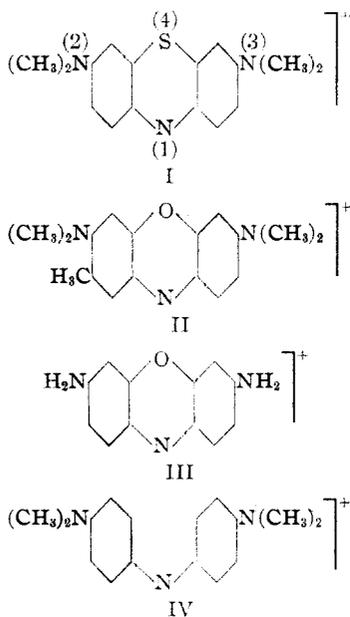


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Methylene Blue and Other Indicators in General Acids. The Acidity Function

BY GILBERT N. LEWIS AND JACOB BIGELEISEN

Methylene blue is not a striking indicator. If to a neutral or alkaline solution in water, which is blue-green, we add sulfuric acid, we find that at about normal acid the green becomes less bluish, while in sulfuric acid of 65% or more by weight a yellow-green is obtained. However, when examined spectroscopically, we find a series of bands the interpretation of which gives an answer to some interesting chemical problems. Let us write down the formulas of methylene blue (I) and the closely related substances capri blue (II), oxonine (III), and Bindschedler's green (IV).



We see that there are four basic spots where a proton or other acid can add: the central nitrogen, the two amino nitrogens, and the sulfur (or oxygen). These will be numbered as indicated in formula I, it being noted that the basic spot (4) is absent in Bindschedler's green. Most chemists would guess, as several already have, that on acidifying one of these dyes the first H^+ will go to the (2) or (3) position. On the other hand, Schwarzenbach and Michaelis have concluded¹ that in the case of Bindschedler's green the basic spot (1) is first occupied. If we represent by D^+ any one of the ions I-IV, we may represent by D^1H^{++} a compound formed by the addition of

(1) Schwarzenbach and Michaelis, *THIS JOURNAL*, **60**, 1667 (1938).

H^+ at the central nitrogen and by D^2H^{++} or D^3H^{++} one produced by addition at one of the amino nitrogens. The extension of this nomenclature to other acids and to more than one addition will be evident as we proceed.

Now by studying the absorption spectrum of the dye and its first acid addition product we have a direct means of deciding this question. If the proton or other acid adds at (1) or (4) the original positive charge will be forced to a greater extent into the positions (2) and (3). The effect is bathochromic by a principle stated by Lewis and Calvin² and illustrated by them by the examples of auramine, malachite green, crystal violet and its compound with hydrogen ion. On the other hand, acid addition at one of the amino nitrogens will presumably have a hypsochromic effect, although by no means so large as that suggested by Schwarzenbach and Michaelis¹ in the case of Bindschedler's green, for we believe that they have over-emphasized the importance of symmetry in color resonance.

When acid is added to an aqueous solution of methylene blue the peak at 6650 Å. ($\bar{\nu} = 15040 \text{ cm.}^{-1}$) begins to disappear and a new peak begins to appear at 7420 Å. ($\bar{\nu} = 13470 \text{ cm.}^{-1}$). We may therefore decide at once that the H^+ addition is at one of the central positions (1) or (4) and since it seems hardly likely that the sulfur will act as a base at these low acid concentrations we may ascribe to the new substance the formula D^1H^{++} . At 0.4 *M* sulfuric acid D^+ and D^1H^{++} are present in about equal amounts. With 3 *M* sulfuric acid D^+ has been quantitatively converted into D^1H^{++} and we may obtain the pure spectrum of the latter. In Fig. 1 we give the molar extinction coefficients of the D^+ and the D^1H^{++} forms of methylene blue over a wide frequency range.³ Beer's law was found to hold accurately over a twenty-fold range of concentration. In accord-

(2) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).(3) The ultraviolet region was explored for a purpose which will appear in a later paper, where also we shall discuss the band at about 3700 Å. seen in Fig. 2. The curve for the pure monomer is to be compared with a similar curve obtained by Epstein, Karush, and Rabinowitch, *J. Opt. Soc. Am.*, **31**, 77 (1941), but theirs is for a mixture of monomeric and dimeric ions. In that paper, which at first we had unfortunately overlooked, curves are given for thionine in hydrochloric acid and sulfuric acid which closely resemble corresponding curves for methylene blue given in this paper.

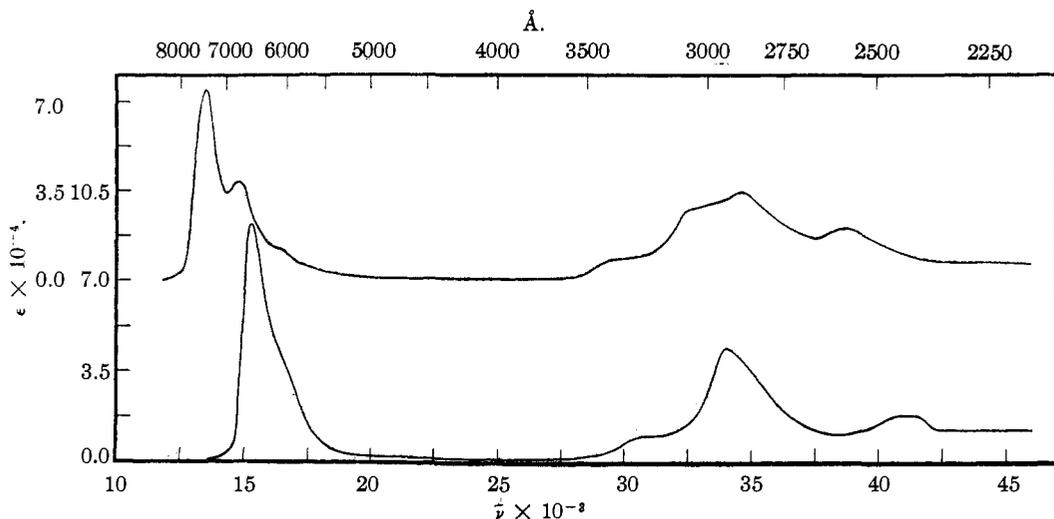


Fig. 1.—The molar extinction coefficients of methylene blue and its first acid addition product: lower curve D^+ in ethanol; upper curve D^+H^{++} in aqueous 3 M H_2SO_4 . Both curves belong to purely monomeric ions. The values of ϵ for D^+H^{++} may have to be raised considerably if there are present in this solution colorless forms of the type discussed in the paper immediately following.

ance with the theory of Rabinowitch and Epstein⁴ it is evident that no dimer could be formed from two doubly charged positive ions.

It was found by Michaelis and Granick⁵ that when oxonine (III) is dissolved in dilute acid a new band appears some 750 \AA . to the red side of the D^+ band. This is very close to the difference that we found for methylene blue. Therefore, for oxonine also we may write for the first product of the addition of H^+ the formula D^+H^{++} .

Capri blue (II) which is so similar to oxonine (III) and to methylene blue (I), and whose absorption curve is identical with that of the latter in all of the visible region, shows a surprisingly different behavior. The addition of acid turns it from blue to red and we find the new band appearing at a higher frequency than the original, namely $\lambda_{\text{max.}} = 5140 \text{ \AA}$. ($\bar{\nu} = 19450 \text{ cm.}^{-1}$). This band has not more than one-half the maximum molar extinction coefficient of the D^+H^{++} band of methylene blue but is much broader. The color change comes in about the same range of acid concentration as in the case of methylene blue.

Because of the hypsochromic change we conclude that the new band at 5140 \AA . is due to the addition of H^+ at one of the amino nitrogens, say D^2H^{++} . At first sight it would seem that the extra methyl group in capri blue would have little influence upon its behavior, but Professor Melvin Calvin has reminded us of the considerable steric

effect of an ortho methyl group upon a dimethyl-amino group which tends to throw the latter out of the plane, thus diminishing its resonance with the ring and, therefore, increasing its basicity.^{5a} It seems probable that it is this effect which causes the difference in behavior of capri blue and oxonine.

Now it cannot be supposed that methylene blue forms only the D^+H^{++} or that capri blue produces only D^2H^{++} , but rather that each dye gives both of these isomers in greater or lesser amount. On account of the shape of the absorption curve it would be hard to detect a small amount of D^2H^{++} in methylene blue. On the other hand, the absorption curve of the acid form of capri blue in 3 M sulfuric acid falls off very sharply to the left and it therefore seemed possible that by using an extremely concentrated solution of capri blue the D^+H^{++} band might be found. This hope was realized, a new band appearing at about the same wave length as that of the D^+H^{++} of methylene blue. This concentrated solution could be studied only up to $17 \times 10^3 \text{ cm.}^{-1}$. The solution was then diluted fifty-fold and the measurements were continued to $33 \times 10^3 \text{ cm.}^{-1}$. Then correcting for concentration we obtain the full absorption curve. To display this whole curve within reasonable space we plot in Fig. 2 the logarithm of the extinction against the fre-

(5a) Thus Branch and Calvin (Branch and Calvin "The Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p. 267) explain the high basic strength of dimethyl-ortho-toluidine found by Davies and Addis (*J. Chem. Soc.*, 1622 (1937)).

(4) Rabinowitch and Epstein, *THIS JOURNAL*, **63**, 69 (1941).

(5) Michaelis and Granick, *ibid.*, **63**, 1636 (1941).

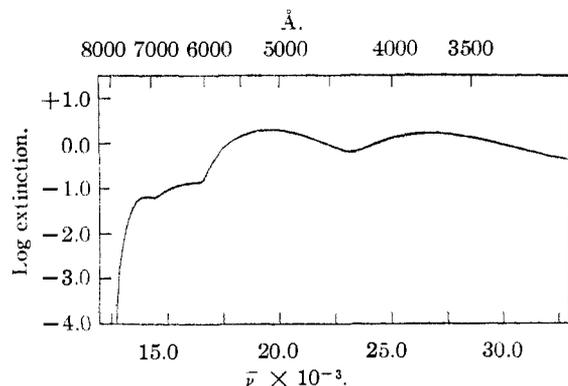


Fig. 2.—Logarithm of extinction of capri blue in 3 *M* H₂SO₄ showing³ the main bands of D¹H⁺⁺ at 14030 cm.⁻¹ and that of D²H⁺⁺ at 19450 cm.⁻¹. Extinction is in arbitrary units.

quency. If we correct the left-hand part of the curve for the contribution of the D²H⁺⁺ from the remaining curve for pure D¹H⁺⁺ is similar in shape to the corresponding curve of methylene blue but displaced a little toward the violet, λ_{\max} can be taken as 7125 Å. ($\bar{\nu} = 14030$ cm.⁻¹). Assuming that the ratio of ϵ 's for D¹H⁺⁺ and D² is the same as for methylene blue we find the ratio of the two isomers D¹H⁺⁺/D²H⁺⁺ as about 0.015.

The Second Proton Addition

As we proceed to higher concentrations of acid, a second hydrogen ion adds to the dye and new bands appear, and in 78% sulfuric acid the DH⁺⁺ species is gone. The spectrum for methylene blue is now the one shown in Fig. 3. Here also we have investigated Beer's law and find the whole curve unchanged by a change in concentration, except possibly at the small subsidiary band at 16×10^3 cm.⁻¹. This small region needs further study.

We have found no way of accounting for the three bands "A," "B," and "C" of Fig. 3 except on the assumption that they belong to three different substances. In this case there are four possible isomers but we shall not attempt at present to ascribe the bands to the several isomers. When such attempt is made attention must be given not only to the position of these bands but also to their great breadth.

Studying capri blue also in 78% sulfuric acid we found only two bands. The first is at 5900 Å. ($\bar{\nu} = 16900$ cm.⁻¹) and the second at 4200 Å. ($\bar{\nu} = 23800$ cm.⁻¹). The first has a half width of 1300 Å.; the second with a 50% higher extinction has a half width of 1000 Å.

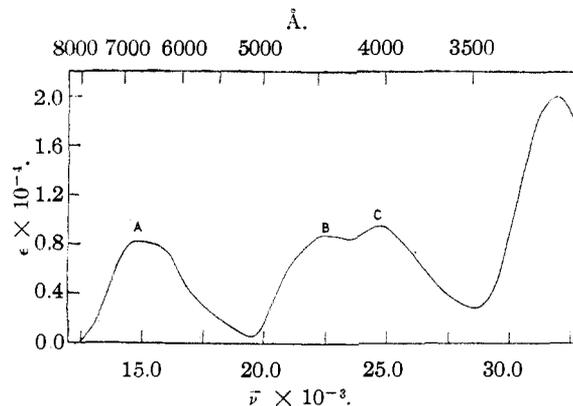


Fig. 3.—The molar extinction coefficient of methylene blue in 78% H₂SO₄. The values of ϵ are calculated and plotted as though only one substance were present. If bands "A," "B," and "C" represent, as we suppose, three different substances and if these have about the same molar extinctions and if these have about the same molar extinctions, then the true ϵ for each would be about three times as great as here shown.

Looking for a third acid addition we studied the spectrum of methylene blue all the way into fuming sulfuric acid. No new band was found and the absorption curves were extraordinarily similar to that of Fig. 3. The only observable differences were in the relative heights of the three maxima. Assuming that the individual ϵ 's are constant, we can see how the relative amounts of the three isomers change with changing medium, as shown in the following table.

TABLE I
RELATIVE HEIGHTS OF "A," "B," AND "C" BANDS AT
THREE ACID CONCENTRATIONS

	A/B	A/C	B/C
78% H ₂ SO ₄	0.95	0.88	0.93
96% H ₂ SO ₄	.93	.84	.90
H ₂ SO ₄ + 15% SO ₃	.83	.73	.88

Addition of Other Acids than the Proton

Although the phenomenon was first discovered by Meyer⁶ in 1908 and was strongly emphasized by Lewis⁷ in his paper on "Acids and Bases" it is not generally realized how inadequate is a titration, even if carried out spectrometrically, to show what acid is being added to a basic indicator. Meyer showed that benzaurin (as well as fuchson) gives the same absorption spectrum⁸ when dissolved in concentrated aqueous sulfuric

(6) K. H. Meyer, *Ber.*, **41**, 2568 (1908).

(7) Lewis, *J. Franklin Institute*, **226**, 293 (1938).

(8) The rule is not universal. For example, when the acid atom is the boron of boric acid or a metallic ion, and the indicator base is a dye of the alizarin type or any other that forms chelated rings, new colors appear. Many of these are mentioned in Feigl's "Qualitative Analysis by Spot Tests," 2nd English edition, Nordemann Publishing Co., New York, N. Y., 1939.

acid and in a chloroform solution of stannic chloride. In the first case presumably H^+ is added to the indicator, in the second stannic chloride.

In this section we shall give several illustrations of this remarkable phenomenon. Our first experiments were with methylene blue in acetone to which boron trichloride was added as acid. In addition to the curve for D^+ which is identical with that in ethanol (Fig. 1) a second maximum appeared at 7400 Å. It coincides with the band given in Fig. 1 for D^1H^{++} , but now our ion is $D^1-(BCl_3)^+$. In this experiment the dye was slowly being destroyed by the boron trichloride. Our next experiments, therefore, were made with stannic chloride, as acid, dissolved in methyl cyanide.

In Fig. 4 we give the molar extinction coefficients of methylene blue (1) in methyl cyanide with 0.1 *M* stannic chloride and (2) in aqueous sulfuric acid 3 *M*. The two substances are $D^1-(SnCl_4)^+$ and D^1H^{++} . It will be seen how extraordinarily similar the two curves are as to the position of the main bands and of the subsidiary vibrational bands, and as to the absolute extinction coefficients.

Since both acetone and methyl cyanide are in some degree capable of assuming tautomeric forms containing labile hydrogen, we also tried phenyl cyanide and stannic chloride. The curve obtained was very similar to those of Fig. 4.

The experiments with non-aqueous solvents were carried out on the vacuum bench, great pains being taken to exclude traces of water and hydrochloric acid, but these precautions were really unnecessary as we later found that even if the greater part of our stannic chloride had been converted into hydrochloric acid there would not have been enough of the latter to convert all of the D^+ into D^1H^{++} . In fact it takes approximately 1 *M* hydrochloric acid in methyl cyanide to eliminate the D^+ band. This solution gives once more an entirely similar absorption curve. The results in the four cases are shown in Table II where $\bar{\nu}$ shows the first absorption maximum, $\bar{\nu}'$ another vibrational peak. The last column shows the vibrational separation.

TABLE II

	$\bar{\nu}$ in cm^{-1}	$\bar{\nu}'$ in cm^{-1}	$\bar{\nu}' - \bar{\nu}$
Aqueous 3 <i>M</i> H_2SO_4	13500	14750	1250
HCl in CH_3CN	13600	15050	1450
$SnCl_4$ in CH_3CN	13340	14500	1160
$SnCl_4$ in C_6H_5CN	13150	14430	1280
BCl_3 in $(CH_3)_2CO$	13540	Not measured	

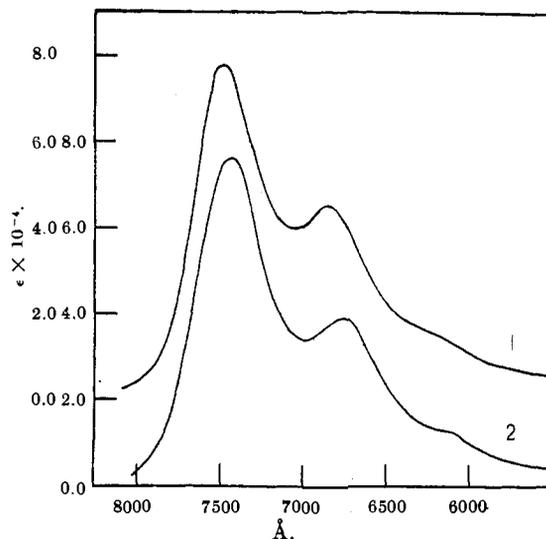


Fig. 4.—Molar extinction coefficients of methylene blue: (1) in CH_3CN and 0.1 *M* $SnCl_4$; (2) in 3 *M* H_2SO_4 ; (1) is the curve of the ion $D^1SnCl_4^+$; (2) of D^1H^{++} .

Capri Blue.—It seemed important to make similar experiments with capri blue in order to see how the ratio of the two isomers changes with the nature of the medium and of the acid. Using first hydrochloric acid in methyl cyanide and then stannic chloride in methyl cyanide we obtained curves entirely similar to that of Fig. 2 with almost the same values of $\bar{\nu}_{max}$, but differing in the relative amounts of the two isomers. In aqueous sulfuric acid we found $D^1H^{++}/D^2H^{++} = 0.015$; with hydrochloric acid in methyl cyanide we find $D^1H^{++}/D^2H^{++} = 0.033$; but with stannic chloride in methyl cyanide we find a much larger ratio of 0.13 for $D^1(SnCl_4)^+/D^2(SnCl_4)^+$. We shall not comment on the small change in going from water to methyl cyanide as solvent, but in the latter solvent the change in going from hydrochloric acid to stannic chloride is not only striking but was in fact predicted. When $SnCl_4$ adds to the nitrogen which is already attached to the ring and also to the two methyl groups, there must be some steric opposition, diminishing the tendency of the acid to add at this spot. If this is the chief reason for the difference in ratios with H^+ and stannic chloride we may estimate the increase in free energy of $D^2(SnCl_4)^+$ due to the steric effect, as 0.8 kcal.

We have not commented on the fact that many of our results show the untenability of the view that a monotonic scale of acid and base strengths can be accurately set up.⁹ Lewis and Seaborg¹⁰

(9) Luder, *Chem. Rev.*, **27**, 547 (1940).

(10) Lewis and Seaborg, *THIS JOURNAL*, **62**, 2122 (1940).

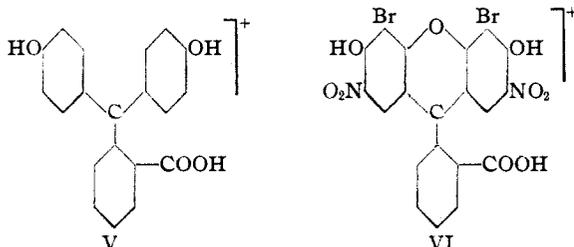
showed that ammonia is specifically a very strong base toward *m*-dinitrobenzene because of the great coulombic interaction (hydrogen bond formation) in the addition compound. In the steric repulsion, that we have just mentioned, we see an opposite effect. Indeed, we can imagine a very strong acid that might be unable to neutralize a very strong base because of such a steric influence.^{10a}

We may mention here a few experiments with Bindschedler's green.¹¹ This dye in water shows maximum absorption at 13810 cm.⁻¹. In 3 *M* sulfuric acid a completely new band was found, which, however, is very near to the former one. Its maximum is at 14100 cm.⁻¹. This experiment had to be performed at -25° in order to avoid too rapid decomposition of the dye. The next experiments were in methyl cyanide and in methyl cyanide with stannic chloride. Here the values of $\bar{\nu}_{\max}$ were practically identical with those in water, namely: 13810 cm.⁻¹ and 14140 cm.⁻¹.

We believe that in spite of the small hypsochromic shift the acid addition products are D¹H⁺⁺ and D¹SnCl₄. In this case it seems probable that the acid addition causes a diminution in the angle between the phenyl groups, thus shortening their distance, and diminishing the polarizability of the molecule and λ_{\max} .

Titration in Concentrated and Fuming Sulfuric Acid: the Acidity Function

There is another class of compounds that we may use to illustrate the rule that acid addition at one of the main auxochromes gives rise to an absorption at higher frequency, while addition at the central atom has a bathochromic effect. As examples we may take phenolphthalein (V), eosin, and dinitro-dibromofluorescein (VI).



We give the formula of the substance as it exists in 96% sulfuric acid, where each substance has a

(10a) Cf. Brown and Bartholomay, *J. Chem. Phys.*, **11**, 43 (1943).

(11) Our sample of Bindschedler's green does not show the large indicator effects found by Schwarzenbach and Michaelis¹ between pH 2 and 4.5.

yellow color. All three can be used as reversible indicators in the range from 96% to fuming acid. With increasing fractions of sulfur trioxide the phenolphthalein becomes colorless. The visible absorption band has been replaced by one in the near ultraviolet and here we see that the only acid addition can be at one of the hydroxyl groups. On the other hand, with increasing sulfur trioxide the other two indicators develop a reddish color, and the new absorption bands are at lower frequency than the original ones. Here we suppose that the acid adds at the central oxygen.

The whole color change in phenolphthalein occurs before we reach 100% sulfuric acid (50 mole % SO₃). In the case of eosin the color change is all in the range very close to 100% sulfuric acid while the dinitro-dibromofluorescein is only 60% converted when the mole fraction of sulfur trioxide is 0.508 and 80% at mole fraction 0.534, as determined from complete spectrograms. In the most fuming acids the indicator is attacked, but not fast enough to interfere with our measurements. It is probable that with tetranitrofluorescein a considerable further range of fuming sulfuric acid could be explored.

It occurred to us that we might use dinitro-dibromofluorescein to extend and interpret the interesting series of measurements used by Hammett and Deyrup¹² in establishing their acidity function, which must, through the greater part of the acid range they investigated, give a good approximation to the logarithm of the activity of H⁺. However, as they approached 100% sulfuric acid where log *a*_{H⁺} should be nearly at a maximum (as indicated by the dotted curve in Fig. 5) their -*H*₀ shows an enormous increase.

We are convinced that with all of the three indicators they used in their strongest acids their color change was due in part to the addition of H⁺ and in part to the addition of a quite different acid, sulfur trioxide, until as they approached 100% sulfuric acid only the latter species was important.

In Fig. 5 we have replotted the results of Hammett and Deyrup with their last three indicators, showing -*H*₀ as a function of the mole fraction of sulfur trioxide (moles SO₃ to moles H₂O + SO₃). It will be seen that near 50 mole per cent. their curve is nearly vertical but begins turning again at their last point at 50.14 mole per cent. Although our measurements do not claim the high

(12) Hammett and Deyrup, *This Journal*, **54**, 2721 (1932).

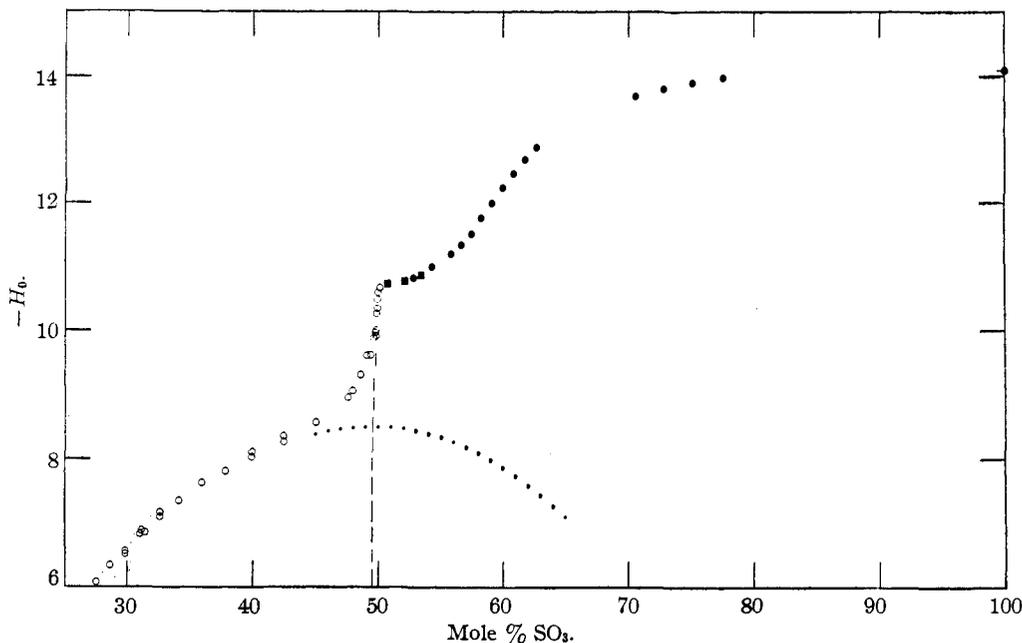


Fig. 5.—The acidity function ($-H_0$) obtained by Hammett and Deyrup with their last three indicators and replotted against mole % SO_3 , open circles. Also our extension of their results with dinitrodibromofluorescein as indicator, squares. Also 14.56 plus the logarithm of the vapor pressure (atm.) of SO_3 , solid circles. The dotted curve and points to the left give approximately $\log a_{\text{H}^+}$, the broken curve and points to the right, $\log a_{\text{SO}_3}$ plus 14.56 (standard state SO_3 gas, 1 atm.).

accuracy attained by Hammett and Deyrup, we have extended their curve by fitting our point at 50.0 mole per cent. to theirs. Our other three points are shown by the squares. That the great increase in $-H_0$ at about fifty mole per cent. really indicates a large increase in the "acidity" of the solution was shown by Hammett and Deyrup when they compared their results with the observations of others on the decomposition of malic and oxalic acids, which demonstrate that the catalytic effect also increases enormously in this region. In fact we may note the observation of Lichty¹³ that at a little more than fifty mole per cent. the decomposition of oxalic acid was too rapid to measure at 0°. There is undoubtedly a great increase in the activity of some acid in this range but it is not H^+ .

In order to show that the acid that causes the indicator and catalytic effects is sulfur trioxide we have added to Fig. 5 the logarithm of the vapor pressure¹⁴ of sulfur trioxide above fuming sulfuric acid solutions, to which has been added a constant to fit this to our other curve. The right-hand portion of the curve together with the nearly

vertical continuation shown by the somewhat schematic broken curve measure $\log a_{\text{SO}_3}$. The jog in the curve and the fact that $\log a_{\text{SO}_3}$ approaches minus infinity, not at fifty mole per cent., but at a lower concentration, is due to the partial dissociation of pure sulfuric acid, producing sulfur trioxide.

The fact that we can thus get a satisfactory acidity function over the whole range from pure water to pure sulfur trioxide shows the desirability of attempting to construct a monotonic series of acids even though we have pointed out that it never can be exact and that there may be some very large specific variations.

Experimental

Absorption spectra from 8100 to about 4000 Å. were measured by methods previously described.¹⁵ Measurements over the whole spectral range were made with only a little less accuracy by means of a Beckman quartz photoelectric spectrophotometer.

The dyes used were commercial samples. In the case of methylene blue many severe tests showed the absence of any other dye. In determining its molar extinction coefficient a sample was used that had been moderately dried and then analyzed. The analysis accorded best with the assumption of a monohydrate and on this basis a calculation of concentrations was made. When the D^1H^{++}

(13) Lichty, *J. Phys. Chem.*, **11**, 225 (1907).
 (14) These values were all obtained from the "International Critical Tables" except the point at pure sulfur trioxide which is extrapolated from the values of Berthoud, *Helv. Chim. Acta*, **5**, 513 (1922).

(15) Lewis, Lipkin, and Magel, *THIS JOURNAL*, **63**, 3005 (1941).

band of capri blue was first found it seemed necessary to show that this band could not be due to an impurity. Some of the capri blue was converted into leuco base at pH 7.5, was partially shaken out with purified ether, and later partially reoxidized. In spite of the considerable opportunities for fractionation thus afforded the ratio of ϵ_{\max} for the two bands was within 3% the same as before. The sample of dinitrodibromofluorescein that we first employed was an old commercial sample that we distrusted. A new sample was therefore prepared by the standard method¹⁶ and fractionated. The absorption spectrum was identical with that given by the old sample, both in fuming sulfuric acid and in dilute alkali, although in the latter case our sample showed a little sharper maximum and therefore presumably was a little purer.

In the experiments on the vacuum bench the stannic chloride was fractionally distilled, the middle portion being employed. The tube containing the dye was exhausted, dry methyl cyanide was distilled in, and then the desired amount of stannic chloride was distilled in and the tube sealed off for the spectrometric measurements. It was impossible to obtain high enough concentrations of stannic chloride to give the second acid addition, since the methyl cyanide is a sufficiently strong base to neutralize stannic chloride to form a white compound, not extremely soluble.

Summary

When in aqueous solution acid is added to dyes of the type of methylene blue the first addition of H^+ is at the central nitrogen, giving a band of lower frequency than that of the original dye. But with capri blue the first addition is to one of the amino nitrogens and a band of higher frequency than the original. These facts are interpreted in terms of a rule of Lewis and Calvin. In the case of capri blue, however, a small amount of

(16) See Colour Index No. 771.

the isomeric form, with H^+ on the central nitrogen, is found. In more than 70% sulfuric acid a second H^+ adds. Here there are several isomers possible of which two are found with capri blue, three with methylene blue and the change in the relative amounts of the latter in going from 78% to fuming sulfuric acid is found.

In experiments in which the added acid is not H^+ but boron trichloride or stannic chloride in acetone, and methyl and phenyl cyanides, the extraordinary similarity but not complete identity of the absorption curves of these addition compounds and those with H^+ is exhibited in the cases of methylene blue, capri blue, and Bindschedler's green. In the case of capri blue an interesting steric repulsion between stannic chloride and the dimethylamino group is exhibited.

Another class of dyes, phenolphthalein, eosin and dinitrodibromofluorescein, are indicators in the range from 95% to fuming sulfuric acid and illustrate further the difference between acid addition at central and end positions.

By using dinitrodibromofluorescein as indicator, we have been able to extend the determination of the acidity function of Hammett and Deyrup well into fuming sulfuric acid. It is shown that in the more concentrated acids used by those authors a large part of the color change results from the addition not of H^+ but of another acid, namely, sulfur trioxide. In the range of our titrations and presumably all the way to pure SO_3 the acidity function ($-H_0$) measures not $\log a_{H^+}$ but $\log a_{SO_3}$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Dimeric and Other Forms of Methylene Blue: Absorption and Fluorescence of the Pure Monomer¹

BY G. N. LEWIS, O. GOLDSCHMID, T. T. MAGEL AND J. BIGELEISEN

In order to understand the absorption spectra of dyes as a class it is desirable to analyze the absorption of a few typical dyes in the fullest detail. Having studied in the preceding paper the spectra of compounds between methylene blue and acids, which compounds are obviously stoichiometrically different from the parent dye, it remains to

(1) This paper is a collection of sporadic work done through a period of four years. The first experiments on absorption and the study of the fluorescence spectrum were carried out by O. G. The construction of the spectrophotometer and the first experiments on the molecular polymer were made by T. T. M. All the remaining experiments were made by J. B.

consider those forms that are, or appear to be, stoichiometrically identical.

This task is simplified by the work of Rabinowitch and Epstein² on the dimeric ion, which they conclude exists in considerable amount in a solvent of high dielectric constant, such as water, where the coulombic repulsion is not great enough to overcome the addition forces.

In ethanol or 95% ethanol no appreciable amount of dimer was found, at least in the en-

(2) Rabinowitch and Epstein, *THIS JOURNAL*, **63**, 69 (1941).