derivatives melting at the same point. In general the method of O'Gee and Woodburn[5] was superior to that of Aspinall.[6]

N-Isopropyl- and N-*n*-butylethylenediamine were prepared by the method of O'Gee except that the free amines were dried with sodium before distillation.

N-*n*-propylethylenediamine was obtained by the courtesy of Dr. H. M. Woodburn at the University of Buffalo. It was redistilled over sodium.

The amines were fractionated through an eleven-inch column packed with stainless steel spiral and had the following boiling ranges

N-Alkylethylenediamines ($RNHCH_2CH_2NH_2$) R	B.p., °C.
Me	114–115
Et	125–126
i-Pr	137–138
n-Pr	152–153
n-Bu	75–77 (20 mm.)

These agree well with those reported by O'Gee and Woodburn.[5]

Preparation of Solutions and Titrations.—The amines were diluted with distilled water until they were 3 to 5 molar and then standardized against standard acid by means of conductometric titrations. The primary standard for all acid–base titrations was a sample of 99.96% potassium hydrogen phthalate obtained from the Bureau of Standards.

The constant ionic strength nitric acid solution containing barium nitrate was made by preparing a solution approximately 0.1 *N* in boiled nitric acid and adding reagent grade chemicals to make the solution 0.50 *M* in KNO_3 and 0.05 *M* in $Ba(NO_3)_2$. The nitric acid was then titrated against standard base using phenolphthalein as the indicator.

A Beckman *p*H meter model G was standardized against Beckman standard buffers at a *p*H of 4.00 and 9.00 before each run. A Beckman 1190–90 glass electrode was used which is accurate to *p*H's of 11 without corrections in the absence of sodium ion. The solutions were maintained at a constant temperature by means of a constant temperature bath at 25 ± 0.1° and by an intimate mixture of ice and water at 0 ± 0.1°.

The titration of the standard nitric acid solution with standard amine was accomplished by means of a microburet capable of being read to ± 0.001 ml. The hydrogen ion was followed by means of a *p*H meter which could be read to ± 0.02 *p*H unit.

A sample titration at the appropriate regions of *p*H along with calculated values of pK_1 and pK_2 are indicated in Table I. One notices the good agreement of the various *pK* values. In each case these values were checked by determining the respective *p*H's of two separate solutions which fall in the first dissociation constant range and in the second dissociation constant range. The constants calculated from these solutions agreed with those obtained from the titration within ±0.01 *pK* unit.

The dissociation constants at 0 and 25° along with the heats of neutralization are summarized in Table II. A graphic representation of these *pK* values is shown in Fig. 1. Although these compounds have comparable dissociation constants, it does appear that with the straight chain alkyls there is a gradual change in going from methyl to butyl with a slight maximum in the region of N-ethylethylenediamine. It is likewise noteworthy that although one may expect a more marked change in case of the pK_2 values as compared to changes in pK_1, this was not observed.

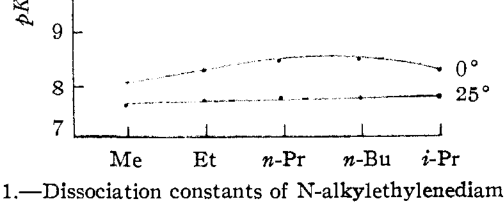

Fig. 1.—Dissociation constants of N-alkylethylenediamines.

TABLE I

DISSOCIATION CONSTANTS OF N-ETHYLETHYLENEDIAMINE AT 0°

Diamine, ml.	*p*H	C_{En}	C_{H}	pK_1
1.002	7.91	0.06223	0.10254	8.16
1.039	8.00	.06449	.10247	8.16
1.077	8.10	.06679	.10239	8.16
1.111	8.19	.06886	.10232	8.16
1.150	8.28	.07123	.10224	8.17
1.187	8.36	.07346	.10217	8.17
1.220	8.43	.07545	.10210	8.17
1.252	8.50	.07739	.10204	8.17
1.291	8.57	.07974	.10196	8.16
1.328	8.65	.08197	.10189	8.16
			Av.	8.16
				pK_2
2.050	10.50	0.12477	0.10048	11.12
2.085	10.53	.12681	.10041	11.11
2.120	10.55	.12885	.10034	11.10
2.160	10.59	.13110	.10026	11.11
2.191	10.62	.13300	.10006	11.11
2.337	10.72	.14146	.09992	11.10
2.413	10.77	.14585	.09978	11.11
2.481	10.80	.14976	.09965	11.10
2.594	10.85	.15624	.09944	11.10
2.709	10.90	.16282	.09922	11.08
			Av.	11.11

TABLE II

DISSOCIATION CONSTANTS AND HEATS OF NEUTRALIZATION OF N-ALKYLETHYLENEDIAMINES

$RNHCH_2$-CH_2NH_2 —R—	pK_1 0°	pK_1 25°	pK_2 0°	pK_2 25°	Δ*H*, kcal. pK_1	Δ*H*, kcal. pK_2
Me	8.00	7.56	10.83	10.40	− 6.55	− 6.30
Et	8.16	7.63	11.11	10.56	− 7.90	− 8.20
n-Pr	8.24	7.54	11.04	10.34	−10.4	−10.4
n-Bu	8.11	7.53	10.93	10.30	− 8.65	− 9.40
i-Pr	8.30	7.70	11.15	10.62	− 8.95	− 7.90

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

---

[5] R. C. O'Gee and H. M. Woodburn, THIS JOURNAL, **73**, 1370 (1951).

[6] S. R. Aspinall, *ibid.*, **63**, 852 (1941).

Chromatographic Investigations Related to Photographic Theory. II. Adsorption of Developing Agents and Sodium Sulfite[1]

BY T. H. JAMES AND W. VANSELOW

RECEIVED JANUARY 12, 1952

In a preceding paper,[2] the technique of elution chromatography was used to show that the photographic developing agents, *p*-phenylenediamine and hydrazine, are adsorbed by silver bromide. These agents displaced the adsorbed dyes, phenosafranin and 3,3′-diethyloxacarbocyanine, from the silver bromide surface. Hydroquinone and catechol, on the other hand, caused the dyes to be held even more tightly, and this suggested a coöperative adsorption of the negatively-charged developing agent

---

[1] Communication No. 1473 from the Kodak Research Laboratories.

[2] T. H. James and W. Vanselow, THIS JOURNAL, **73**, 5617 (1951).

and the positively-charged dye. In these experiments, therefore, no evidence was obtained that hydroquinone or catechol is adsorbed by silver bromide in the absence of the positively-charged dye molecules.

The investigation has now been extended to include dyes which do not have a positive charge and hence would not attract the negatively-charged developer ions. The results obtained show that hydroquinone, catechol and hydroxylamine displace some adsorbed dyes from the silver bromide surface and hence must themselves become adsorbed by that surface.

Experimental Procedure

The preparation of the silver bromide columns and the general technique of charging and developing the columns were the same as those described in the preceding paper. The length of the silver bromide column was standardized at 20 cm. When aqueous solutions of developers were to be used, the columns were charged with dye in aqueous solution, and the charging and developing operations were carried out in the absence of oxygen in the apparatus described in the preceding paper.

The merocyanine dye, 4-[3-ethyl-2(3H)-benzothiazolylidene)-ethylidene]-3-methyl-1-(*p*-sulfophenyl)-5-pyrazolone (sodium salt), was used in most of the experiments. Each tube was charged with 2 cc. of 10^{-4} *M* dye solution. The eluate was collected in acetic acid solution to prevent oxidation of the developing agent on contact with air.

Results

Hydroquinone in 0.01 *M* aqueous solution could be used as a chromatographic developer at *p*H 8.0 and below without causing reduction of the silver bromide. When a solution of *p*H 9.0 was used, a slight amount of reduced silver formed toward the end of the experiment. Hydroquinone displaced the merocyanine dye, and its effectiveness increased with increasing *p*H of the solution. Some data are given in Fig. 1, where the amount of dye eluted in terms of the percentage of dye originally present in the column is plotted against the volume of eluate. It is seen that, even at *p*H 6, more dye was eluted by the hydroquinone solution than by an equal volume of water. The cause of the breaks observed in the curves representing *p*H 8 and 9 is not clear, but may be associated with the existence of two types of surface of somewhat different adsorptive properties. The break is not specific for hydroquinone, but has been obtained with other chromatographic developers (*e.g.*, dilute potassium bromide solutions), where the ratio of displaced dye to eluate volume is about the same. No breaks were observed when this ratio was either considerably larger or considerably smaller. Displacement of other dyes by hydroquinone has been observed, *e.g.*, eosin.

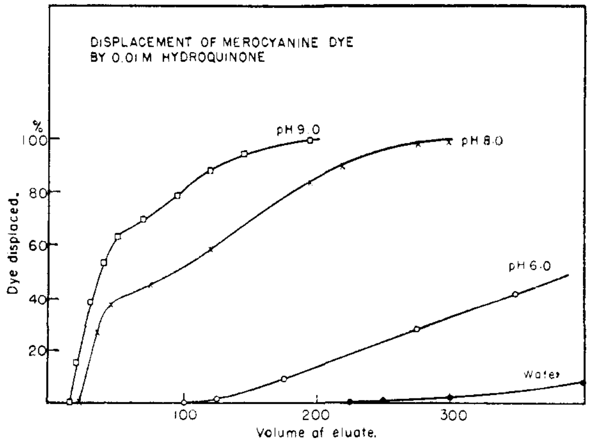

Fig. 1.—Displacement of merocyanine by 0.01 *M* hydroquinone at various *p*H values.

Figure 2 illustrates results obtained with catechol, hydroxylamine and resorcinol. A hydroquinone curve is included for comparison. The displacement of the merocyanine dye by catechol at *p*H 6.0 (not shown) was only slightly greater than that by hydroquinone at the same *p*H. The displacement by catechol at *p*H 8.0 was about the same as that by hydroquinone at *p*H 9.0. A break was not observed in the catechol curve for *p*H 8.0, but some reduction of silver bromide occurred in the later stages of the experiment, and the presence of a break may have been obscured by the appearance of developer oxidation product. Hydroxylamine was less effective than hydroquinone in displacing the dye, but its action was greater at *p*H 10 than at 8, showing that a *p*H-dependency exists for this agent as well. The displacement by water alone showed little or no dependency upon *p*H. Resorcinol was much less effective as a chromatographic developer than hydroquinone or catechol. A solution at *p*H 8 was no more effective than water, and a solution at *p*H 10 was less effective than one of hydroquinone at *p*H 8.

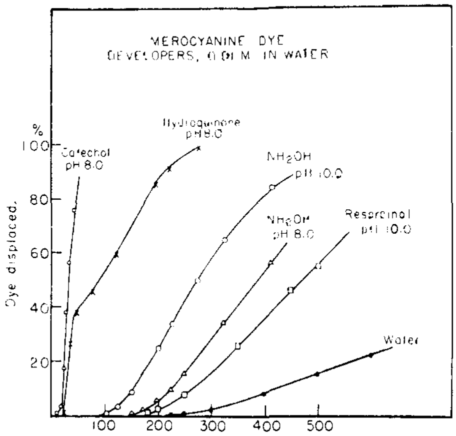

Fig. 2.—Displacement of merocyanine by various developing agents.

Sodium sulfite, which showed some coöperative adsorption with the positively-charged dyes, displaced the merocyanine, but was less effective than the photographic developing agents. Some data are given in Fig. 3. A sodium sulfate solution, on the other hand, was somewhat less effective than pure water in displacing the dye.

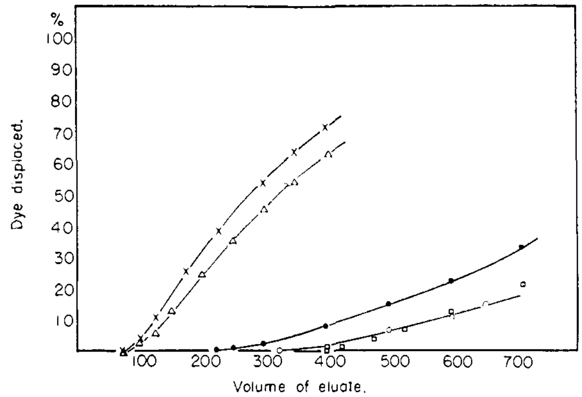

Fig. 3.—Displacement of merocyanine by sodium sulfite: -X-X-, 0.001 *M* Na_2SO_3; -Δ-Δ-, 0.01 *M* Na_2SO_3; -O-O-, 0.005 *M* Na_2SO_4; -□-□-, 0.0005 *M* Na_2SO_4; -●-●-, water.

It was shown previously that *p*-phenylenediamine in aqueous solution displaces phenosafranin and 3,3′-diethyloxacarbocyanine from the silver bromide surface. Some reduction of silver bromide occurred in the later stages of the elution, however. In an effort to avoid such reduction, solutions of *p*-phenylenediamine in acetone have been tried with success. In these experiments, the silver bromide tubes were first washed with three 5-cc. portions of acetone after the water had been expelled. The tubes were then charged with dye from acetone solution, and 2 cc. more of acetone used to rinse out the tube. Development by the *p*-phenylenediamine solution was then carried out in the usual manner. The dye in the eluate could be determined directly without the addition of acid.

The curves obtained with the *p*-phenylenediamine developer are regular in shape, resembling those of hydroxylamine in Fig. 2. A concentration series was run over a range of 100-fold. The dependence of elution upon concentration of *p*-phenylenediamine is illustrated in Fig. 4. Here, the logarithm of the maximum slope of the elution curve is plotted against the logarithm of the concentration of the *p*-phenylenediamine. A straight line of slope of 0.55 was obtained for each dye. If the maximum slope of the elution curve is a measure of the amount of *p*-phenylenediamine adsorbed, the straight lines in Fig. 4 would show that the adsorption is following the Freundlich isotherm. Similar results were obtained for the displacement of merocyanine dyes.

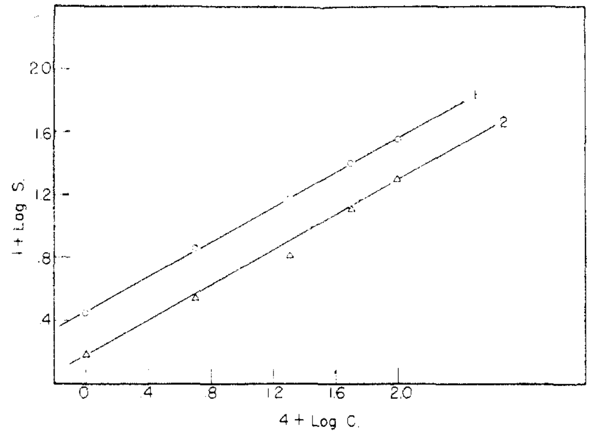

Fig. 4.—Dependence of displacement of dyes upon the concentration of *p*-phenylenediamine: curve 1, displacement of phenosafranin; curve 2, displacement of 3,3′-diethyloxacarbocyanine.

Some tests were made on the displacement of phenosafranin by 4-amino-3-methyl-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline. The displacement curves obtained are similar in form to those obtained with *p*-phenylenediamine. The maximum slopes are 1.76 and 0.50 for developer concentrations of 0.01 and 0.001 *M*, respectively. If these data are plotted in the same way as the *p*-phenylenediamine data in Fig. 4, the slope of the straight line is 0.54, in excellent agreement with the value of 0.55 for the *p*-phenylenediamine. It is of interest to compare this concentration-dependence with that found by Fortmiller and James[3] for the development of liquid emulsions by derivatives of *p*-phenylenediamine. A log–log plot of their data yields a straight line of slope 0.54.

Discussion

The dye displacement experiments have demonstrated that hydroquinone, catechol, hydroxylamine, hydrazine, *p*-phenylenediamine and 4-amino-3-methyl-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline are adsorbed by silver bromide. This supports the suggestion of Sheppard and Meyer[4] that adsorption of photographic developing agents by silver halide precedes the reduction of the silver salt in photographic development. The *p*H-dependence of displacement by hydroquinone and catechol indicates that these agents are adsorbed in the ionized form. Kinetic evidence indicates that the ionized forms of the developing agents likewise are involved in photographic development. Resorcinol is much less effective than hydroquinone and catechol, both in displacing the merocyanine dye and in photographic development. The low developer activity of the resorcinol can depend only in part on its lower adsorption, however, since the oxidation of this agent by silver ions from solution is much slower than the oxidation of hydroquinone and catechol.

ROCHESTER, N. Y.

---

(3) L. Fortmiller and T. H. James, *PSA Journal*, **17B**, 102 (1951).

(4) S. E. Sheppard and G. Meyer, THIS JOURNAL, **42**, 689 (1920).

Remarks on Spectra of Stilbene Derivatives

BY JOHN R. PLATT

Application of first-order perturbation theory[1] to the spectra of stilbene derivatives as given by Beale and Roe[2] leads to some important conclusions. For an allowed even–odd transition in a centrally symmetric molecule, such as the longest wave length transition in *trans*-stilbene, the oscillator strength is the square of a transition moment vector, M.[3] A small perturbation by a substituent, a, at a particular position introduces an additional perturbation vector, m_a. The total intensity becomes the square of the vector sum, $M + m_a$. If there is an angle, θ_a, between the vectors, the oscillator strength in suitable units is

$$\begin{aligned} f &= (M + m_a \cos\theta_a)^2 + (m_a \sin\theta_a)^2 \\ &= M^2 + 2Mm_a \cos\theta_a + m_a^2 \end{aligned}$$

and the increment is

$$\Delta f = 2Mm_a \cos\theta_a$$

if m_a is relatively small.

For two substituents at opposite positions, the perturbation vectors will be parallel and the intensity increments will add linearly. (For an even–even transition, they would subtract. For a forbidden even–odd, where M is zero, the perturbation vectors would add linearly, but the intensity increments would go up as the square of the vector sum.[4]) For two substituents at any positions, the total intensity increment will be approximately the sum of the independent increments, in this first-order theory, as long as m_a and m_b are small compared to M.

Examination of Beale and Roe's *f*-values in the light of these remarks leads to the following conclusions.

(1) **The longest wave length singlet–singlet transition in *trans*-stilbene is necessarily even–odd** (in agreement with all theoretical predictions and with the high intensity. Reason: the 4-methylstilbene intensity is greater than that of stilbene; and the 4,4′-dimethyl intensity is greater still (in arithmetic progression) and not less.

(2) **The $N(CH_3)_2$ perturbation is larger than the** methyl (as noted by Beale and Roe) **and in addition it has the same sign.** Reason: the 4,4′-increments for these substituents add, and do not subtract. The same result has been found[5] for these substituents as they affect the benzene 2600 Å. bands; but the $N(CH_3)_2$ group had a relatively larger effect there.

---

(1) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

(2) R. N. Beale and E. M. F. Roe, THIS JOURNAL, **74**, 2302 (1952).

(3) R. S. Mulliken and C. A. Rieke, *Rep. Prog. Phys.*, **8**, 231 (1941).

(4) J. R. Platt, *J. Chem. Phys.*, **19**, 263, 1484 (1951).

(5) J. R. Platt, unpublished.