Summary

Experiments on the oxidation of glucose by yeast in the presence of isotopic acetate or bicarbonate lead to the following conclusions.

At least half and probably much more of glucose undergoing complete oxidation passes through the intermediate stage of acetate.

The tricarboxylic acid cycle is a common pathway for the complete oxidation of both glucose and acetate.

Intermediates of the fermentation process in yeast are not in equilibrium with acetate.

Assimilation of carbon dioxide occurs but is of minor importance in the formation of succinate from glucose.

The data are in accord with the postulate that fermentation and oxidation of glucose diverge at acetaldehyde.

PHILADELPHIA, PENNSYLVANIA RECEIVED JUNE 16, 1948

[CONTRIBUTION FROM THE PHILADELPHIA QUARTZ COMPANY]

Spectral Changes of Some Dyes in Soluble Silicate Solutions

BY REYNOLD C. MERRILL AND ROBERT W. SPENCER

The spectral changes of the dyes pinacyanol chloride, toluidine blue O and Rhodamine 6G in sodium silicate solutions were reported recently.[1] The present paper reports the effect of sodium silicates on the spectra of eleven additional dyes and the influence of two potassium silicates and of seven sodium silicates of different SiO_2/Na_2O ratios, on the absorption spectrum of 1×10^{-5} M pinacyanol chloride. The influence of sodium chloride, sulfate, and orthophosphate on the spectrum of pinacyanol chloride in water and in a silicate solution (0.00598 M $Na_2O{\cdot}3.33\ SiO_2$) is also studied.

Experimental

Compositions of the soluble silicates used are summarized in Table I. The sodium oxide content was determined by titration with standardized hydrochloric acid to the methyl orange endpoint. Silica was determined gravimetrically. The remainder of each silicate is almost entirely water. Impurities were usually less than 0.1%. The orthosilicate, sesquisilicate, and metasilicate are white free flowing solids; the others are aqueous solutions. "Kasil #1," "E" and "Star" are clear and transparent. "BW," "S" and "Kasil #6" are opalescent due mainly to a small amount of impurities. The sodium hydroxide, chloride, sulfate and orthophosphate were J. T. Baker reagent grade chemicals.

TABLE I

COMPOSITION OF THE SOLUBLE SILICATES

Name[a]	Mol. formula	Mol. wt.[b]	Percentages Na_2O	Percentages SiO_2
Na orthosilicate	Na_4SiO_4	185.4	61.35	29.40
Metso 99	$Na_2O{\cdot}0.590SiO_2$	148.2	36.12	24.62
Metso crystals	$Na_2SiO_3{\cdot}5H_2O$	122.4	29.24	28.20
BW	$Na_2O{\cdot}1.71SiO_2$	164.8	19.35	32.09
Star	$Na_2O{\cdot}2.62SiO_2$	219.6	10.34	26.29
E	$Na_2O{\cdot}3.33SiO_2$	262.0	8.72	28.13
S	$Na_2O{\cdot}3.95SiO_2$	291.7	6.58	25.16
Kasil 1	$K_2O{\cdot}3.79SiO_2$	321.6	7.77[c]	18.72
Kasil 6	$K_2O{\cdot}3.27SiO_2$	290.8	12.82[c]	26.76

[a] Philadelphia Quartz Co. trade names (except Na orthosilicate which was a product of the Dow Chemical Co.). [b] Molecular weights determined on the basis of Na_2O and SiO_2 determinations. Theoretical percentages for pure "orthosilicate" 184.0 and for pure sodium metasilicate 122.05. [c] K_2O for Kasils.

All of the dyes were commercial products and used without further purification. Crystal violet (C. I. 681), basic fuchsin (C. I. 677), malachite green, phenosafranin (C. I. 840), quinaldine red, and pinacyanol chloride were purchased from the Eastman Kodak Co. Nile blue A (C. I. 913), thionin (C. I. 920) and niagara sky blue 6B (C. I. 518) were obtained from Eimer and Amend. The safranine O (C. I. 841) and toluidine blue O were obtained from A. H. Thomas and the methylene blue from Merck. Most of the dyes were manufactured by the National Aniline Division of the Allied Chemical and Dye Corp. According to the supplier the total dye content of basic fuchsin was 91%, of crystal violet 93%, nile blue A 86%, thionin 86%, safranine O 94%, and toluidine blue O 66%. The molar concentrations are given on the basis of actual dye content assuming the remaining dyes were pure.

The absorption spectra were obtained at room temperature (~22°) with a General Electric Co. recording spectrophotometer. Molar extinction coefficients, ϵ_m, were calculated from the transmission curves using the equation $\epsilon_m = 1/cd \log_{10} I_0/I$, where c is the molar concentration of dye, d the width of the cell (1.00 cm.), and I_0 and I the intensity of the incident and transmitted light. Stock solutions of the dyes and silicates were mixed immediately before the transmission curves were determined in order to avoid or minimize possible errors due to fading of some of the dyes. Basic fuchsin, malachite green, nile blue A and crystal violet fade in less than one-half hour at pH's above 12 so that their absorption spectra in 0.020M sodium metasilicate and 0.0158M sodium hydroxide were not determined. Any fading of the other dyes during our experiments was considered negligible.

Results

Absorption spectra of the thiazine dyes, methylene blue, toluidine blue O and thionin in solutions of the more siliceous silicates, $Na_2O{\cdot}3.33SiO_2$ and $Na_2O{\cdot}3.95SiO_2$, show pronounced differences from those for the same concentration of dye in water or in dilute sodium hydroxide solutions of the same pH as the silicate solutions. The molar absorption curve of 1×10^{-5} M methylene blue in water shows the α band maximum at 662 mμ with ϵ_m = 67,600 and indications of the β band at 615 mμ where ϵ_m = 37,200 (Fig. 1). The absorption curve is practically the same for this concentration of methylene blue in 0.0158 M so-

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[1] R. C. Merrill, R. W. Spencer and R. Getty, THIS JOURNAL, **70**, **2460** (1948).

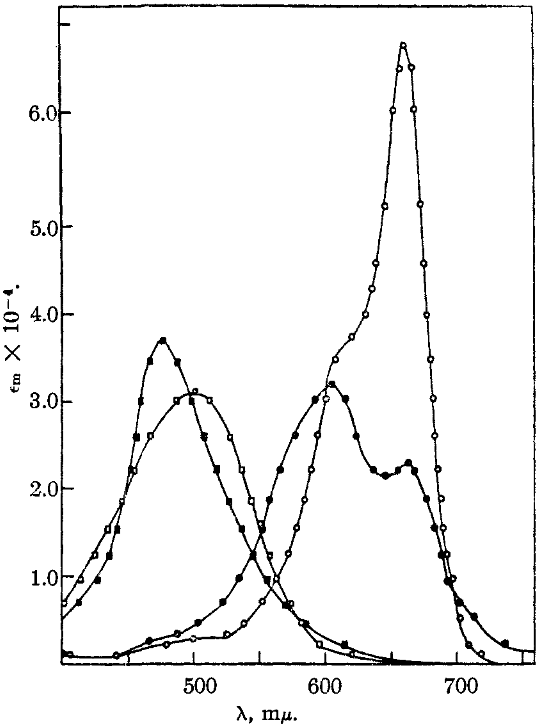

Fig. 1.—Molar extinction coefficients of 1×10^{-5} *M* methylene blue and quinaldine red: methylene blue in H_2O ○—○, in 0.00598 *M* $Na_2O{\cdot}3.33SiO_2$ ●—●, quinaldine red in H_2O □—□, in 0.00598 *M* $Na_2O{\cdot}3.33SiO_2$ ■—■.

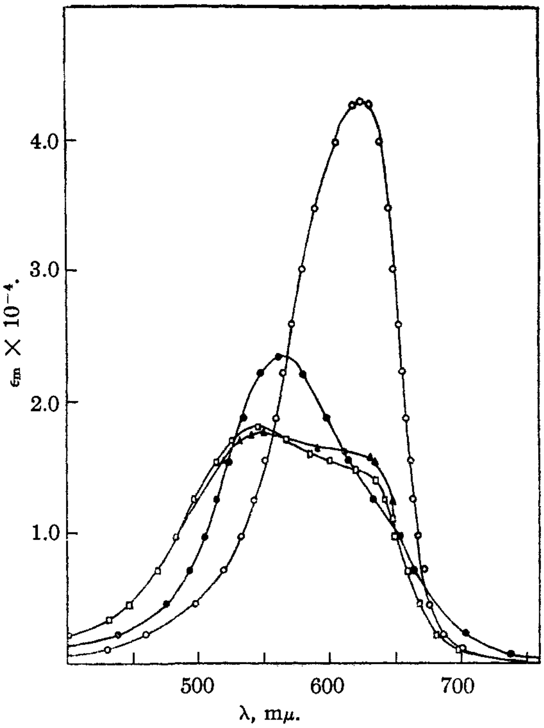

Fig. 2.—Molar extinction coefficients of 1×10^{-5} *M* toluidine blue O: in H_2O ○—○, in 0.00598 *M* $Na_2O{\cdot}3.33SiO_2$ ●—●, in 0.020 *M* Na_2SiO_3 □—□, in 0.0158 *M* NaOH ▲—▲.

dium hydroxide or 0.020 *M* sodium metasilicate as in water except that ϵ_m for the α band is reduced about 2 and 4%, respectively, and the absorption between 400 and 570 mμ is somewhat less. When the same concentration of dye is dissolved in 0.00598 *M* $Na_2O{\cdot}3.33SiO_2$ or 0.00522 *M* $Na_2O{\cdot}3.95SiO_2$ the intensity of the α band is reduced by 65 and 62%, respectively, as compared with that in water; the β band becomes well defined, is reduced in intensity only 14 and 11%, respectively, and is shifted to 605 and 607 mμ. These differences are apparent to the eye for these solutions are purple in contrast to the blue color of the dye in water, 0.0158 *M* sodium hydroxide, or 0.020 *M* metasilicate. The *p*H's of these two siliceous silicate solutions are intermediate between those of the metasilicate and water. The differences in the spectra of the dye in these solutions and in water are thus due to the presence of colloidal silica rather than to the alkalinity. All of these silicate solutions contain the same amount (0.12%) of soluble silica (SiO_2).

The differences in the absorption spectra of 1×10^{-5} *M* toluidine blue O in water and in 0.020 *M* sodium metasilicate (Fig. 2) are due mainly to the alkalinity of the metasilicate since the absorption spectra in 0.0158 *M* sodium hydroxide, which has approximately the same *p*H, is closely similar. The spectra of a 1×10^{-5} *M* toluidine blue O solution in 0.00598 *M* $Na_2O{\cdot}3.33SiO_2$ shows a single maximum at 562 mμ with ϵ_m = 23,600; in 0.00522 *M* $Na_2O{\cdot}3.95SiO_2$ the maximum is at 569 mμ with ϵ_m = 22,600. In a 0.00058 *M* sodium hydroxide solution, which has approximately the same *p*H as the 0.00598 *M* $Na_2O{\cdot}3.3SiO_2$, the absorption curve is similar to that in water except that the intensity of the main band is reduced 7.5%. Again the silicate solution has an effect not due to its *p*H.

Thionin fades rapidly in 0.0158 *M* sodium hydroxide or 0.020 *M* sodium metasilicate solutions so that it was not studied in these solvents. The intensity of the band maxima of thionin is decreased by the addition of 0.00058 *M* sodium hydroxide; its intensity is decreased much more in 0.00598 *M* $Na_2O{\cdot}3.33SiO_2$ (which has about the same *p*H and in addition the short wave length or β band becomes more prominent.

The absorption spectrum of 1×10^{-5} *M* nile blue A, an oxazine dye containing a naphthalene ring, in 0.00598 *M* $Na_2O{\cdot}3.33SiO_2$ shows a maximum at 574 mμ with ϵ_m = 16,700 as contrasted with the maxima in water at 634 mμ where ϵ_m = 38,000 (Fig. 3). In 0.00058 *M* sodium hydroxide solution, which has about the same *p*H as the $Na_2O{\cdot}3.33SiO_2$ solution, ϵ_m of the main band is only 17,700 but it occurs at the same wave length as in water.

Quinaldine red differs from the other dyes studied in that the molecular extinction coefficient at the band maxima is higher in both the siliceous silicate solutions than in water (Fig. 1). The curve in 0.00522 *M* $Na_2O{\cdot}3.95SiO_2$ is similar to

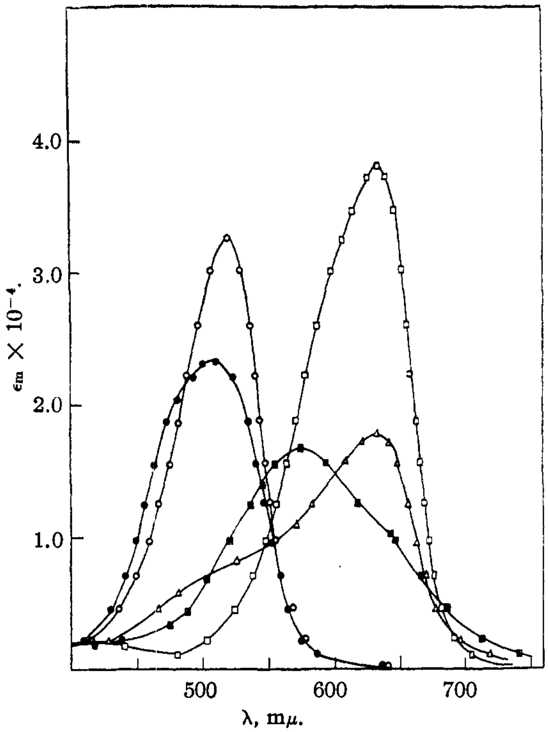

Fig. 3.—Molar extinction coefficients of 1 × 10^{-5} *M* safranine O and nile blue A: safranine O in H_2O O—O, in 0.00598 *M* $Na_2O \cdot 3.33SiO_2$ ●—●; nile blue A in H_2O □—□, in 0.00598 *M* $Na_2O \cdot 3.33SiO_2$ ■—■, in 0.00058 *M* NaOH △—△.

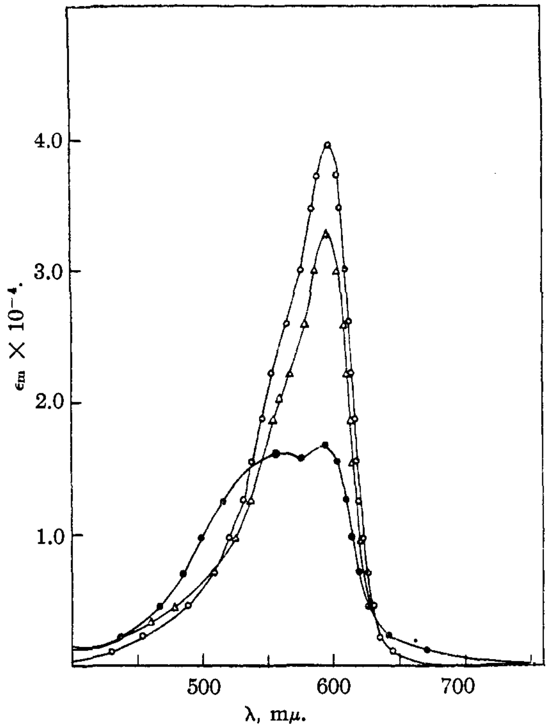

Fig. 4.—Molar extinction coefficients of 1 × 10^{-5} *M* thionin: in H_2O O—O, in 0.00598 *M* $Na_2O \cdot 3.33SiO_2$ ●—●, in 0.00058 *M* NaOH △—△.

that shown in Fig. 1 for the dye in the 3.33 ratio silicate except that the maximum is at 474 mμ where ϵ_m = 35,200.

Two safranine and three triphenylmethane dyes were studied—safranine O, phenosafranine, fuchsin, malachite green and crystal violet. As shown in Fig. 3, the band maxima for a 1 × 10^{-5} *M* safranine O solution occurs at 520 mμ with ϵ_m = 32,700 whereas in 0.00598 *M* $Na_2O \cdot 3.33SiO_2$ the maxima is at 509 mμ with ϵ_m = 23,400. The curve in 0.00522 *M* $Na_2O \cdot 3.95$ is similar to the latter curve with a maximum at 506 mμ where ϵ_m = 23,700. These differences are not due to the alkalinity of the silicates because the curves in 0.0158 *M* sodium hydroxide and 0.020 *M* metasilicate are the same as those in water except that ϵ_m for the maximum is about 6% greater for the former and 4% for the latter. It is interesting that 1 × 10^{-5} *M* solutions of the closely related dye, phenosafranine, show practically the same absorption curve in water, 0.0158 *M* sodium hydroxide, 0.020 *M* metasilicate and 0.00522 *M* $Na_2O \cdot 3.95SiO_2$ except that the absorption maximum, which occurs at 520 mμ, is about 6% lower in solutions of the 3.95 ratio silicate. Likewise, the absorption curves of 1 × 10^{-5} *M* solutions of malachite green and fuchsin in 0.00522 *M* $Na_2O \cdot 3.95SiO_2$ have the same shape as those in water or 0.00058 *M* sodium hydroxide although the intensities of the band maxima are reduced, particularly with the

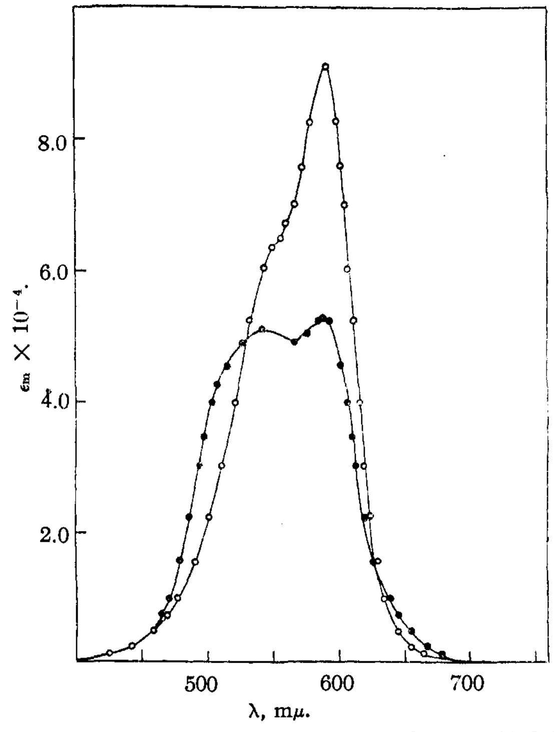

Fig. 5.—Molar extinction coefficients of 1.0 × 10^{-5} *M* crystal violet; in H_2O O—O, in 0.00598 *M* $Na_2O \cdot 3.33SiO_2$ ●—●.

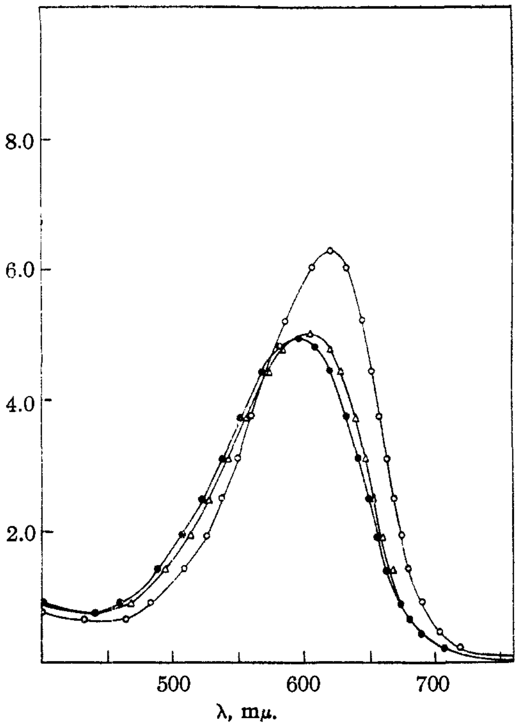

Fig. 6.—Molar extinction coefficients of 5.0 × 10^{-5} niagara sky blue; in H_2O ○—○, in 0.00598 *M* $Na_2O·3.33SiO_2$ ●—●, in 0.00058 *M* NaOH △—△.

latter dye. However, this reduction in intensity suggests some type of interaction between the dye and silicate.

The spectrum of 1 × 10^{-5} *M* crystal violet in 0.00598*M* $Na_2O·3.33SiO_2$ shows that the intensity of the α band at 590 mμ is reduced 42% and shifted slightly as compared with that in water; the β band at 542 mμ is better developed in the silicate solution (Fig. 5). Again this is not a *p*H effect because the curve in a sodium hydroxide solution having the same *p*H as the silicate solution is the same as in water except that the intensity of the band maxima is reduced 4%.

The absorption spectrum for niagara sky blue 6B, which differs from the other dyes used in this paper by being anionic, in 0.00598 *M* $Na_2O·3.33SiO_2$ is about the same as in a sodium hydroxide solution of nearly the same *p*H (Fig. 6).

That the interaction of quinaldine red and pinacyanol chloride with potassium silicates resembles that with sodium silicates of comparable ratio and concentration is shown in Fig. 7.

Effect of Salts.—The effects of 0.10 *M* sodium chloride, 0.033 *M* sodium sulfate and 0.00167 *M* trisodium phosphate on the absorption spectra of 1 × 10^{-5} *M* pinacyanol chloride in water and in 0.00598 *M* $Na_2O·3.33SiO_2$ are illustrated in Figs. 8, 9 and 10. All of these solutions have the same ionic strength. Each salt lowers the intensity of

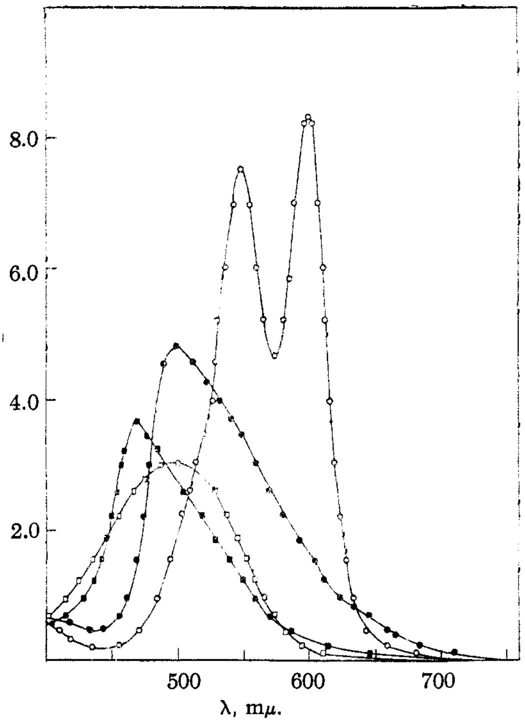

Fig. 7.—Molar extinction coefficients of 1 × 10^{-5} *M* pinacyanol chloride and quinaldine red: pinacyanol chloride in H_2O ○—○, in 0.00522 $K_2O·3.79SiO_2$ ●—●; quinaldine red in H_2O □—□, in 0.00608 *M* $K_2O·3.27SiO_2$ ■—■.

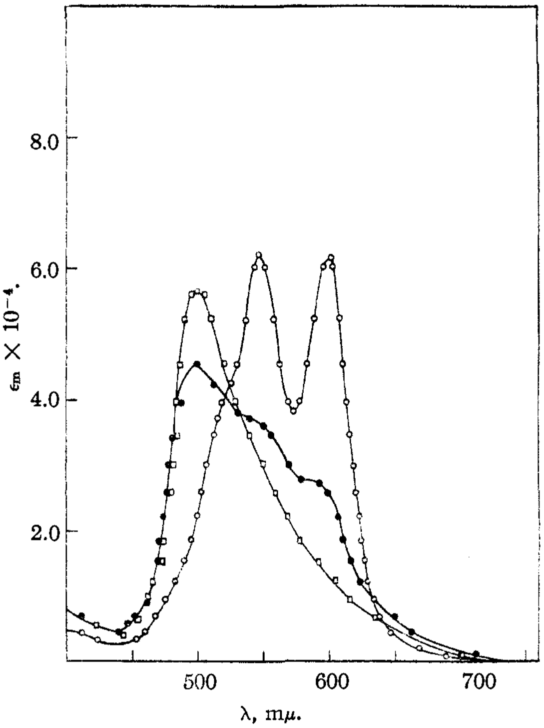

Fig. 8.—Effect of sodium chloride on absorption spectrum of 1 × 10^{-5} *M* pinacyanol chloride in $Na_2O·3.33SiO_2$: in 0.10 *M* NaCl alone ○—○, in 0.00598 *M* $Na_2O·3.33SiO_2$, □—□, in 0.10 *M* NaCl + 0.00598 *M* $Na_2O·3.33SiO_2$ ●—●.

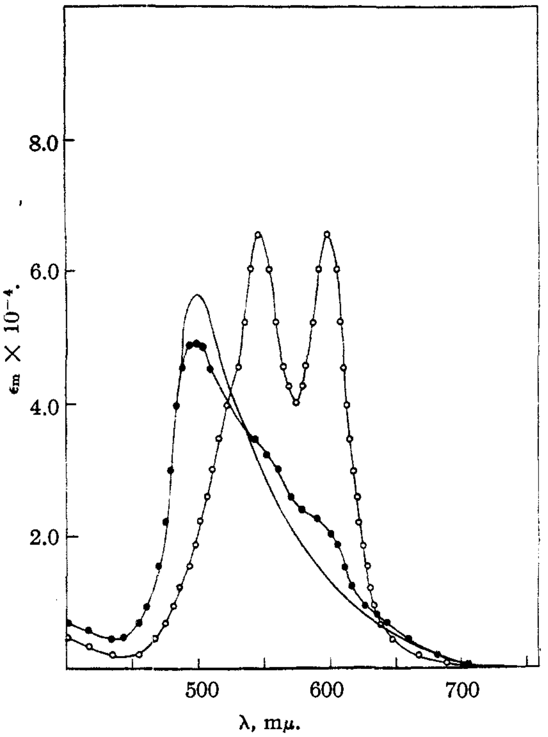

Fig. 9.—Effect of sodium sulfate on absorption spectrum of 1 × 10^{-5} *M* pinacyanol chloride in $Na_2O \cdot 3.33SiO_2$: in 0.0333 *M* Na_2SO_4 O—O, in 0.0333 *M* Na_2SO_4 + 0.00598 *M* $Na_2O \cdot 3.33SiO_2$ ●—●, solid line in 0.00598 *M* $Na_2O \cdot 3.33 SiO_2$ alone.

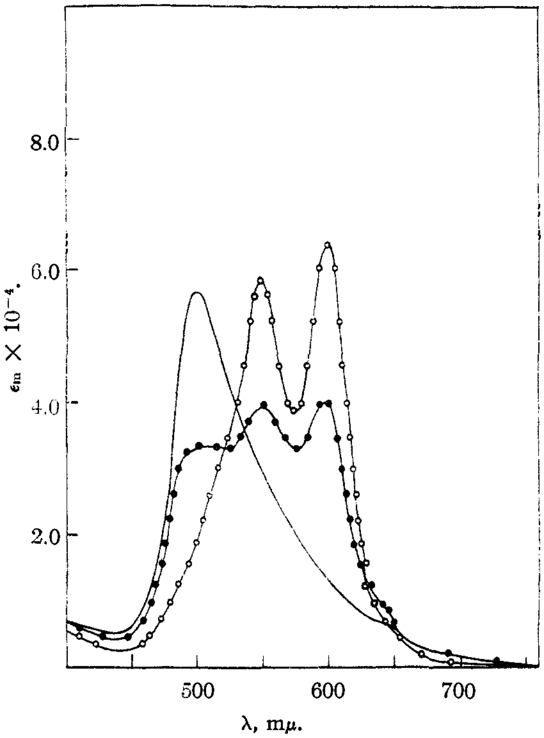

Fig. 10.—Effect of trisodium phosphate on absorption spectrum of 1 × 10^{-5} *M* pinacyanol chloride in $Na_2O \cdot 3.33SiO_2$: in 0.0167 *M* Na_3PO_4 O—O, in 0.0167 *M* Na_3PO_4 + 0.00598 *M* $Na_2O \cdot 3.33SiO_2$ ●—●, solid line in 0.00598 *M* $Na_2O \cdot 3.33SiO_2$ alone.

the α and β bands at 599 and 547 mμ, respectively, as compared to that in water, and alters the relative intensity of the bands to a small but significant extent. Sodium sulfate decreases the effect of the 0.00598 *M* $Na_2O \cdot 3.33SiO_2$ on the dye least, sodium chloride intermediate, and trisodium phosphate most at an ionic strength of 0.1. It is clear that the interaction of the dye and silicate is not dependent only on the total ionic strength of the medium.

Effect of Different Silicates.—The effects on the absorption spectra of 1 × 10^{-5} *M* pinacyanol chloride of silicates of different silica to alkali (Na_2O) ratio, each of which contains the same amount (0.12%) of silica, is illustrated in Fig. 11. Since sodium hydroxide at equivalent *p*H's has comparatively little effect on the absorption spectrum of the dye, the effects observed must be due to the silica occurring in different forms depending on the silica to alkali ratio. As the silica to alkali ratio increases at a constant silica concentration the intensity of the α and β bands of pinacyanol chloride in these silicate solutions decreases; a γ band first becomes apparent at the 1:1 or metasilicate ratio and increases in intensity with ratio. The wave length at which this γ band occurs apparently changes from 492 mμ to 500 mμ with increase in ratio. An α′ band at around 630 mμ is apparent at silica to alkali ratios above one.

Discussion

Most of the dyes used in this investigation, such as toluidine blue O, are biological stains. Their use for this purpose depends on the same dye staining different histological elements in different colors or shades, the phenomenon which P. Ehrlich called "metachromasy." It is interesting and significant that these dyes show the same color changes in the presence of highly charged inorganic colloids, such as the sodium silicates, as they do in the presence of biological materials. Such color changes occur in the presence of carbohydrate high polymers partially esterified with sulfuric acid,[2] the sodium salt of carboxymethylcellulose,[3] polymeric polyphosphates[4] and soaps and synthetic detergents above the concentration where micelle formation occurs.[3,5,6,7] These cationic dyes would probably show similar color changes in the presence of any colloid with a high negative charge.

(2) L. Lison, *Arch. biol.*, **46**, 599 (1935); L. Lison, *Protoplasma* **24**, 453 (1935); L. Lison, "Histochimie animale," Gauthier, Paris, 1936.

(3) L. Michaelis in "Cold Spring Harbor Symposia on Quantitative Biology," Vol. XII.

(4) J. M. Wiame, THIS JOURNAL, **69**, 3146 (1947).

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

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

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

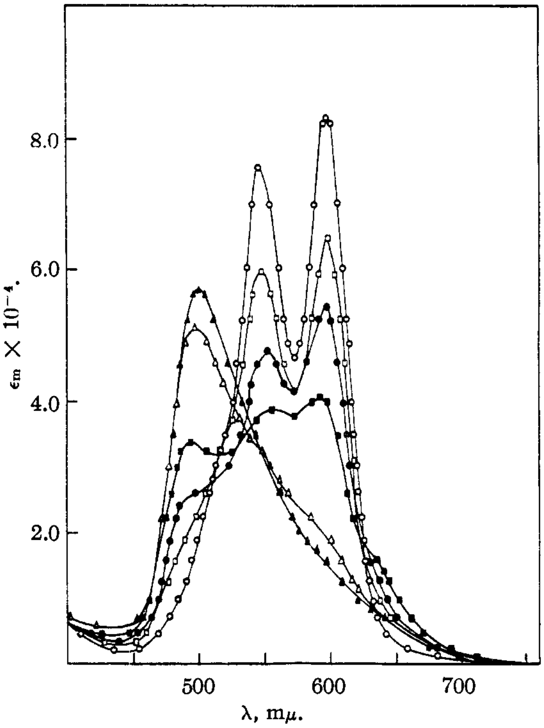

Fig. 11.—Molar extinction coefficients of 1×10^{-5} *M* pinacyanol chloride in solutions of various silicates having same silica concentration (0.12% SiO_2): in H_2O ○—○, in 0.0182 *M* Na_3HSiO_4 □—□, in 0.02 *M* Na_2SiO_3 ●—●, in 0.0120 *M* $Na_2O \cdot 1.71SiO_2$ ■—■, in 0.00761 *M* $Na_2O \cdot 2.62SiO_2$ △—△, in 0.00522 *M* $Na_2O \cdot 3.95SiO_2$ ▲—▲.

The ability of the dye to change color in the presence of highly charged colloids is attributable to the existence in aqueous solution of an equilibrium between at least two forms of the dye, one of which interacts preferentially with the colloid. One of the forms may be produced by the addition of a proton and the color change be due to a difference between the hydrogen ion concentration at the surface of the micelle near the sorbed dye molecule and the bulk solution. For most, if not all, of the dyes, studied in this work the two or more different forms are monomers, dimers and probably higher association products of the dye ions or molecules.

Comparison of our results with those of Michaelis and Granick[8] shows that those dyes showing color changes in solutions of the siliceous silicates also show color changes in the presence of agar and disobey Beer's law in aqueous solution. Those showing no color changes in siliceous silicate or agar solutions obey Beer's law. Failure to conform to Beer's law is due to the formation of molecular aggregates of the dye with increasing concentration. Similarly, Corrin and Harkins concluded[7] that color change of dyes at the critical concentration for micelle formation was "related to the existence of an equilibrium mixture of the dye in aqueous solution from which one form is preferentially solubilized by the soap micelle." However, the siliceous silicates, polymeric phosphates,[4] sodium carboxymethylcellulose,[3] agar[8] and other polymeric carbohydrate sulfates produce color changes comparable to those observed in micellar soap and detergent solutions and yet are not solubilizers. Production of these pronounced color changes is observed only when electrostatic interaction between oppositely charged micelles and dye ions can occur. In solubilization only van der Waals–London forces and hydrogen bonding need be involved.

Combination between colloids and dye ions of the same sign does occur. However, even when the colloid contains a minor fraction of ionic groups of opposite sign, the changes in color and intensity are small compared to those occurring when dye and colloid are of opposite sign.

With most of the cationic dyes studied the effect of the silicate was to increase the relative intensity of the low wave length or β band generally regarded as due to the presence of dimers, to broaden it and to displace the band toward shorter wave lengths. Siliceous silicates, like agar,[8] increase the proportion and size of the dye polymers by combining with the polymeric dye molecules in complexes of continuously varying composition as indicated by gradual changes in the intensity, position and shape of the bands generally attributed to polymers. A reviewer of this paper suggests that a smaller ionization constant of the dimer may be responsible for its greater tendency to associate with colloidal dye anions.

The effect of sodium metasilicate on the absorption spectra of pinacyanol chloride is more comparable to that of the colloidal silicates than that of the simple chloride, sulfate or phosphate ions. This suggests that association products are present in sodium metasilicate solutions although these are probably not sufficiently large to be called micelles.[9] Such an interpretation is in agreement with the work of Roller and Ervin[10] who found it necessary to assume a high tendency of the metasilicate to associate in dilute alkaline solution in order to explain their experimental data on the system, calcium oxide–silicate–water.

The fact that the 3.95 ratio silicate often has less effect on the absorption spectrum of cationic dyes than does the 3.33 ratio silicate may be attributed to a lower density of charge on the larger silicate anionic micelles.

Summary

Colloidal sodium and potassium silicates produce marked changes in the absorption spectrum of

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

(9) Likewise the large effect of very dilute soap solutions on the absorption spectrum of pinacyanol chloride,[6] and the difference in color between Sky Blue FF in water, micellar soap solutions, and ordinary salt solutions as compared with very dilute soap solutions[7] suggests that small aggregates of some type form in soap solutions more dilute than the "critical concentration for micelle formation." Other work also indicates some aggregation in very dilute soap solutions (for references see R. C. Merrill and R. Getty, *J. Phys. and Colloid Chem.*, **52**, 774 (1948).

(10) P. S. Roller and G. Ervin, THIS JOURNAL, **62**, 461 (1940).

those cationic dyes which do not conform to Beer's law in aqueous solution. Usually the silicates increase the relative intensity of the low wave length or β band, broaden it and displace this band toward even shorter wave lengths. The changes are not due to the alkalinity of the silicates. They are attributed to interaction, probably involving both electrostatic and van der Waals forces, of a dimeric or polymeric form of the dye with the oppositely charged silicate micelles.

The addition of sodium chloride, sulfate or trisodium phosphate decreases the interaction of the dye, pinacyanol chloride, and silicate. This effect of salts is not due entirely to the ionic strength of the solution.

Sodium silicates of different silica to alkali ratio have widely varying effects on the absorption spectra of pinacyanol chloride even when the silica concentration is the same.

PHILADELPHIA 6, PA. RECEIVED JUNE 4, 1948

[CONTRIBUTION NO. 75 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Chain Transfer in the Polymerization of Styrene. IV. The Effect of Chain Length on the Reaction of Styrene and Carbon Tetrachloride

BY FRANK R. MAYO

The first paper of this series,[1] on the basis of literature data, indicated the existence of a quantitative relation between solvent: monomer ratio in a reaction mixture and the solvent fragment content of the polymer. Work was at once undertaken to determine the limitations of this relation and its applicability to the preparation of very low molecular weight compounds. Breitenbach and Maschin[2] had previously obtained fractions containing as much as 22% chlorine, and Kharasch and co-workers have recently reported a polymer containing 7.6% chlorine,[3a] but only by the use of the more reactive bromotrichloromethane instead of carbon tetrachloride has a 1:1 product been isolated.[3b] These products are mixtures of compounds of the type, $Cl_3C\text{–}(CH_2\text{–}CHC_6H_5)_n\text{–}Cl$(or Br). The second paper[4] in this series showed that both the over-all second order rate constant and the transfer constant for the polymerization of styrene in carbon tetrachloride are independent (at low conversions and within experimental error) of average polymer chain lengths ranging from about one hundred to many thousands. It follows that either all the individual rate constants in the polymerization (initiation, growth, transfer, termination) are independent of chain length, as has been commonly assumed, or else there is mutual compensation of trends. In the present extension of the above studies to the very low molecular weight range, the ratio of the rate constants for chain growth and chain termination is found to vary little, if at all, as the average number of styrene units in the growing free radical decreases from twenty to two. On the other hand, the ratio of the rate constants for chain transfer with carbon tetrachloride and for chain growth of the radical, $Cl_3C\text{–}(CH_2\text{–}CH_6H_5)_n\cdot$, increases markedly with chain length as n increases from one to three, then remains constant to the largest values of n found.

Equations.—All the reactions considered between the peroxide catalyst (Cat.), monomer (M), and solvent (S) are represented by the following equations, where Cat.: represents radical from the catalyst, M· represents the free radical formed by the addition of any radical to a monomer, and S· is the radical formed by removal of an atom from the solvent by chain transfer. In this paper S· is $Cl_3C\cdot$ as shown by identification of disproportionation and coupling products of the radical containing one styrene unit.

$$\text{Cat.} \longrightarrow 2\ \text{Cat.}\cdot \tag{1}$$

$$2\ \text{Cat.}\cdot \longrightarrow \text{products (first order combination)} \tag{1a}$$

$$\text{Cat.}\cdot + M \longrightarrow M\cdot \tag{2}$$

$$\text{Cat.}\cdot + S \longrightarrow S\cdot \tag{2a}$$

$$M\cdot + M \longrightarrow M\cdot \tag{3}$$

$$M\cdot + S \longrightarrow S\cdot \tag{4}$$

$$S\cdot + M \longrightarrow M\cdot \tag{5}$$

$$2M\cdot \longrightarrow \text{products} \tag{6}$$

$$2S\cdot \longrightarrow \text{products} \tag{6a}$$

When the kinetic chains are long (and the contribution of chain initiation and termination to the composition of the product can be neglected) and when essentially all polymer chains end by transfer

$$\frac{d[M]}{d[S]} = \frac{k_3[M\cdot][M] + k_5[S\cdot][M]}{k_4[M\cdot][S]} \tag{7}$$

Since $k_4[M\cdot]\,[S] = k_5[S\cdot]\,[M]$ and since the transfer constant, C, is defined as k_4/k_3[5]

$$\frac{d[M]}{d[S]} = \frac{[M]}{C[S]} + 1 \tag{8}$$

In the previous papers this 1 term has been neg-

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[1] Mayo, THIS JOURNAL, **65**, 2324 (1943).

[2] Breitenbach and Maschin, *Z. physik. Chem.*, **187A**, 175 (1940).

[3] (a) Kharasch, Jensen and Urry, THIS JOURNAL, **69**, 1100 (1947); (b) Kharasch, Reinmuth and Urry, *ibid.*, 1105.

[4] Gregg and Mayo, *ibid.*, **70**, 2373 (1948). Paper III, on transfer with hydrocarbons, will appear shortly in *Trans. Faraday Soc.*

[5] This equation is identical in form with the differential equation for the copolymerization of the monomers M_1 and M_2 when the monomer reactivity ratio of $M_2\cdot = 0$ and the monomer reactivity ratio of $M_1\cdot$ is $1/C$; *cf.* Alfrey, Mayo and Wall, *J. Polymer Sci.*, **1**, 581 (1946).