standard hydrogen electrode at 25°. Extrapolating to a *pa*H of zero and a pyrophosphate concentration of unity on the basis of experimental data previously presented yields a value of +1.15 v. as the "formal" oxidation potential for the reaction in equation (9) at 25°. Strictly speaking this potential is not the formal potential, since the hydrogen ion activity and not its concentration was extrapolated to zero. Nor is it the standard potential since the concentrations and not activities of the complex ions and pyrophosphoric acid are used. As the activity coefficients are not known, the standard potential cannot be solved but is probably close to 1.15 v.

Although the data will not permit an accurate evaluation of the instability constants, an approximation may be made of their ratios. On the basis of the standard potential of 1.51 v. for the aqueous manganese(III)/manganese(II) couple determined by Grube and Huberich,[8,9] the following relation between the instability constants K_{III} for tri-dihydrogen pyrophosphatomanganate(III) complex and K_{II} for di-dihydrogen pyrophosphatomanganate(II) is obtained

$$1.15 \text{ v.} = 1.51 + 0.0591 \log \frac{a_{\mathrm{Mn}^{+3}}}{a_{\mathrm{Mn}^{+2}}} =$$

$$1.51 \text{ v.} + 0.0591 \log \frac{K_{\mathrm{III}} a_{\mathrm{Mn^{III}C}}\, a_{\mathrm{H_4P_2O_7}}{}^{3}}{K_{\mathrm{II}} a_{\mathrm{Mn^{II}C}}\, a_{\mathrm{H_4P_2O_7}}{}^{2}} \text{ volts} \qquad (11)$$

Since the standard potential is calculated for all substances in the last term at unit activity the following relation is obtained

$$K_{\mathrm{III}} = 10^{-6} K_{\mathrm{II}} \ (ca.) \qquad (12)$$

Summary

The couple tripyrophosphatomanganic(III) acid/dipyrophosphatomanganic(II) acid was shown to behave reversibly at a platinum electrode. The influence of the total pyrophosphate concentration, ratio of manganese(III)/manganese(II) concentrations, and *pa*H were studied. At a *pa*H near zero, the equilibrium was shown to be essentially

$$\mathrm{Mn(H_2P_2O_7)_2}^{-2} + \mathrm{H_4P_2O_7} \rightleftharpoons \mathrm{Mn(H_2P_2O_7)_3}^{-3} \text{ (violet)} + 2\mathrm{H}^+ + \mathrm{e} \qquad (9)$$

The potential of a platinum electrode in a solution containing equal concentrations of manganese (II) and manganese(III) in a solution 0.4 *M* in pyrophosphate having a *pa*H of 2.06 is +1.013 ± 0.003 v. *versus* the standard hydrogen electrode. The standard potential for the reaction indicated in equation (9) is E_0 = (*ca.*) −1.15 v. (Lewis and Randall convention).

As the *pa*H approaches 7, the manganese(III) complex becomes increasingly brown amber in color, due to the ionization of additional hydrogen ions from the complex. In an alkaline solution, the manganese(III) complex is unstable disproportionating to form manganese dioxide and manganese(II) ion.

A new method for determining manganese by means of a potentiometric titration of tripyrophosphatomanganic acid with iron(II) sulfate is described.

MINNEAPOLIS, MINNESOTA RECEIVED FEBRUARY 9, 1948

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[8] G. Grube and K. Huberich, *Z. Elektrochem.*, **29**, 17 (1923).

[9] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 221.

[CONTRIBUTION FROM THE PHILADELPHIA QUARTZ CO.]

The Effect of Sodium Silicates on the Absorption Spectra of Some Dyes

BY R. C. MERRILL, R. W. SPENCER AND R. GETTY

That certain dyes change color in the presence of various colloids has long been known. Familiar examples are the variation in color of a biological stain depending on the nature of the stainable substrate, which P. Ehrlich called metachromasy, and the protein error of indicators. Micellar solutions of colloidal electrolytes, such as cetyl pyridinium chloride[1] and long chain sulfonates and sulfates[2,3] change the color of pinacyanol chloride and other dyes.[4,5] This paper reports the effects of another group of colloidal electrolytes, the sodium silicates, on the absorption spectra of the dyes, pinacyanol chloride, toluidine blue O, Rhodamine 6G, and the sodium salt of 2,6-dichlorobenzenone indophenol.

Experimental

All of the sodium silicates used were commercial products of the Philadelphia Quartz Co. Their composition is summarized in Table I. The sodium metasilicate pentahydrate was in the form of pure white free flowing crystals which have a melting point of 72.2°. The "E" and "Star" silicates are clear, transparent, aqueous solutions and the "S" is an opalescent solution. The sodium oxide content is determined by titration with standardized hydrochloric acid to the methyl orange end-point. Silica

TABLE I

COMPOSITION OF SODIUM SILICATES

Name	Formula	M. W.	Na_2O, %	SiO_2, %
Metso crystals	$Na_2SiO_3 \cdot 5H_2O$	122	29.1	28.2
Star	$Na_2O \cdot 2.6SiO_2$	217	10.5	26.3
E	$Na_2O \cdot 3.3SiO_2$	262	8.6	27.7
S	$Na_2O \cdot 4.0SiO_2$	305	6.3	24.6

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[1] S. E. Sheppard and A. L. Geddes, *J. Chem. Phys.*, **13**, 63 (1945).

[2] M. L. Corrin, H. B. Klevens and W. D. Harkins, *ibid.*, **14**, 480 (1946).

[3] M. L. Corrin and W. D. Harkins, THIS JOURNAL, **69**, 679 (1947).

[4] G. S. Hartly, *Trans. Faraday Soc.*, **30**, 444 (1934).

[5] J. E. Smith and H. L. Jones, *J. Phys. Chem.*, **38**, 243 (1934).

TABLE II

THE INTENSITIES OF BAND MAXIMA IN 2 × 10^{-5} MOLAR SOLUTIONS OF PINACYANOL CHLORIDE

Solvent	pH	α Band		α′ Band		β Band		γ Band	
		λ(mμ)	$\epsilon m \times 10^4$	λ(mμ)	$\epsilon m \times 10^4$	λ(mμ)	$\epsilon m \times 10^4$	λ(mμ)	$\epsilon m \times 10^4$
H_2O	5.92	599	5.94	...	..	546	7.33	...	..
0.020 *M* NaOH	12.24	599	5.65	630	1.84	546	5.03	490	2.08
.020 *M* Na_2SiO_3	12.23	599	3.90	630	2.36	556	2.73	486	2.34
.020 *M* $Na_2O{\cdot}2.6SiO_2$	11.02	593	3.49	630	2.24	...	..	492	3.65
.020 *M* $Na_2O{\cdot}4.0SiO_2$	10.83	584	2.62	630	1.25	...	..	502	3.64
2 × 10^{-5} *M* $Na_2O{\cdot}3.3SiO_2$	6.78	599	5.87	...	..	546	6.88	...	..
2 × 10^{-4} *M* $Na_2O{\cdot}3.3SiO_2$	9.17	599	3.07	...	..	~550	2.72	490	1.20
2 × 10^{-3} *M* $Na_2O{\cdot}3.3SiO_2$	10.20	584	2.48	630	1.37	...	..	488	2.41
6 × 10^{-3} *M* $Na_2O{\cdot}3.3SiO_2$	10.40	582	3.45	630	1.69	...	..	492	3.46
2 × 10^{-2} *M* $Na_2O{\cdot}3.3SiO_2$	10.85	587	3.47	630	1.98	...	..	493	3.92

is determined gravimetrically. The sodium hydroxide was J. T. Baker analyzed C.P. grade.

The dyes were all commercial products and used without further purification. The pinacyanol chloride and sodium salt of 2,6-dichlorobenzenoneindophenol were purchased from the Eastman Kodak Co. Rhodamine 6G (C.I. No. 752) was obtained from the National Aniline division of the Allied Chemical and Dye Corp. The toludine blue O was the certified dye stain sold by the Coleman and Bell Co. which contained 66% dye. The molar concentrations of the solutions are given on the basis of actual dye content, assuming that the first three dyes were pure. The pH of the dye solution was determined with a Beckman pH meter.

The absorption curves were obtained with a General Electric Co. recording spectrophotometer. From the transmission curves thus obtained the molar extinction coefficients, ϵ_m, were calculated at 10 mμ intervals and at maxima and minima from the equation $\log_{10} I_0/I = \epsilon_m Cd$ where C is the molar concentration of the dye, d the width of the cell (0.50 cm.), and I_0 and I the intensity of the incident and transmitted light. All the absorption curves were obtained at room temperature (around 22–23°).

Results

The absorption spectra of 2 × 10^{-5} *M* pinacyanol chloride in water and in 0.02 *M* solutions of sodium hydroxide, sodium metasilicate and silicates with silica to alkali (Na_2O) ratios of 2.6 and 4.0 are shown in Fig. 1. The effect of four concentrations, including 0.02 *M*, of the 3.3 ratio silicate on the absorption spectra of 2 × 10^{-5} *M* dye is illustrated in Fig. 2. Table II gives the intensities of the band maxima for these solutions. All solutions were diluted fivefold immediately prior to being placed in the spectrophotometer after

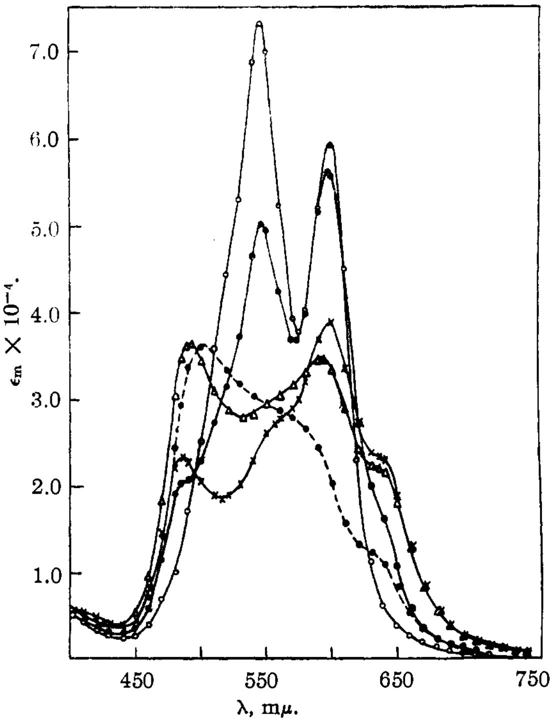

Fig. 1.—Molar extinction coefficients of 2 × 10^{-5} *M* pinacyanol chloride: ○—○ in H_2O, ●—● in 0.02 *M* NaOH; ×—× in 0.02 *M* Na_2SiO_3, △—△ in 0.02 *M* $Na_2O{\cdot}2.6\ SiO_2$, ●---● in 0.02 *M* $Na_2O{\cdot}4.0\ SiO_2$.

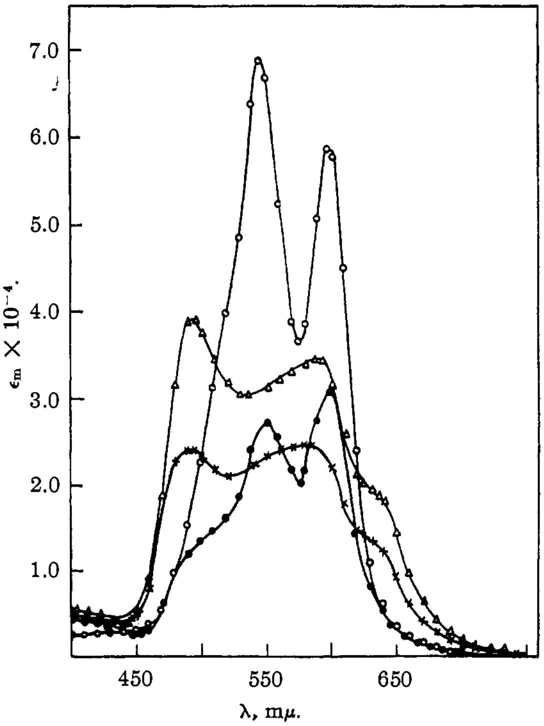

Fig. 2.—Molar extinction coefficients of 2 × 10^{-5} *M* pinacyanol chloride in varying concentrations of $Na_2O{\cdot}3.3\ SiO_2$: ○—○ 2 × 10^{-5} *M*, ●—● 2 × 10^{-4} *M*, ×—× 2 × 10^{-3} *M*, △—△ 2 × 10^{-2} *M*.

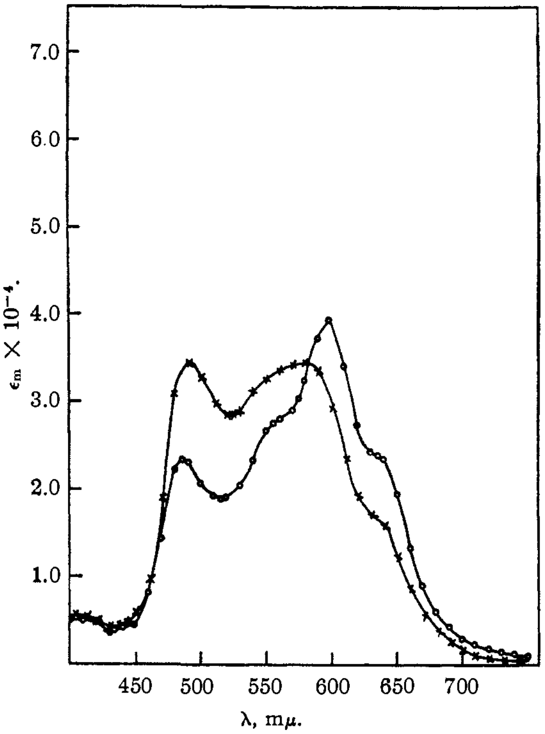

Fig. 3.—Molar extinction coefficients of 2×10^{-5} *M* pinacyanol chloride in Na_2SiO_3 and $Na_2O{\cdot}3.3\ SiO_2$ solutions containing the same amount of SiO_2: O—O 0.02 *M* Na_2SiO_3, ×—× 0.006 *M* $Na_2O{\cdot}3.3\ SiO_2$.

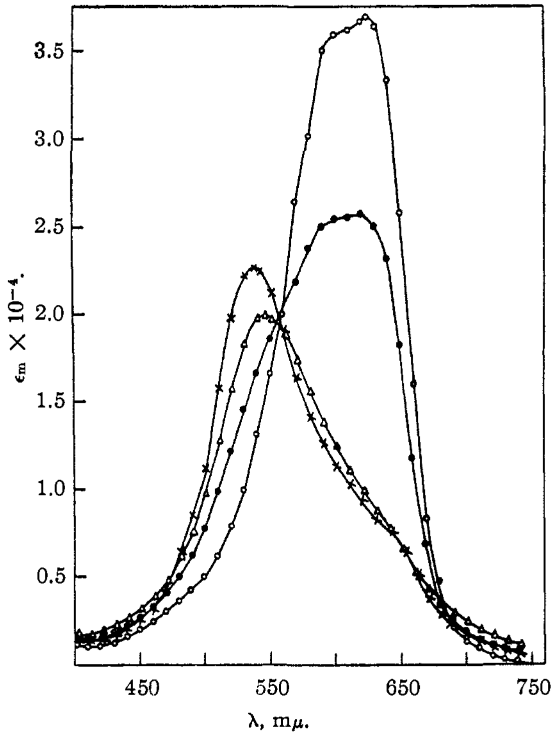

Fig. 4.—Molar extinction coefficients of 2.5×10^{-5} *M* toluidine blue O in water and varying concentrations of $Na_2O{\cdot}3.3SiO_2$: O—O in H_2O, ●—● in 5×10^{-4} *M* $Na_2O{\cdot}3.3SiO_2$, △—△ in 5×10^{-3} *M* $Na_2O{\cdot}3.3SiO_2$, ×—× in 5×10^{-2} *M* $Na_2O{\cdot}3.3SiO_2$.

having stood about fifteen hours at the higher concentration. Our absorption curve for pinacyanol chloride in water is in excellent agreement with that expected by interpolation from the curves given by Sheppard[6] for different concentrations of dye.

The effect on the dye's absorption spectrum of increasing the silica to alkali ratio of the 0.02 *M* silicates is to decrease greatly the intensity of the α band at about 595 mμ, and even more that of the β band at 546 mμ. New bands, α' at 630 mμ and γ at about 490 mμ, appear in the metasilicate solution. The intensity of the γ band is about 50% greater in solutions of the higher ratio silicates whereas that of the α' band becomes progressively less with increasing silica to alkali ratio. The effect of increasing the concentration of the 3.3 ratio silicate parallels that of increasing the silica to alkali ratio at a given concentration in that the intensity of the α band is greatly decreased and that of the β band even more. Their effects differ in that the intensities of both the α' band, which becomes apparent in a 2×10^{-3} *M* silicate solution, and the γ band, first being evident in a 2×10^{-4} *M* silicate, increase progressively with increase in concentration. Both the α and β bands appear to have a minimum intensity at a silicate concentration about 2×10^{-3} *M*. The visual color of the dye solutions changes from blue to purple as the silica to alkali ratio or the silicate concentration is increased.

The differences in the absorption spectra of 2×10^{-5} *M* pinacyanol chloride in 0.020 *M* sodium metasilicate and 0.006 *M* 3.3 ratio silicate (Fig. 3) both of which contain the same amount of silica, show clearly that the silica is in a different form in the two solutions.

The differences in the absorption spectra of 2.5×10^{-5} *M* toluidine blue 0 in 0.01 *M* sodium metasilicate and varying concentrations of the 3.3 ratio silicate as compared with that in water (Figs. 4 and 5) are similar to those observed in solutions of the polymeric sodium "hexametaphosphate"[7] and agar.[8] Results with this dye suggest that the addition of small amounts of colloidal electrolytes greatly decreases the intensity of the two only partially resolved bands, α at 624 mμ and β (which at this concentration in water occurs at 600 mμ), and gradually decreases the wave length at which the β band maxima occurs. At higher concentrations the intensity of the band at around 540 mμ increases, and in "hexametaphosphate" solutions[7] goes through a maximum. The effects of the silicates on the intensities of the band maxima of 2.5×10^{-5} *M* toluidine blue 0 solutions are summarized in Table III. The dye

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(6) S. E. Sheppard, *Rev. Mod. Physics*, **14**, 303 (1942).

(7) J. M. Wiame, This Journal, **69**, 3146 (1947).

(8) L. Michaelis and S. Granick, *ibid.*, **67**, 1212 (1945).

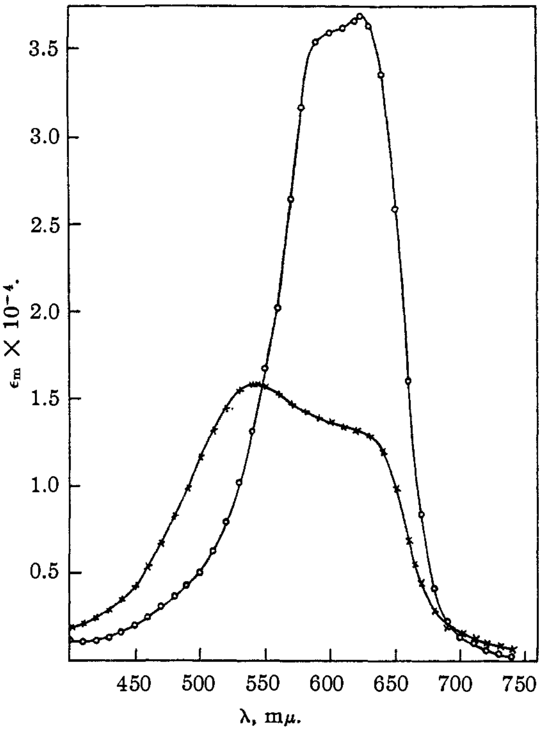

Fig. 5.—Molar extinction coefficients of 2.5×10^{-5} *M* toluidine blue O: O—O in H_2O, ×—× in 0.01 *M* Na_2SiO_3.

appears blue in water and in the 5.0×10^{-4} *M* 3.3 ratio silicate solution, but is purple at all other silicate concentrations studied.

TABLE III

THE INTENSITIES OF BAND MAXIMA IN 2.5×10^{-5} MOLAR SOLUTIONS OF TOLUIDINE BLUE O

		α Band		β Band	
Solvent	*p*H	λ (mμ)	ϵm × 10^4	λ (mμ)	ϵm × 10^4
H_2O	6.53	624	3.69	600	3.59
5.0×10^{-4} *M* $Na_2O \cdot 3.3SiO_2$	9.49	622	2.57	600	2.54
1.0×10^{-3} *M* $Na_2O \cdot 3.3SiO_2$	9.91	...	..	546[a]	1.98
5.0×10^{-3} *M* $Na_2O \cdot 3.3SiO_2$	10.11	...	..	546[a]	2.00
5.0×10^{-2} *M* $Na_2O \cdot 3.3SiO_2$[b]	11.12	...	..	538[a]	2.27
1.0×10^{-2} *M* Na_2SiO_3	11.96	624	1.31	5.44	1.58

[a] May be new band. [b] There is an indication of a new band at around 640 mμ at this silicate concentration.

Figure 6 shows the absorption spectra of 1×10^{-4} *M* Rhodamine 6G and 1×10^{-4} *M* sodium 2,6-dichlorobenzenone indophenol in water and in 0.010 *M* solutions of $Na_2O \cdot 3.3SiO_2$. The addition of this concentration of silicate appears to shift by about 6 mμ toward shorter wave lengths, the band (or unresolved bands) of Rhodamine 6G occurring from about 460 to 540 mμ. The water spectrum is probably somewhat complicated by the dye's fluorescence. Rhodamine 6G is orange and fluorescent in water and red and non-fluorescent in micellar solutions of anionic detergents and in solutions of various silicates including the metasilicate.

A 1×10^{-4} *M* solution of sodium 2,6-dichlorobenzenone indophenol has a single band maximum in the visible occurring at 605 mμ with a molar extinction coefficient of 18.2×10^4. The addition of 0.010 *M* $Na_2O \cdot 3.3SiO_2$ to this dye produces practically no change in the color of the solution but *increases* the intensity maximum 3%. Unlike other dyes used in this investigation, the dye ion in this case has the same charge as the silicate ions and micelles.

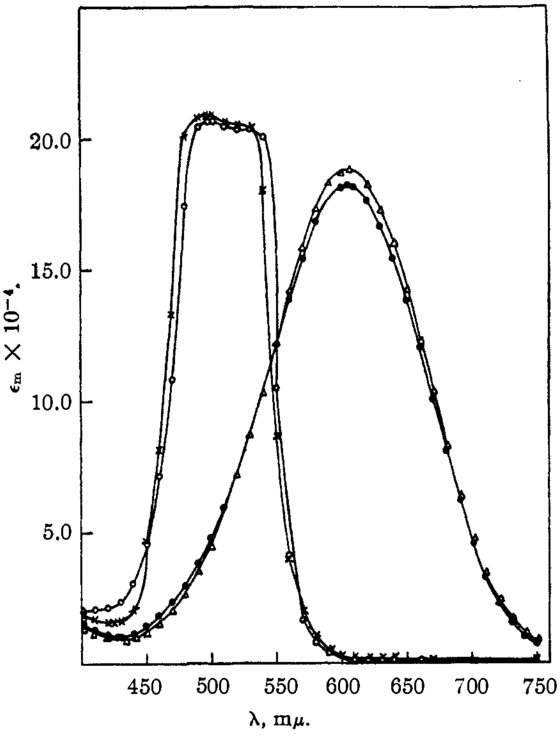

Fig. 6.—Molar extinction coefficients of 1×10^{-4} Rhodamine 6G and 1×10^{-4} *M* sodium 2,6-dichlorobenzenone indophenol: Rhodamine 6G O—O in H_2O, ×—× in 0.01 *M* $Na_2O \cdot 3.3SiO_2$; sodium 2,6-dichlorobenzenone indophenol ●—● in H_2O, △—△ in 0.01 *M* $Na_2O \cdot 3.3SiO_2$.

Discussion

The reduction in intensity of the α and β bands of solutions of pinacyanol chloride and toluidine blue 0 of as much as 50% by silicate solutions as dilute as 2×10^{-4} *M* is much larger than that observed for ordinary electrolytes. For example, the height of the main band of methylene blue in water is decreased only 5% when the solution is made 1*M* in potassium chloride and somewhat less with 1*M* potassium nitrate.[9] Lewis, *et al.*,[9] suggest that salts increase the formation in aqueous solution of a colorless form of the dye produced by simultaneous, reversible addition of hydrogen and hydroxyl ions. It appears that this suggestion does not explain the large reductions due to colloidal electrolytes, especially since, as Lewis states, one must also assume polymerization of the colorless substance in order to explain effects

[9] G. N. Lewis, O. Goldschmid, T. T. Magel and J. Bigeleisen, THIS JOURNAL, **65** 1150 (1943).

as large as 5%. A more likely explanation (*cf.* ref. 10) is that the dye and colloidal electrolyte interact in such a manner as to restrict free rotation of some part of the molecule involved in the electronic transitions giving rise to the bands. This decreases the number of fully extended planar ions suitably oriented per unit time to the electric vector of the light rays.

Probably sorption of colloidal particles is involved but the interaction is at least partially electrostatic for effects plainly visible to the eye occur only when the charges on the dye ion and colloidal particles are opposite in sign. Precipitation or flocculation occurs rapidly at dye and silicate concentrations greater than those reported in Tables II and III; the higher concentrations in these tables precipitated after standing a day or two.

The addition of silicates alters the relative intensities of the α and β band maxima of pinacyanol chloride. Thus, the ratio of the maximum molar extinction coefficients of the α to β band is 0.81 in water, 0.85 in 2×10^{-5} M $Na_2O \cdot 3.3SiO_2$ and 1.13 in 2×10^{-4} M $Na_2O \cdot 3.3SiO_2$. Some investigators regard the α band as characteristic of the monomer dye ion, the β band as peculiar to a dimer, and the γ band peculiar to high polymers.[11,12,13,14] Since these bands are generally apparent in organic solvents where there is no evidence of dimerization or polymerization it appears more likely that the β and γ bands are not new bands peculiar to dimers or polymers, but are vibrationally coupled transitions proper to the monomeric ions which are, however, enhanced in the dimer or polymer.[10] Because electrolytes generally increase the extent of formation of associated ions in aqueous systems, it would be expected that, if the first hypothesis is true, the ratio of the intensities of the α to β bands would decrease on the addition of electrolytes. That the opposite effect occurs on the addition of both sodium hydroxide and silicates is evidence that the bands are not peculiar to dimers or polymers. That the relative intensity of the α and β bands of thionine is not affected by the addition of a chloride[14] is a further indication.

Silicates also produce a shift in the wave length at which the band maxima appear and causes new bands to become evident thus producing a visual change in the colors of the solutions. The color change of toluidine blue in agar solutions is attributed to the adsorption of molecular aggregates of dye larger than the dimer by agar.[8] In "hexametaphosphate" solutions the color change has been attributed to a linear complex polymer produced by each dye ion reacting with a phosphate group.[7] The color change of dyes in soap solutions is attributed to preferential solubilization of one form of dye from the equilibrium mixture by the soap micelle.[3] Since silicates do not solubilize water-insoluble dyes and still produce comparable color changes, it is evident that the intimate type of interaction producing solubilization is not necessary to give a change in color. A reasonable explanation is that these color changes are also due to sorption at the surface of the colloidal silica particle and/or chemical combination of the dye cation with the negative ionic groups of the colloid. The change in the wave length at maximum intensity of the various bands with concentration indicates that the complexes responsible for their appearance vary in composition.

Summary

The addition of various sodium silicates to a pinacyanol chloride solution changes the absorption spectra by decreasing the intensity of the α and β bands to different extents, and by forming new α' and γ bands. The visual color change is from blue to purple. Their addition to a solution of toluidine blue 0 reduces the intensity of the absorption band and shifts the band maxima from 620 mμ to about 540 mμ, causing a visual change from blue to purple. Silicates shifted the band maxima of Rhodamine 6G about 6 mμ toward the violet but did not alter the intensity by more than 2%. This dye was orange and fluorescent in water and red and non-fluorescent in silicate solutions. Silicates had little effect on the absorption spectra of the sodium 2,6-dichlorobenzenone indophenol. The silicates used had the molecular formulas Na_2SiO_3, $Na_2O \cdot 2.6SiO_2$, $Na_2O \cdot 3.3SiO_2$ and $Na_2O \cdot 4.0SiO_2$. Their effects are attributed to sorption and electrostatic interaction of the dye ion with the silicate ions and micelles.

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(10) S. E. Sheppard and A. L. Geddes, THIS JOURNAL, **66**, 2003 (1944).

(11) G. Scheibe, *Kolloid Z.*, **82**, 1 (1938).

(12) W. L. Lewschin, *Acta Physicochim. U. R. S. S.*, **1**, 685 (1934).

(13) H. O. Dickinson, *Trans. Faraday Soc.*, **43**, 486 (1947).

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