JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY • Volume 40, Number 3, May/June 1996

Correlation of the Photographic Performance of Indocarbocyanine Dyes with Their Electrochemical Properties and Aggregation Behavior

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The correlation of photographic performance of indocarbocyanine dyes having different substituent groups on the benzene ring and the heterocyclic nitrogen atom with their electrochemical properties and aggregation behavior in solution and on emulsion grains was investigated. The experimental results indicate that the physicochemical properties of the dyes are determined by their skeletons and subtle structure features. The photographic performance of the dyed emulsion depends on the dye's photophysical and electrochemical properties and on the energy level positions of the sensitizer.

Journal of Imaging Science and Technology 40:3 220-229 (1996)

Introduction

The synthesis and application of indocarbocyanines as functional dyes in optical disk recording materials,[1a] as green spectral sensitizers,[1b,c] as infrared spectral sensitizers[1,d–f] and as desensitizers[1g] have been of interest for many years. As compared with symmetrical and unsymmetrical benzothiacarbocyanines, the structure–performance relationships of indocarbocyanine dyes have been much less systematically investigated. An attempt was made to carry out systematic exploratory research on the symmetrical and unsymmetrical indocarbocyanine dyes. The hope was to reveal the major advantages and disadvantages of the dyes in potential applications in the image-recording fields, particularly in photography.

The present study also has academic implications. It is known that spectral sensitization is a complicated process, which involves dye excitation and interaction of the excited dye molecule with the silver halide. In this process, at first, the sensitizer must be suitably adsorbed on silver halide emulsion microcrystals. It is generally considered that dyes on silver halide crystals may be in the M-, H-, or J-state. Many experimental findings have been published, and it is accepted that J-aggregates are essential for the spectral sensitization of silver halide emulsions used in photography.[2] The processes of electron transfer and/or energy transfer take place between the sensitizer and the silver halide lattice under certain conditions. Dye adsorption and aggregation depend on the forces of interaction of molecules—dye molecule with dye molecule, dye molecule with silver halide molecule, dye molecule with additive molecule, and so on. The sensitization depends on the relative energy levels of the frontier molecular orbital of dye and the gap of the forbidden band of silver halide.[3] The aggregation state strongly influences spectral (de)sensitization, and the relative position of energy levels determines the direction of electron transfer, energy transfer, and the resulting sensitization by dyes. Both the aggregation states and the energy levels of the dye molecule are directly related to the structure of the dye molecule.

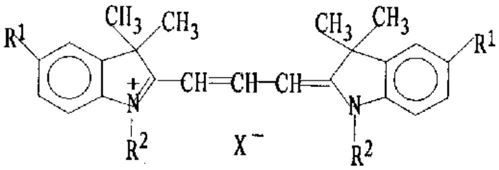
Generally, the information on adsorption is obtained from the absorption spectra and reflectance spectra of the dye molecule. The analytical color fluorescence electron microscope (ACFEM)[2a] and the high-resolution scanning electron microscope (HRSEM)[2b] have also been used. The relative position of energy levels has been estimated extensively from redox potentials, ionization potentials, and HOMO calculations.[4] The dye molecules carrying different substituents have different LUMO and HOMO energies, different positions of energy relative to silver halide, different aggregation states on the same silver halide emulsion microcrystals, and may have different spectral sensitizing efficiencies.

A question arises, among the several important and necessary characteristics (absorption spectra, redox, aggregate state, energy level position, etc.), as to which ones are of the prime importance. Do some parameters have to be met and matched simultaneously or are some parameters necessary conditions, but unlikely to be sufficient conditions for the spectral sensitization?

To extend and deepen the published knowledge of the structure–performance relationships, we synthesized a series of 15 symmetrical indocarbocyanine dyes[5] having the same chromophoric system, but with different substituents, OCH_3, CH_3, H, Cl, and NO_2 in the 5- position of the indolenine ring; CH_3, CH_2CH_3, and $(CH_2)_3SO_3$– on the heterocyclic nitrogen atoms. Much effort was applied to the techniques to determine the aggregate behavior, redox potential, and sensitometric properties. These properties were then correlated with dye sensitizing efficiency and dye uptake (residual dye density) as well.

Experiment

The general formula of the indocarbocyanine dyes studied can be expressed as follows:



The corresponding dyes are tabulated in Table I. The synthesis, purification, and characterization of these dyes have been described elsewhere by the authors.[5]

Original manuscript received April 26, 1995. Revised March 6, 1996.

TABLE I. The Indocarbocyanine Dyes Studied and Elemental Analysis Data

Series	Dye no.	R_1	R_2	X	Molecular formula	Elemental analysis (%) Found (calculated)		
						C	H	N
I	1	OCH_3	CH_3	I^-	$C_{27}H_{33}N_2O_2I$	58.85 (59.53)	6.16 (6.12)	5.15 (4.71)
	2	CH_3	CH_3	I^-	$C_{27}H_{33}N_2I$	62.97 (63.28)	6.43 (6.49)	5.43 (5.47)
	3	H	CH_3	I^-	$C_{25}H_{29}N_2I$	61.52 (61.59)	6.26 (6.03)	5.79 (5.48)
	4	Cl	CH_3	I^-	$C_{25}H_{27}N_2Cl_2I$	53.83 (54.13)	4.92 (4.92)	4.96 (5.06)
	5	NO_2	CH_3	I^-	$C_{25}H_{27}N_4O_4I$	51.84 (52.26)	4.86 (4.70)	9.48 (9.75)
II	6	OCH_3	CH_2CH_3	I^-	$C_{29}H_{37}N_2O_2I$	61.40 (60.84)	6.62 (6.52)	4.76 (4.89)
	7	CH_3	CH_2CH_3	I^-	$C_{29}H_{37}N_2I$	64.48 (64.44)	6.84 (6.90)	5.18 (5.18)
	8	H	CH_2CH_3	I^-	$C_{27}H_{33}N_2I$	62.82 (63.28)	6.45 (6.49)	5.24 (5.46)
	9	Cl	CH_2CH_3	I^-	$C_{27}H_{31}N_2Cl_2I$	54.83 (55.19)	6.47 (6.70)	5.32 (5.51)
	10	NO_2	CH_2CH_3	I^-	$C_{27}H_{31}N_4O_4I$	53.56 (53.77)	5.29 (5.19)	9.15 (9.30)
III	11	OCH_3	$(CH_2)_3SO_3^-$	$^+NHEt_3$	$C_{37}H_{55}N_3S_2O_8$	59.23 (59.08)	7.26 (7.58)	5.35 (5.59)
	12	CH_3	$(CH_2)_3SO_3^-$	$^+NHEt_3$	$C_{37}H_{55}N_3S_2O_6 \bullet 2H_2O$	60.12 (60.16)	7.72 (7.72)	5.83 (5.69)
	13	H	$(CH_2)_3SO_3^-$	$^+NHEt_3$	$C_{35}H_{51}N_3S_2O_6 \bullet 1/2\ H_2O$	61.30 (61.58)	7.62 (7.62)	5.98 (6.15)
	14	Cl	$(CH_2)_3SO_3^-$	$^+NHEt_3$	$C_{35}H_{49}N_3Cl_2S_2O_8 \bullet H_2O$	54.78 (55.19)	6.44 (6.70)	5.28 (5.52)
	15	NO_2	$(CH_2)_3SO_3^-$	$^+NHEt_3$	$C_{35}H_{49}N_5S_2O_{10}$	55.12 (55.05)	6.13 (6.42)	9.11 (9.19)

Photographic Tests. A thick tabular iodobromide (AgI 2 mol%) emulsion was precipitated, using the double-jet method with automated control of pAg, at an initial gelatin concentration of 2%, temperature 60°C, pBr = 1.0 for a period of 40 min, then coagulated, washed, redispersed, and chemically sensitized with S + Au sensitizers. Portions were spectrally sensitized with selected volumes of Dyes 1–15 in 0.1% methanol dye solution, 40°C, for a given 50 g of emulsion, coated on film base, dried, exposed sensitometrically (1/20 s Xian Feng sensitometer, Shanghai, China), developed in D-19b developer at 20°C for 5 min, fixed in F-11 fixing bath at 25°C for 1 h, and sensitometrically measured on a CMT Densito (China). The resulting data are given in Table II. An electron micrograph of the emulsion micro-crystals is shown in Fig. 1. The pH and pAg of the emulsion were 6.5 and 7.8, respectively. The average grain size diameter was 1.0 μm.

UV-VIS Spectra. It has been customary[6] to attribute the molecular absorption of unperturbed transitions obtained in highly dilute aqueous or alcoholic dye solutions (normally 10^{-5}mol/L) to the M-band and to define as H-bands (H for hypsochromic) those blue-shifted transitions, including D-bands (D for dimers), that frequently appear when the dye's concentration is increased (normally to 10^{-3} to 10^{-2}mol/L). Depending on the dye structure, such a concentration increase may cause the appearance of a new, narrow, and intense maximum at wavelengths much longer than the M-band (such a maximum band often accompanies resonance fluorescence), i.e., the J-band. The spectral band for an adsorbed monomer on the silver halide surface is shifted 20 to 30 nm (bathochromically) from that

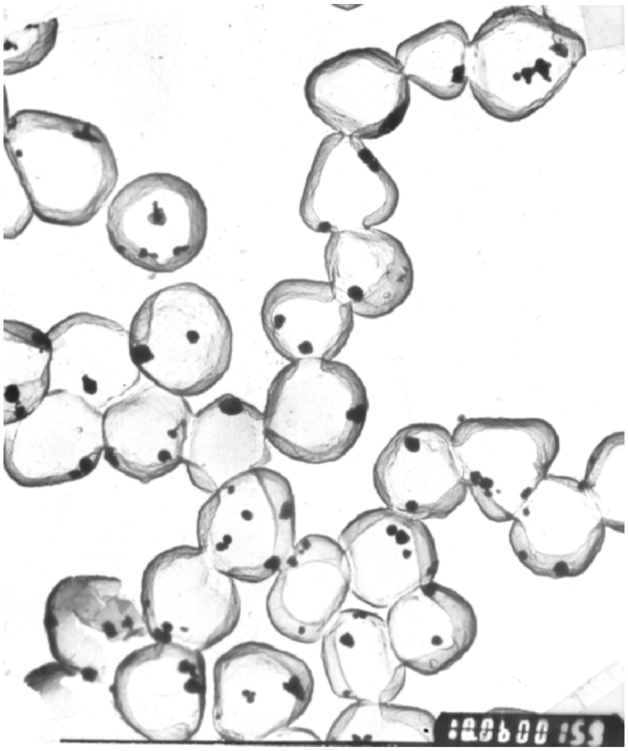


Figure 1. An electron micrograph of silver halide grains (magnification ×10,000).

TABLE II. The Photographic Performance of Indocarbocyanine Dyes 1–15

Series	Dye no.	V (mL)	D_0	D_{max} (DIN)	S (ISO)	ΔS	Contrast	Residual color
		o	0.08	7.10	320		4.0	no
I	1	1	7.00	7.10				
		3	7.00	7.10				
	2	1	6.20	7.00				
		3	6.20	7.00				
	3	1	0.20	>7.00	250	–70	3.8	yes
		3	0.30	>7.00	200	–120	3.7	yes
	4	1	0.11	>7.00	64	–256	4.0	heavy
		3	0.10	>7.00	16	–304	3.9	heavy
	5	1	0.04	4.15	20	–300	3.0	no
		3	0.06	3.00	12	–308	2.4	no
II	6	1	7.00	7.10				
		3	7.00	7.10				
	7	1	6.10	7.10				
		3	6.10	7.10				
	8	1	0.20	7.00	200	–120	2.8	heavy
		3	0.29	7.00	200	–120	3.0	heavy
	9	1	0.17	7.00	100	–220	4.2	heavy
		3	0.30	7.00	25	–295	4.0	heavy
	10	1	0.08	4.25	40	–280	3.7	no
		3	0.07	5.30	8	–312	3.4	no
III	11	2	6.90	7.10				
		4	6.90	7.10				
	12	2	6.70	7.00				
		4	6.70	7.00				
	13	2	0.08	>7.00	400	+80	4.0	no
		4	0.07	>7.00	250	–70	4.9	no
		6	0.06	>7.00	100	–220	4.0	no
		8	0.06	>7.00	100	–220	4.3	no
	14	2	0.10	>7.00	320	0	3.1	slight
		4	0.11	>7.00	320	0	2.8	yes
	15	2	0.07	5.70	64	–256	3.0	no
		4	0.07	5.80	80	–240	3.8	no

V(mL) = the number of milliliters of 0.1% methanol solution of dye added to 50 g emulsion.
D_0, D_{max} = the minimum and maximum densities, respectively, of film strips.
S = the sensitivity, defined by the following equation,

$$S = 10 \log(1/H_{D_0} + 0.1),$$

in which *H* represents the amount of exposure necessary to obtain a density of 0.1 above fog.

TABLE III. Electronic Spectroscopic Data of Dyes 1–15

Dye No.	In methanol ($C = 1 \times 10^{-5}$ mol/L)		Dyed emulsion strip			
	λ_{max} (nm)	$\varepsilon \times 10^{-5}$ (L • mol^{-1} • cm^{-1})	λ_{max} (nm) (second peak)	M	H	J
1	570	1.0453	600 (560)	V	V	
2	552	1.1407	600 (540)		V	V
3	542	1.9873	580 (530)	V	V	
4	550	1.3451	605 (554)	V		V
5	562	1.2455	620			V
6	572	1.0955	556 (590)	V	V	
7	554	1.0874	604 (548)		V	V
8	544	1.5479	580 (540)	V		
9	552	1.4878	598 (560)			V
10	562	1.0955	622			V
11	574	1.0980	542 (580)	V	V	
12	558	1.2427	528		V	
13	548	1.9020	532 (554)	V	V	
14	664	1.3748	560 585 (526)	V	V	
15	564	1.7637	580 628 (530)	V	V	V

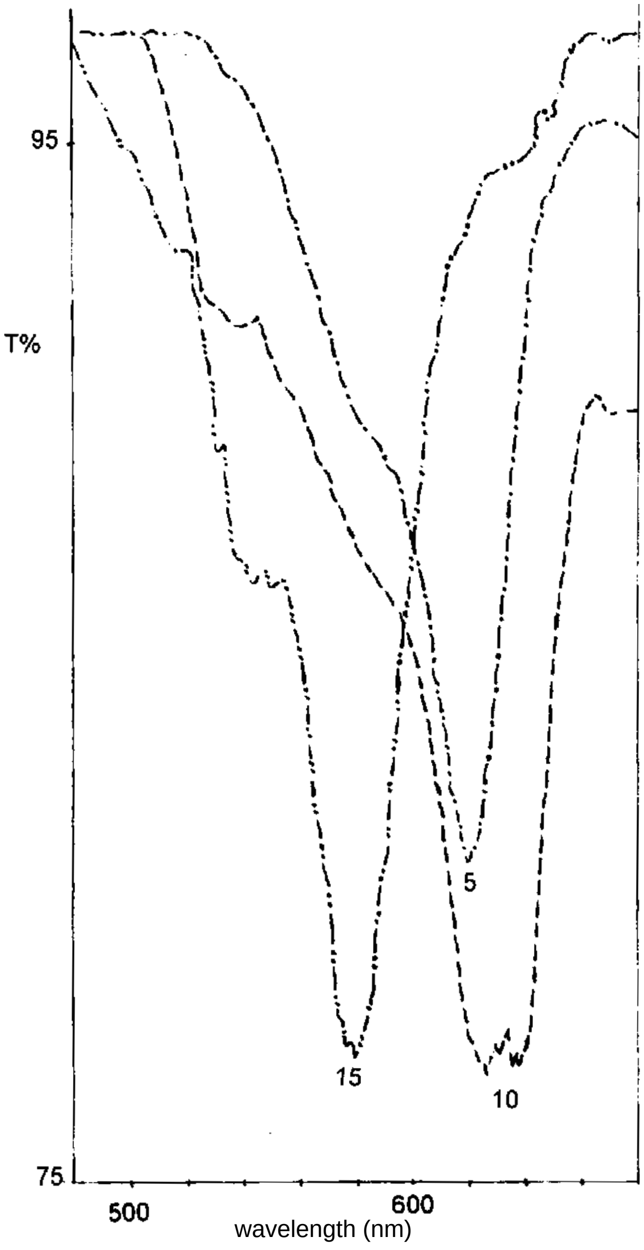


Figure 2. The reflection spectra of dyed emulsion strips. The reference was a base strip coated with emulsion without dye. The numbers in this figure refer to the dyes as denoted in Table I.

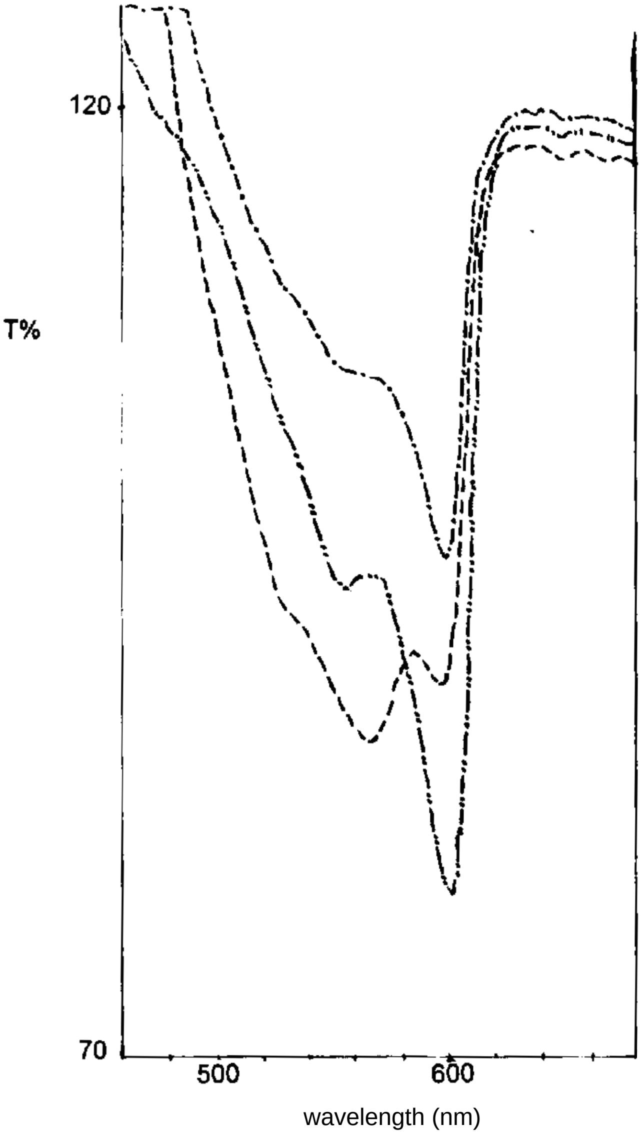


Figure 3. The reflection spectra of emulsion strips dyed with Dye 9 in various amounts.

— • — 2×10^{-5}g dye/g emulsion

— • • — 6×10^{-5}g dye/g emulsion

— — — 1×10^{-4}g dye/g emulsion

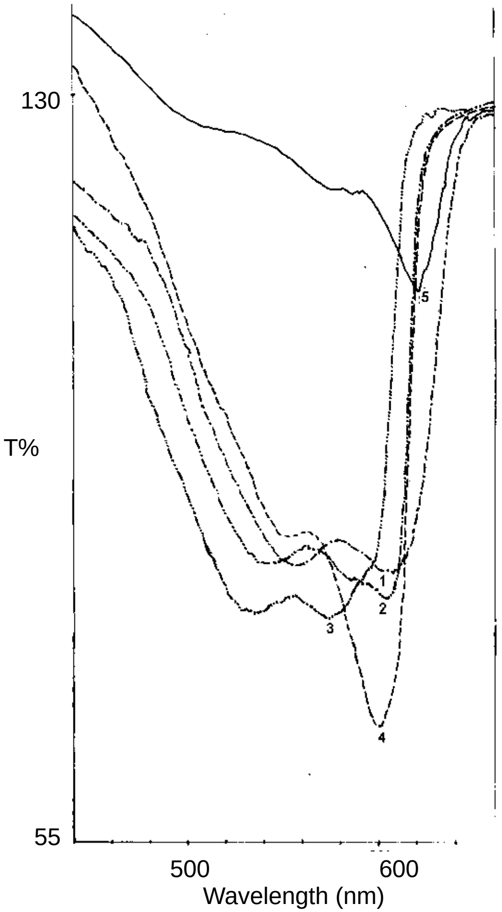
of the monomer in aqueous or methanol solution. For the J-aggregates of sensitizing dye on a silver halide surface, a larger bathochromic shift can be also observed, either by absorption or by reflection spectroscopy. The reflectance spectra of dyed emulsion strips made above were measured on a Hitachi-557 spectrophotometer (Figs. 2, 3, and 4). The absorption spectra of dyes in solution were recorded on a Hitachi UV-8451A spectrophotometer at room temperature. The experimental results are compiled in Table III and shown in Figs. 5 through 9.

The Reduction Potential. The reduction potentials were determined on an oscilloscope polarographer (Shichun, China, Model JP-2). The basic construction and operational procedures are described in Ref. 7. The only exception is that a dropping mercury electrode is used in the present study as the working electrode. The concentration of dye in aqueous methanol (5% water) is approximately 10^{-4} mol/L. KCl (0.2%) is added to the dye solution as the supporting electrolyte. A three-electrode system incorporating a dropping mercury electrode, a platinum counter electrode, and a 212 saturated calomel reference electrode, was used at 25°C.

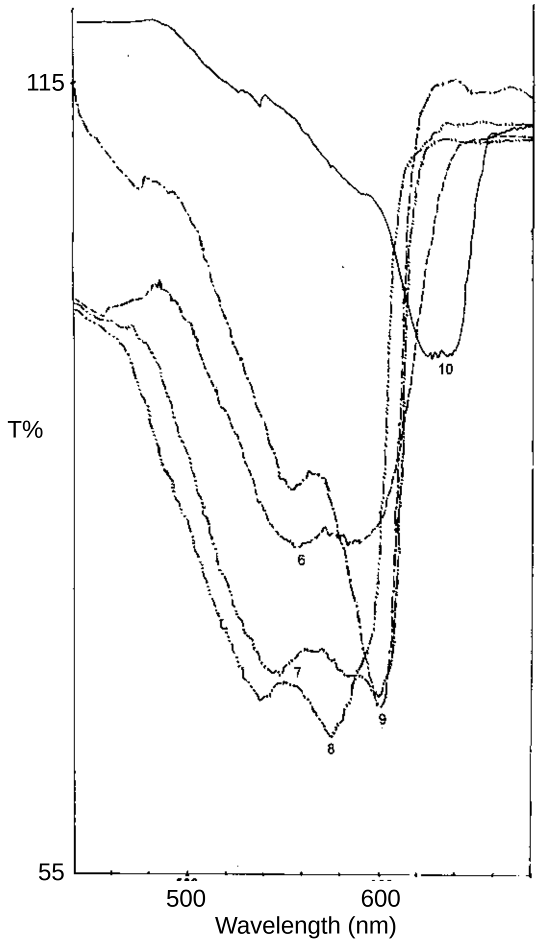
In the experiment, the solution was deaerated for 10 min. before measurement under bubbling nitrogen. Two typical cathodic oscillopolarograms for Dye 11 and Dye 13 are shown in Figs. 10(a) and 10(b). The experimental values of reduction potential are listed in Table IV.

Results and Discussion

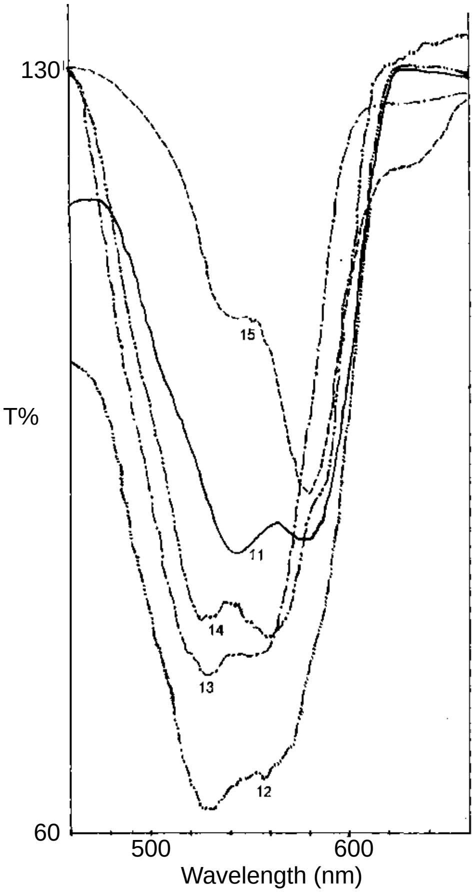
The Photographic Performance. The sensitization by indocarbocyanine dyes listed in Table I depends fundamentally on their structure, especially on the nature of substituent R_1. Dyes 1, 2, 6, 7, 11, and 12, having the electron-donating OCH_3 and CH_3 groups on the indolenine ring, induced severe fog under the experimental conditions, regardless of the substituent on the heterocyclic nitrogen atom. On the other hand, Dyes 4, 5, 9, 10, 14,



(a)



(b)



(c)

Figure 4. The reflection spectra of emulsion strips dyed with the dyes in (a) Series I and (b) Series II, containing 6 × 10^{-5}g dye/g emulsion. (c) Series III, containing 8 × 10^{-5} g dye/g emulsion. The numbers refer to the dyes as denoted in Table I.

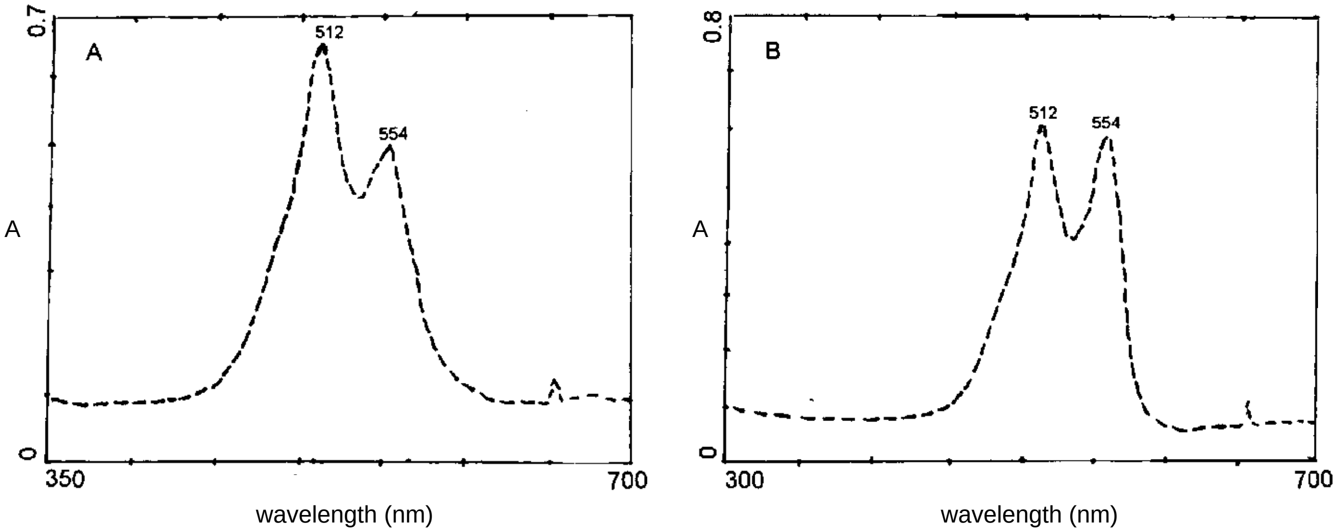


Figure 5. The absorption spectra of Dye 12, dye concentration ≈ 1 × 10^{-2} mol/L. (a) The dye is in aqueous KNO_3 solution. (b) The dye is in water. Both H-aggregate and monomer exist together.

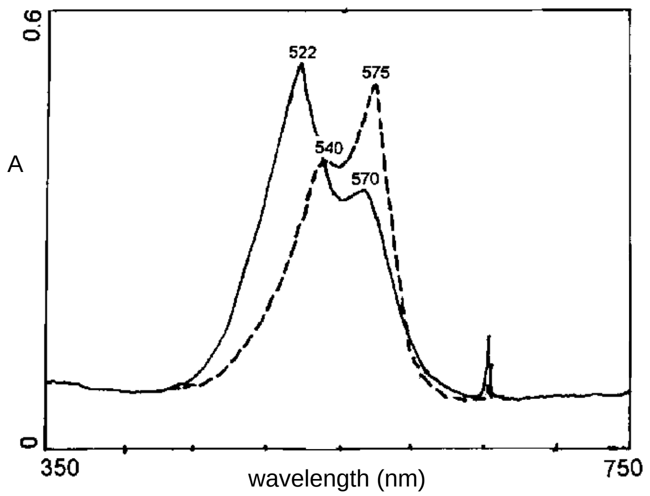


Figure 6. The absorption spectra of Dye 11. — The concentration of dye is 10^{-2} mol/L. The dye forms H-aggregates both in aqueous KNO_3 and in water. ——— The dye concentration is about 10^{-5} mol/L. The dye exists in monomer.

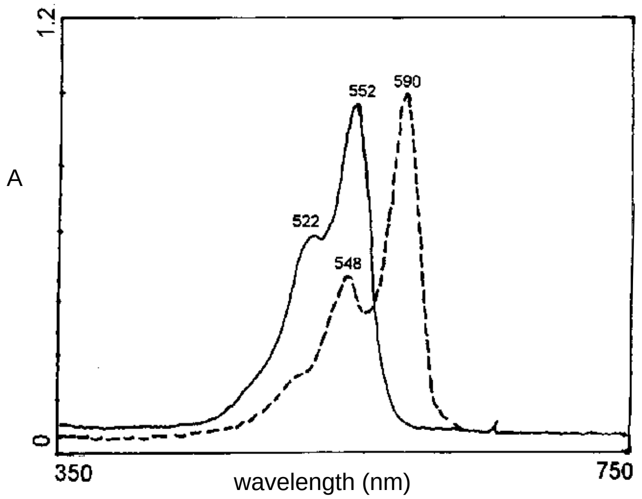


Figure 8. The absorption spectra of Dye 14. —— The concentration of dye is about 10^{-5} mol/L. The dye exists in monomer state. ——— The dye concentration is about 10^{-2} mol/L. The dye exists mainly in J-aggregates with or without added KNO_3.

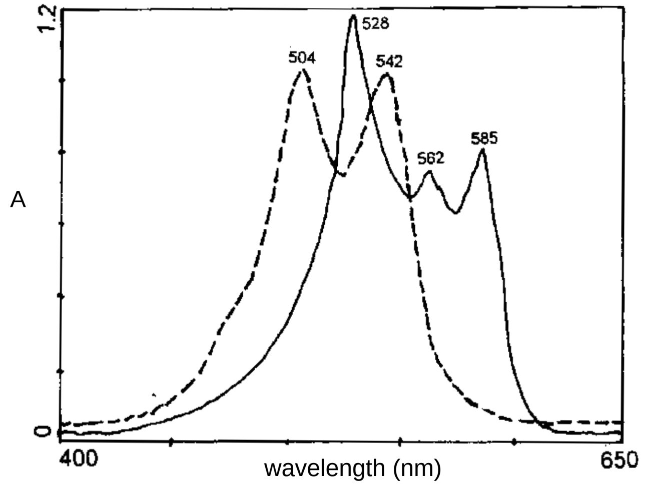


Figure 7. The absorption spectra of Dye 13 in water. ——— Concentration of dye is 7.5 × 10^{-3} mol/L, only the H-aggregate is formed. —— Concentration of dye is 1 × 10^{-2} mol/L; three states, H, monomer, and J, exist in aqueous KNO_3 solution.

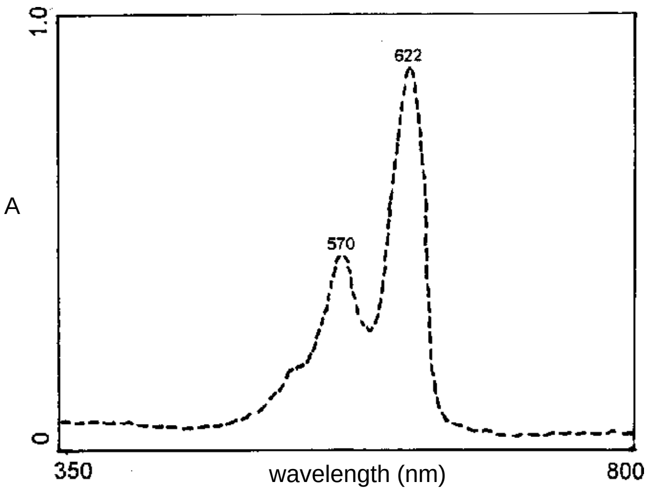
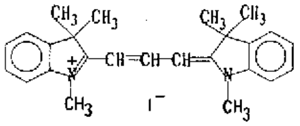
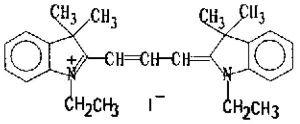
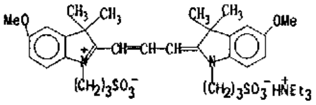
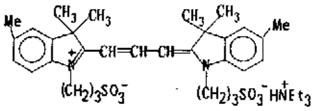
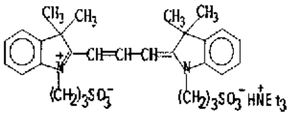
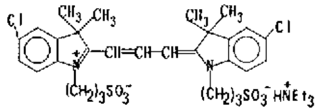
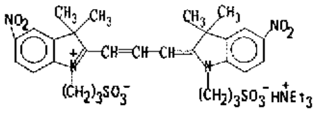


Figure 9. The absorption spectrum of Dye 15. The concentration is 5 × 10^{-3} mol/L. The dye exists mainly in J-aggregates, both in aqueous KNO_3 solution and in water.

TABLE IV. Electron-donating and Electron-accepting Properties

Dye no.	Structure	E_{tr} (eV)	E_{red} (VS, SFC)	E_{LU} (eV)	E_{HO} (eV)	σ_p
	AgBrI: E_{cb},< -3.23 ev, E_{vb},< -5.76 ev[9a]					
1		2.175	–1.26	–3.25	–5.42	
6		2.167	–1.28	–3.23	–5.39	
11		2.160	–1.60	–2.91	–5.07	–0.27
12		2.222	–1.40	–3.11	–5.33	–0.17
13		2.263	–1.36	–3.15	–5.41	0.00
14		2.238	–1.33	–3.18	–5.42	0.23
15		2.199	–0.82	–3.69	–5.88	0.78

and 15, carrying the electron-withdrawing Cl or NO_2 as substituents on the indolenine ring, displayed different patterns of desensitization with respect to undyed emulsion strips. The extent of desensitization strengthens as the amount of added dye increases. In particular, Dyes 5, 10, and 15, carrying the nitro group in the indolenine ring, which strongly reduced fog and sensitization (as compared to undyed emulsion) and left no residual color density, are good desensitizers. The extent of desensitization varied with the substituent in the heterocyclic nitrogen. Dye 4 and Dye 9, substituted by Cl and unsubstituted dyes (Dye 3 and Dye 8) not only produced desensitization, but also residual color density. Owing to heavy residual color density, these dyes are not useful desensitizing agents. The sensitivity of the emulsion strip dyed by Dye 13, which has sulfopropyl groups on the heterocyclic nitrogens, is 80 (ISO), higher than that of the undyed emulsion strip. The emulsion strip dyed by Dye 14 had almost the same sensitivity as the undyed emulsion strip, when 2 mL of 0.1% methanol solution of dye was added to 50 g emulsion.

From the experimental results listed in Table II, we can see that with a higher quantity of added dye, the sensitization of the dyed emulsion is lower and the residual color is heavier. The main cause may be that the solubility of iodide salts (Dyes 3, 4, 8, and 9) in water is much less than that of triethylammonium salts (Dyes 13 and 14). It is difficult with Dyes 3, 4, 8, and 9 to remove the residual color from the film strip in the process of development, fixation, and washing. The slight residual color of Dye 14 is probably due to the high quantity of dye added (6 mL dye solution to 50 g emulsion).

Reflectance Spectra. The reflectance spectra of dyes adsorbed on emulsion grains are generally accepted to indicate the states of aggregation of the dye. As seen in Fig. 2, when 3 mL of 0.1% methanol solution of Dye 5 and Dye 10 were added, respectively, to 50 g emulsion, the sensitized emulsions exhibited very strong J-aggregation peaks at 620 and 630 nm. These peaks were stronger than that of Dye 15, regardless of the quantity of Dye 15 added. The relative sensitivities of emulsion strips dyed with 3 mL/50 g emulsion Dye 5 and Dye 10 were reduced by 300 and 280 (ISO), whereas the sensitivity of the emulsion strip dyed with Dye 15, adding 4 mL dye to 50 g emulsion, was only 240 (ISO) less than that of the undyed one. The amounts of Dye 5 and Dye 10 adsorbed on AgBrI emulsion, which result from Van der Waals force of the conjugated aromatic system, are more than that of Dye 15. Among factors in desensitization by Dyes 5 and 10, holetrapping desensitization is quite severe, aside from electron-trapping desensitization.[8] Perhaps the strong J-aggregation is a fundamental indication of a strong cyanine desensitizer.

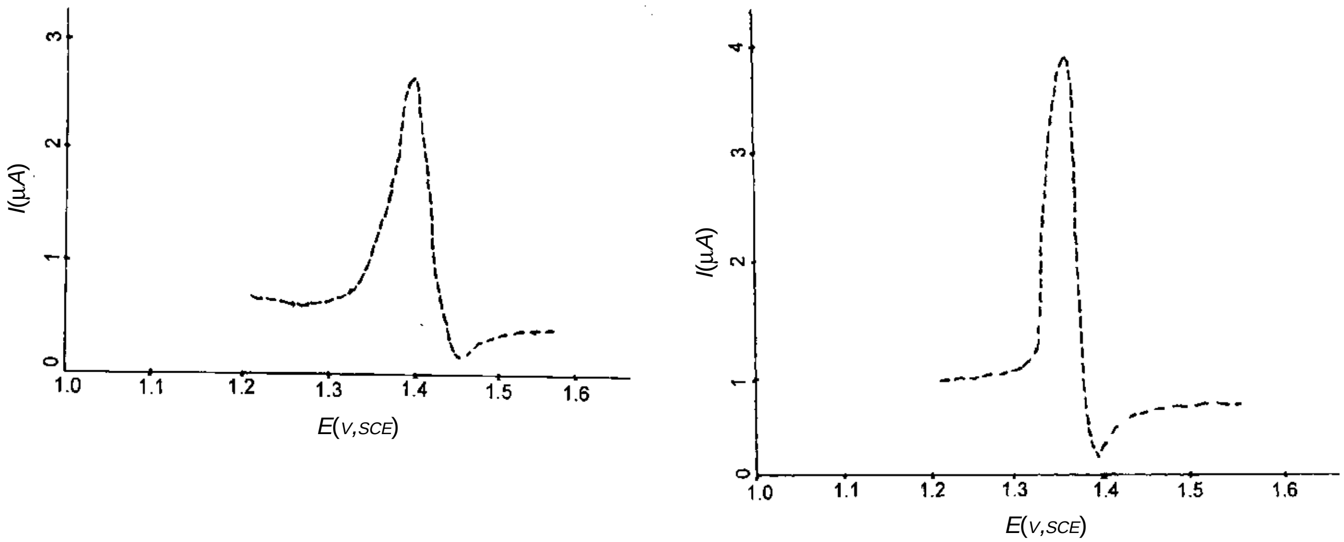


Figure 10. The cathodic oscillopolarography of (a) Dye 11, and (b) Dye 13, in aqueous methanol, dye concentration ≈ 1×10^{-4} mol/L; scan rate, 5 mV/s; SCE reference electrode.

Dyes 4, 9, and 14, which have the same substituent on the 5-position of the indolenine ring and different groups on heterocyclic nitrogen, result in various aggregation behaviors and sensitization effects. As shown in Figs. 4(a), 4(b), and 4(c), these dyes were adsorbed on emulsion in certain proportion of monomer, H-aggregation, and J-aggregation; the main states are J-aggregation for Dyes 4 and 9 and monomer for Dye 14. The addition of Dye 4 and Dye 9, like Dye 5, Dye 10, and Dye 15, led to stronger desensitization, whereas Dye 14, having sulfopropyl on the N atom, desensitized slightly. The same case and conclusion are also obtained with the unsubstituted Dye 3, Dye 8, and Dye 13.

The reflectance spectra of emulsion strips dyed, respectively, with Dyes 1, 2, 6, 7, 11, and 12, which resulted in extremely high fog, display higher H-aggregation peaks. These dyes readily exist on emulsion microcrystals as dimer, trimer, tetramer, etc.

As shown in Fig. 3, with increasing dye added to the emulsion, the J-aggregation state saturates; then, as the aggregate of the H-state and M-state increase, the proportion of the J-aggregation decreases. Note that there is an optimum concentration of dye for forming larger proportion J-aggregation and for better spectral sensitization.

Absorption Spectra. The states of the dyes in solution at higher concentration of dyes were investigated by using Dyes 11 through 15. Figures 5 through 9 show the absorption spectra of Dyes 11 through 15, respectively, in water or in KNO_3 solution, with the dye concentration about 10^{-2} mol/L. The dyes exhibited hypsochromic or bathochromic shifts to various extents with respect to the peak absorption wavelength of the dye monomer. The maximum absorption peaks of Dye 11 and Dye 12, shown in Fig. 5 and Fig. 6, are at 522 and 514 nm, respectively, which we assign to H-aggregation, suggesting that Dyes 11 and 12 exist mainly in the H-aggregation state. The experimental results in aqueous solution are not substantially different from those of dyes on silver halide emulsion. The maximum absorption peaks of Dyes 14 and 15, shown in Figs. 8 and 9, are at 590 and 622 nm, respectively, which relate to the appearance of J-aggregation states of these dyes, and these J-absorption peaks appear readily, whether or not KNO_3 is added to the dye solution. Finally, as shown in Fig. 7, it is difficult for Dye 13 in aqueous solution to exhibit the absorption peak of J-aggregation. With the addition of KNO_3 to the dye aqueous solution, the 586-nm peak appears, and the three states exist together. The results in solution differ slightly from those on the emulsion strips.

Reduction Potential. At present, estimates of energy levels for silver halide and dyes adsorbed to silver halide still rely mainly on electrochemical data obtained from the unaggregated dye in solution. Although there are some exceptions and deviations, these data are generally acknowledged and can be used to anticipate the approximate sensitizing effects of the dyes.

According to many reports, the reduction potentials of dyes having CH_3 and CH_2CH_3 on heterocyclic nitrogen and the same substituent groups elsewhere are almost identical, and they are slightly less negative in value than those of dyes having sulfoalkyl groups on heterocyclic nitrogen.[9b] Our experimental results are consistent with these reports.

The reduction potentials of seven dyes were measured. In our experiment, the reduction potential was obtained

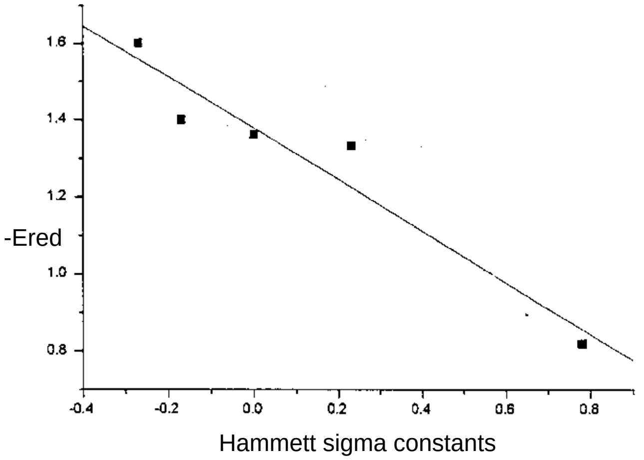


Figure 11. Correlation of the reduction potentials (E_{red}) of dyes in Series III and the Hammett sigma constants (σ_p) of the substituent R_1.

polarographically. We can see from Figs. 10(a) and 10(b) that only reduction peaks occur. The electrochemical potentials measured are irreversible, and these values are more negative than those that have been reported previously.[10] The lowest vacant and the highest occupied electronic energy levels of dyes, E_{LU} and E_{HO}, are, respectively, estimated as follows[11]:

$$E_{LU} = -E_{red} - 4.51,$$
$$E_{HO} = -E_{red} - E_{tr} - 4.51.$$

The data are summarized in Table IV. From these data we conclude that the redox properties of the dyes are closely related to the type of substituent on the indolenine ring. Figure 11 shows that the reduction potentials of dyes in Series III vary linearly with the Hammett sigma values for these substituents (σ_p), and the correlation coefficient is –0.9651.

Dye 15 may be taken as an example of a strong desensitizer. Its E_{LU} (–3.69 eV) is much lower than E_{cb} AgBrI (–3.23 eV); the difference amounts to 0.46 eV. It is impossible for Dye 15 to inject electrons into the conduction band of silver halide; in contrast, it is very easy for it to trap electrons from the surface of silver halide, leading to strong desensitization by the electron-trapping process. The observed strong desensitizing efficiency of Dye 15 is in very good agreement with the theoretical expectation. The same situation and the same conclusion are probably so with Dye 5 and Dye 10.

Dye 13 can be considered as typical of sensitizers or nondesensitizers. Its E_{LU} (–3.18 eV) is higher than the E_{cb} AgBrI (–3.23 eV), which is favorable to the electron-injection process from dye to the conduction band of silver halide, showing a positive sensitizing efficiency. The same is true for Dye 14, but it by no means implies that the greater the difference between the dye E_{LU} and silver halide E_{cb} AgBrI is, the higher the sensitizing efficiency. The E_{LU} of Dye 11 (2.91 eV) is much higher than E_{cb} AgBrI (–3.23 eV); $E_{cb} - E_{LU} = -0.32$ eV. The electron-donating capacity of Dye 11 is so strong that the unexposed silver halide can be reduced, giving extremely high fog values.

As far as the ways of forming heavy fog are concerned, there are several possible assumptions and explanations. First, this reduction leading to high fog values cannot be attributed to the possible contamination by foreign reducing substances left during the synthesis procedures, because the elemental analysis and other data listed in Table I have shown that all of the synthesized dye samples are of high purity; in our opinion, this effect ought to be excluded. Second, the possible direct reduction of silver halide grains by dye molecules in an alkaline medium very close to the development conditions was considered. A special test indicated that Dye 11 at the pH of development lacked the capacity to initiate and produce such heavy fog levels. Third, the effect of dye molecules on the nucleation and growth of fogging centers ought to be considered.

According to contemporary concepts, the fogging centers can be classified into two different types: emulsion fog and development fog.[12] Their respective chemical nature, composition, fog scope, and extent may be entirely different. To clarify which type's growth contributed the high fog level is quite difficult, given only the experimental results of the present study. Special research on this interesting topic will follow in the near future.

In the present study there are several dyes (Dyes 1, 2, 6, 7, and 12) with very strong reducing tendencies and they act much like Dye 11, indicating that sensitizing dyes with comparatively high E_{LU} (E_{cb}–E_{LU} = 0.1 to 0.2 eV) favor or enhance the sensitizing efficiency, but E_{cb}– E_{LU} > 0.3 eV, on the contrary, can be of great harm to the normal developing and the sensitizing efficiency. In extreme cases, the emulsion strips can be fogged and entirely blackened.

From the present aggregation state results, one can conclude that the capacity to form J-aggregates is a prerequisite for an effective sensitizing dye, such as Dye 13, but it is not necessarily a sufficient condition. For example, Dye 15 ($\lambda_{\max}$ = 580 nm) is notable for its high capacity to form J-aggregates, but it has very negative E_{LU}. This dye is a strong desensitizer. It is interesting to note here that the capacity to form J-aggregates is probably also required for a strong desensitizer.

As far as the extent of residual dyeing is concerned, it can be seen from Table II that the indocarbocyanine dyes having Cl and NO_2, respectively, at the 5-positions of the indolenine rings demonstrated completely contradictory results. The Cl group strengthens, but the NO_2 group weakens the dyeing tendency. Introduction of $(CH_2)_3SO_3^-$ group on the heterocyclic nitrogen atom in place of the alkyl group helped to reduce, even to eliminate completely, the dyeing capacity. If a comparison is made between the rules of residual dyeing capacity of the benzoxacarbocyanine dyes[13] and the indocarbocyanine dyes, we can see that the presence of Cl and OCH_3 at the 5-positions of benzoxazole rings causes no residual dyeing density at all for the benzoxacarbocyanine dye. On the contrary, the same substitution at the 5-positions of the indolenine rings leads to severe dyeing by the indocarbocyanine dyes. Probably the difference in dyeing capacity for these two different classes of carbo-cyanine dyes may be attributed to a distinction in adsorption kinetics on silver halide. The problem of explaining the rules governing the residual behaviors awaits further comparative investigation.

Considering the different photographic, electrochemical, and sensitometric characteristics as a whole, one can conclude that an effective sensitizing dye must meet the following major requirements simultaneously:

1. Reasonable absorption spectra.
2. Strong tendency to form J-aggregate states.
3. Appropriate redox potentials.
4. Proper interaction state between the dye and silver halide microcrystals with different habits.
5. No residual dyeing density on the processed emulsion strips.

The present systematic survey and investigation have deepened our knowledge of the structure–sensitizing efficiency relationship. Further effort will be made toward new insight to comprehend and optimize the screening of indocarbocyanines, especially unsymmetrical indocarbocyanine dyes having good sensitometric performance, washout properties, and suitability for image recording. A special study of the unsymmetrical indocarbocyanine dyes will be reported in detail elsewhere.

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