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

Rules for the Absorption Spectra of Dyes

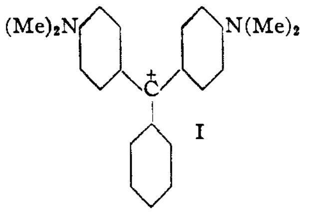
BY GILBERT N. LEWIS

While some have hoped that the relation between color and chemical constitution will ultimately be found by the exact methods of quantum mechanics, it is worth while, in the meantime, to see what may be accomplished by quasi-classical methods.

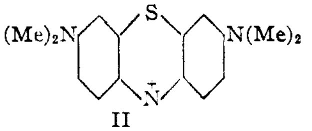
Hausser[1] showed that, for a very large number of substances of the polyenic type, the wave length of maximum absorption, plotted against the number of double bonds, gave the same curve for all substances of this class. The functional nature of this curve was shown by Lewis and Calvin,[2] who found λ^2 to be linear with the number of double bonds, an equation that has recently been corroborated by Heilbron, Jones and Raphael.[3]

It was further found by Lewis and Calvin that for nearly linear molecules of another type, the cyanines, the wave length of maximum absorption is linear with the number of connecting double bonds, and this has been confirmed in many instances by Brooker[4] and co-workers, for symmetrical molecules. Molecules whose formulas do not possess a right and left symmetry cannot be brought under ordinary rules. In fact, their absorption spectrum varies from solvent to solvent, especially if, in the normal state, the molecule has a considerable dipole moment.[2,5] This paper will deal henceforth only with substances of the symmetrical or nearly symmetrical type.

Turning to the more common kind of dyes, the older theories have been excellently presented by Wizinger.[6] For a treatment somewhat similar to the present one, but based on an entirely different theory, reference may be made to a number of papers by Moir.[7] Aside from the azo dyes, which, because of their broad absorption bands and because of the coexistence of *cis-* and *trans*-isomers, are not easily subject to analysis, the most important classes of dyes can be brought into a single family which will be the subject of this paper. Two examples of this family are malachite green (I) and methylene blue (II).



I



II

In such dyes, according to the quasi-classical theory of Lewis and Calvin,[2] an excited state produced by the absorption of light is characterized by an oscillation of the electronic cloud, *i. e.*, an alternating current, along some axis of the molecule. In malachite green the first absorption band in the red corresponds to an excited state in which the oscillation is horizontal as Formula I is written. The second band (*y* band) corresponds to a vertical oscillation, the third (*x′* band) corresponds to a second horizontal, of higher amplitude. The positions of the *y* and the *x′* bands are, at least roughly, calculable, as shown by Lewis and Bigeleisen.[8,9] This paper will be concerned primarily with the main *x* band.

The solution offered by Lewis and Calvin of the old problem as to why malachite green, with only two auxochromes, absorbs farther toward the red than crystal violet, with three auxochromes, gives a clue to the behavior of all the dyes of the family we are considering. The characteristic positive charge (deficiency of one electron), which is formally assigned to the central carbon atom in Formula I, does not wholly or even chiefly remain on that atom. Resonance carries it partly into the lower phenyl group, and largely to the two NR_2 auxochromes. If it all remained on the central carbon, this would be the only acid spot, but in fact the acidity is distributed to various parts of the molecule. While it would be difficult to define numerically the amount of such acidity, one can ask, without ambiguity, as to the fraction of the characteristic positive charge which is to be assigned, say, to one NR_2 group. This is equivalent to asking the fraction of double-bondedness in the bond between that nitrogen and the carbon of the ring. There are other charges in the molecule, indeed we shall discuss many dyes with ionic substituents, such as SO_3^- and CO_2^-, but these will be ignored in order to focus attention upon that particular positive charge that has been indicated in the formulas.

Considering the first absorption band of a dye like malachite green, and assuming that λ increases with any increase in the fraction of the characteristic charge located at the two auxo-

---

[1] Hausser, *Z. tech. Physik.*, **15**, 10 (1934).

[2] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

[3] Heilbron, Jones and Raphael, *J. Chem. Soc.*, 139 (1944). These authors also confirm the rules of Lewis and Calvin regarding the *x* bands of the polyenes.

[4] Brooker, *Rev. Mod. Physics*, **14**, 275 (1942).

[5] Brooker and Sprague, THIS JOURNAL, **63**, 3214 (1941).

[6] Wizinger, "Organische Farbstoffe," Dümmlers Verlag, Berlin u. Bonn, 1933.

[7] Moir, *Trans. Roy. Soc. S. Africa*, **17**, 51 (1928).

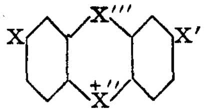
[8] Lewis and Bigeleisen, THIS JOURNAL, **65**, 2102 (1943).

[9] Lewis and Bigeleisen, *ibid.*, **65**, 2107 (1943).

chromes, we may understand the effect of various substituents in the lower phenyl, φ'', of malachite green. If in the para position of this phenyl (designated as p'') a nitro group is substituted, this acid group, by its resonance, largely eliminates the positive charge from φ''. Thus more of the characteristic charge passes into the rest of the molecule and to the two auxochromes. With this substitution λ changes from 621 mμ for malachite green to 646 mμ for the p'' nitro derivative.[7]

On the other hand, if a basic group is placed in the p'' position, the effect is in the opposite direction, and this effect increases[8] in the order: methyl, methoxy, dimethylamino (crystal violet). Meanwhile the y band has been progressing to larger λ, and in crystal violet where the three auxochromes are identical, the x and y bands become identical. If we place in the p'' position a somewhat stronger auxochrome such as diethylamino, the first or x band now corresponds to oscillations in the vertical direction and the second or y band to oscillations in the horizontal.

Now we are going to extend these ideas to the whole family of dyes represented by the skeleton formula III



III

Rule I.—Since all of the molecules of the family have about the same horizontal dimension, it is postulated that the wave length of the main absorption band depends solely upon the fraction of the characteristic charge that is on the two auxochromes, and that λ is larger when this fraction is larger.[10]

It readily may be seen that the rule is in all cases qualitatively in agreement with our available data. Let us consider first the auxochromes X and X′ themselves. With one minor exception, we shall deal only with the symmetrical dyes in which X and X′ are identical. With X and X′ as OH, OR, O^-, NH_2, NR_2, we have the well-known series of basic auxochromes,[6] λ increasing in the order given. This is roughly the order of the basic strength of these radicals, each having a greater tendency than its predecessors to form a double bond with the phenyl carbon, thus acquiring a larger part of the characteristic positive charge of the dye.

When the two main phenyl groups are linked by O, S, or NR, in the X‴ position, there is a shift toward lower values of λ and this is due, not to the mere fact of linking, as supposed by Wizinger,[6] but to the fact that these are basic groups tending to form double bonds with the adjacent carbons and thus acquire some part of the available characteristic charge, leaving less for the auxochromes. O and S are about equally basic and in fact produce the same hypsochromic, or, as we shall say, *negative* effect on λ. NR is much more strongly basic and produces an enormous negative effect.

Finally, we have a strong positive effect when at X″ we replace CR by N. In the former type of dyes a considerable part of the characteristic charge is held by the central carbon atom. In other words Formula I represents one of the important resonating forms of the molecule. On the other hand, nitrogen has much less tendency than carbon to act as an acid. Thus, in methylene blue, Formula II must be regarded as having relatively little weight among the resonating forms. It must not be supposed, however, that even in this case the nitrogen has none of the characteristic charge. By adding hydrogen ion at this central nitrogen, most of the remaining characteristic charge is driven into the rest of the molecule and instead of λ = 665 mμ for methylene blue, λ = 742 mμ in strong acid.[18] Here it is safe to assume that the fraction of the characteristic charge left on the central nitrogen is negligible.

Before proceeding to a quantitative study, we must decide whether to include dyes in which there are substituents in the two main phenyls, φ and φ'. Halogens produce considerable positive shift (compare fluorescein and eosin); so do isopropyl groups. Even methyl causes a small positive shift, which, however, we shall ignore. Since these effects are hard to treat theoretically, only those dyes will be included which, except for the two auxochromes X and X′, are either unsubstituted, or have one or more methyl groups, in the two main phenyl groups.

The quantitative treatment of the absorption spectra of all these dyes has been greatly facilitated by the discovery of a remarkably simple rule which is purely empirical, namely: Any change in X and X′, or in X″ or X‴, produces the same change in λ, regardless of the character of the rest of the molecule. It is therefore possible to obtain additive constants which enable us to correlate known absorption maxima and to calculate new ones. These additive values must themselves be determined empirically, but we shall note that in every case they correspond qualitatively to the rule that λ is determined solely by the fraction of the characteristic charge possessed by the auxochromes X and X′.

We shall take as standard auxochrome NR_2 where R is any alkyl group or a benzyl group, which latter may have any substituents, such as sulfonate groups. It is true ethyl makes an amino group a little more basic than methyl and

---

(10) This may be an oversimplification. The electronic motion which characterizes the excited state is not merely between auxochrome and auxochrome, but throughout the whole molecule, including, for example, the lower phenyl of malachite green. Discrepancies in cases 26, 27, and 28 possibly are consequences of this oversimplification. Moreover, the scope of electronic oscillation may be a little greater when X and X′ are NR_2 than when they are O^-, thus offsetting the greater basicity of the latter.

in every known case the substitution of ethyl for methyl in the auxochromes produces an increase in λ, but we shall ignore this in our simplified table and treat all the alkyls, including benzyl, as identical. As our standard dye we shall therefore take one of the malachite green type in which X and X′ are dialkyl amino groups, X″ is CR and X‴ is absent. For such a dye we shall take λ = 620 mμ.

a. When the alkyl groups in these auxochromes are replaced by hydrogen, the groups become much less basic, and there is a negative shift in λ. We shall assume that each replacement of an alkyl will cause the same shift, *a*, in λ. Thus if X and X′ are both NHR the shift is 2*a*, and when X is NR_2 and X′ is NH_2 the shift is also 2*a*. This is the only case in which we include unsymmetrical dyes. When all four alkyls are replaced by hydrogen, the shift is 4*a*. Taking the average for all the dyes, we write: For each replacement of an alkyl by a hydrogen in amino auxochromes: $a = -13$ mμ.

It is tempting to include the considerable number of dyes in which there is a phenyl or other aromatic group on the auxochrome nitrogen. This could be done in a purely empirical way but is beyond the scope of the present investigation; because (1) such groups increase the size of the resonating system, and (2) they give a hybrid, in the sense that, choosing one center, the dye might, for example, be regarded as a triphenylmethane derivative, or, choosing another center, it might be regarded as a diphenylamine derivative.

b. The weak auxochromes OH and OR will not be treated in this paper. However, O^- according to chemical evidence is more basic than NH_2. The two prove to be about the same as auxochromes,[10] thus we find: For replacing both NR_2 groups in X and X′ by O^-, $b = -69$ mμ.

c. Turning now to dyes in which the X‴ position is occupied, we might expect O and S in this position to be about equally basic. They prove to be so, and we may write: For inserting O or S in the X‴ position, $c = -72$ mμ.

d. The very basic group NR in the X‴ position produces an enormous negative shift, indicating that a considerable part of the characteristic charge has gone to that position. We should expect a greater shift when R = H than when R = φ''', and this seems to be the case, but the data are meager and we shall lump them all together and write: For inserting NR in the X‴ position, $d = -157$ mμ.

e. Finally, when we come to the important classes of dyes with a central nitrogen, we have a large positive shift and find: For substituting N for CR in the X″ position, $e = +108$ mμ.

With these simple rules we can now obtain a good approximation to the observed values of λ in our various classes of dyes. However, since a large fraction of the dyes that have been studied have X″ = Cφ'', with various substituents in φ'', a more accurate calculation of the absorption maxima, as well as greater confidence in our theoretical conclusions, can be obtained by considering the effect of such substituents.

f. If the *p*″ in φ'' is occupied by the ammonium ion-, or alkyl ammonium ion-group, the effect, largely coulombic, is to drive a part of the characteristic charge out of the φ'' and toward the auxochromes. This produces a positive shift in λ and we write: For substituting NH_3^+ or NR_3^+ in the *p*″ position, $f = +14$ mμ.

g. When the *p*″ position is occupied by a negative ionic group, namely, SO_3^-, the coulombic effect is in the opposite direction, but this is more than offset by the conjugation of the acid group, which tends to drive from the φ'' some part of the characteristic charge. This results in a positive shift, which, however, is by no means as large as the one that we have already noted when the uncharged acid group NO_2 is substituted in the *p*″ position. We write: For substituting SO_3^- in the *p*″ position, $g = +6$ mμ.

h. An *o*″ substituent has a very interesting effect that is chiefly of steric character. The substituent forces the φ'' group away from the nearly coplanar configuration, thus diminishing its part in the general resonance, and forcing some of its part of the characteristic charge toward the auxochromes. We should not expect, nor do we find, that the shift is the same for CH_3, Cl, COO^-, or SO_3^-, nor that the shift is independent of the presence or absence of a *p*″ substituent. Nevertheless the differences are small and we shall write: For one substitution in the *o*″ position, $h = +11$ mμ.

Finally we must consider the effect of replacing the unsubstituted φ'' by hydrogen or alkyl. The experimental data are meager, and the theory is uncertain. Perhaps here we find a small error in our fundamental assumptions of the type already discussed.[10] For the present we shall take all these groups as equivalent, although in the dyes numbered 26, 27 and 28 in the table, a considerable discrepancy is thus produced.

About half of the data presented in Table I are taken from the Schultz[11] tables which are a little more complete than the Color Index.[12] The best of these data were those of Formánek.[13] Most of these absorption maxima were obtained visually but are nevertheless surprisingly good. Where some values are in error we may suspect the identification and purity of the dye, rather than the spectroscopic measurements. Of the more modern data those of Auškāps[14] are important because of their number and accuracy. The remainder of the data have been collected

[11] Schultz, "Farbstoff Tabellen," 7th edition, Akademische Verlagsgesellschaft, Leipzig, 1931.

[12] "Color Index," Society of Dyers and Colourists, 1924.

[13] Formánek, "Untersuchung und Nachweis Organische Farbstoffe," Julius Springer, Berlin, 1911.

[14] Auškāps, "Acta Universitatis Latviensis," Riga, 1930, p. 279.

TABLE I

	Sch.	C. I.	Ausk.	Acid or alk.	Ref.	λ in mμ	λ (calcd.)	Δ	Terms used	Structural data
I, Triphenyl-(or diphenyl)-methane dyes, X‴ absent; X″ = CR										
1	754	657	1, 2		14	621	620	1		. .
2	755	658				633	631	2	h.	D_1
3	756	659				628	631	−3	h.	D_1, D_2
4	757	661	7		14	627	631	−4	h.	D_8, D_{10}
5	760	662	3		14	623	620	3		B_4
6	761	664	6		14	627	631	−4	h.	A_2, B_2, D_1, D_2
7	762	663	5		14	609	605	4	2a,h.	A_2, B_3, D_1
8	763	669				629	626	3	g.	B_6, D_4
9	764	666	13		14	618	620	−2		B_7
10	765	670	16		14	631	626	5	g.	B_7, D_4
11	767	667	14		14	631	631	0	h.	B_7, D_1
12	769	672	9		14	636	637	−1	h,g.	B_4, D_3, D_4
13	770	671	15		14	628	631	−3	h.	B_7, D_3
14	771	673	12		14	636	637	−1	h,g.	B_7, D_3, D_4
15	772	674				619	620	−1		D_{12}
16	773	675				617	620	−3		D_{13}
17	826	712	10			637	637	0	h,g.	B_4, D_3, D_4, D_7
18	827	714	17			634	637	−3	h,g.	B_5, D_3, D_4, D_7
19	828	715				613	611	2	2a,h,g.	A_2, B_3, D_3, D_4, D_7
20			4		14	631	631	0	h.	D_1
21			11		14	612	611	1	2a,h,g.	A_2, B_3, D_3, D_4, D_7
22					7	562	568	−6	4a.	B_1
23					7	590	594	−4	2a.	B_8
24					17	576	579	−3	4a,h.	B_1, D_3
25					17	604	605	−1	2a,h.	B_3, D_3
26				Ac.	9	600	620	−20		C_1
27				Ac.	7	548	568	−20	4a.	B_1, C_1
28				Ac.	7	574	594	−20	2a.	B_8, C_1
29	780	676		Ac.		578	582	−4	4a,f.	A_1, B_1, D_{14}
30	782	678		Ac.		582	582	0	4a,f.	A_2, B_1, D_9, D_{14}
31	785	681		Ac.		631	634	−3	f.	D_{16}
32	787	682		Ac.		640	634	6	f.	B_4, D_{17}
33	788	684				636	634	2	f.	D_{15}
34	790	686			7	634	634	0	f.	A_1, D_{15}
35				Alk.	7	553	551	2	b.	B_{12}
36				Alk.	15	558	562	−4	b,h.	B_{12}, D_4
37				Alk.	15	572	562	10	b,h.	A_2, B_{12}, D_4
38				Alk.	15	553	562	−9	b,h.	B_{12}, D_5
II, Xanthene Dyes, X‴ = O; X″ = CR										
39	853	739				550	548	2	c.	C_1
40	854	740				548	522	26	2a,c.	B_2, C_1
41	858	743				546	548	−2	c.	C_2
42	862	746				531	533	−2	2a,c,h.	A_2, B_2, D_1
43	863	748				568	565	3	c,g,h.	B_4, D_3, D_4
44	864	749			18	555	559	−4	c,h.	B_4, D_5
45	865	750				556	559	−3	c,h.	B_{10}, D_5
46	866	752				529	533	−4	2a,c,h.	B_3, D_6
47	867	751				559	559	0	c,h.	B_4, D_6
48	868	753				535	533	2	2a,c,h.	A_1, B_8, D_5
49			45		14	552	559	−7	c,h.	B_4, D_5
50			47		14	565	565	0	c,g,h.	B_4, D_3, D_4
51	880	766		Alk.	9	490	490	0	b,c,h.	B_{12}, D_5
52	884	764		Alk.		485	490	−5	b,c,h.	A_3, B_{12}, D_5
III, Acridine Dyes, X‴ = NR; X″ = CR										
53	901	785				455	411	44	4a,d.	A_2, B_1, C_1, E_3
54	902	788				497	463	34	d.	C_1, E_3
55	903	787				481	437	44	2a,d.	A_1, B_8, C_1, E_3
56	909					460	411	49	4a,d.	A_2, B_1, E_3

TABLE I (*Concluded*)

	Sch.	C. I.	Ausk.	Acid or alk.	Ref.	λ in mμ	λ (calcd.)	Δ	Terms used	Structural data
IV, Diphenylamine Dyes, X''' absent; X'' = N										
57	938	819			5, 18	726	728	− 2	e.	
58		In water		Alk.	5	628	659	−31	b,e.	B_{12}
		In methanol		Alk.	5	640	659	−19	b,e.	
V, Oxazine and Thiazine Dyes, X''' = O or S; X'' = N										
59	991	876			9	661	656	5	c,e.	A_1, E_1
60	1038	922			16, 9	657	656	1	c,e.	E_2
61	1041	925				640	630	10	2a,c,e.	A_1, B_5, E_2
62			50		14	660	656	4	c,e.	E_1
63			52		14	628	630	− 2	2a,c,e.	A_2, B_3, E_2
64					16	600	600	0	4a,c,e.	B_2, E_2
VI, Azine Dyes, X''' = NR; X'' = N										
65	946	825			15	533	545	−12	2a,d,e.	A_1, B_8, E_3
66	955	838				526	545	−19	2a,d,e.	A_1, B_8, E_4
67	957	839				578	558	20	a,d,e.	B_{11}, E_4
68	959	842				557	545	12	2a,d,e.	B_8
69	960	847				590	571	19	d,e.	B_4
70	963	844				551	545	6	2a,d,e.	A_1, B_8
71	964	843	56		14	547	545	2	2a,d,e.	A_1, B_8
72	967	841	55		14	516	520	− 4	4a,d,e.	A_2, B_1
73	970	852				555	545	10	2a,d,e.	A_4, B_8, E_5
74			54		14	519	519	0	4a,d,e.	B_1

NOTES ON STRUCTURAL DATA.—The only permitted substituents in ϕ and ϕ' are indicated by: A_1, 3-CH_3. A_2, 3-CH_3, 3'-CH_3. A_3, 3-$CH_2C_6H_5$. A_4, 2'-CH_3, 5'-CH_3.

The auxochromes X and X' in the 4 and 4' positions are identical, and, moreover, are both $N(Me)_2$, except when specified as follows: B_1, NH_2. B_2, N(H, Me). B_3, N(H, Et). B_4, $N(Et)_2$. B_5, N(Et, benzyl). B_6, N(Me, *p*-sulfonated benzyl). B_7, N(Et, *p*-sulfonated benzyl). B_8, X = NH_2, X' = $N(Me)_2$. B_9, X = NH_2, X' = $N(Et)_2$. B_{10}, X = $N(Et)_2$, X' = N(H, Et). B_{11}, X = $N(Me)_2$, X' = N(H, Et). Finally, B_{12}, O^-.

When X'' is CR we have the cases: C_1, R = H. C_2, R = CH_2CH_2COOH. In all other cases R is phenyl, which may contain substituents as follows: D_1, 2''-Cl. D_2, 5''-Cl. D_3, 2''-SO_3^-. D_4, 4''-SO_3^-. D_5, 2''-COOH. D_6, 2''-$COOC_2H_5$. D_7, 5''-OH. D_8, 5''-NO_2. D_9, 5''-CH_3. D_{10}, 2''-CH_3. D_{11}, 4''-CH_3. D_{12}, 5''-COOH. D_{13}, a complex azo-group. D_{14}, 4''-NH_3^+. D_{15}, 4''-$N(Me_3)^+$. D_{16}, 4''-$N(H, Me_2)^+$. D_{17}, 4''-$N(H, Et_2)^+$. D_{18}, 4''-$N(Me_2, Et)^+$.

When the X''' position is occupied, we have the cases: E_1, X''' = O. E_2, X''' = S. When X''' is NR we have the cases: E_3, X''' = NH. E_4, X''' = NCH_3. Otherwise R is phenyl, in which there may be the substituent: E_5, 2'''-CH_3, 4'''-CH_3.

from numerous papers[15,16,17,18,19] in addition to those already cited.

Table I shows in the second column the number of the dye in the Schultz tables; in the third, the Color Index number; the fourth, Auškāps number; the fifth column shows that measurements were made in an acid or an alkaline solution; the sixth gives the footnote for the several references; the seventh, the observed λ in mμ; the eighth, the calculated values; the ninth gives the difference between the observed and calculated values; the tenth column shows the various terms which, added algebraically to 620 mμ, give the calculated values; and the last column has notes from which in each given family the whole structure of the dye can be obtained. (These specifications should be unique, but the dyes 70 and 71, prepared differently, are assigned the same structure in the literature.) Most of the values were obtained in water solution, but some in ethanol. The difference is usually small and may be in either direction. In the case of the azine dyes the values in ethanol have been preferred.

The most striking feature of the table is the great departure of observed and calculated values of λ in class III, the acridine dyes. Now this is the only class in the whole family of dyes in which there is a large part of the characteristic positive charge both on X'' and on X'''. It therefore seems likely that in the acridine dyes the electronic oscillation of lowest energy, corresponding to the *x* band, is not the horizontal but the vertical one. The calculated values would then be, not for the (vertical) *x* band, but for the (horizontal) *y* band. In fact Formanek found for Dye 53 (acridine yellow, with methyl groups in φ and φ') a second band at 417 mμ, agreeing well enough with the calculated value, 411 mμ. It may be predicted that the *y* bands of other acridine dyes will correspond to the calculated values.

Considering the five remaining classes, the average value of Δ for all dyes is less than 5 mμ. The

---

(15) Brode, THIS JOURNAL, **46**, 581 (1924).

(16) Rabinowitch and Epstein, *ibid.*, **63**, 69 (1941).

(17) Mohler, Forster and Schwarzenbach, *Helv. Chim. Acta*, **20**, 654 (1937).

(18) Lewis and Bigeleisen, THIS JOURNAL, **65**, 1144 (1943).

(19) Unfortunately it has seemed undesirable to use the numerous data of Orndorff, Gibbs and co-workers (references: *ibid.*, **50**, 2798 (1928)) since their values of λ are always higher than those of other observers by 10 to 20 mμ.

discrepancies in dyes 26, 27 and 28 have already been discussed. The case of no. 58 (phenolindophenol) cannot be interpreted until the cause of the great difference in absorption of the water and methanol solutions is found. Some of the remaining large discrepancies are doubtless due to experimental error. If we arbitrarily exclude the eight cases with the largest Δ, the average value of Δ becomes 3 mμ. It may therefore be reasonably predicted that when new members of these five great classes of dyes are investigated, the average difference between calculated and observed values will not be over 3 mμ. Indeed, if we should consider the various factors that we have noted but not used, this difference would probably be reduced to 2 mμ.

Summary

Six great classes of dyes are brought together into one family. The wave length, λ, of the main absorption band of any member of the family is determined by two rules. The first, theoretical, states that λ is always greater, the greater the fraction of the characteristic positive charge that is on the auxochromes. The second, empirical, states that the effect upon λ of various groups is additive. Thus a number of additive constants are obtained, from which λ can be calculated, and which are all qualitatively consistent with the theoretical rule.

However, in the acridine dyes the calculation applies, not to the first (*x*) band, but to the second (*y*) band. With this proviso, the table shows that with new dyes of the family λ can be predicted with an average error of not more than 3 mμ.

BERKELEY, CALIFORNIA RECEIVED DECEMBER 29, 1944

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

The System Octadecylamine–Acetic Acid

BY W. O. POOL, H. J. HARWOOD AND A. W. RALSTON

The present investigation is a continuation of work dealing with the properties of high molecular weight aliphatic compounds and reports the behavior of binary mixtures of octadecylamine and acetic acid.

Method

Preparation of Materials.—Anhydrous acetic acid was prepared by partially freezing 99.5% glacial acetic acid and allowing the liquid portion to drain from the crystals. The freezing point of the acid used was 16.63°.

Fatty acid from hydrogenated soybean oil was converted to nitrile which was then hydrogenated to amine. After a preliminary distillation the octadecylamine was fractionated in a Stedman-packed column. The freezing point (53.02°) of the fraction used was in good agreement with the best literature value[1] (53.06°).

The octadecylammonium acetate was prepared in benzene and after several crystallizations had a freezing point of 84.4°.

Determination of Equilibrium Temperatures.—Mixtures containing more than 55 mole % of acetic acid were prepared by weighing octadecylammonium acetate and acetic acid into small glass tubes which were then sealed. Octadecylamine and acetic acid were used to prepare samples containing 3 to 53 mole % of acetic acid. Mixtures having less than 3 mole % of acetic acid were prepared from octadecylamine and octadecylammonium acetate. Equilibrium temperatures were obtained by observation of the tubes as they were rotated vertically about their short axes in a water-bath. The temperature of the bath was electrically controlled and was subject to very nice adjustment. A condition of equilibrium was proved by noting the temperature at which a solid phase disappeared as the sample was warmed slowly and comparing this temperature with that at which a trace of crystals definitely exhibited growth as the sample was cooled slowly. These two temperatures were always within a few tenths of a degree of each other. The filled circles in Fig. 1 represent the upper or solution temperatures. In some cases unstable crystals transformed to the stable modifications with such speed that true solution temperatures could not be obtained. To secure an approximate solution temperature, the tube was warmed in hot water until the contents were entirely liquid. The tube was then placed in the bath which had a fixed temperature slightly below the melting point of the most stable modification. The mixture would generally supercool and remain liquid. The tube was then removed from the bath, immersed momentarily in cold water and replaced immediately in the bath. If the crystals, which had formed by the rapid cooling, went into solution, the fixed temperature of the bath was lowered, and the entire procedure was repeated. In this way two temperatures were obtained, an upper at which the unstable crystals remelted, and a lower at which the unstable crystals remained or underwent a transformation to a more stable modification. The upper of these two temperatures, which were usually within 0.5° of each

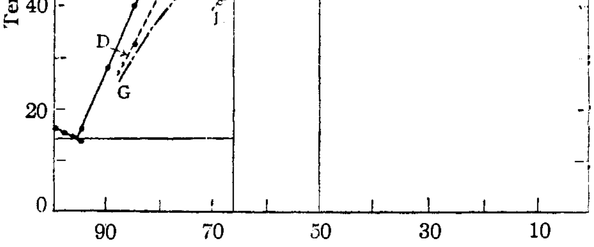


Fig. 1.—The system octadecylamine–acetic acid.

---

[1] Ralston, Hoerr, Pool and Harwood, *J. Org. Chem.*, **9**, 102 (1944).