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Chromatographic Investigations Related to Photographic Theory[1]

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Elution chromatography has been applied to the separation of a series of photographic sensitizing and desensitizing dyes, using silver bromide as the adsorption medium and aqueous pyridine solutions as the chromatographic developer. The following water-soluble dyes were used to determine relative adsorption of various colorless compounds by silver bromide: phenosafranin, 3,3'-diethyloxacarbocyanine chloride, methylene blue, 3,3'-diethylthiacarbocyanine *p*-toluenesulfonate, 1,1'-diethyl-2,2'-carbocyanine chloride. The ease of displacement of the dyes from the silver bromide column decreases in that order. The chemical sensitizer, allylthiourea, displaces all five dyes with about equal ease and is more strongly adsorbed than any of them. Thiourea is not so strongly adsorbed as the allyl derivative. The photographic developers, hydrazine and *p*-phenylenediamine, displace phenosafranin and 3,3'-diethyloxacarbocyanine, showing that these agents are themselves adsorbed. Hydroquinone and catechol in aqueous solution at *p*H 8 mordant the dyes, showing that these developing agents are adsorbed in the presence of the dyes. Gelatin displaces phenosafranin and 3,3'-diethyloxacarbocyanine but not the other dyes. The antifoggant, 6-nitrobenzimidazole, is more strongly adsorbed than benzimidazole. Data also were obtained for the following compounds: glutathione, *dl*-methionine, benzothiazole, benzotriazole, lauryl pyridinium *p*-toluenesulfonate, sodium sulfite, sodium thiosulfate and ammonia.

Adsorption of several classes of substances plays, or is believed to play, an important role in the chemistry of the photographic process. The sensitizing dyes must be adsorbed by the silver halide grains before optical sensitization can occur.[2] Adsorption of gelatin and of ripening restrainers plays a dominant role in determining the growth and shape of the silver halide grains during the preparation of the photographic emulsion.[1] It has been suggested that adsorption of antifogging agents is an important factor in determining the relative antifogging action of these agents.[3] It has also been suggested that the photographic developing agents are adsorbed by the silver halide prior to chemical reaction[4a,b] and that chemical sensitizers are adsorbed by the silver halide prior to the formation of the sensitivity centers.[5] Comparative data on the adsorption of these various agents by silver halides are scanty, however, and have been confined largely to sensitizing and desensitizing dyes.[2,6]

In the present investigation, the technique of elution chromatography was employed. Columns of precipitated silver bromide were prepared and charged with various dyes. The rate of elution of the dyes by aqueous solutions of various substances was then followed. In the first stage of the investigation, aqueous pyridine was chosen as the standard chromatographic developer, and the relative order of displacement of a series of ten dyes was determined. In the second stage of the investigation, five of these dyes were chosen to form a standard dye series, and the relative efficacy of various substances as developers in aqueous solution was determined in terms of the rates of elution of the various dyes.

Experimental Procedure

Preparation of the Column.—The silver bromide was prepared and used under darkroom conditions (illumination by a Wratten No. 0 safe light) as follows: One hundred seventy grams of silver nitrate dissolved in a liter of water was added to a solution of 120 g. of potassium bromide in a liter of water over a period of 2 minutes, with vigorous mechanical agitation. The stirring was continued for 15 minutes. The silver bromide was washed by decantation five times, 3 liters of water being employed each time. The halide grains were then permitted to age under water at room temperature for at least 5 days prior to use in the columns.

The aged silver bromide was packed into glass tubes of 6-mm. internal diameter, partly closed at one end by fire polishing. A wad of glass wool was inserted into this end to prevent the silver bromide particles from being forced out of the tube. The tubes were approximately 30 cm. in length, and the silver bromide column usually was 16 to 18 cm. in length. Two hundred milliliters of distilled water was forced through each tube under 5 lb. of pressure before use.

The specific surface of the silver bromide was determined in terms of adsorption of 3,3'-diethyl-9-methylthiacarbocyanine chloride. One gram of the silver bromide adsorbed 0.5×10^{-3} millimole of the dye. Sheppard, Lambert and Walker[7] found that one molecule of this dye covered approximately 86 square Å. Thus, the specific surface of the silver bromide sample used in the present experiments is approximately 2.6×10^{19} square Å. or 2.6×10^{3} sq. cm.

Not all of the surface of the free silver bromide precipitate was available for dye adsorption in the packed column, however. A column containing 4.3 g. of silver bromide adsorbed only 1.6×10^{-3} millimole of dye. When the silver bromide was removed from the column and treated with more dye solution, a further amount of 0.6×10^{-3} millimole of dye was adsorbed. Thus, the total dye adsorption (2.2×10^{-3} millimole) agrees well with the previously found value of 0.5×10^{-3} millimole per gram of silver bromide.

Charging and Development.—The dyes employed, together with their code designation, are given in Table I. In the experiments to determine the relative displacement of the various dyes, mixtures of two or three dyes were used, and the dyes were present in equal molecular amounts. Each tube was washed with 5 cc. of ethanol, then charged with 10^{-3} millimole of dye mixture dissolved in 1 cc. of ethanol. This was followed by a 2-cc. water-wash before development was started. In the experiments to determine the relative effectiveness of various developers, a mixture of equal molar quantities of Dyes P, II, MB, I and VI was used. In some of these experiments, the tubes were washed with ethanol, then charged with 1 cc. of 10^{-3} *M* dye solution in ethanol. In others, 10 cc. of 10^{-4} *M* dye solution in water was used, and the preliminary ethanol wash was omitted. The dyes were more readily removed by weak developers when the ethanol charge method was employed, possibly because of a difference in the state of the dye on the surface when adsorbed from ethanol instead of from water, or possibly because of an effect of ethanol upon the silver bromide surface. Thus, 90 to 100 cc. of water was required to remove phenosafranin from an ethanol-charged tube, as compared with 165 to 175 cc. from a water-charged tube. Dye II was removed from an ethanol-

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(1) Presented at the Meeting of the American Chemical Society, April 4, 1951, in Boston, Mass.

(2) C. E. K. Mees, "Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1942.

(3) S. M. Solov'ev and V. A. Smirnova, *J. Appl. Chem.* (*U. S. S. R.*), **20**, 439 (1947).

(4) (a) S. E. Sheppard and G. Meyer, THIS JOURNAL, **42**, 689 (1920); (b) P. Wulff and K. Seidl, *Z. wiss. Phot.*, **28**, 239 (1930).

(5) S. E. Sheppard, R. H. Lambert and R. L. Keenan, *J. Phys. Chem.*, **36**, 174 (1932).

(6) W. West, B. H. Carroll and D. L. Whitcomb, to be published.

(7) S. E. Sheppard, R. H. Lambert and R. D. Walker, *J. Chem. Phys.*, **7**, 265 (1939).

charged tube by 425 cc. of water, whereas 800 cc. was insufficient to remove it from a water-charged tube. On the other hand, no difference was noted when a strong developer, such as allylthiourea, was used.

Table I

List of Dyes

Code	Name
P	Phenosafranin
I	3,3′-Diethylthiacarbocyanine *p*-toluenesulfonate
II	3,3′-Diethyloxacarbocyanine chloride
III	3,3′-Diethyl-4,5,4′,5′-dibenzothiacarbocyanine bromide
VI	1,1′-Diethyl-2,2′-carbocyanine chloride (pinacyanol)
VII	3,3′-Diethylthiazolinocarbocyanine *p*-toluenesulfonate
X	3,3′-Dihexyloxacarbocyanine perchlorate
XI	3,3′-Diethyl-5,5′-di-*t*-amyloxacarbocyanine perchlorate
XIII	3,3′-Diethyl-4,5,4′,5′-dibenzoöxacarbocyanine bromide
MB	Methylene blue

Unless otherwise specified, all operations were carried out at room temperature (23–24°). For development, a 200-cc. pipet filled with the developer solution was placed above the column and attached to it by rubber tubing. Development was carried out generally under 5 lb. of pressure supplied by tank nitrogen, and the eluate was collected in a graduate placed just below the tip of the tube. The tubes were generally wrapped with black tape so that development could be carried out in daylight. Successive samples of eluate were collected and the dyes present in the eluate samples determined from the spectral-transmittance curves read on the General Electric Automatic Spectrophotometer.

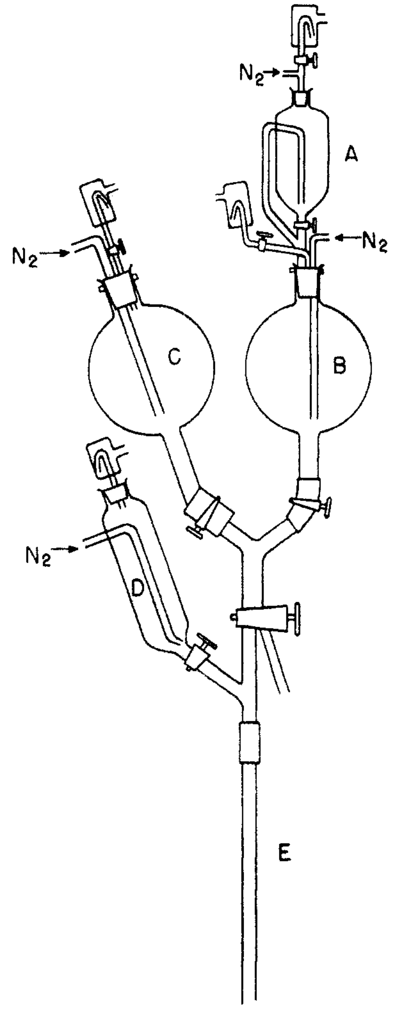

Fig. 1.—Apparatus for chromatographic development with oxygen-free solutions.

When the developer was susceptible to oxygen oxidation, as when photographic developing agents were used, the solutions were prepared and used in the apparatus illustrated in Fig. 1. The developing agent in acid solution was placed in bulb B, and the alkali necessary to give the desired final *p*H was placed in bulb A. Bulb C contained distilled water; and bulb D, the dye solution. All solutions were deaerated by passage of nitrogen through them. The silver bromide column, E, was then washed with approximately 75 cc. of deaerated water under 5 lb. of pressure, the dye solution (10^{-3} millimole of dye dissolved in 10 cc. of water) was added from bulb D, 10 cc. more water was passed through the column from C, and then the developing solution obtained by mixing the contents of A and B was passed through the silver bromide column. The eluate was collected in tubes containing 6 *M* acetic acid to prevent oxygen oxidation.

Experimental Results

Determination of Order of Displacement of Dyes.—The dye mixture usually formed bands as it passed into the column, and the relative adsorption of the dyes could then be determined from the position of the bands. However, some dye bands overlapped considerably, and others were too nearly the same color to be distinguished with certainty. Accordingly, elution development was carried out with all dye mixtures, and, when the identity of any dye was in doubt, absorption spectra of the eluates were obtained.

Development was started with a 0.2% aqueous pyridine solution. Weakly adsorbed dyes were displaced by this solution, whereas the dyes which were more strongly held remained in the column. When the eluate became colorless, or if no dye was displaced, development in this solution was discontinued, and a 0.5% solution of pyridine was substituted. If dye was displaced by this solution, development was continued until the eluate became colorless; then the strength of the pyridine solution was increased to 1%. Subsequent developments were carried out with 1.5, 2, 4, 6, 10 and 15% pyridine if necessary. In this way, the following relations were obtained between the various dyes tested, where, in each instance, the dye preceding the symbol > is more strongly held by the silver bromide than the dye following it: $\mathrm{III} > \mathrm{I} > \mathrm{II}$; $\mathrm{VI} > \mathrm{I} > \mathrm{II}$; $\mathrm{I} > \mathrm{MB} > \mathrm{II}$; $\mathrm{II} \geqslant \mathrm{VII} > \mathrm{P}$; $\mathrm{X} > \mathrm{II}$; $\mathrm{XIII} > \mathrm{XI} > \mathrm{II}$; $\mathrm{XIII} > \mathrm{VI} > \mathrm{I}$; $\mathrm{I} \geqslant \mathrm{XI}$; $\mathrm{III} > \mathrm{XIII}$; $\mathrm{X} \geqslant \mathrm{MB}$.

From this series of relations, the following composite arrangement of dyes can be derived: $\mathrm{III} > \mathrm{XIII} > \mathrm{VI} > \mathrm{I} \geqslant \mathrm{XI} > \mathrm{X} \geqslant \mathrm{MB} > \mathrm{II} \geqslant \mathrm{VII} > \mathrm{P}$.

Results Obtained with Various Developing Agents.—On the basis of the preceding results, five dyes were chosen as reference dyes for use in determining the relative effectiveness of colorless developing agents. The dye series is the following

$$\mathrm{VI} > \mathrm{I} > \mathrm{MB} > \mathrm{II} > \mathrm{P}$$

These dyes have a solubility of about 10^{-3} *M* or more in water. The absorption peaks are well separated, so that the concentrations of each in a mixed solution can be determined easily. The following method of quantitative expression was adopted: The partial optical density of each dye was determined from spectral-transmittance curves for each sample of eluate. Graphs were constructed for each dye by plotting the density of the absorption maximum against the volume of eluate. Such graphs are illustrated in Figs. 2 to 6. The volume of developer required to displace the major portion of any particular dye from the silver bromide was determined as the sum of all eluate cuts in which the density of the particular dye was 10% or more of the maximum density for that dye. The volumes so obtained agreed well with those determined visually when a fairly sharp separation of the various dyes was obtained.

The data in Table II illustrate the reproducibility of the results obtained with one particular developer (0.01 *M* benzothiazole at *p*H 5.9). The values given represent the volumes of developer required to elute the particular dyes. The table also includes data obtained with a column which had been charged with only 0.3×10^{-3} millimole of the dye.

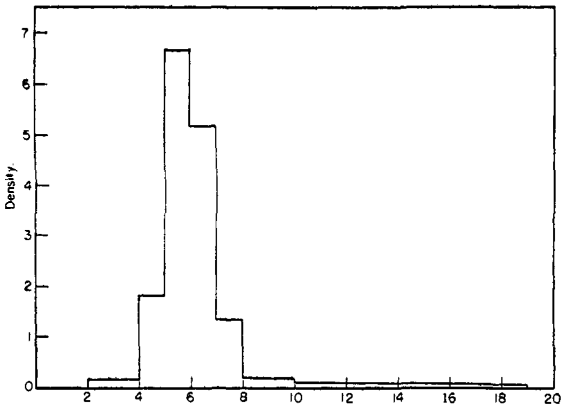

Fig. 2.—Elution of Dye VI (pinacyanol) by 0.001 *M* allylthiourea at *p*H 8.0.

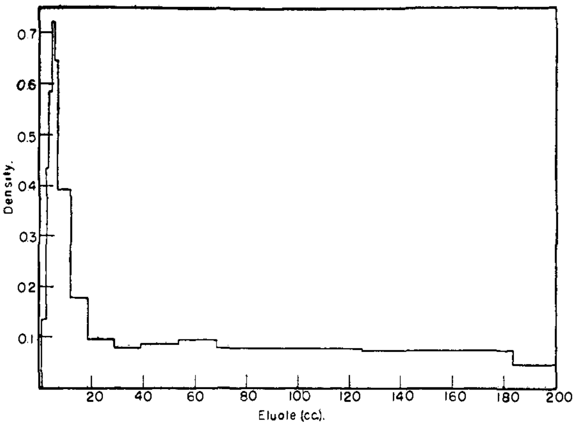

Fig. 3.—Elution of Dye VI by 0.001 *M* thiourea at *p*H 8.0.

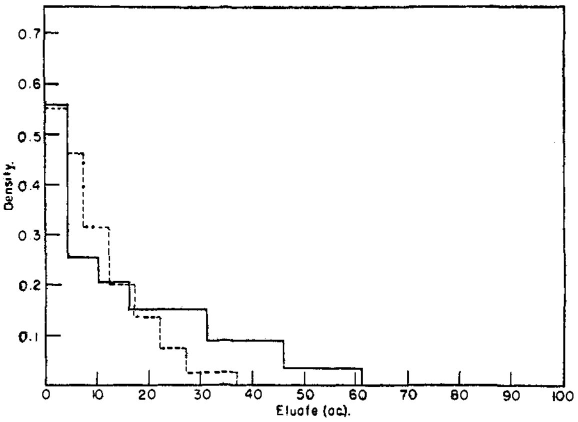

Fig. 4.—Elution of phenosafranin by 0.5% gelatin solution at *p*H 6.2: solid curve, 22°; broken curve, 48°.

It is seen that the volume of developer required to displace a given dye is roughly independent of the amount of dye present, within the limits of the experiment.

TABLE II

DISPLACEMENT OF DYES BY 0.01 *M* BENZOTHIAZOLE AT *p*H 5.9

Column no.	Dye used, millimoles × 10³	Volume developer required to displace P	II	MB	I
61	1.0	2	8	25	174
63	1.0	4	8	18	166
62	0.3	4	8	17	(140)[a]

[a] Visual estimate.

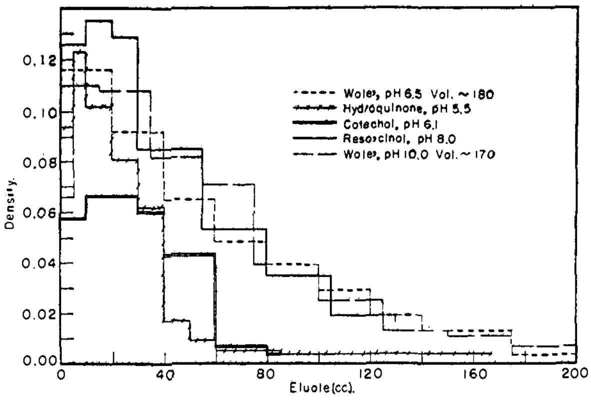

Fig. 5.—Elution curves for phenosafranin: ---- water, *p*H 6.5; -/-/- hydroquinone, *p*H 5.5; ▬ catechol, *p*H 6.1; —— resorcinol, *p*H 8.0; — — water, *p*H 10.0.

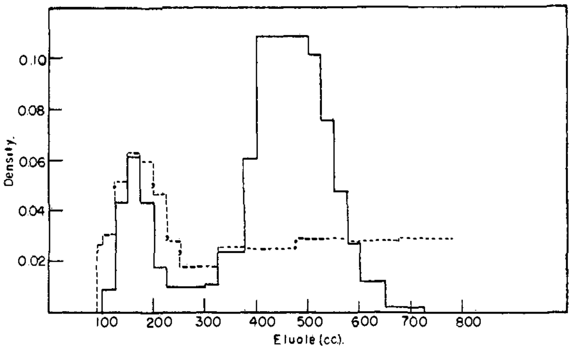

Fig. 6.—Elution of Dye II by: ---- water, *p*H 3.5; —— 0.002 *M* benzimidazole, *p*H 3.5.

Displacement of the dyes by solvent action, *e.g.*, no absorption of the developer, shows little dependence upon *p*H. Visual determinations with 40% ethanol as developer showed no definite difference in the displacement of the dyes at *p*H 3.5 and at *p*H 10. The following volumes of water were required to displace phenosafranin: 100 cc. at *p*H 3.5, 165 cc. at *p*H 6, 165 cc. at *p*H 10. More than 800 cc. of water was required to displace Dye II at any of the three *p*H values.

Thiourea and Allylthiourea.—The chemical sensitizer, allylthiourea, displaced all five dyes simultaneously. The displacement plots for II, MB, I and VI have roughly the same form, and about the same volume of developer is required for each. The data are tabulated in Table III, for 0.001 *M* and 0.0001 *M* allylthiourea at *p*H 6 and 8. (In this and all subsequent tables, values given in parentheses refer to maximum densities.) Eight to ten times the volume of 0.0001 *M* developer as of the 0.001 *M* solution is required to displace the dyes. The data also show that the allylthiourea is more effective at *p*H 6 than at *p*H 8. This same *p*H effect appears with some of the other developing agents, although no effect of *p*H was noticed with either water or 40% ethanol as developer between *p*H 6 and 10, and the quaternary salts tested were more effective at the higher *p*H.

TABLE III

DISPLACEMENT OF DYES BY THIOUREA AND ALLYLTHIOUREA

Developer	Concn.	*p*H	Vol. developer required to displace P	II	MB	I	VI
Allylthiourea	0.001	8.0	3	5	4	4	4
			(3.7)	(14.6)	(8.2)	(13.5)	(6.7)
	.0001	8.0	25	38	32	32	44
			(0.53)	(1.6)	(0.86)	(1.4)	(0.67)
	.0001	6.0	23	26	18	25	25
			(0.64)	(2.6)	(1.1)	(2.0)	(1.12)
Thiourea	.001	8.0	6	6	20	28	180
			(4.2)	(13.8)	(1.46)	(1.9)	(0.72)

After development by the allylthiourea had been completed, the columns were washed with water and the silver bromide was removed. The silver bromide was then titrated with 3,3′-diethyl-9-methylthiacarbocyanine bromide. The amount of 0.001 *M* dye solution required in each titration was approximately 0.6 cc. This, as already discussed, appears to be a blank required to cover silver bromide surface which, in the column, is mechanically protected from dye or developer. No dye was adsorbed by silver bromide which had been treated with allylthiourea outside the column.

The titration experiments with the allylthiourea-treated samples show that, apart from the blank, no dye is adsorbed. This shows that the silver bromide surface is covered with allylthiourea which prevents adsorption of the thiacarbocyanine dye, and displacement of the allylthiourea by the thiacarbocyanine does not occur.

Thiourea is less effective than allylthiourea, as shown by the data in Table III. Although phenosafranin and Dye II are readily displaced by the thiourea, the other dyes are displaced with more difficulty. The displacement graphs given in Figs. 2 and 3 show another point of interest, namely, the long "tail" in the displacement of Dye VI by thiourea (Fig. 3), as compared with the substantial lack of "tail" in the displacement by allylthiourea (Fig. 2). After 19 cc. of thiourea had passed through the column, the density of Dye VI had dropped to about one-eighth of the maximum value, but the density then remained nearly constant for 165 cc. This long "tail" suggests that the dye coming off in the later stages of development is more strongly adsorbed than that displaced in the early stages and is displaced by the thiourea only with difficulty. It is, however, displaced readily by the more strongly adsorbed allylthiourea, and the "tail" obtained with this developer is short. Long "tails" of lower density also were obtained in the development of Dye I and methylene blue by thiourea.

Gelatin.—Sheppard, Lambert and Keenan[5] found that gelatin was held so tightly by silver bromide grains from a photographic emulsion that not all of it could be removed by boiling with water for several hours or by digestion with 10% sulfuric acid for 6 hours. However, the gelatin does not prevent adsorption of sensitizing dyes, nor does it prevent rapid reduction of the silver bromide grains by active photographic developers.

A series of tests was included in the present investigation, in which gelatin solutions were used as the chromatographic developer. The results are given in Table IV and in Fig. 4. Development was carried out both at 22 and 48°. The experimental procedure at the higher temperature was the same as that previously employed. The complete apparatus was jacketed, and temperature was maintained by circulating water through the jackets. The tubes were charged with ethanol dye solution.

TABLE IV

DISPLACEMENT OF DYES BY GELATIN

Concn. of gelatin, %	*p*H	Temp., °C.	Volume developer to displace P	II
0		24	91 (0.26)	425 (0.13)
0.1	6.4	22	77 (.18)	320 (.16)
.5	6.2	22	46 (.56)	225 (.29)
.5	4.0	22	13 (1.75)	89 (.80)
0		48	41 (0.46)	190 (.32)
.5	6.2	48	27 (.55)	116 (.44)
2.0	6.1	48	18 (.80)	105 (.70)

Gelatin will displace both phenosafranin and Dye II, but relatively large amounts are required. Gelatin is more effective on the positive side of the isoelectric point (*p*H 4.0) than on the negative (*p*H 6.2). The gelatin is more effective at 48° than at 22° by a factor of about 2, but the same factor applied to removal of the dyes by water. In none of the experiments was there any evidence of displacement of methylene blue or any of the more strongly adsorbed dyes.

An experiment was carried out in which the silver bromide column was charged with gelatin before the dyes were added. The column was treated with 100 cc. of 0.5% gelatin at 22°, after which the dye was added in aqueous solution. Development was carried out with 0.10 *M* pyridine. The data are given in Table V. Comparison of the data with results obtained in the absence of gelatin with the same developer indicates that the dyes are somewhat more readily displaced in the presence of gelatin.

TABLE V

EFFECT OF GELATIN ON DISPLACEMENT OF DYES DEVELOPER, 0.10 *M* PYRIDINE

Column contg.	Volume required to displace P	II	MB
Plain AgBr	4 (2.6)	21 (2.6)	>200 (0.05)
Gelatin-coated AgBr	4 (3.9)	12 (5.0)	110 (.32)

Photographic Developing Agents.—The photographic developing agents could not be tested as chromatographic developers in the *p*H range where they are useful photographically because of their attack upon the silver bromide. However, several of the agents could be used at lower *p*H. Hydrazine could be used at *p*H 8.0 with the standard technique, since no special precautions to exclude oxygen were necessary. The other agents used were too readily attacked by oxygen, however, and, to avoid loss of developing agent and possible complications from oxidation products, these agents were used in the apparatus shown in Fig. 1.

Hydrazine at *p*H 8.0 displaced phenosafranin and Dye II but did not displace any of the other dyes. The hydrazine displaced dye from gelatin-coated silver bromide much more readily than from the plain silver bromide. Data are given in Table VI. The figures for the water control immediately following the hydrazine data apply to a column charged with dye from alcohol solution. Examination of the columns after the hydrazine development showed that no significant reduction of silver bromide had occurred.

TABLE VI

DISPLACEMENT OF DYES BY PHOTOGRAPHIC DEVELOPING AGENTS

Developer	Concn.	*p*H	Treatment AgBr	Volume to displace P	II
Hydrazine	0.01	8.0	None	15 (0.96)	>115 (0.28)
	.10	8.0	None	8 (1.7)	172 (0.55)
	.10	8.0	Gelatin	3 (4.1)	7 (6.1)
Water	..	...	None	91	425 (0.13)
p-Phenylenediamine	0.01	8.0	None	40	100
	.01	8.0	Ferricyanide	60	125
	.01	8.0	Gelatin	45	70
Water	..	...	None	180	>500

Data for development by *p*-phenylenediamine are also given in Table VI, together with the water control for a column dyed from aqueous solution. Phenosafranin and Dye II are completely eluted by the *p*-phenylenediamine solution, but none of the other dyes was displaced. Some reduction of silver bromide occurred during the later stages of displacement of Dye II. In an attempt to prevent this, a column was washed with potassium ferricyanide solution to destroy any silver centers which might be present in the silver bromide. The column was then thoroughly washed with water and used as before. The start of reduction of the silver bromide was delayed somewhat by the ferricyanide treatment, but a significant amount was occurring at the end of the experiment. However, considerable dye had been displaced in both experiments before any reduction could be detected, and the reduction occurring in the later stages should not invalidate the general conclusion that *p*-phenylenediamine displaces both phenosafranin and Dye II.

Experiments were carried out with 0.01 *M* solutions of hydroquinone and catechol at *p*H of 8.0 and of approximately 6. Experiments were also carried out with resorcinol at *p*H 8.0 and 10.0. Adsorption of the latter compound by silver bromide has been reported in the literature.[4a,8] No dye was displaced by either the hydroquinone or catechol solution at *p*H 8.0. All but 11% of the phenosafranin was displaced by 400 cc. of the resorcinol solution at *p*H 8.0. At this point, the eluate was substantially colorless, and no trace of Dye II had appeared. No destruction of dye by the developing agents had occurred, since the dyes could be recovered quantitatively by extraction of the silver bromide with pyridine solution.

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(8) H. Ukihashi and S. Kikuchi, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **52**, 240 (1949).

At *p*H 5.55, 430 cc. of hydroquinone solution eluted 49% of the phenosafranin, and at *p*H 6.1, 300 cc. of catechol solution eluted 45% of the phenosafranin. The elution curves compared with the water controls are given in Fig. 5. No Dye II appeared in the eluate with either catechol or hydroquinone. Resorcinol at *p*H 10.0 failed to displace any dye.

Miscellaneous Organic Compounds.—A group of water-soluble organic compounds of photographic interest was tested as chromatographic developers. Results obtained with these compounds are given in Tables VII and VIII. All of the agents displace phenosafranin and Dye II, although none is as effective as the thioureas. All except methionine displace methylene blue from the ethanol-charged columns, and most of them cause some displacement of Dye I.

TABLE VII

DISPLACEMENT OF DYES BY MISCELLANEOUS ORGANIC COMPOUNDS

Column charged from ethanol solution

			Volume developer required to displace			
Developer	Concn.	*p*H	P	II	MB	I
Water		6.5	91	425	.....	....
Dye II	0.001		2	....	57	>80
			(6.4)		(0.57)	(0.30)
Glutathione	.001	8.0	12–15	14	>200	
			(1.1)	(3.4)	(0.04)	
	.001	3.5	4	14	34–49	
			(3.7)	(6.5)	(1.05)	
dl-Methionine	.001	6.3	28	148	.....	
			(0.62)	(0.26)		
Benzothiazole	.01	5.9	4	8	18	166
			(3.2)	(6.4)	(1.13)	(0.33)
Benzotriazole	.01	5.5	15	34	98	
			(1.7)	(1.8)	(0.21)	(0.12)
6-Nitrobenzimidazole	.001	8.05	8	25	>400	None
			(2.0)	(2.0)	(0.035)	
Pyridine	.01	8.4	12	100		
			(1.3)	(0.90)		
	.10	9.0	4	21	>200	
			(2.6)	(2.6)	(0.05)	
Lauryl pyridinium p. t. s.	.001	4.7	5	12	50	96
			(2.9)	(3.3)	(1.0)	(0.63)
	.01	3.8	3	3	115	180
			(4.7)	(20.7)	(0.28)	(0.26)
	.10	3.3	4	4	97	140
			(3.0)	(14.7)	(0.28)	(0.38)

TABLE VIII

COMPARISON OF BENZIMIDAZOLE AND 6-NITROBENZIMIDAZOLE AS DEVELOPERS

Tube charged from water solution of dye

	Volume to displace								
	P at *p*H			II at *p*H			MB at *p*H		
Developer (2×10^{-3} *M*)	3.5	6	8	3.5	6	8	3.5	6	8
Water	100	165	165	>800	....	....	....	....	....
	(0.27)	(0.11)	(0.11)	(0.06)					
Benzimidazole	100	6	8	550	63	95	....	....	....
	(0.29)	(2.4)	(1.9)	(0.11)	(0.65)	(0.30)			
6-Nitrobenzimidazole	6	3	4	6	8	17	72	78	>300
	(2.7)	(6.1)	(6.0)	(3.7)	(5.8)	(1.8)	(0.37)	(0.33)	(0.03)

Displacement of Dye II by benzimidazole at *p*H 3.5 shows the unusual behavior illustrated in Fig. 6. After passing through the customary maximum, displacement passes through a minimum and then rises to a second maximum. This behavior is also shown by columns charged only with Dye II and by columns prepared with silver bromide which had been previously saturated with Dye II. Water development also yields a second maximum with Dye II, although it is not so pronounced as that obtained with benzimidazole development. A second maximum in the displacement of methylene blue was observed with 6-nitrobenzimidazole development. The existence of the second maximum may be taken as further indication of some difference in the strength of adsorption on different parts of the silver bromide surface.

Inorganic Compounds.—Displacement of phenosafranin by ammonia solution was slower than by water. Approximately 195 cc. of 0.10 *M* ammonia was required (visual determination) in comparison with 120 cc. for the water control. Dye II was not displaced by ammonia. Displacement of phenosafranin by 0.01 *M* sodium sulfite solution was slower even than by ammonia. Less than half of the phenosafranin was displaced by 650 cc. of the solution. Dye II was not displaced. Sodium thiosulfate used in 0.001 *M* solution failed to displace any dye in 200 cc. of eluate. When the concentration was increased to 0.01 *M*, using the same column, both phenosafranin and Dye II were displaced, but the rate of displacement was still well below that by water. Approximately 400 cc. of the 0.01 *M* solution was required to eliminate the phenosafranin. At this point, the developer was replaced by 0.10 *M* thiosulfate. This was more effective in displacing Dye II than the weaker solution, but displacement was not complete after a total of 975 cc. had passed through the column. None of the other dyes had been displaced, and at this point the solvent action of the thiosulfate had seriously loosened up the column so that the developer was passing through at about 10 times the initial rate.

No dye was displaced in 400 cc. of 0.001 *M* potassium bromide. A solution of 0.001 *M* silver nitrate displaced phenosafranin and Dye II readily, requiring 10 cc. for the former, 18 cc. for the latter. Weak displacement of methylene blue occurred, but no displacement of Dyes I or VI. Sodium sulfate, in 0.01 *M* solution, showed essentially the same developer activity as pure water.

Discussion

The more rapid displacement of the dyes by the various developing solutions than by water is primarily a matter of adsorption displacement, since the developing agents in most cases are present in too small concentrations to change the solubility of the dyes in water appreciably. The relative ease of displacement of the dyes by the developing agents, accordingly, supplies information on the adsorption of those agents by the silver bromide.

Allylthiourea displaces all five dyes indiscriminately and evidently is more strongly adsorbed by the silver bromide than any of the dyes. Thiourea itself is strongly adsorbed but displaces a portion of the pinacyanol only with difficulty. Gelatin and the photographic diamine developing agents displace only the two dyes which are removed by water itself, but the elution of the dyes by the gelatin and the diamine solutions is considerably faster than by water alone. These agents, accordingly, are adsorbed by the silver bromide.

Hydroquinone and catechol at *p*H 8.0 and resorcinol at *p*H 10.0 prevent the elution of phenosafranin and Dye II, which would occur if plain water were used. This "mordanting" action implies that these agents are themselves adsorbed and are acting to hold the dye more tightly than the pure silver bromide surface. The fact that the mordanting action depends on the *p*H suggests that ionized hydroquinone, catechol and resorcinol are involved. This is reasonable, since the positively charged dye ion would attract the negatively charged developer ion. The concentration of hydroquinone and catechol ion at *p*H 8 would be relatively low, since the *pK* values are 9.9 and 9.1, respectively, and it would be even lower at *p*H 6. However, ionization may be strongly promoted in the vicinity of positively charged adsorbed dye layer. Resorcinol, although its *pK* value is the same as that of catechol, shows much less mordanting effect at a given *p*H, which may be associated with a weaker adsorption.

The present results do not demonstrate unequivocally that hydroquinone and catechol are adsorbed by silver bromide in the absence of adsorbed dye, although such adsorption seems highly probable. The results are of special interest, however, in view of the accelerating effect which the dyes have on photographic development by hydroquinone and, to a smaller extent, catechol.

Other negatively charged ions which are adsorbed by silver bromide mordant the dyes. Thus, no dye is eluted by 0.001 *M* bromide solution. The mordanting effect of the thiosulfate and sulfite ions may stem from the same cause. It is probable that these ions are adsorbed by silver halide because of the complexes which they form with silver ions. Sulfate, which does not form a complex and which is not adsorbed by silver bromide to any significant extent, has little effect upon the rate of elution of the dyes. On the other hand, the positively charged silver ion promotes elution of the dyes.

The quaternary salt, lauryl pyridinium *p*-toluenesulfonate, shows unusual behavior in two ways. Its effectiveness in displacing the dyes increases with increasing *p*H, and the dependence of rate of displacement on the concentration of the solution is slight. It is possible that the latter effect is associated with the tendency of the quaternary salts to form colloidal micelles in more concentrated solution. The solvent action of the quaternary salt on the silver bromide apparently increases with *p*H, and this may be responsible for the more effective displacement of the dyes at the higher *p*H.

The comparison between benzimidazole and 6-nitrobenzimidazole given in Table VIII is of interest because benzimidazole is relatively ineffective as an antifoggant, while 6-nitrobenzimidazole is a good antifoggant in photographic developing solutions. At a given *p*H, the 6-nitro derivative is much more effective in displacing the dyes than is the parent substance. This indicates that 6-nitrobenzimidazole is more strongly adsorbed by the silver bromide than is benzimidazole itself. Solov'ev and Smirnova[3] reached the same conclusion on the basis of experiments carried out on simultaneous adsorption of 2-methylbenzimidazole and 3,3′-diethyl-9-methylthiacarbocyanine iodide by silver bromide and of 6-nitro-2-methylbenzimidazole and the dye by silver bromide. Their results indicate that the 6-nitro compound expelled the dye from the surface or prevented its adsorption, whereas the 2-methylbenzimidazole did not. They conclude that the stronger adsorption of the 6-nitro compound is an important factor in determining its antifogging activity.

The *p*H dependence of the displacement of dyes by benzimidazole contrasts sharply with that of the 6-nitro derivative. The effectiveness of the benzimidazole is much greater at *p*H 6 than at *p*H 3.5, whereas the effectiveness of the 6-nitro derivative is about the same at the two *p*H values. Both agents show some loss of effectiveness in going from *p*H 6 to *p*H 8.

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Determination of Rho and Sigma Constants for Quinoline Carboxylic Acids and Their Methyl Esters[1]

BY ROBERT C. ELDERFIELD AND MALCOLM SIEGEL

The relative pK_a values for the seven quinoline monocarboxylic acids in 50% methanol have been determined. Alkaline hydrolysis rate constants for the methyl esters of the acids have been determined. From these data tentative values of ρ and σ for the quinoline compounds have been calculated.

A considerable fund of information concerning the effects of substituents on reactions of given groups in the benzene series is available.[2] On the basis of these data, it is possible to correlate such effects by a simple mathematical treatment, and to express the magnitude of such effects by unique constants. Thus a constant, σ, measures a change in electron density produced by a substituent, and a second constant, ρ, measures the susceptibility of the reaction in question to changes in electron density. In contrast to this situation in the benzene series, little or no information on similar effects in heterocyclic systems is at hand. In many of the heterocyclic nuclei, the problem is further complicated by the presence of hetero atoms which themselves are capable of producing changes in electron density. As a start on the major problem of providing such information for various heterocyclic systems, the quinoline carboxylic acids and their esters have been chosen for study with the hope that the results obtained might be of use in explaining and predicting the chemistry of the quinoline compounds. The present investigation has been confined to the determina-

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[1] The material presented herein is taken from a dissertation submitted by Malcolm Siegel in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184 ff.