Spectral Sensitization and Photographic Characteristics of 9-Phenyl-3,3'-Bis(3-Sulfopropyl)-4,5,4',5'-Naphthothiazolo Carbocyanine Triethyl Ammonium Salt

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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, speed, 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.

Keywords : red sensitizing dye, spectral sensitization, J-state,
              photographic characteristics.

1. 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
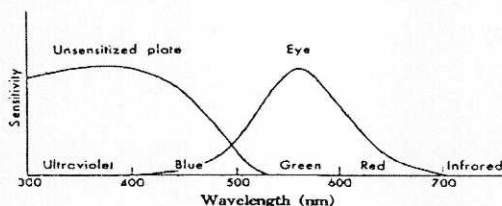

Fig. 1. Wavelength vs. sensitivity curve of an unsensitized photographic emulsion compared with that of the normal human eye.

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 tone 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 Vogel, of Berlin, in 1873. 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 without 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 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 Fig. 2 wedge spectra show the effect of sensitizing chloride, bromide, and iodobromide emulsions with erythrosin and with a thiacarbocyanine dye.
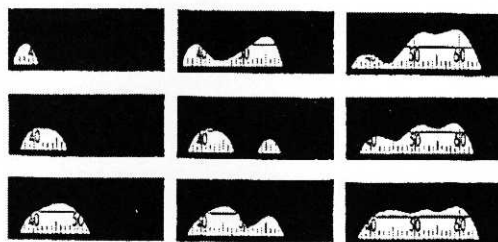

Fig. 2. Wedge spectrograms of chloride, bromide, and iodobromide emulsions.: First column, unsensitized; second column, sensitized with erythrosin; third column, sensitized with 3,3'-diethyl-9-methylthiacarbocyanine bromide.

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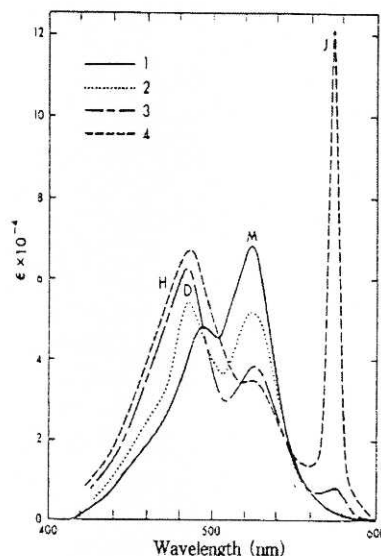

Fig. 3. Absorption spectrum of aqueous solutions of 1,1'-diethyl-2,2'-cyanine chloride at 25℃.: (1) 1.3×10^{-5} M; (2) 1.3×10^{-3} M; (3) 7.1×10^{-3} M; (4) 1.4×10^{-2} M.

The spectrum of the very dilute aqueous solution (Curve 1) closely resembles that of the alcoholic solution, with a maximum near 525nm, a secondary maximum about 490nm, 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 490nm, 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 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 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 the 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 reasionably 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 is called a J-band[7-10], and the aggregated state associated with the band can be referred to as the J-state. Hence the structure suggested for the J-aggregate is an array of dye molecules with their molecular planes parallel to each other, arranged to form a threadlike aggregate. By co-operation of the individual molecules, an oscillator inclined to the molecular axes and parallel to the axis of the aggregate is generated and this oscillator gives rise to the J-band. Further details of the J-aggregate structure have been derived by Hoppe from the x-ray analysis of dried gels of the dye. According to this analysis, the planes of the individual molecules are tilted about 35 degrees from the normal to the axis of the thread and are spaced 4.5 A. apart. Moreover, it been deduced from the adsorption of the J-aggregate on mica that alternate molecules are displaced with respect to each other perpendicularly to the axis of the thread so as to form a staggered configuration in which the carbon atom of the

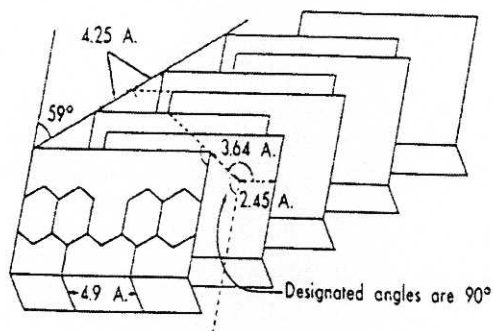quinoline ring of its neighbor (Fig. 4).

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

Absorption within the J-band involves the co-operation of all the molecules in the aggregate, and absorbed energy traverses the whole aggregate[11]. 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 9-phenyl-3,3'-bis(3-sulfopropyl)-4,5,4',5'-naphthothiazolo carbocyanine triethyl ammonium salt (PNCTAS) were examined.

2. Experimental

Methanol, silver nitrate, potassium chloride, triethylamine, m-cresol triethyl orthobenzoate and sodium thiosulfate were purchased from Aidrich. Potassium bromide and sodium chloride were purchased from SIGMA and 2-methyl-3-sulfopropyl-4,5-naphthothiazolium (inner salt) was purchased from H. W. SANDS corporation. Dye of PNCTAS was synthesized in this laboratory[12].
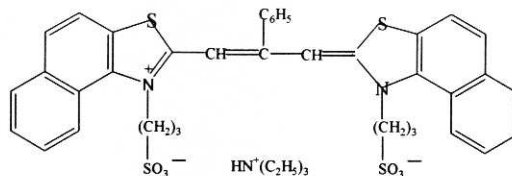
Scheme 1. Molecular structure of PNCTAS.

Scheme 1 shows a structure of PNCTAS molecule. The absorption spectra were recorded by using a Shimadzu UV 256 spectrophotometer. Absorption spectrum of PNCTAS in 10% aqueous methanol solutions containing 10^{-2}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 PNCTAS, 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% dye methanol solution per 0.03 mol of silver. Spectral sensitization and photographic characteristics were measured by using a spectral sensitometer and reflection densitometer.

3. Results and Discussion

Absorption spectrum of PNCTAS 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 600 nm.
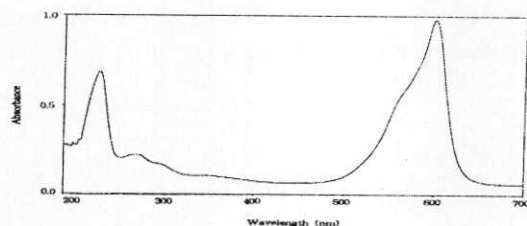
Fig. 5. UV-Vis spectrum of PNCTAS in methanol solution.

In the Fig. 6, maximum absorption spectrum of dye in 10% aqueous methanol solution containing 10^{-2}M potassium chloride shows 674 nm, and strong J-band was observed.
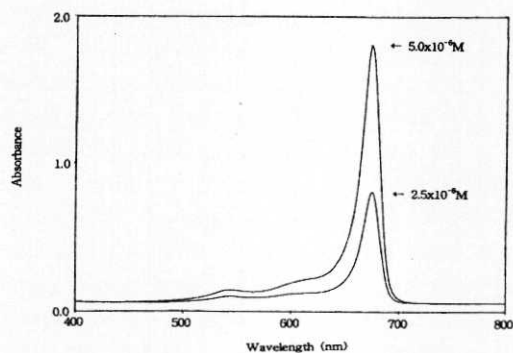

Fig. 6. UV-Vis spectrum of PNCTAS solutions of 2.5×10^{-6}M and 5×10^{-6}M concentrations in 10% methanol containing 10^{-2}M KCl showing the monomer-J-aggregate equilibria.

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 sensitization shows 545 nm ~ 695 nm, and maximum spectral sensitization was observed 665 nm[15].

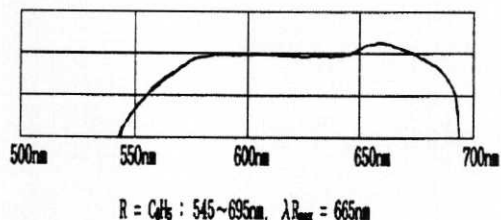$R = C_2H_5 : 545 \sim 695nm, \ \lambda R_{max} = 665nm$

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

As compared with the maximum absorption peak of the monomer in methanol solution, the maximum spectral sensitization specrtrum of PNCTAS has red shift of 65 nm.

Maximum absorption spectrum of the dye in electrolyte solution has red shift 74 nm more than that of the monomer in methanol solution.
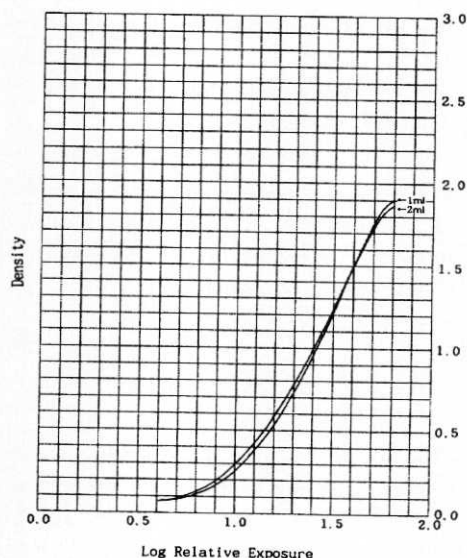

Fig. 8. Photographic characteristic curves of the color paper added to 0.1% dye (1ml, 2ml respectively) per 0.03 mol of silver.

In the Fig. 8, photographic characteristics of the color paper added dye (1ml, 2ml respectively) to photographic emulsion were shown contrast (2.5), speed (60), maximum density (1.90), fog (0.08) and contrast (2.8), speed (62), maximum density (1.87), fog (0.08), respectively.

4. Conclusions

It was concluded that PNCTAS can be used as red-sensitizing dye for the spectral sensitization of photographic emulsion. However, the dye has a little residual color after development and fixation. The amount of residual color in the coated layer also depends upon the dye structure. The dye was observed strongly J-band in electrolyte solution.

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