

---

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

---

VOLUME 66

DECEMBER 15, 1944

NUMBER 12

---

[COMMUNICATION NO. 966 FROM THE KODAK RESEARCH LABORATORIES]

## Effect of Solvents upon the Absorption Spectra of Dyes. IV. Water as Solvent: A Common Pattern

BY S. E. SHEPPARD AND A. L. GEDDES

The Beer-Lambert law, which affords the empirical basis for the definition of a molecular extinction coefficient, has been largely validated for dyes in organic solvents. Notable deviations, with which we shall be concerned, have been found in aqueous solutions of many dyes of several types or classes. From a theoretical point of view the formulation expresses a "limiting law," for gases at relatively low pressures, or for not too concentrated solutions. In this respect it resembles Boyle's law,  $pv = \text{constant}$ , actually presuming that interaction between the gaseous or dissolved molecules is negligible. The theoretical approach to the definition of a measurable extinction coefficient was outlined by G. Kortüm<sup>1</sup> on the basis of classical dispersion theory. Intermolecular influence as between the gaseous state, and different solvents, could be large,<sup>2</sup> but nothing in classical physical theory anticipates the large differences in behavior, notably in spectral behavior, between dyes in organic solvents and in water.

From the chemical standpoint, differences are to be anticipated, and even in some degree, their character. Dyes are organic molecules of considerable magnitude, of molecular weight ranging from about 300 upward, and, a most important factor, having usually only a small proportion of water-miscible to water-immiscible groups. The former, capable, in general, of *ionizing* in water, comprehend, beside the auxochromes  $-\text{NH}_2$  and  $-\text{OH}$ , the acidic groups  $-\text{COOH}$  and  $-\text{SO}_3\text{H}$ , of which the last is indeed principally employed to make soluble in water otherwise insoluble dyes. Consequently, in most organic liquids, the bulk of the molecule is readily "homologated" to the solvent, to use McBain's term.<sup>3</sup> In other words,

it tends to be completely solvated and, up to relatively high concentrations, insulated from its fellows. On the other hand, in water, only the rather sparse and isolated hydrophile groups will be definitely solvated.

It is not surprising that on any adequate occasion, *e. g.*, the introduction of inorganic salts, the hydrophobe parts of dye molecules agglutinate. A very important nuance in their typically amphipathic behavior<sup>4</sup> results from the fact that dyes, as molecular resonance systems,<sup>5</sup> are in most part very definitely *planar* in shape, favoring, in general, a strongly orienting disposition of the amphipathic groups. The hydrophile groups may be accumulated at one side of a planar extension, or they may be symmetrically distributed about it, but in any case there are apt to be organophile surfaces or areas, contrasted with hydrophile peripheries or edges.<sup>6</sup> There results the possibility of two contrasting types of oriented aggregates (i) ion aggregates via the hydrophile groups and water molecules, and (ii) organic aggregates via the essential resonance circuits of aliphatic or cyclic systems of double bonds.

The former of these, as pointed out by G. N. Lewis, T. T. Magel and D. Lipkin,<sup>7</sup> are liable to appear in solutions of ionized dyes in organic solvents of low polarity. The latter are responsible for closer coupling, which may extend from the formation of dimers in solution to the separation of paracrystalline and crystalline phases. Whereas the former type of aggregation

(4) G. S. Hartley has referred to such molecules as "amphipathic."

(5) G. Schwarzenbach, *et al.*, *Helv. Chim. Acta*, **20**, 490 (1937); *cf.* also *Z. Elektrochem.*, **47**, 40 (1941).

(6) The planar extensions will consist usually of aromatic and heterocyclic rings. Geometrically, in such relatively aliphatic types as the polyenes, the organophile areas may degenerate to lines, the hydrophile peripheries to end-groups.

(7) G. N. Lewis, T. T. Magel and D. Lipkin, *THIS JOURNAL*, **64**, 1778 (1942).

(1) G. Kortüm, *Z. physik. Chem.*, **B33**, 243 (1936).  
(2) *Cf.* Pt. I, "Effect of Solvents upon the Absorption Spectra of Dyes. Chiefly Polymethine Dyes," S. E. Sheppard, P. T. Newsome and H. R. Brigham, *THIS JOURNAL*, **64**, 2023 (1942).

(3) J. McBain, *Colloid Symposium Monograph*, **4**, 7 (1926).

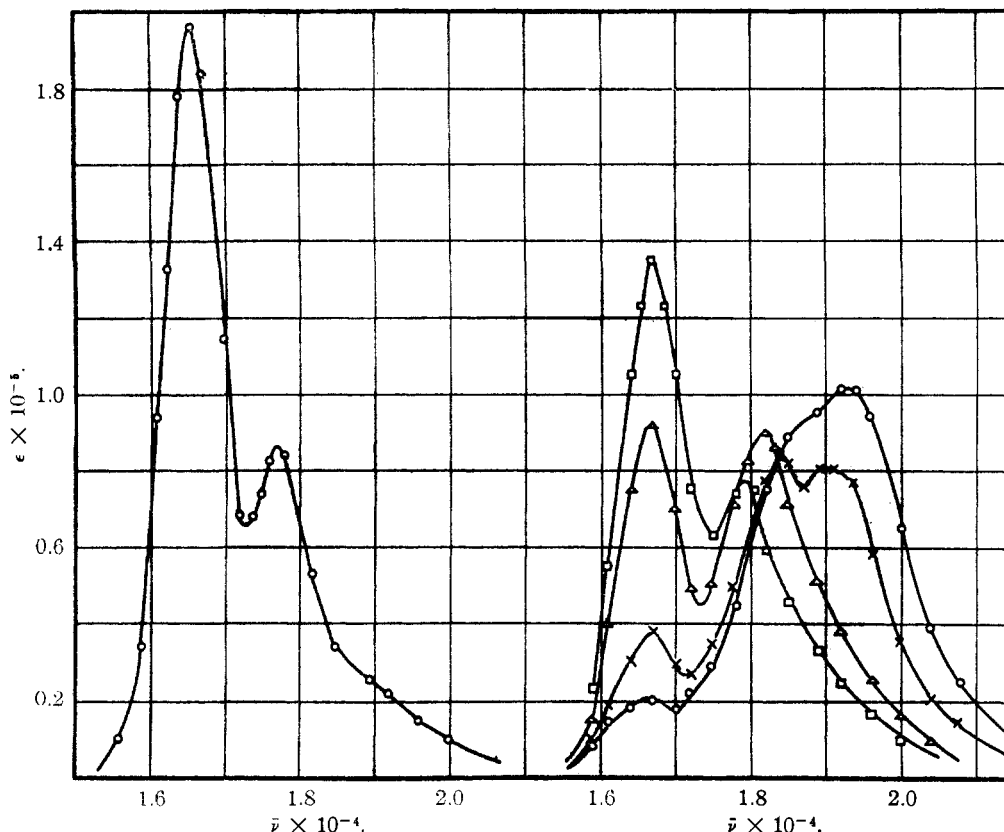
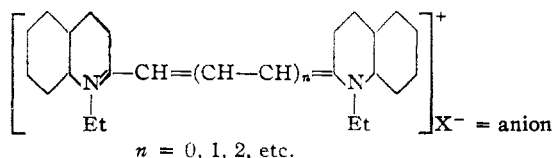


Fig. 1.—Spectral absorption of Dye VIIa (1,1'-diethylcarbo-cyanine chloride): left side, in methyl alcohol; right side, in water;  $\odot$ ,  $4.65 \times 10^{-4} M$ ;  $\times$ ,  $1.0 \times 10^{-4} M$ ;  $\Delta$ ,  $1.0 \times 10^{-5} M$ ;  $\square$ ,  $1.0 \times 10^{-6} M$ .

has, so far as is known, only minor effects on absorption spectra,<sup>5</sup> the latter has very notable ones.

Apparently, the first observations on such deviations (from Beer's law) were made in 1908 and 1909.<sup>8</sup> Spectrophotometric measurements made then by Sheppard on cyanine (polymethine) dyes exhibit a pattern of behavior, for change of concentration or change of temperature, which, by increase of the number of spectrophotometric measurements, is shown to be general and consistent, albeit more or less clearly revealed according to certain characteristics of the individual dye.

In Fig. 1 are compared the absorption spectra of Dye VIIa (pinacyanol or 1,1'-diethylcarbo-cyanine chloride) in methanol and in water (at pH 7), respectively. The structure of the absorption bands of the symmetrical, homologous cyanines, of the type



(8) J. Formánek and E. Grandmougin, "Untersuchung und Nachweis org. Farbstoffen auf Spektroskopischem Wege," Erste Teil (Berlin, 1908) but only qualitative. S. E. Sheppard, *Phot. J.*, **48**, 300 (1908); *Proc. Roy. Soc. (London)*, **A82**, 256 (1909).

is very similar to that of the left-hand curve in Fig. 1.<sup>9</sup> The strongest or primary band at lowest frequency is displaced to lower frequency with increase of  $n$ . Each band has a fairly well-marked secondary maximum at a wave-number higher than the primary band *ca.* 1250  $\text{cm.}^{-1}$  and a feeble tertiary (clear for  $n = 0$ ,  $n = 1$ ) observed in mere asymmetry for higher numbers, as the primary band strengthens with increasing chain length.<sup>10</sup> The effect of temperature change on aqueous solution of *pinacyanol*, of *pinachrome* and of *orihochrome-T* (1,1'-diethyl-4,4'-dimethylisocyanine bromide) was found to be similar to that of change of concentration. It was reversible; at higher temperatures the spectrum approached that in alcohol, while on lowering the temperatures (as on increasing the concentration), the primary band decreased in strength, and bands at higher frequency gained.

Some measurements by Söderborg<sup>11</sup> in 1913 on aqueous solutions of *eosin* (2,4,5,7-tetrabromo-fluorescein) indicated a similar behavior in aqueous solution. A band of higher frequency (by about 1500  $\text{cm.}^{-1}$ ) gained in strength with concentration, while the main band (at 518  $\text{m}\mu$ )

(9) N. I. Fisher and F. M. Hamer, *Proc. Roy. Soc. (London)*, **A154**, 703 (1936).

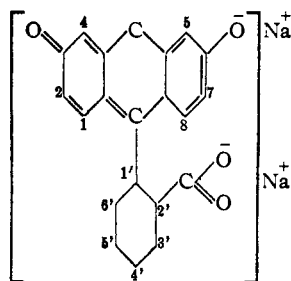
(10) R. S. Mulliken, *J. Chem. Phys.*, **7**, 570 (1939).

(11) B. Söderborg, *Ann. Physik*, **346**, 381 (1913).

declined. Söderborg's measurements were between  $4.5 \times 10^{-6} M$  and  $3.8 \times 10^{-3} M$ . His values at higher concentrations are unreliable.

These aberrations were shown to be a consequence of a dominantly aqueous medium. In acetone-water mixtures, containing 30% acetone by volume, a spectrum was obtained at all concentrations similar to that of a very dilute solution of the dye in water, and Beer's law was followed over a wide range of concentration.

Later observations by W. C. Holmes,<sup>12</sup> on phenolphthalein and resorcinphthalein (fluorescein) dyes in water, are not entirely in agreement with Söderborg's observations on eosin. The structural formula for the fluorescein skeleton (unsubstituted) may be written, for the disodium salt



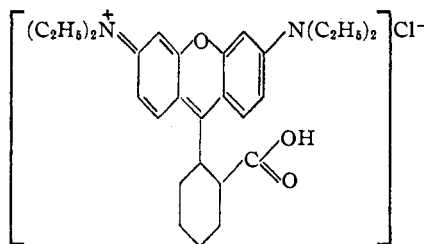
Substitution positions in the phthalic anhydride residue are marked 3', 4', 5' and 6', and in the resorcin residue, 2, 4, 5 and 7. Holmes states "The absorptions of fluorescein, both in the form of color acid [replace  $-O^-$  by  $-OH$ ] and alkali salts, and those of the alkali salts of pure tetrachloro-, tetrabromo-, and tetraiodofluorescein, for substitution in the *phthalic anhydride residue* [*i. e.*, 3', 4', 5', 6' and include with these Phloxin and Rose Bengal] are found to be decidedly modified by change in concentration [in water];" whereas, *per contra*, he asserts that those [fluoresceins] substituted by halogens in the resorcinol part of the molecule, or in both [the resorcinol and the phthalein residues], are *optically stable*. This last group would obviously include eosin, as tetrabromofluorescein, which is in contradiction with Söderborg, also with observations of Speas.<sup>13</sup> Tabulating, we have

TABLE I

Beer's law	Aberrant
Eosin (?) at high pH	Fluoresceins substituted
Rose Bengal	in phthalic anhydride
Octabromofluorescein	only
Octaiodofluorescein	Rhodamine-B
Erythrosin	Eosin, at medium pH

For the same group (fluoresceins) Rhodamine-B having the structure

(12) W. C. Holmes, *Ind. Eng. Chem.*, **16**, 85 (1924).  
 (13) W. E. Speas, *Phys. Rev.*, **31**, 569 (1928).



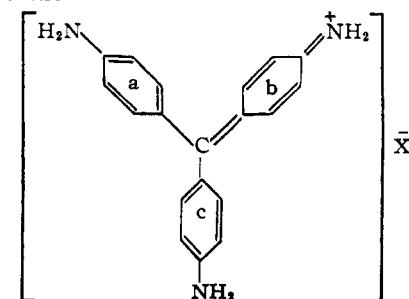
was found by Speas<sup>13</sup> to show very considerable sensitivity both in regard to concentration and to temperature. On increasing the concentration, the band toward the red—the  $\alpha$ -band—decreases in intensity while the small band, the  $\beta$ -band, toward the violet, grows and becomes the more intense of the two. Increase in temperature of a relatively concentrated solution had the same effect as dilution. The relative change of molecular extinction coefficients indicates the magnitude of the deviation.

In respect of this same group of dyes (fluoresceins), Sheppard, Lambert and Walker<sup>14</sup> in recent measurements on *erythrosin* found that at sufficiently high pH, *erythrosin*, as alkali erythrosinate, obeys Beer's law between  $10^{-6}$  and  $10^{-3}$  molar. There is some tendency to hydrolysis of the simple salts, whereby the acid tends to separate in dilute solutions. The acid, soluble in alcohol, but hardly so in water, shows significant spectral differences. So far as they go, they confirm Holmes' statement. The cause for the difference between dyes of the same basic constitution, differing only because of substitutions, will be discussed later.

#### Tri- and Diphenylmethane Dyes

Rather closely related to the fluorescein (resorcinphthalein) and phenolphthalein dyes are the triphenylmethane dyes. In this class also, while many of the dyes examined give the characteristic instability or anomaly, yet closely related ones, differing only by substitutions, appear to be stable, *i. e.*, follow Beer's law, over a wide range of concentration. Holmes<sup>10</sup> remarks: "Both the relatively stable and the unstable groups of these dyes include examples of both basic and acid character and of both symmetrical and unsymmetrical constitution."

So far as present evidence goes, it may be summarized by reference to the graphic structure of *p*-rosaniline

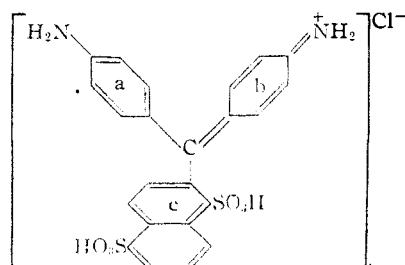


(14) S. E. Sheppard, R. H. Lambert and R. D. Walker, *J. Chem. Phys.*, **11**, 263 (1943).

TABLE II

Concentration	Rhodamine-B at 20°		Temperature, °C.	Rhodamine-B at $2.1 \times 10^{-4} M$	
	$\epsilon_{\alpha}$	$\epsilon_{\beta}$		$\epsilon_{\alpha}$	$\epsilon_{\beta}$
$2.1 \times 10^{-3} M$	$2.6 \times 10^4$	$2.6 \times 10^4$	0	$2.4 \times 10^4$	$3.03 \times 10^4$
$2.1 \times 10^{-6} M$	$4.07 \times 10^4$	$1.46 \times 10^4$	90	$2.7 \times 10^4$	$1.87 \times 10^4$

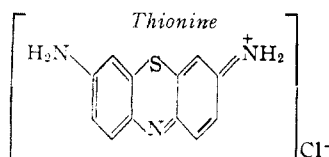
This substance and congeners with substitution in the phenyl nuclei, as, *e. g.*, Fuchsine (one- $\text{CH}_3$ ), New Fuchsine (two- $\text{CH}_3$  groups), Acid Magenta (one- $\text{CH}_3$ , two- $\text{SO}_3\text{H}$  groups), give aqueous solutions obeying Beer's law, and displaying no anomaly, over the range investigated.<sup>15</sup> But substitution in the amino groups, by alkyl, aryl, alkyl-aryl, and derivative groups, *e. g.*, from tri- to penta- and hexamethyl or -ethyl, leads to the characteristic optical anomaly, *viz.*, as the concentration of an aqueous solution is increased, the long wave band yields in intensity to one of lesser wave length. The interval between these two bands is of the order of  $1300 \text{ cm.}^{-1}$  to  $1600 \text{ cm.}^{-1}$ . In alcohol and acetone usually only a shoulder appears, apparently corresponding to the band of higher frequency. Beer's law is followed and the spectrum resembles that of the dilute aqueous solution. However, relative stability in aqueous solution may be restored to such triamino-substituted dyes by addition of alkyl chloride to one of the alkylamino-groups. For example, Crystal Violet,  $\text{N}(\text{CH}_3)_2$ , replacing  $\text{NH}_2$  shows the anomaly in water but is stabilized on conversion to Methyl Green, with  $\text{MeCl}$  added to one  $\text{—N}(\text{Me})_2$  group, *e. g.*, on *c*. Not only is a divalent positive ion produced, but the dye becomes effectively a diamino triphenylmethyl derivative, resonance being confined between *a* and *b*. It is also interesting to note that dyes with structures such as



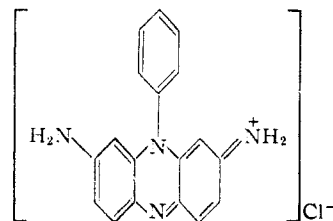
show appreciably stable aqueous solutions. This appears to be in line with a statement<sup>14</sup> to the effect that *diamino* derivatives of triphenyl- and diphenylnaphthylmethane in water show little appreciable alteration in the location of the absorption maxima other than, with increasing concentration, a slight but progressive asymmetry indicative of the development of a band or bands toward the shorter wave lengths.

**Azine Dyes.**—Azine dyes for which any spectrophotometric data are available, including *oxazines*,<sup>16</sup> *thiazines*,<sup>17</sup> and *azines*, show definite concentration anomaly in water, a shoulder or

band on the higher frequency side of the principal band becoming stronger and the former weakening, with increase of concentration or reduction of temperature. The phenomenon has been rather fully investigated for the thiazines, *thionine* and *methylene blue*, as will be noted later. Here it is of interest to observe that in this group also, as in the triphenylmethyl and in the fluorescein groups, the degree of the anomaly is relative to the positions and characters of substituents in the skeletal framework of the dye molecule. For example, the effect is strongly marked with thionine but still more with methylene blue where  $\text{—N}(\text{CH}_3)_2$  is substituted for  $\text{—NH}_2$



Whereas, with phenosafranine



the anomaly in aqueous solution is less. Over the range  $1.8 \times 10^{-6} M$  to  $3.8 \times 10^{-3} M$  it consists, compared with the alcoholic solution, in a displacement of the maximum toward higher frequency, as the asymmetry increases in the same direction. Thereby  $\epsilon_{\text{max}}$  falls and there is progressive departure from Beer's law (*cf.* Fig. 2). This behavior seems general in the safranines and rhodulines, compared with the parent azines, or the comparable thiazines.

**The Azo Dyes.**—No very notable spectral anomalies are recorded for aqueous solutions of azo- and disazo dyes. This is the more interesting, since this group has furnished much of the evidence for the formation of colloidal (micellar) electrolytes from dyes. It is very possible that more intensive spectrophotometric study will reveal the presence of spectral anomalies in this group of the same type, though less pronounced, as in the others. This is indicated by the behavior of two isomeric disazo dyes, benzo-purpurine and *meta*-benzopurpurine. The specimens examined were of high purity, having been used for calibration of a diffusion apparatus.<sup>18</sup>

(15) Which quite possibly has not been sufficiently extensive.

(16) L. Michaelis and S. Granick, *THIS JOURNAL*, **63**, 1636 (1941).

(17) E. Rabinowitch and L. F. Epstein, *ibid.*, **63**, 69 (1941).

(18) We are glad to thank Dr. Samuel Lenber of E. I. du Pont de Nemours & Co. for the gift of these samples.

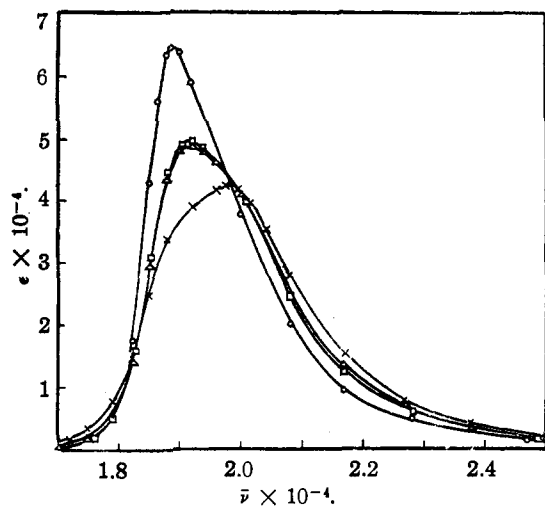


Fig. 2.—Spectral absorption of phenosafranin:  $\circ$ , in methyl alcohol;  $\times$ ,  $3.83 \times 10^{-3} M$ ;  $\Delta$ ,  $1.9 \times 10^{-4} M$ ;  $\square$ ,  $1.8 \times 10^{-6} M$  in water.

In Fig. 3 are compared the spectral dilution curves of the two dyes, and with each the graphic formula. It will then be noted that the *meta*-isomer has the two  $-\text{CH}_3$  groups so near that steric hindrance in this case would prevent complete planarity of the whole molecule. The two halves must be twisted perhaps  $40$  to  $50^\circ$  about a lateral axis, which would considerably reduce resonance for the total conjugated system.

This is conformable to the contours of the absorption curves. The *meta* sterically hindered molecule has an absorption band at higher frequency and lower extinction than is found for the unhampered isomer. It shows slightly greater deviation from Beer's law, but it cannot be said that in either case there is pronounced increase of asymmetry or "typical" concentration anomaly in water.

The data on molecular aggregation found by Robinson and Molliet<sup>19</sup> and by Robinson and Garrett<sup>20</sup> from conductance measurements indicate a lower degree for the *meta* dye than for its isomer, as shown in Table III.

TABLE III

Molar concentration $\rightarrow$	MINIMUM AGGREGATION NUMBERS ( $n$ )			
	0.005	0.01	0.02	0.03
<i>Meta</i> benzopurpurine	1.0	1.2	1.4	1.4
Benzopurpurine 4B	1.93	1.94	1.94	1.92

The values for  $n$  are for *degree*, not for *order*, but they certainly suggest aggregation: (a) not higher than 2 (dimerization), (b) in lower degree for the *meta* dye than for the fully planar isomer. Similarly, the maximal aggregation numbers from Table IV of Robinson and Garrett indicate for the *meta* dye a value not greater than 2, but also for

(19) C. Robinson and J. L. Molliet, *Proc. Roy. Soc. (London)*, **A143**, 630 (1934).

(20) C. Robinson and H. E. Garrett, *Trans. Faraday Soc.*, **25**, 771 (1929).

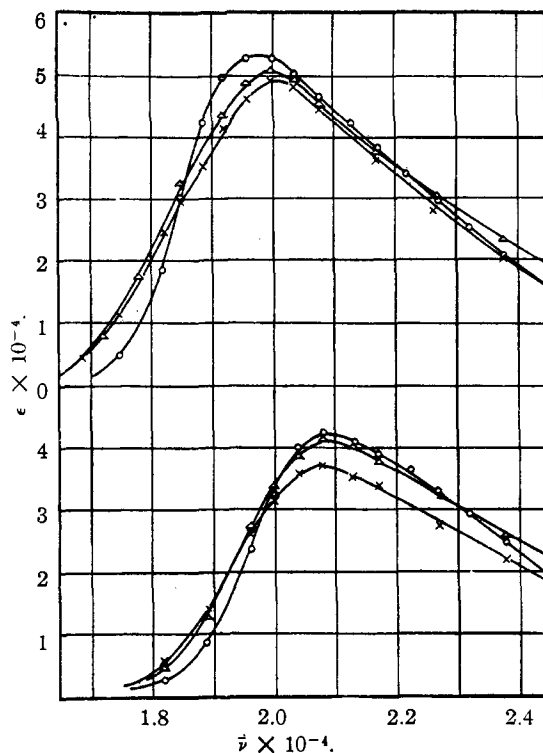
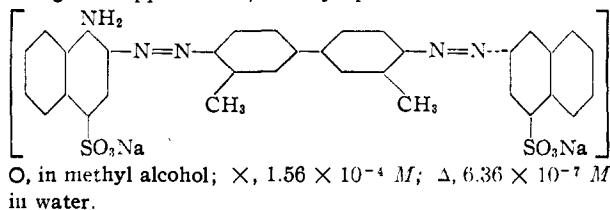
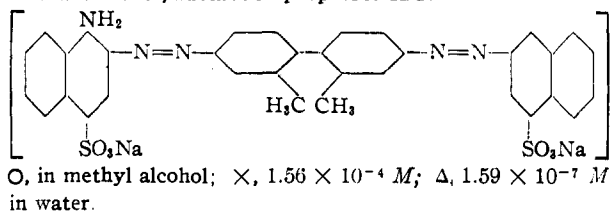


Fig. 3.—Upper curves, Benzopurpurine 4B:



Lower curves, Metabenzopurpurine 4B1:



its isomer a value not less than 2—which last observation suggests that this isomer may not disperse molecularly in water—although greater aggregation probably supervenes at higher concentrations. One can deduce from comparison of the spectral behavior of these two isomeric dyes with their aggregation in aqueous solution that a higher degree of planarity may favor aggregation, even as it increases resonance and light absorption. But it is not clear from these observations that aggregation *per se* necessarily leads to spectral anomaly in aqueous solution, still less to the development of "new" absorption bands.

The porphyrines and phthalocyanines contrast with the azo-dyes in offering remarkable examples amongst dye molecules of centric sym-

metry—more so even than the triphenylmethane derivatives. In order to study their behavior in water, it is necessary to use sulfonated derivatives, which in this respect may be well considered as in the relation of benzene sulfonic acids to benzene itself. The spectra of the porphyrines, exemplified by that of the synthetic tetrazophorphyrine, *phthalocyanine*, resemble that of benzene in many respects.<sup>21</sup> Sulfonation, which induces solubility in water, has but small effect upon the spectrum (*cf.* Fig. 4)—no more than in analogous cases, such as the sulfonation of indigo,<sup>22</sup> but it enables us to observe the influence of concentration, of temperature, and of *pH* on the absorption spectrum of the aqueous solutions.

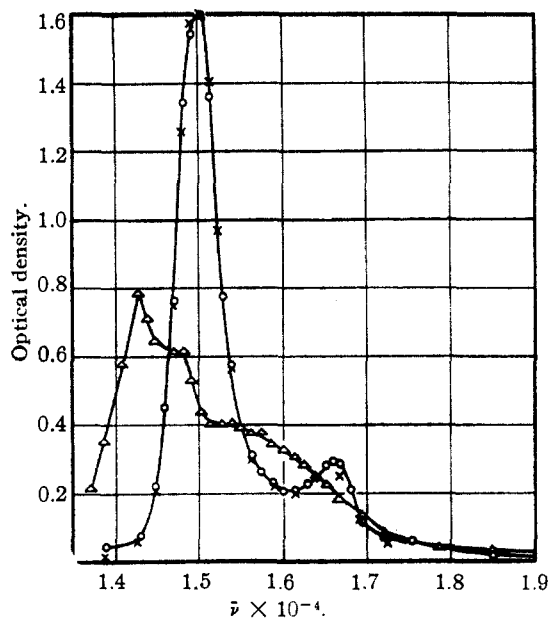


Fig. 4.—Spectral absorption of zinc phthalocyanine sodium sulfonate in methyl alcohol; O, saturated solution; X, diluted 1:10, (cell thickness increased tenfold); Δ, acidified with sulfuric acid (shown in displacement of zinc by hydrogen).

Two sets of curves for the influence of temperature (Fig. 5) will exemplify this, as do also the data for *pH*, at the same concentration (Fig. 6), that the aggregation anomaly is strongly developed in aqueous solutions of zinc phthalocyanine *tri-, tetrasulfonate*. The intensity of absorption in the principal low-frequency band is diminished with concentration, to pass over into an adjacent band of higher frequency. This behavior is important, as showing that (a) formation of peripheral hydrating points not concerned in the resonance system need not prevent aggregation,<sup>23</sup> (b) nor are sulfonated dyes precluded from aggregation, and the optical anomaly associated there-

(21) *Cf.* R. P. Linstead, *et al.*, *J. Chem. Soc.*, 1719 (1936).

(22) J. M. Eder and E. Valenta, *Photochemische Untersuch.*, 1, 407 (1904).

(23) In the acidified state, as  $-\text{SO}_3\text{H}$  groups, they might favor it through intermolecular hydrogen bridge formation.

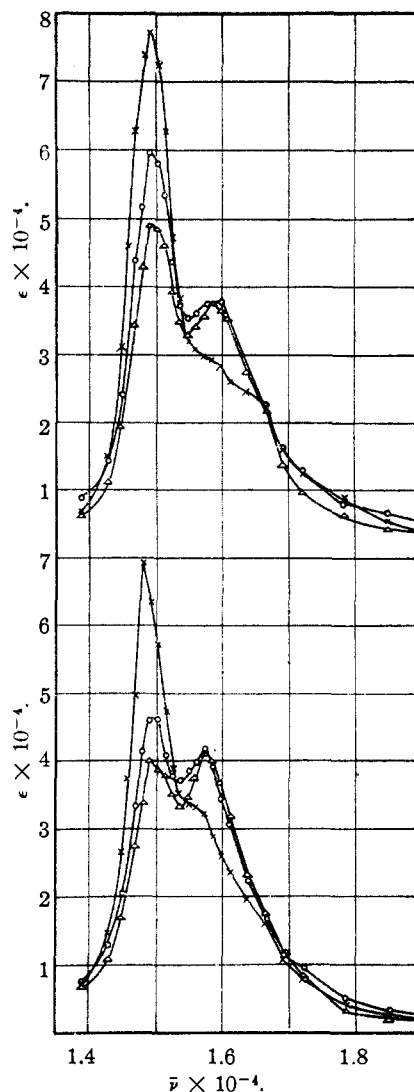


Fig. 5.—Spectral absorption of zinc phthalocyanine sodium sulfonate in water: lower curves, *pH*, 6.1; upper curves, *pH*, 9.8; X, 75°; O, 25°; Δ, 2°.

with. This particular pattern of behavior of dyes in water has, and even more has had, considerable importance in optical sensitizing. To illustrate we show a series of spectrograms (Fig. 7). It is quite clear that the higher frequency bands of the dye *in aqueous solution* have developed, with increasing concentration, their own specific sensitizing action.

The overtone bands of the dye are recorded spectrographically because they are imprinted by adsorption on the silver halide.<sup>9</sup>

#### Experimental

The absorption measurements detailed in Figs. 1 to 3 were made with a Bausch and Lomb spectrometer, having a constant deviation prism, and to which a photocell had been fitted. For most measurements the absorption cells were thermostated. The absorption values at maximum extinction may be low, in extreme cases by about 5%, because of insufficient dispersion. The measurements of the

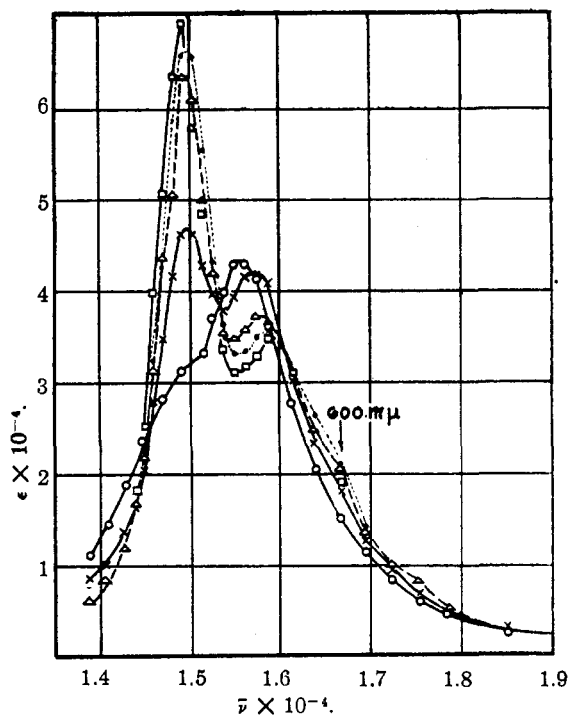


Fig. 6.—Spectral absorption of zinc phthalocyanine sodium sulfonate in water, concn.,  $4.53 \times 10^{-5} M$ , pH values:  $\circ$ , 4.2;  $\times$ , 6.1;  $\Delta$ , 8.0;  $\bullet$ , 10.0;  $\square$ , 11.9.

phthalocyanine solutions (cf. Figs. 4, 5, 6) were made with a Gaertner constant deviation spectrometer lined up with a König-Martens (visual) photometer. The error due to dispersion was of about the same order. The wedge spectra of Fig. 7 were made<sup>24</sup> with a transmission grating replica spectrograph.

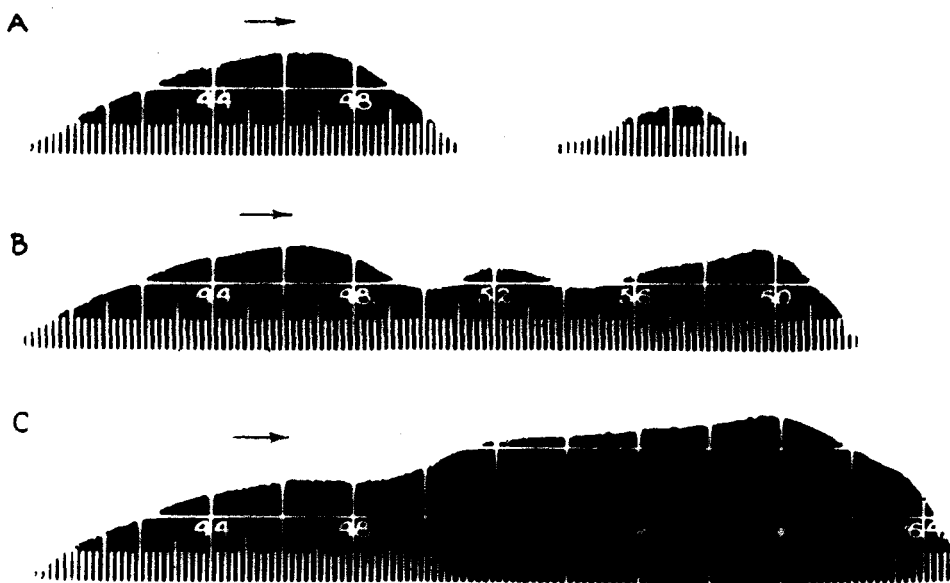


Fig. 7.—Spectral sensitivity of emulsion sensitized with Dye Xa (3,3'-diethylthiacarbocyanine); A,  $1 \times 10^{-5}$  mole/liter of emulsion; B,  $5 \times 10^{-5}$  mole/liter of emulsion; C,  $25 \times 10^{-5}$  mole/liter of emulsion. Arrow indicates blue-violet sensitivity of undyed emulsion.

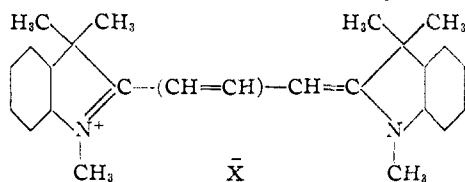
### Discussion

The survey of different classes shows that the aberrations from Beer's law in aqueous solution appear in all classes of water-soluble dyes, but that in all classes also are dyes which approach to conformity. Deviations with increasing concentration may vary from relatively slight fall in the main absorption peak, accompanied by increasing asymmetry on the higher frequency side, to strong and progressive fall of the lowest frequency peak accompanied by increasing strength of bands of higher frequency. The deviations, with one or two doubtful exceptions, appear, therefore, to be variants of a general pattern, of which one extreme variant—of zero degree—is conformity to Beer's law. The conditions for this conformity are interesting as having something in common. Thus in the *fluoresceins* conformity is improved by substitution of halogen atoms in the resorcin part of the molecule, and therewith, from chlorine to bromine to iodine. Although these atoms are not directly concerned in the resonance, they are indirectly or electromerically,<sup>25</sup> and, therefore, will tend to be coplanar with the ring system. This will increase the interval between parallel ions or molecules to a value soon making optical coupling difficult or impossible. Let the minimum interval tolerable between the planes of two planar dye ions be  $3.5 \text{ \AA}$ ., and the maximum permitting optical coupling  $4.0 \text{ \AA}$ .. Taking the radius of a chlorine atom as  $0.97 \text{ \AA}$ ., this involves an additional separation of  $1.94 \text{ \AA}$ .—for bromine,  $2.26 \text{ \AA}$ .; for iodine,  $2.70 \text{ \AA}$ .. It is evident that so long as the halogen atoms remained coplanar with the main structure of the dye, coupling would be slight

(24) Thanks to Mr. R. D. Walker, formerly of this Laboratory.

(25) Cf. A. L. Sklar, *Rev. Modern Phys.*, **14**, 232 (1942).

or negligible.<sup>26</sup> Similar conditions for *intermolecular steric hindrance* obtain for the cyanine dye,



astraphloxin, because of the dimethyl groups.<sup>27</sup> Only at very high concentrations is there any evidence for deviations from Beer's law.<sup>28</sup> The same condition obtains for dye molecules whose own structure is non-planar.<sup>29</sup> In the case of dyes with an azine structure, the safranines and rhodulines appear to be largely sterically hindered and show little aberration. In the case of the triphenyl- and diphenylmethane dyes there are complications from the fact that a less rigid (cross-linked) conjunction of resonating groups appears. The absence of aberration (relatively) for the triamino dyes might possibly be attributed to the fuller hydration possible to these peripheral groups, lessening the probability of the ions getting into parallel fixation. Conversely, then, this parallel fixation is favored on substitution in the amino-groups of alkyl, etc., so that they become less hydrophile. The "blocking" of one amino-group (as in methyl green) makes the dye effectively in line with diphenylmethane congeners, so that now only two of the phenyl groups have to be coplanar for full resonance, and the peculiar quasi-centric symmetry of the triphenylmethane dyes is lost. Even so, it is not immediately apparent why diamino derivatives of triphenylmethane dyes should show such reduced aberration that on increase of concentration only small but progressive increase of asymmetry occurs on the higher frequency side of the main band. This does indicate the potentiality of further band development. In any case, there appear to be possible complications of a stereochemical character with triphenylmethane dyes, such as Crystal Violet, which have been discussed

(26) If the  $-C-X$  bond took on a certain degree of electrostatic character, i. e., of  $-C^+X^-$  character, the repulsive effect would be still greater, since the ionic radii of these atoms are much greater. Another way of expressing this is to consider the bond as hyperconjugated because of electron migration.

(27) Also for Quinoline Red—here because of ring binding of the N atoms.

(28) G. Scheibe, *Kolloid-Z.*, **82**, 1 (1938); cf. also *Z. angew. Chem.*, **52**, 631 (1939).

(29) S. E. Sheppard, R. H. Lambert and R. D. Walker, *J. Chem. Phys.*, **9**, 96 (1941).

recently by G. N. Lewis, T. T. Magel and D. Lipkin.<sup>7</sup>

The evidence from the general survey points to the formation of optically coupled plane-parallel molecules or ions, separated by an interval of about 4 Å., as responsible for the typical aberration in aqueous solution on increase of concentration. Evidently, the type of equi-distant plane-parallel coupling suggested could be secured for molecules not themselves planar, provided that all planar parts of the molecules could arrange themselves appositely without steric hindrance occurring. This evidence is largely of a negative character, in that steric conditions which would inhibit such dimerization also accompany conformity to Beer's law, and conversely. It does not appear necessary to assume that the spectral modification by change of concentration is caused by the development of new bands peculiar to the dimer. The bands in question overlap too consistently with vibration coupled overtones of the main absorption band for this to be a mere casual coincidence. It appears to be causal rather than casual, and made possible by vibrational excitation of the individual ionic partners of dimerization. The eventual nature of the process will be considered more fully in a following paper dealing with quantitative studies of specific dyes.

### Summary

Many dyes, of several different classes, *viz.*, azo- to disazo-, triphenylmethane, fluorescein, azine and polymethines and azoporphyrine dyes, exhibit marked aberrations from Beer's law in aqueous solutions. The aberrations appear to have a common pattern, deriving from a similar causation. In each class there appear also dyes of which the aqueous solutions conform to Beer's law. Examination of the conforming types indicates that the aberration is probably due to the formation of optically coupled pairs of ions, or dimers, which is not possible to the conformist dyes because of intermolecular steric hindrance. Certain examples cited of specific dyes, *e. g.*, resorciuphthalein and *tri-*, *diphenylmethane* dyes which appear from the literature to deviate from the rules suggested, were not studied over a sufficient range of pH. When due consideration is taken of the importance of pH for intermolecular hydrogen bond formation, *e. g.*, with carboxylic and sulfonic groups—it is believed that such exceptions will fall in line.

ROCHESTER, N. Y.

RECEIVED MARCH 6, 1944