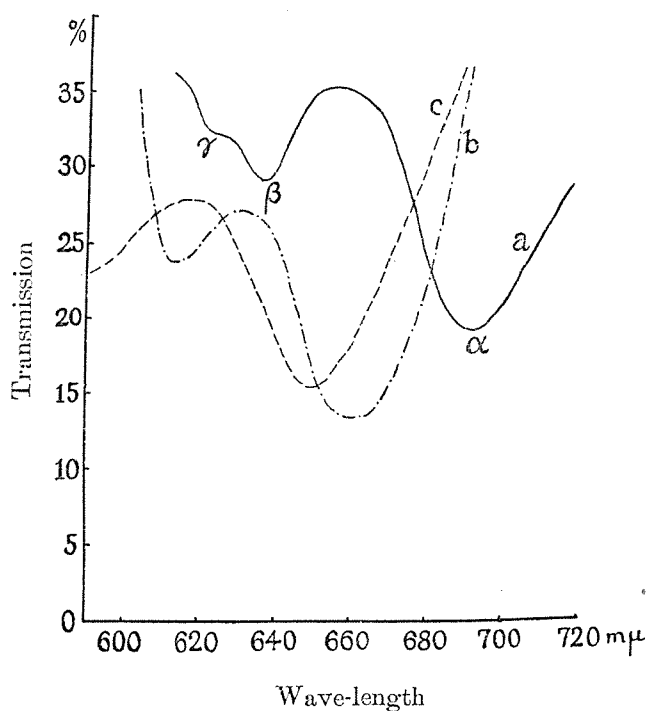


Fig. 1. Absorption curves of Dicyanine-A
a; on Rock-salt, b; in Alcohol, c; in Water.

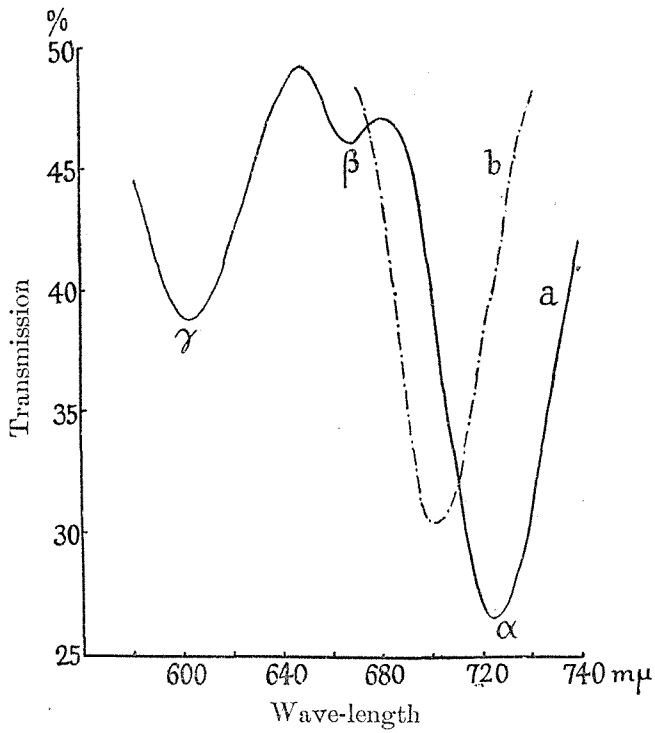


Fig. 2. Absorption curves of Kryptocyanine. a; on Rock-salt, b; in Alcohol.

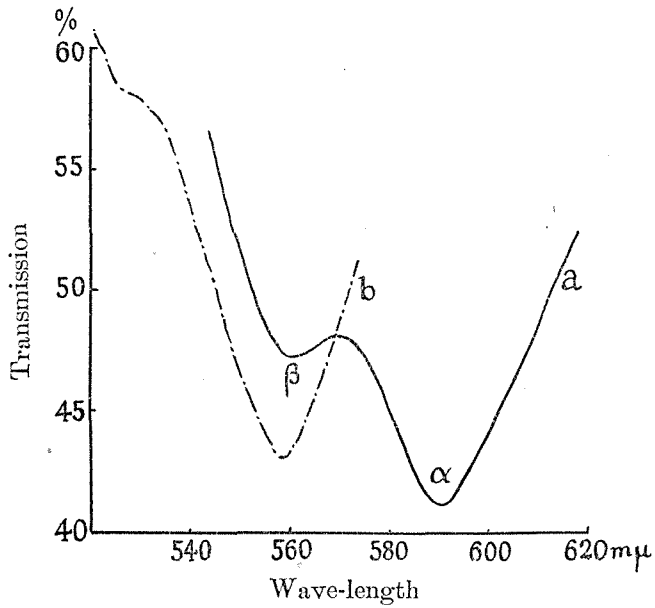


Fig. 3. Absorption curves of Phenosafranine. a; on Rock-salt, b; in Alcohol.

(2) Photo-conductive effects

Spectral sensitivity of photo-conductivity of rock-salt crystals which adsorbed these dyes, were measured by the arrangement shown in Fig. 4. In this case, suitable filters were used instead of the above-mentioned grating monochromator, since intensities of light transmitted through the monochromator were too weak. A 750 watt projection lamp was set 30 cm. apart from the sample (D) and various filters were inserted between the lamp and samples successively. A photo-current produced in the dyed crystal (N) was

led to the same amplifier used in the absorption experiment. The dark resistance of rock-salt crystals was found to depend on the humidity of the surrounding atmosphere, and the ease of measurement of the photo-currents depended on this resistance. As very low humidity was associated with high crystal resistance, a desiccative (A) was inserted inside the measuring apparatus and the electric resistance of the crystal was maintained to $10^{14} \sim 10^{15} \Omega/\text{cm}$. Since our measurements were performed at about 25°C , the amplifier was balanced initially to keep off the effects of electrolytic currents by these thermal influences.

As the width and coefficient of transmission bands are independent among each filter, photo-currents measured through these filters do not show absolute spectral sensitivity. Absolute amounts of energy of the light transmitted through these filters set in the position of the samples were measured by means of Moll's micro-thermopile which was calibrated against a standard Hefner lamp (7), the energy of Hefner lamp at 1 m. distance per cm^2 being $22.6 \times 10^{-6} \text{ cal/sec.} (= 9.46 \times 10^2 \text{ erg/sec.})$. But, in our arrangement, the thermopile used produced $1.252 \times 10^{-5} \text{ V}$ which corresponded to $6.386 \times 10^{-6} \text{ cal/sec} = 2.763 \times 10^2 \text{ erg/sec}$ considering its receiving area.

From these relations, photo-currents in the case when a unit energy is transmitted through each filter, may be calculated and spectral regions showing photo-current may be deduced. This is shown in Table 2. It is seen that photo-current increases in the regions of the filters VR1 and VR2 corresponding to the region of absorption bands α and β of Dicyanine-A in adsorbed states.

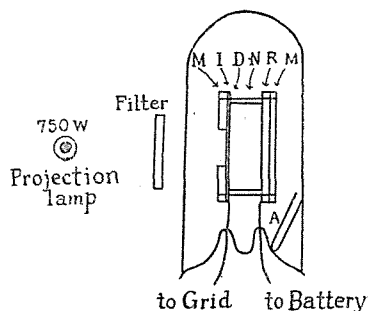


Fig. 4. Apparatus measuring photo-conductive currents.

M; metal plate, I; mica insulator, D; dyes, N; rock-salt crystal, R; rubber, A; desiccative.

TABLE 2. Photo-conductive effect of rock-salt which adsorbs Dicyanine-A

| Filters | Mazda | | | | Wratten 740 | |
|-------------------------------------|-------|------|------|------|----------------|---|
| | VB1 | VG1 | VR2 | VR1 | | |
| Energy transmitted through filters | 687 | 702 | 1962 | 1526 | 1461 | 10^2 erg/sec. |
| | 1962 | 3290 | 9198 | 7154 | 6847 | μ V/sec. |
| Rock-salt which adsorbs Dicyanine-A | 2 | 2 | 20 | 20 | 5 | Direct reading of galvanometer: 10^{-10} A. |
| | 9.4 | 5.6 | 20 | 25.7 | 6.7 | Relative amount of photo-current. |
| Photo-current | 2 | 2 | 20 | 20 | 5 | Absolute photo-current: 10^{-14} A. |

(3) Photo-electric effects

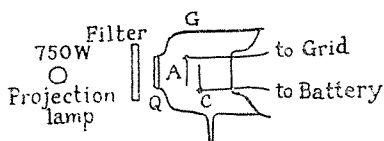


Fig. 5. Apparatus measuring photo-electric currents.

A; anode (molybdenum wire), C; cathode (silver plate coated with dyes), Q; quartz plate, G; glass bulb.

system was put in a glass bulb (G) which was evacuated and then tipped off. Then this arrangement was connected to the same amplifier used in the absorption experiment. Filtered light was sent on the sample through the quartz window (Q). Then photo-electric currents produced by these dyes were measured, and dividing photo-current by the number of incident photons, efficiency (8) was calculated for the case of Dicyanine-A. This amounts to 10^{-9} , which is very small in comparison with ordinary photocell, (which is about 10^{-4}).

Results are shown in Tables 3, 4, and 5. It is seen that maximum regions showing photo-electric effect are $430 \sim 440 \text{ m}\mu$ (corresponding to its absorption $420 \sim 430 \text{ m}\mu$) in the case of Dicyanine-A, $480 \sim 500 \text{ m}\mu$ in the case of Kryptocyanine and $230 \sim 240 \text{ m}\mu$ in the case of Phenosafranine.

In order to measure the photo-electric effects of these dyes and of rock-salt crystals containing F-centers respectively, an arrangement shown in Fig. 5 was used. In the case of dyes, a silver plate on which these were evaporated thickly, was served as a cathode (C) and a molybdenum wire as an anode (A). The whole

TABLE 3. Photo-electric effect of Dicyanine-A

| Filters | UVD1 | Wratten 435 | VP1 | VB1 | Wratten 500 | VG1 | |
|--|------|-------------|------|------|-------------|------|--|
| Energy transmitted through filters | 401 | 2527 | 396 | 1178 | 2774 | 1203 | 10^2 erg/sec |
| | 1880 | 11843 | 1857 | 3363 | 12999 | 5641 | μ V/sec |
| Photo-current by Mazda filters | 2 | | 9 | 8 | | 4 | Direct reading of galvanometer: $\frac{1}{4} \cdot 10^{-10}$ A |
| | 6 | | 28 | 13.2 | | 4 | Relative amount of photo-current |
| Photo-current by Wratten monochromatic filters | | 4.5 | | | 3.5 | | Direct reading of galvanometer: $\frac{1}{4} \cdot 10^{-10}$ A |
| | | 4.9 | | | 3.5 | | Relative amount of photo-current |
| Photo-current | 0.5 | 1.1 | 2.25 | 2 | 0.9 | 1 | Absolute photo-current: 10^{-14} A |
| Efficiency | 225 | 39 | 1420 | 434 | 54 | 160 | $10^{-12}/m\mu$ width |
| Half width of absorption curves of filters | 50 | 30 | 90 | 100 | 30 | 100 | $m\mu$ |

TABLE 4. Photo-electric effect of Kryptocyanine

| Filters | VP1 | VB1 | Wratten 500 | VG1 | Wratten 546 | |
|--|------|-----|-------------|-----|-------------|--|
| Energy transmitted through filters | 56.0 | 105 | 383 | 174 | 418 | 10^2 erg/sec |
| | 262 | 496 | 1798 | 817 | 1962 | μ V/sec |
| Photo-current by Mazda filters | 0.5 | 2.5 | | 1.5 | | Direct reading of galvanometer: $\frac{1}{4} \cdot 10^{-10}$ A |
| | 4.3 | 8.3 | | 3 | | Relative amount of photo-current |
| Photo-current by Wratten monochromatic filters | | | 4.5 | | 1.5 | Direct reading of galvanometer: $\frac{1}{4} \cdot 10^{-10}$ A |
| | | | 10 | | 3 | Relative amount of Photo-current |
| Photo-current | 0.1 | 0.6 | 1.1 | 0.4 | 0.4 | Absolute photo-current: 10^{-14} A |

Photo-electric effects of rock-salt crystals have already been studied by P. Tartakowsky (9) and others (10). According to them, differences of energy between levels of zero state and ground state of F-center of rock-salt crystals is about 4.4 eV. We repeated experiments and verified their results: Photo-currents were not obtained by the light through filters transmitting longer than 300 $m\mu$, but were obtained by the light through Br₂ gas filter transmitting 240~350 $m\mu$ region, thus showing the maximum sensitivity is at 4.9~4.4 eV in accordance with Tartakowsky.

TABLE 5. Photo-electric conductivity of Phenosafranine.

| Filters | C ₂ H ₅ OH | CH ₃ OH | Glycerine | Mazda UV1 |
|---|----------------------------------|--------------------|-----------|-----------|
| Shortest wave-length of transmitted light | 210 $m\mu$ | 220 | 240 | 250 |
| Deflection of galvanometer | 115 mm | 210 | 210 | 20 |

Light source: Mercury lamp.

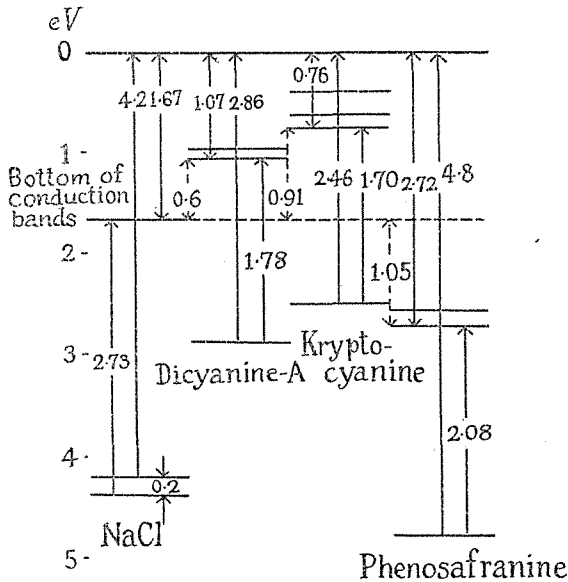


Fig. 6. Electronic energy levels.

excited levels are situated above the lowest conduction level of rock-salt, electrons raised to their excited levels by absorption of light have some probability to fall down to the conduction band of rock-salt leading to

4. Conclusion

According to these results, the electronic energy levels shown in Fig. 6 are obtained for rock-salt crystal, Dicyanine-A, Kryptocyanine and Phenosafranine, by taking their zero levels side by side. In terms of these levels, the mechanism of photo-sensitization of rock-salt crystals which adsorb Dicyanine-A or Kryptocyanine, may be explained as follows: since their lowest ex-

electric conduction in rock-salt crystals. Thus, the rock-salt crystal which adsorbs these dyes, becomes sensitive at only 1.8 eV corresponding to their absorption of light, while pure rock-salt crystal just becomes photo-sensitive at 9 eV, and that containing F-centers at 2.7 eV.

In the case of Phenosafranine, photo-conductivity does not occur. This may be understood from the electronic energy levels. For the lowest excited level of this dye is situated lower than the conduction level of rock-salt by about 1 eV and electrons may not be transferred from this excited level of the dye molecule to the conduction band of the rock-salt. Next, when Dicyanine-A and Phenosafranine are used in mixture, photo-conductivity is not found. The reason may be that electrons transferred to excited levels of Dicyanine-A are directly transferred to those of Phenosafranine and may be difficult to be transferred to the conduction levels of rock-salt.

Probably, the above-described mechanism of sensitization and desensitization of photo-conduction applied to rock-salt crystals, may be extended to silver-halides in photographic emulsion. For the fundamental process of latent image formation in silver-halides is a production of conduction electrons in silver-halides and in the case of dyed emulsion this may be effected by electrons of the dye molecules by the same mechanism shown in the case of rock-salt. In this connection, experiments on large single crystals of silver-halides are anticipated in future.

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