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SPECTRAL SENSITIZATION AND PHOTOGRAPHIC CHARACTERISTICS OF NAPHTHOTHIAZOLO CARBOCYANINE DYE

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Abstract — In this paper, it was studied about the red-sensitive layer. UV-Vis data of the dye at monomeric and J-state were considered with respect to their performance(contrast, density and fog) in photographic emulsion. The sensitizing effect of the dye is found to be strongly structure-dependent. Naphthothiazolo carbocyanine dye can be used as red-sensitizing dye for the spectral sensitization of photographic emulsion.

INTRODUCTION

Whereas the human eye is sensitive to that portion of the electromagnetic spectrum which lies approximately between 400 and 700 nm (the visible spectrum, Fig. 1), the finely divided halides of silver which constitute the sensitive element in most photographic processes have, in general, significant sensitivity only to the ultraviolet, violet, and blue. Since they are unaffected by green, yellow, orange, and red light, such color-blind materials give photographs in black-and-white in which one values are distorted, red, for example, being rendered almost indistinguishably from black. Furthermore, such blue sensitive materials obiously could not be made the basis for color photography. It is to remedy these situations that sensitizing dyes are used.

The solution of the problem stems from a chance discovery made by H. W. Vogel, of Berlin, in 1873.

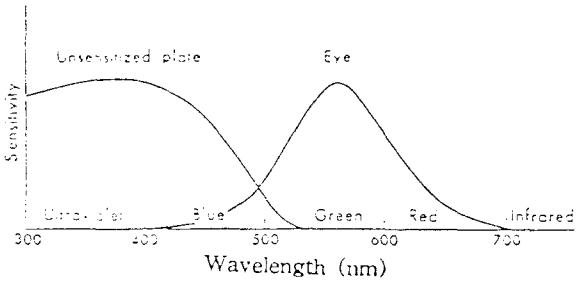

Figure 1. Wavelength vs. sensitivity curve of an unsensitized photographic emulsion compared with that of the normal human eye.

While investigating some collodion dry plates, he noticed that exposure to the solar spectrum revealed sensitivity in the green which he traced to the presence in the emulsion of a yellow dye that had been added to prevent halation.[1,2] Vogel sought to reproduce the effect by impregnating a silver bromide plate with a dye coralline for the purpose, he found that the plates behaved as he had hoped. The experiment was repeated using dyes which absorbed red, and among the green aniline dyes, which absorbed red strongly, Vogel found one which sensitized emulsions to the red portion of the spectrum.

It is hardly possible to overestimate the importance of Vogel's discovery, for the greater part of modern photography would not be possible without sensitizing by means of dyes. His discovery aroused considerable interest, although at first a number of investigators attempted to repeat his experiments with out success. But others confirmed them, and it gradually became recognized that for the effect to be clearly observed, the dye should be in a high state of purity and used in rather high dilution, conditions that were undoubtedly not fulfilled in much of the early work.

Sensitizing dyes are adsorbed at the surface of the silver halide particles.[3] The aggregated state of sensitizing dyes will be mentioned here because of its great practical importance in photographic spectral sensitization. Some sensitizing dyes are able to form aggregates of molecules in which the flattish dye molecules are stacked one against the other rather

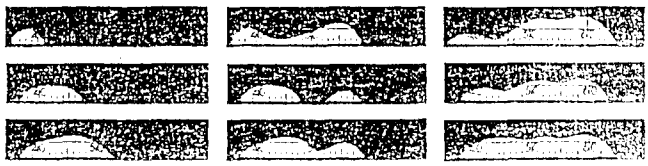

Figure 2. Wedge spectrograms of chloride, bromide, and iodobromide emulsions.: First column, unsensitized; second column, sensitized with erythrosin; third column, sensitized with 3,3'-diethyl-9-methylthiacarbocyanine bromide.

like a row of books on a shelf. Such aggregates may separate from solution or may appear more readily when the dye is adsorbed to the surface of silver halide grains. These aggregates are frequently characterized by adsorption bands of extraodinarily high selectivity and sharpness, and in favorable circumstances give rise to sensitizing bands which are correspondingly sharp, particularly when the dye is supersensitized.

In Figure 2 wedge spectra show the effect of sensitizing chloride, bromide, and iodobromide emulsions with erythrosin and with a thiacarbocyanine dye.

The changes in the absorption spectrum of aqueous solution of sensitizing dyes, 1,1'-diethyl-2,2'-cyanine chloride are illustrated in Figure 3.

The spectrum of the very dilute aqueous solution (Curve 1) closely resembles that of the alcoholic solution, with a maximum near 525 nm, a secondary maximum about 490 nm, and traces of shoulders at shorter wavelengths. This spectrum is to be ascribed to the isolated dye molecule, as perturbed by the solvent, but free from mutural interactions between dye molecules, as is indicated by adherence to Beer's law. The subsidiary maximum and the shoulders very probably represent a progression of vibrational bands originating in the simultaneous excitation, along with the electronic excitation, of certain vibrations associated with the atoms in the conjugated chain.

The first spectral change observed on increasing the concentration of the dissolved dye is the appearance of a new maximum, D, displaced somewhat to shorter wavelengths from the subsidiary vibrational maximum at 490 nm, with a concomitant decrease in the absorption of the molecular maximum, M. With increase in the temperature, the spectrum tends to return reversibly to that of the very dilute solution.

This type of change is observed in dyes of many classes, including,besides the cyanine, merocyanines, triphenylmethane dyes, xanthenes, rhodamines azines, oxazines, and thiazines. The band that first appears at shorter wavelength is probably, for all

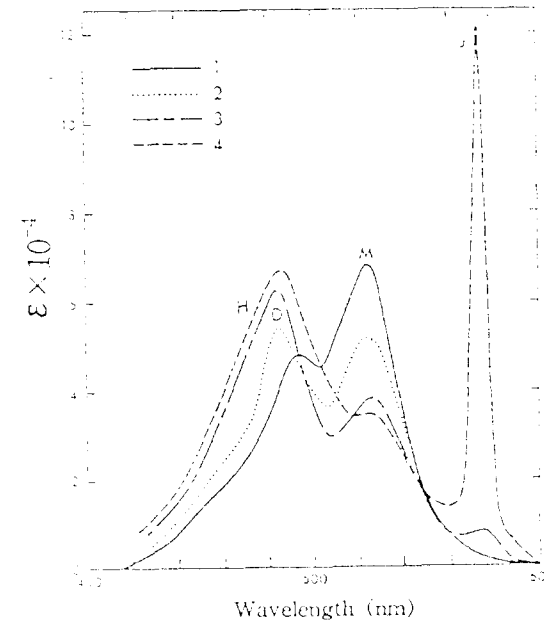

Figure 3. Absorption spectrum of aqueous solutions of 1,1'-diethyl-2,2'-cyanine chloride at 25°C.: (1) 1.3×10^{-5} *M*; (2) 1.3×10^{-3} *M*; (3) 7.1×10^{-3} *M*; (4) 1.4×10^{-2} *M*.

these dye classes, to be ascribed to a dimer; the absorption maximum falls near the wavelength of the first subsidiary molecular vibrational maximum or shoulder. For many dyes, including the present example and many other cyanines, the dimer stage is followed by a higher stage of aggregation, shown by a further hypsochromic displacement of the maximum from the dimeric maximum and a broadening of the band. The equilibrium between monomeric and dimeric molecules often persists over too small a concentration range to allow the corresponding eqilibrium constant to be observed, but for some dyes in aqueous solution, for example, thionine, methylene blue, acridine orange, fluorescein, eosin, rhodamine B, the existence of a monomer-dimer eqilibrium has been proved. Dimeric eqilibrium costants over the concentration range 10^{-6} to 2×10^{-4} *M* or higher can be deduced from the changes in th absorption spectrum with concentration of several cyanine and merocyanine dyes.[4-6] The broadening of the short-wavelength dimeric band and its displacement to shorter wavelengths as the concentration of dye is increased can reasonably be attributed to the formation of multimolecular aggregates. These aggregates may be called H-aggregates, and corresponding absorption bands, H-band. For the dye, 1,1'-diethyl-2,2'-cyanine chloride, illustrated in Fig. 3 , at concentrations above those at which the aggregation effects at short wavelength appear, an intense, remarkably sharp absorption maximum was found by Jelley[7] and by Scheibe[8] to

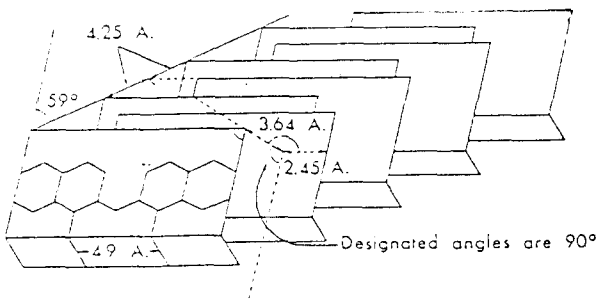

Figure 4. Arrangement of molecules in the J-state of 2,2'-cyanine dyes, according to Scheibe.

appear at wavelength about 573 nm, displaced to longer wavelengths from the molecular band The new band is called a J-band, and the aggregated state associated with the band can be referred to as the J-state. With the appearance of absorption within the J-band involves the co-operation of all the molecules in the aggregate, and absorbed energy traverses the whole aggregate.[10] The process may be an example of exciton propagation, whereby a state of electronic excitation achieved by absorption of a molecule in a closely coupled periodic aggregate is rapidly transferred from molecule to molecule in an interval less than the period of a molecular vibration. Consistent with the rapid migration of energy throughout the molecules of the aggregate is the observation of measurable quenching of the fluorescence of the J-aggregate by concentrations of catechol as low as one molecule of quencher to 10^3 or 10^6 molecules of dye.

In this report, spectral sensitization and photographic characteristics of naphthothiazolo carbocyanine dye were examined.

MATERIALS AND METHODS

Materials. Methanol, silver nitrate, potassium chloride and sodium thiosulfate were purchased from Aldrich. Potassium bromide and sodium chloride were purchased from SIGMA. Dye of 9-methyl-3,3'-bis(3-sulfopropyl)-4,5,4',5'-naphthothiazolo carbocyanine triethyl ammonium salt was synthesized in this laboratory.[11,12]

Experimental methods . The absorption spectra were recorded by using a Shimadzu UV 256 spectrophotometer. Absorption spectrum of 9-methyl-3,3'-bis(3-sulfopropyl)-4,5,4',5'-naphthothiazolo carbocyanine triethyl ammonium salt in 10% aqueous methanol solutions containing 10^{-3}M potassium chloride was measured.[13,14] The photographic emulsion for color paper prepared to double-jet method in our laboratory.The tabular grain emulsion was precipitated using the double-jet method with automated control of pAg, then coagulated, washed, redispersed, chemically sensitized with sodium thiosulfate, spectrally sensitized with 9-methyl-3,3'-bis(3-sulfopropyl)-4,5,4',5'-naphthothiazolo carbocyanine triethyl ammonium salt, coated on the paper base, dried, exposed, developed in developer. The spectral sensitizer used in the red-sensitive silver halide emulsion layer may preferably be in an amount of 0.1% methanol solution per 0.03 *M* of silver. Spectral sensitivity and photographic characteristics were measured by using a spectral sensitometer and sensitometer.

RESULTS AND DISCUSSION

Absorption spectrum of 9-methyl-3,3'-bis(3-sulfopropyl)-4,5,4',5'-naphthothiazolo carbocyanine triethyl ammonium salt in methanol solution was determined (dye concentration about 5×10^{-5} mol/L). In the Fig. 5, maximum absorption spectrum of dye was observed near 573 nm.[12]

In the Fig. 6, maximum absorption spectrum of dye in 10% aqueous methanol solution containing $10^{-2}M$ potassium chloride shows 658 nm, and strong J-band was observed.

The light-sensitive material has a blue-sensitive layer, green-sensitive layer and a red-sensitive layer. The blue-sensitive layer has the maximum spectral sensitivity at a wavelength within the range of 415 nm to 470 nm. The green-sensitive layer has the maximum spectral sensitivity at a wavelength within the range of 530 nm to 560 nm. The red-sensitive layer has the maximum spectral sensitivity at a wavelength within the range of 595 nm to 700 nm. In this paper, it was studied about the red-sensitive layer.

In the Fig. 7, spectral sensitivity shows 524 nm ~ 685 nm, and maximum spectral sensitivity was observed 655 nm.[15]

As compared with the maximum absorption peak of

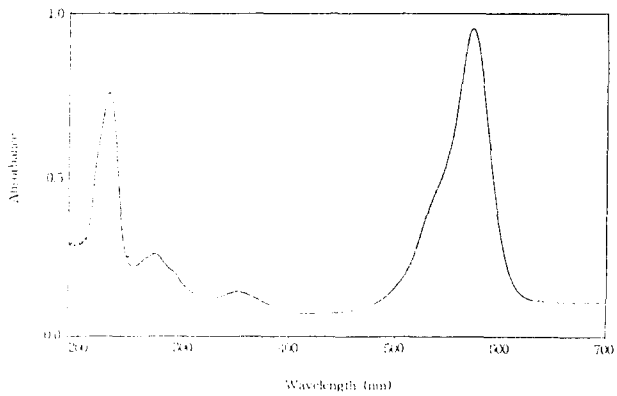

Figure 5. UV-Vis spectrum of 9-methyl-3,3'-bis(3-sulfopropyl)- 4,5,4',5'-naphthothiazolo carbocyanine triethyl ammonium salt.

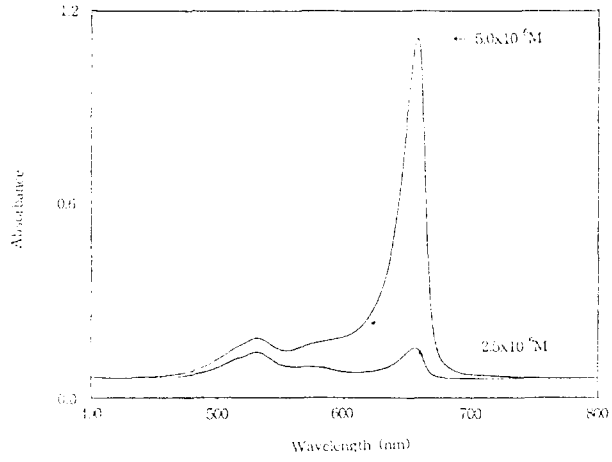

Figure 6. UV-Vis spectrum of 9-methyl-3,3'-bis(3-sulfopropyl)-4,5,4',5'-naphthothiazolo carbocyanine triethyl ammonium salt solutions of $2.5 \times 10^{-6}M$ and $5 \times 10^{-6}M$ concentrations in 10% methanol containing $10^{-2}M$ KCl showing the monomer-J-aggregate equilibria.

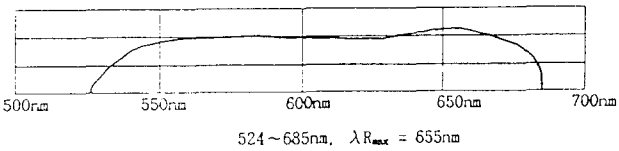

Figure 7. Wedge spectrogram of the color paper added to dye (1ml, 0.1%) per 0.03 mol of silver.

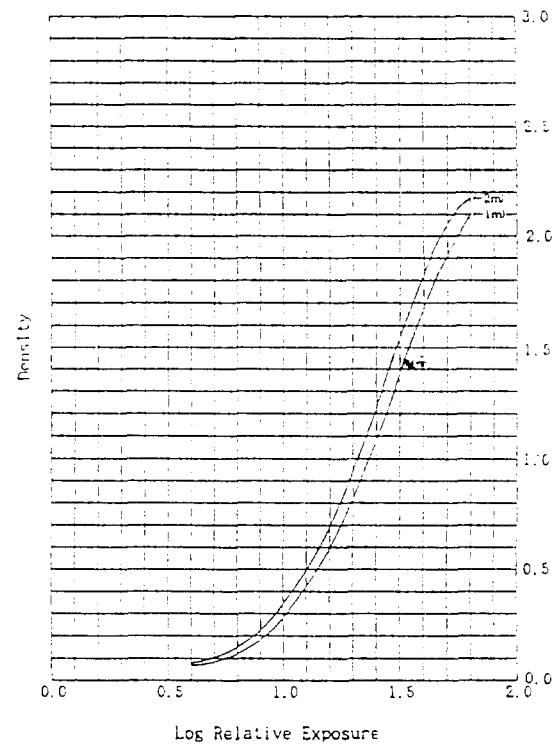

Figure 8. Photographic characteristic curves of the color paper added to 0.1% dye (1ml and 2ml, respectively) per 0.03 mol of silver.

the monomer in methanol solution, the maximum spectral sensitivity specrtrum of 9-methyl-3,3'-bis(3-sulfopropyl)-4,5,4',5'-naphthothiazolo carbocyanine triethyl ammonium salt has red shift of 82 nm. Maximum absorption spectrum of the dye in electrolyte solution has red shift 85 nm more than that of the monomer in methanol solution.

In the Fig. 8, photographic characteristics of the color paper added dye(1mL~2mL) to photographic emulsion were shown contrast (2.7), maximum density (2.10), fog (0.07) and contrast (2.8), maximum density (2.17), fog (0.08), respectively.

CONCLUSION

The amount of residual color in the coated layer also depends upon the dye structure; the dye has no residual color after development and fixation. It was concluded that 9-methyl-3,3'-bis(3-sulfopropyl)-4,5,4',5'-naphthothiazolo carbocyanine triethyl ammonium salt can be used as red-sensitizing dye for the spectral sensitization of photographic emulsion.

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