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Effect of Solvents upon the Absorption Spectra of Dyes. V. Water as Solvent: Quantitative Examination of the Dimerization Hypothesis

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The spectral anomaly[1] in water has been most intensively studied, in the case of polymethine dyes, by G. Scheibe and collaborators,[2] by Sheppard and co-workers;[3] and in the case of thiazines, by Rabinowitch and Epstein,[4] also to some extent, by G. N. Lewis, *et al.*[5] While Sheppard[3] had regarded the anomaly as a consequence of some form of molecular aggregation, other early investigators, as Merritt,[6] Speas[7] and Holmes[8] concluded that a tautomeric equilibrium was responsible. This seems excluded for an isothermal dilution change, for which only aggregation is likely. Scheibe[2] suggested that a process of "reversible dimerization" is responsible for the β-band with pinacyanol (*cf.* Part IV) and a higher "polymer" for the γ-band—comprising perhaps ten or more dye cations. Scheibe proposed two methods of experimentally testing applications of the mass law to the equilibrium $2D^+ \rightleftarrows D_2^{++}$. He assumed that the extinction of the peak of the α-band was proportional to the concentration of the monomer, *i. e.*, $c_{\text{mono}} = \epsilon_\alpha/\epsilon_\infty \cdot C$, where ϵ_α is the extinction for the total molar concentration C, and ϵ_∞ is the extinction at infinite dilution, when the dimer is supposed to be totally dissociated. The mass law was then tested by plotting log c_{mono} against log $(1 - c_{\text{mono}})$, the dissociation residue. This should give a straight line, the slope of which should be an integral number, the order of molecular aggregation, *e. g.*, 2 for a dimer.

To obtain the unknown value ϵ_∞, Scheibe assumed that this would be the same as ϵ_α for alcoholic solution, which obeys Beer's law and is supposed to contain only monomeric ions. He concluded that certain data obtained with pinacyanol (*cf.* below, Dye VIIa) approximately verified this version over *part* of the concentration range, failing at higher concentrations "because of formation of higher polymers." We have tested these assumptions by spectrophotometric measurements with the following polymethine dyes: Va, 1,1′-diethylcyanine chloride; IIb, 3,3′-dimethyl-9-ethylthiacarbocyanine bromide; IVb, 3,3′-diethyl-9-ethylthiacarbocyanine bromide; VIIa, 1,1′-diethylcarbocyanine chloride; and VIIIb, 1,1′-diethyl-6,6′-dimethylisocyanine (Orthochrome T). Our results did not confirm Scheibe's hypothesis. Where a straight line could be obtained for some of the data, the slope did not have the value 2, but some value between 1 and 2. In other cases the best fitting line was a curve.

An improvement on Scheibe's procedure was proposed by Rabinowitch and Epstein,[4] in application to the thiazine dyes, *thionine* and *methylene blue*. Instead of taking ϵ_∞ from the alcoholic solution, they found a value by empirical approximation from the absorption curves in water itself. Although this appeared to represent, for $n = 2$, the data of Rabinowitch and Epstein, it can be shown that in their approximation procedure, and in a modification by M. L. Huggins[9] the value of the equilibrium constant (K) used must be taken from only one experimental point, that at the highest concentration: the values of K from other points are not constant, but vary widely.

The dyes used in our further investigations were

Ref. No.	Formula
Va	1,1′-diethylcyanine chloride
VIIa	1,1′diethylcarbocyanine chloride
XXXIVa	1,1′-diethyldicarbocyanine chloride
IXa	3,3′-diethylthiacyanine chloride
Xa	3,3′-diethylthiacarbocyanine chloride
XIa	3,3′-diethylthiadicarbocyanine chloride
XIIa	3,3′-diethylthiatricarbocyanine chloride
	Thionine
	Methylene blue

We have preferred to deduce ϵ_∞ (in water) by purely empirical extrapolation, from such families of curves as are shown for two cyanine dyes in Figs. 1 and 2, and for methylene blue in

TABLE I

VALUES OF EXPONENT n WITH VARIOUS DYES

Dye	Temp., °C.	n
IXa	5	1.57
IXa	25	1.49
IXa	50	1.48
IXa	70	1.45
IXa	90	1.40
Xa	25	1.75
XIa	25	1.79
Va	25	1.57
VIIa	25	1.84
XXXIVa	25	1.87
Thionine	25	1.83
Methylene blue	25	1.57

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(1) *Cf.* Part IV, THIS JOURNAL, **66**, 1995 (1944).

(2) G. Scheibe, *Kolloid. Z.*, **82**, 1 (1938); also *Angew. Chem.*, **50**, 212 (1937).

(3) S. E. Sheppard, *Proc. Roy. Soc.* (London), **A82**, 256 (1909); *Rev. Mod. Phys.*, **14**, 303 (1942).

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

(5) G. N. Lewis, *et al.*, *ibid.*, **65**, 1150 (1943).

(6) W. E. Merritt, *Phys. Rev.*, **28**, 684 (1926).

(7) W. E. Speas, *ibid.*, **31**, 569 (1928).

(8) W. C. Holmes, *Ind. Eng. Chem.*, **16**, 35 (1924).

(9) M. L. Huggins, unpublished work, Eastman Kodak Research Laboratories.

Fig. 3. From the equation expressing the mass law

$$\left(\frac{\epsilon_\alpha C}{\epsilon_\infty}\right)^n = \left(1 - \frac{\epsilon_\alpha}{\epsilon_\infty}\right) C \qquad \text{(I)}$$

a plot of log $\epsilon_\alpha C/\epsilon_\infty$ *vs.* log $(1 - \epsilon_\alpha/\epsilon_\infty)\ C$ should give a straight line with a slope equal to n. Such graphs are shown in Figs. 4 and 5 for two classes of dyes. The graphs are quite reasonably linear, but the values of n are not integral, but vary from 1.40 to 1.86. (They also show a slight increase of n with decrease of temperature.)

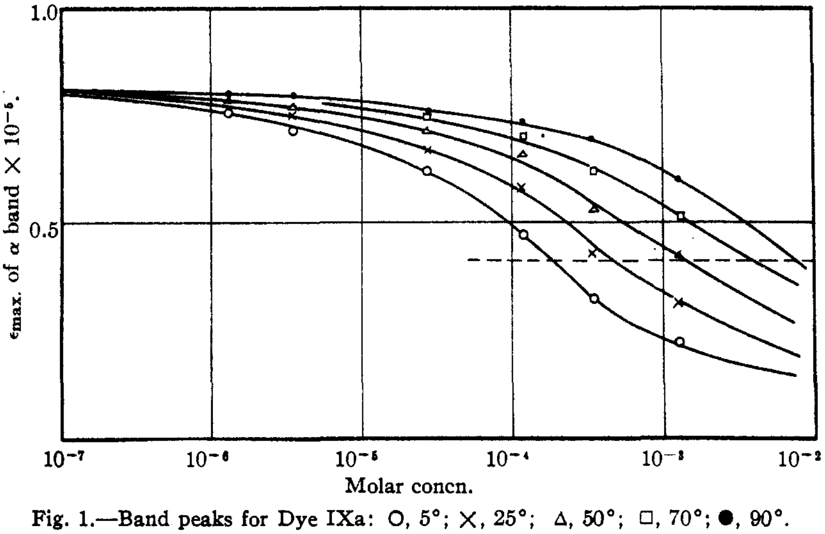

Fig. 1.—Band peaks for Dye IXa: O, 5°; ×, 25°; △, 50°; □, 70°; ●, 90°.

It does not appear that the comparative failure to fulfill simple application of the mass law is due to the error involved in extrapolating to log ϵ_∞. If we change equation I to

$$\epsilon_\alpha{}^2 C = K\epsilon_\infty{}^2 - K\epsilon_\infty\epsilon_\alpha \qquad \text{(II)}$$

on the assumption that $n = 2$, it is evident that $\epsilon_\alpha{}^2C$ should vary linearly with ϵ_α, and that values of K and ϵ_∞ could be calculated from the slope and intercept of such graphs. They are plotted for the data with Dye IXa at five temperatures in Figure 6. Since a family of smooth curves is obtained rather than one of straight lines, it again appears that the simple application of the mass law to the spectrophotometric data is inadequate. It does not seem likely that methods of approximation[10] could add anything further, since, for most of our data, plots of x *vs.* ϵ_α (where x is calculated from the mass law equation) were curves rather than straight lines, or else values of ϵ_∞ obtained by extrapolation of the curves to $x = 1$ were unreasonably low. We have attempted to choose arbitrary values of ϵ_d, the contribution (overlap) of the dimeric (β) band to ϵ_α, which would give a constant value for K, but without success. Curved lines were obtained in all cases. Evidently, overlap of the β-band—attributed in one form of the dimerization hypothesis to the dimer—cannot afford complete explanation for the failure of the mass law as so far applied.

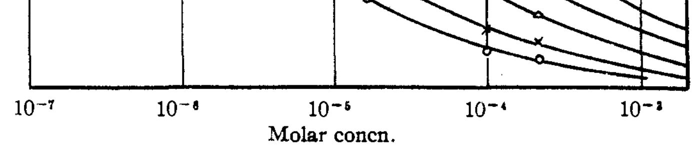

Fig. 2.—Band peaks for Dye XXXIVa: O, 5°; ×, 25°; △, 50°; □, 70°; ●, 90°.

Another procedure proposed by Scheibe[2] is determination of the partition of the dye between water and a sufficiently immiscible organic solvent. One experimental difficulty here is to get a sufficiently immiscible solvent, which at the same time is a good enough solvent for the dye. Hydrocarbons are practically non-solvents, and Scheibe's use of such liquids together with alcohols introduces a complication. It is probable that one or other of the chlorinated alkyls would be satisfactory, provided it is sufficiently stable in the presence of water. We have used hexyl alcohol, which is less than one per cent. soluble in water at 25°. Alcohol concentrations of this order did not perceptibly change the absorption of the aqueous solution. The data are given in Table II. According to Scheibe's

TABLE II

DISTRIBUTION OF DYE VIIa IN THE SYSTEM HEXYL ALCOHOL–WATER

C_w	C_{al}	C_w/C_{al}	log C_w	log C_{al}	$\frac{dC_w/C_{al}}{dC_{al}}$
1.1×10^{-3}	5.30×10^{-4}	2.07	−2.96	−3.28	1.72×10^{3}
3.93×10^{-4}	2.54×10^{-4}	1.55	−3.41	−3.60	2.30×10^{3}
1.06×10^{-4}	9.80×10^{-5}	1.07	−3.97	−4.01	3.95×10^{3}
4.10×10^{-5}	5.15×10^{-5}	0.80	−4.39	−4.29	8.60×10^{3}
7.20×10^{-6}	1.84×10^{-5}	.39	−5.14	−4.74	1.68×10^{4}
1.22×10^{-6}	6.65×10^{-6}	.18	−5.91	−5.17	2.28×10^{4}
1.80×10^{-7}	2.53×10^{-6}	.07	−6.74	−5.60	2.66×10^{4}

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[10] Such as that of Rabinowitch and Epstein, (ref. 4) or of M. L. Huggins.

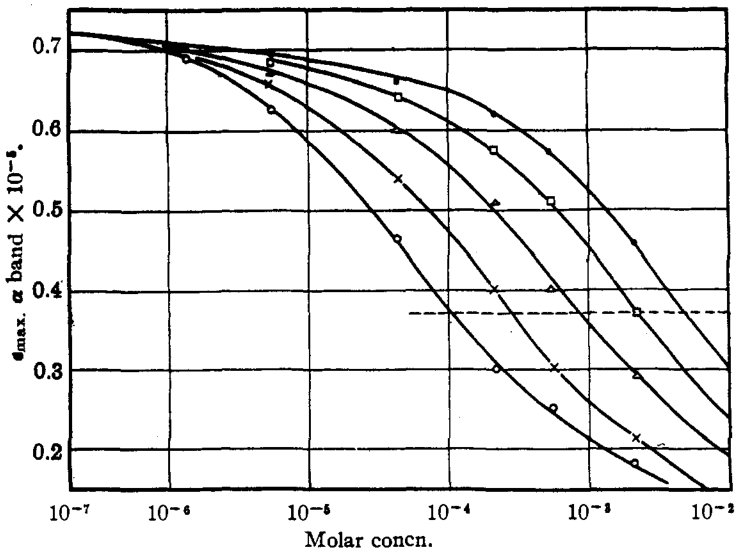

Fig. 3.—Band peaks for methylene blue: O, 5°; ×, 25°; Δ, 50°; □, 70°; ●, 90°.

application of the mass law, $C_w^n/C_{al} = P$, whence a graph of log C_w *vs.* log C_{al} should give a straight line of slope *n*. As observed from Figure 7 this was not found, but a smooth curve of slope less than unity at all points. This might be because of a reversible aggregation of the dye in water.

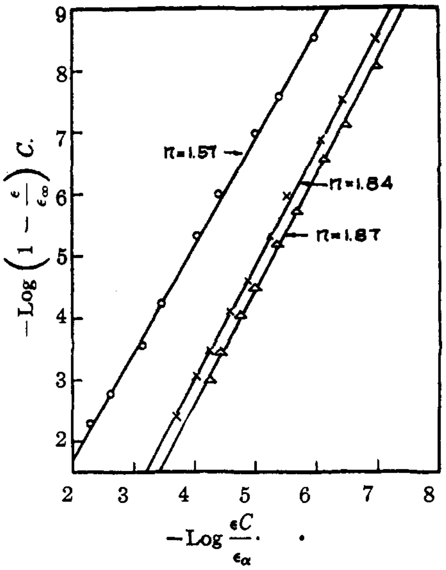

Fig. 4.—O, Dye Va; ×, Dye VIIa; Δ, Dye XXXIVa ($\epsilon = \epsilon_\alpha$ in text).

Assuming that there is no aggregation in the alcohol, then the distribution (of monomer) between the two phases may be represented[11] by the equation $[D']/[D] = K_1$. If *n* be the number of molecules of the polymer in water and $K_2 = [D_n']/[D']^n$ = equilibrium constant for the reversible aggregation $nD' = D_n'$, then $C_w/C_{al} = nK_2K_1^nC_{al}^{n-1} + K_1$. The value of *n*—the *order* of aggregation in water—may be determined by taking arbitrary values until the plot of C_w/C_{al} *vs.* C_{al}^{n-1} gives a straight line, when the intercept K_1 will be the partition coefficient for the monomer. Plots of this kind were made, but no straight line was obtained with any integral value. In particular, the deviation for $n = 2$ was quite large (cf. Fig. 8). If both dimers and trimers are assumed in equilibrium in the system, the general equation becomes

$$C_w/C_{al} = 3K_3K_2K_1^3C_{al}^2 + 2K_2K_1^2C_{al} + K_1$$

whence the graph of the first derivative with respect to C_{al} *vs.* C_{al} itself should give a straight line, but this also failed.

We have then evidence by two independent methods that the application of the simple mass law concept to the state of solution in water of polymethine and thiazine dyes is quantitatively inadequate.

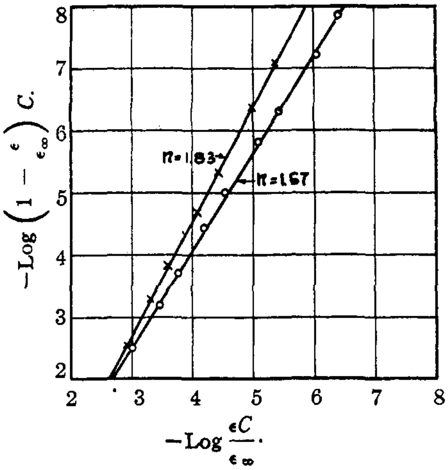

Fig. 5.—O, Methylene blue; ×, thionine ($\epsilon = \epsilon_\alpha$ in text).

Direct application of spectrophotometry to the aqueous phase alone might be vitiated by erroneous assumptions as to the relation between ϵ_α and the concentration of "monomer" but this source of error is absent for the partition experiments, where any spectrophotometric measurements are made only as a calibrated colorimetric analysis. A possible disturbing factor derived from the spectrophotometric analysis must be mentioned, however. It appears that the value of ϵ_∞ in water, for the α-band, as derived by extrapolation[12] is characteristically lower than in alcohol. In Table III are given values for a number of cyanine dyes and also for two thiazine dyes.

It will be seen that the difference between the

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(11) H. I. Almquist, *J. Phys. Chem.*, **37**, 991 (1933).

(12) *Cf.* Figs. 1 and 2.

TABLE III

Dye	ϵ_{max} in Alcohol × 10^5	ϵ_{∞} in Water × 10^5	Ratio
Va	0.75	0.71	0.92
VIIa	1.95	1.60	.82
XXXIVa	2.13	1.58	.74
IXa	0.83	0.81	.97
Xa	1.66	1.58	.95
XIa	2.25	1.80	.80
XIIa	2.05	1.33	.65
Thionine chloride	0.87	0.70	.80
Methylene blue chloride	.90	.73	.81

extinction in the two solvents increases with the length of the chain in a homologous series of polymethine dyes. G. N. Lewis, *et al.*,[5] in dealing with this phenomenon in the case of *thiazines*,

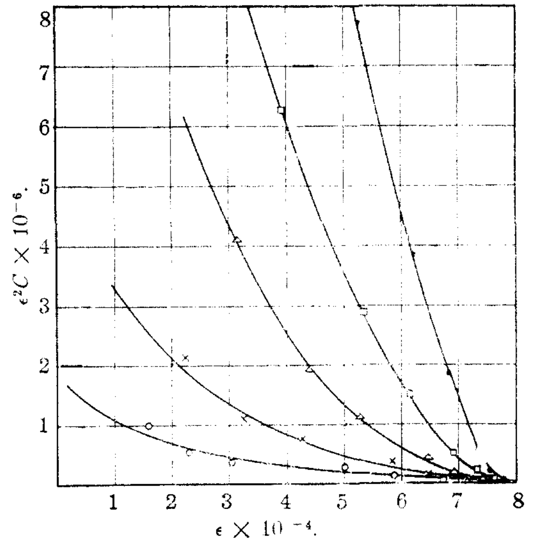
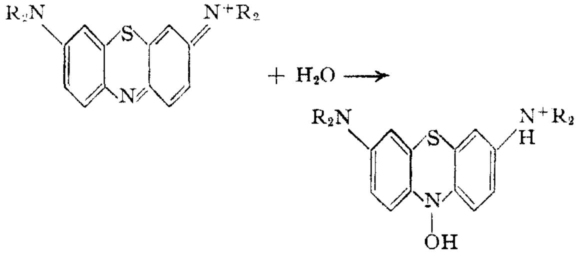
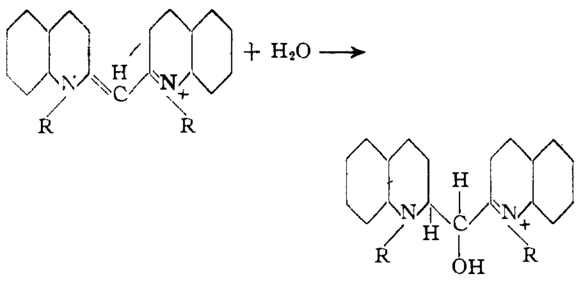


Fig. 6.—Dye O, 5°; ×, 25°; Δ, 50°; □, 70°; ●, 90° ($\epsilon = \epsilon_\alpha$ in text).

have suggested that in water a colorless form of the dye is produced by simultaneous addition of both H^+ and OH^- ions of water. They state there is a "colorless form of the ion obtained by hydrolytic addition in which a hydroxide ion goes to the central nitrogen, and a hydrogen ion to one of the amino nitrogens." Presumably this would be represented by the structural change



but, in the case of the cyanines, the addition is less readily conceived. Apparently the H^+ and OH^- ions must be attached to the methine chain



but may be separated more as the chain lengthens. Although such structures do not seem very probable, they evidently represent removal of color; as to the cyanine dyes, these become increasingly less stable with increased length of chain, so that

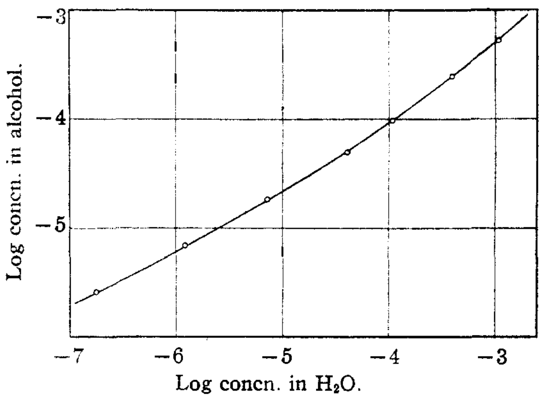


Fig. 7.—Partition of Dye VIIa in the system hexyl alcohol-water.

it is conceivable that the "hydrolation" would actually be increasing the stability relative to the colored form. As an alternative to the chemical addition of the elements of water, we suggest the possibility of greater impedance of

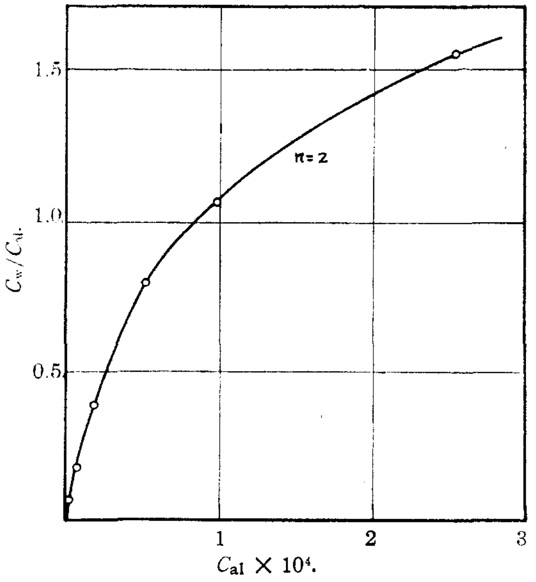


Fig. 8.—Dye VIIa, system hexyl alcohol-water.

free rotation about —CH= bonds of the conjugated chain of dye ions in water, compared with other solvents, because of greater association of the solvent in hydrogen-bonded chains. A consequence of this could be a relatively lower number of fully extended planar ions suitably oriented per unit time to the electric vector of the light ray. Increase of the extinction drop with polymethine chain length is a likely concomitant with the increased probability of such chains becoming *bent* and thereby reducing the transition moment in the dye molecule.[13] In this precise form the physical explanation is not applicable to dyes with a frame like methylene blue. However, in these dyes there is a possibility of bending across a central axis, –S···N–, –O···N–, as is actually observed in crystalline forms of the unsubstituted archetypes. We may suppose, *e. g.*, that hydrogen bridge chains between the $-NR_2$ groups induce a certain degree of this non-planarity and lower transition moment. This kind of explanation seems to line up with the recognition of imperfect solvation of dye molecules or ions in water, compared with organic solvents.[1]

In spite of quantitative discrepancies (in respect of the mass law) we consider that on the whole the dimerization hypothesis so far offers the best interpretation of the dilution anomaly in water. We will show in a later publication that studies of conductance, transport, and diffusion in water of cyanine dyes indicate an order of aggregation not greater than two up to the saturation point or solubility limit—and this for both Dye Va and Dye VIIa (pinacyanol) although these two dyes exhibit growth of a third or γ-band with increased concentration. In fact, we disagree with the interpretation by Scheibe,[2] Rabinowitch[4] and others, of the nature of these bands. We do not consider them to be new bands peculiar to dimers or polymers, but to be vibrationally coupled transitions proper to the monomeric ions, which, however, are enhanced in the dimer. Such auxiliary bands are generally evident in the organic solutions where there is no evidence of dimerization or polymerization. This conception that the spectral anomaly in water consists essentially in a redistribution of transition probabilities in the same molecular spectrum has been previously stated by Sheppard,[3] and by Sheppard, Lambert and Walker.[14] Dimerization is supposed to increase the probability of vibration-coupled electronic transitions. A fully quantitative theory has yet to be developed, but certain suggestions seem in order. (i) The over-all survey of different dye classes, as well as intensive measurements in the cyanines and thiazines, shows the presence of auxiliary bands both in organic solvents and in water.[1] (ii) Auxiliary bands of higher frequency due to vibrational coupling are predicated both for polyene chains and derivatives, as also for polycyclic compounds.[15] (iii) In organic solvents producing complete solvation, collisions between solute molecules would be buffered and relatively elastic. (iv) In water, with local or incomplete solvation, inelastic collisions between unsolvated parts of dye molecules or ions would be probable. (v) Under favoring conditions, these could lead to parallel, optically coupled molecules or ions. (vi) By the collision and coupling, the participant molecules or ions are, so long as they are associated, more vibrationally excited by absorbed light. (vii) Hence, ions absorbing light in the dimerized state have greater absorption, the higher the vibration number available. (viii) Reabsorption of fluorescence is probable with dimerized molecules.

So far, no structure has been proposed for the dimer which would account for a supposed "dimer band" as such. Our hypothesis is economical in this respect, since it simply assumes enhancement of bands already recognized.

Some quantitative support is provided for the redistribution conception by plotting, instead of number of quanta absorbed, *vs.* wave number,[16] the relative *energy* absorbed *vs.* wave number. This means that instead of ϵ we plot $\epsilon\bar{\nu}$ as function of $\bar{\nu}$. Integrating between limits, say $\bar{\nu}_1$ and $\bar{\nu}_2$, for an absorption band, we can compare relative energies absorbed at different concentrations in water. This has been done, for Dye VIIa, at different temperatures, and with Dyes Va, Xa and thionine at different concentrations at 25°. The results are recorded in Table IV.

TABLE IV

INTEGRATED VALUES OF $\epsilon\nu d\nu \times 10^{-33}$

Dye VIIa

Molar concentration	$\int_{\nu_1}^{\nu_2} \epsilon\nu d\nu \times 10^{-33}$ 10°	25°	50°	70°
4.65×10^{-4}	4.68	4.92	3.96	3.96
1.0×10^{-4}	3.56	3.96	3.78	3.83
1.0×10^{-5}	3.47	3.92	3.65	3.70
1.0×10^{-4}	3.83	3.65	3.65	3.65
Average	3.88	4.00	3.76	3.78

Dye Va at 25° Molar concn.	$\int_{\nu_1}^{\nu_2} \epsilon\nu d\nu \times 10^{-33}$	Dye Xa at 25° Molar concn.	$\int_{\nu_1}^{\nu_2} \epsilon\nu d\nu \times 10^{-33}$	Thionine at 25° Molar concn.	$\int_{\nu_1}^{\nu_2} \epsilon\nu d\nu \times 10^{-33}$
3×10^{-3}	3.48	9.6×10^{-4}	3.96	2.02×10^{-3}	2.43
1×10^{-3}	3.29	1.0×10^{-4}	4.14	5.70×10^{-4}	2.14
5×10^{-4}	3.28	1.5×10^{-5}	4.23	1.96×10^{-4}	2.27
1×10^{-4}	3.32	1.2×10^{-6}	3.96	3.90×10^{-6}	2.24
2×10^{-6}	3.25			7.80×10^{-6}	2.33
5×10^{-6}	3.24			1.19×10^{-6}	2.34
1×10^{-6}	3.24				
Average	3.30		4.07		2.29

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[13] Th. Förster, *Z. Elektrochem.*, **45**, 548, 752 (1939); R. S. Mulliken, *J. Chem. Phys.*, **7**, 570 (1939); G. Scheibe, *Z. angew. Chem.*, **52**, 631 (1939).

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

[15] *Cf.* K. W. Hausser, *Z. tech. Phys.*, **15**, 10 (1934).

[16] Which gives on integration, a value of the band strength. In the present case (dilution in water) the "band strength" values are almost as constant as the "band energies," because the mean value of the wave number changes only slightly with dilution.

The constancy of the energy values is not perfect, but on the whole does not vary much more than 5% either way. It seems improbable that even such an approximation to constancy of the energy absorbed could be secured other than by a continuous redistribution.

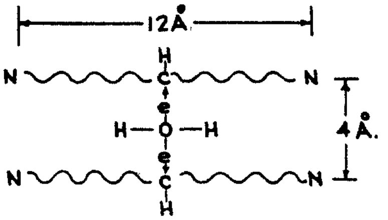

Fig. 9.—Suggested structure of dimer.

Rabinowitch and Epstein[4] have suggested that dimerization in the case of thiazines involves parallel apposition of two molecules (cations) at a distance of 3.5 to 4 Å.; they are supposed to be held together by the dispersion forces (Heitler–London forces) of the labile electrons or "electron clouds" of the two resonating systems. L. Michaelis and S. Granick,[17] referring to oxonines, speak of "dimerization ensuing from intermolecular interaction of the electric oscillators established by the quinone–benzene resonance." Sheppard[3] has suggested the participation of a water molecule in bonding the partners of such dimers. In order that the repulsion of like charges be as small as possible it is evident that in the dimeric ion there must be an alternation of phase of the resonance in each ion such that the charge is alternately at each end of the participating (planar) ions. This will involve a transitional phase of maximum internal repulsion when both charges are, effectively, at the midpoint.[18] This could be buffered by fixation of an intermediate water molecule, as shown schematically in Fig. 9, where *e* and *e* are the counterpoising electrons of the tetrahedral structure of the water molecule suggested by Bernal and Fowler.[19]

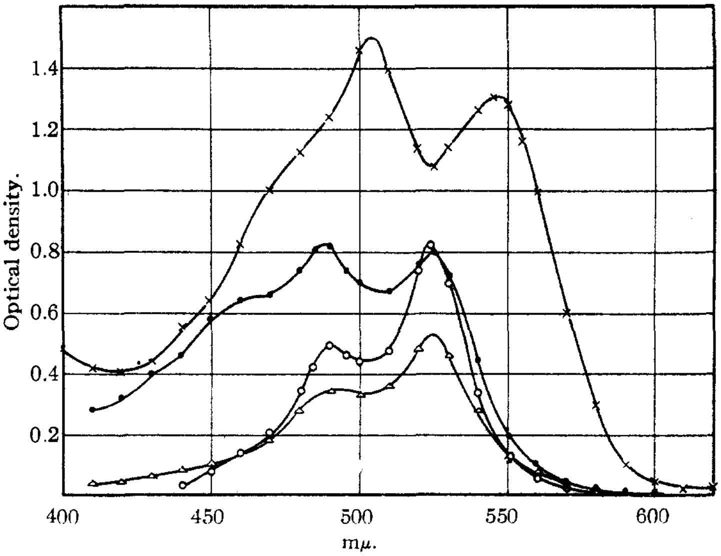

Fig. 10.—Spectral absorption of Dye Vc (1,1′-diethylcyanine iodide): O, dye in alcohol before sublimation; ●, dye in alcohol after sublimation; Δ, sublimed dye in alcohol plus 3% water; ×, sublimed dye as film on glass.

Normally, the spectrophotometry of dyes in mixtures of alcohol and water gives no indication either way as to the inclusion of a water molecule in a dimer. But a peculiar phenomenon was observed in the vacuum sublimation of a dye which seems difficult to interpret on any other basis. In Fig. 10 are shown the spectral absorption curves of: (i), dye in alcohol before sublimation; (ii), sublimed dye dissolved in alcohol; (iii), sublimed dye in alcohol to which 3% water had been added; (iv), sublimed dye as film on glass.

The behavior certainly suggests that in the sublimate a certain number of water molecules were trapped in dimerized pairs. On solution in pure alcohol, the water molecules remained "frozen in," and were only released, with relaxation to equilibrium, *i. e.*, practically zero dimerization, by the addition of a small amount of water dissolved in the alcohol.

Experimental

The spectrophotometric equipment was the same as that described in Part IV.

In the partition measurements, the hexyl alcohol was Eastman Kodak Co. Synthetic and was checked by distillation. The solutions—alcoholic and aqueous—were brought into contact in a tube with an open top, which would accommodate a stirrer. To prevent the formation of large interfacial areas, such as would be formed by shaking, the stirrer was double acting, one set of paddles operating in the alcoholic, the other in the aqueous, phase and at such speed that the interface was never broken. The apparatus was thermostated at 25° and kept in the dark. Samples were withdrawn by pipet and analyzed spectrophotometrically after dilution with known excess of methanol.

Discussion

Application of the mass law in terms of concentrations, does not give complete quantitative support for the dimerization hypothesis. The deviations, however, are not sufficient to require its rejection, but rather suggest the operation of an unrecognized—or inadequately recognized—activity factor.

In fact, it has been pointed out already (*cf.* Part IV of these studies) that the thermodynamic status of aqueous solutions of dyes is different

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(17) L. Michaelis and S. Granick, This Journal, **63**, 1636 (1941).

(18) More exactly, the charge density is a maximum there.

(19) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

from, or in any case the stability is lower than, that of solutions in organic solvents. This is because of the preponderance of the organophile (hydrophobe) portion of a relatively large molecule over the hydrophile portion, and the sterically different location of these disparate parts. The treatment, by partial differentiation of component "interfacial" energies initiated by Langmuir,[20] suggests the direction in which the activity factor may be found, and investigation on such lines is contemplated.

It is not considered probable at present that the mass law deviations derive from total or partial ionic strength factors. Adjustments were made to equal specific conductivity of 4×10^{-4} mhos with Dye VIIa (pinacyanol chloride) and sodium chloride—the latter up to about 3×10^{-3} M. It appeared that little or no alteration of the spectral characteristics was effected. In these and other experiments (with different salts) in which visibly evident "salting out" occurred, this was preceded by fall in total absorption, without, as so far noted, change in the spectral contour. The phenomena merit fuller consideration and will be dealt with elsewhere.

G. N. Lewis[5] has connected the initial fall of band strength on addition of electrolyte with the lower extinction, at infinite dilution, of the principal band of many dyes in aqueous solution. This he attributes to reversible addition of the H^+ and OH^- ions of water.

An alternative suggestion is that of greater internal impedance in water, whereby the *transition moment* of the dye molecule or ion is reduced. For example, in the cyanine dyes it is supposed that a more bent, less extended, configuration[11] is induced, which is in agreement with the progression of the extinction drop in a homologous series. The spectral change associated with dimerization is attributed to increased participation of vibrational energy in the absorption process in the dimer. We were inclined to attribute this to an increased supply of vibrational-rotational energy by an inelastic collision in the dimerization process, but Dr. G. Kornfeld of these laboratories pointed out that retention of such amounts of energy at ordinary temperatures would be very improbable. The coupling (of electronic and vibrational-rotation energies) must occur, therefore, in the excited state. We suppose that in the dimer there is greater probability—perhaps by an internuclear resonance process—of retention of quantized vibrational-rotational energies, which are lost much more rapidly by the monomeric ions (Fig. 11). In this sense the excited dimer may be regarded as a metastable state.[21]

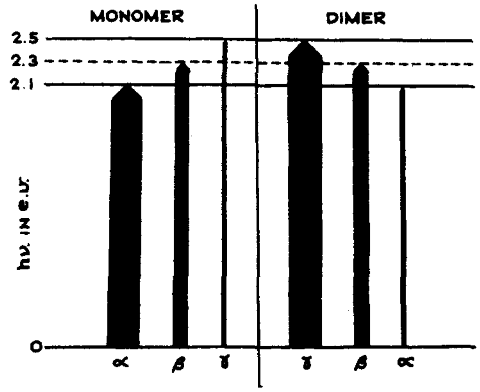

Fig. 11.—Energy levels of Dye VIIa (the intensity of a band is schematically indicated by the breadth).

It is suggested that the process may involve the incorporation of a molecule of water as a hemi-hydrate, but this is not regarded as an essential feature of dimerization under all conditions. There is some evidence[22] for dimerization in alcoholic solutions at low temperatures, but it is quite uncertain whether "alcohol of dimerization" is incorporated.

Summary

An intensive quantitative examination, with several cyanine dyes and with two thiazines, has been made of the dimerization hypothesis for dyes in aqueous solution. It was found that the simple mass law is inadequate, but it is concluded that this is not because the dimerization hypothesis is incorrect *per se*, but that certain "activity" factors have to be taken into account. The possible nature of these is discussed. Also it is concluded that the spectral aberration giving rise to the dimerization hypothesis is not due to the production of "new" polymeric bands, but to vibrational excitation of the ions of the dimer, and consequent enhancement of higher frequency satellites of the main electronic transition. Certain observations indicate the possible incorporation of a molecule of "water of dimerization."

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[20] I. Langmuir, "The Effects of Molecular Dissymmetry on Properties of Matter" in J. Alexander's *Colloid Chemistry*, I, 525 (1926).

[21] This would hold basically for the electrons affected by the Heitler-London dispersion forces.

[22] Part III, S. E. Sheppard and H. R. Brigham, THIS JOURNAL, **66**, 380 (1944).