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Kinetic Investigations of the Reaction of Brilliant Green with Alkalies. Influence of Ionic Strength

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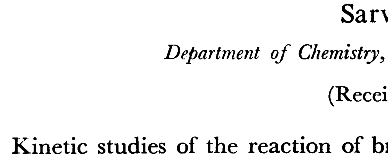
Kinetic studies of the reaction of brilliant green with alkalies have been made by following the reaction spectrophotometrically at 625 mμ. The reaction has been found to be bimolecular but under experimental condition of excess alkali, it obeyed a first order law. The rate constants was independent of the concentration of brilliant green but it varied linearly with the hydroxyl ion concentration. Effect of neutral salt on the rate of reaction was investigated in aqueous and in 40% acetone-water media. The rate was found to decrease progressively with increasing ionic strength in both media. Analysis of the data by Brϕnsted-Christiansen-Scatchard equation yielded a value of -1 for Z_AZ_B indicating thereby that the rate-determining step involves oppositely charged species possessing unit charge. The value of inoic interaction parameter, a_i, corresponded to 1.5 and 4.75 Å in aqueous and 40% acetone-water medium respectively. Without attaching too precise a meaning to a_i it is suggested that B.G. ion is presumably solvated to a greater extent in 40% acetone-water than pure water.

Brilliant green (B.G.), chemically known as 4,4′-bisdiethylaminotriphenyl methyl sulfate belongs to a group of dyes known as triphenylmethane dyes. The physico-chemical[1,2] biological[3,4] and pharmaceutical[5,6] studies of these dyes have attracted the attention of a number of workers. Besides being a compound of biological interest, its major use is in the dye industry where it is used for dyeing and printing all types of fibers, *viz.* cotton, wool, silk, *etc.* Furthermore, it has also been suggested that B.G. can be employed for the colorimetric estimation[7] of Au^{+3}, *etc.*, quantitatively. In biological uses the dye is employed in the biological important pH range 6—7. However, at higher pH the characteristic green color of the dye fades away with time. The kinetic data existing on the instability of B.G. in alkaline solutions are rather scanty[8] while for many other dyes of the series the kinetic data are non-existent. The significance of the stability of these dyes in acidic and alkaline medium, in the course of their biological analytical and dyeing applications, led the author to undertake a systematic kinetic investigation of their reactions. This communication reports the influence of ionic strength, hydroxyl ion concentration and the dye concentration on the reaction responsible for the fading of color of B.G. in alkaline medium, and the data have been employed to detect the species involved in the rate determining step.



Experimental

Materials Used. Brilliant green used was of medicinial quality from British Drug House and was purified by the partition methods[9] described by Lewis, Magel and Lipkin.

Sodium hydroxide employed was a British Drug House 'Anala R' sample.

Potassium nitrate, used for varying the ionic strength of the medium, was a British Drug House 'Anala R' grade reagent which was recrystallized twice from double distilled water.

Acetone employed was a British Drug House 'Anala R' grade reagent and it was further purified[10] before use.

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[1] T. Azami and T. Hinohara, *Nippon Kagaku Zasshi*, **72**, 515 (1951).

[2] R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.*, **1949**, 1724.

[3] C. F. Poe and N. F. Witt, *J. Amer. Water Works Ass.*, **22**, 1365 (1930).

[4] C. N. Stark and L. R. Curtis, *J. Bacteriol.*, **32**, 385 (1936).

[5] F. D. Mann and F. C. Mann, *Amer. J. Digestive Diseases Nutrition*, **6**, 322 (1939).

[6] R. H. Aldrich, *Maine Med., J.*, **28**, 5 (1937).

[7] N. T. Voskresenkaya, *Zh. Anal. Khim.*, **11**, 585 (1956).

[8] N. V. Sidgwick and N. S. Moore, *Proc. Chem. Soc.*, **25**, 123 (1909); *J. Chem. Soc.*, **95**, 889 (1909).

[9] G. N. Lewis, T. T. Magel and D. Lipkin, *J. Amer. Chem. Soc.*, **64**, 1774 (1942).

[10] A. I. Vogel, "A Text Book of Practical Organic Chemistry," Longmans Green & Co. (1948), p. 170.

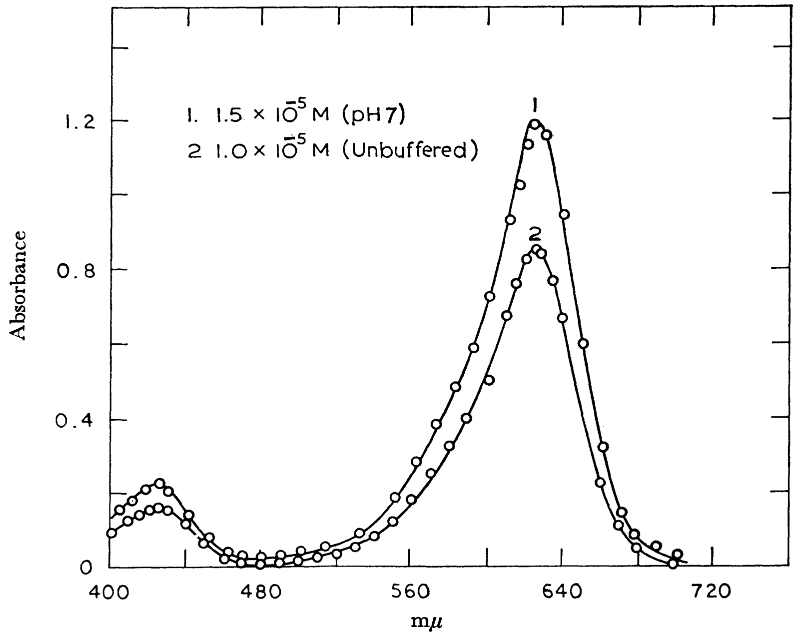

Fig. 1. Absorption spectrum of B.G. in water.

Pre Treatment of Reaction Vessels. B.G. gets adsorbed[11] strongly on the glass surfaces due to which there is a decrease in the effective concentration of the dye. In order to avoid this loss all the vessels used for keeping the solutions of B.G. were coated with a thin layer of purified paraffin wax, which checked the adsorption for sufficiently long durations. The glass cells used for absorbance measurements were rinsed periodically with purified ethanol to remove the adsorbed dye.

Procedure for Following the Reaction. The rate of the chemical change undergone by B.G. in the alkaline medium was studied spectrophotometrically by a Beckman DU spectrophotometer fitted with a dual thermospacer set. The temperature in the cell compartment was regulated by circulating water in the thermospacer set from an external thermostat maintained at 25±0.5°C. The kinetic experiments were carried out in the paraffined flasks kept in the external thermostat and the samples from these flasks were drawn out into 10 mm corex glass cells and their absorbances were noted with time. The absorption measurements were made at λ_{max} of the dye.

Results and Discussion

Absorption Spectrum of Brilliant Green. The absorption spectrum of B.G. in water at two different concentrations in the visible region of the spectrum is given in Fig. 1. It is seen that B.G. exhibits λ_{max} at 625 and 426 mμ. Beer's law held at both these wavelengths as shown by the linear plots of absorbance *vs.* millimicrons in Fig. 2. The value of absorptivity (ε) at 625 mμ corresponded to 8.00×10^4 l mol^{-1}cm^{-1}, which is very high as compared to the absorptivity at 426 mμ. Hence the absorbance measurements during kinetic runs were made at 625 mμ in aqueous solutions. The wavelengths of maximum absorption were unaffected by the buffered or unbuffered nature of the solutions. But in acetone-water mixtures λ_{max} was shifted to 627.5 mμ and therefore the measurements were made at this wavelength in acetone-water mixtures.

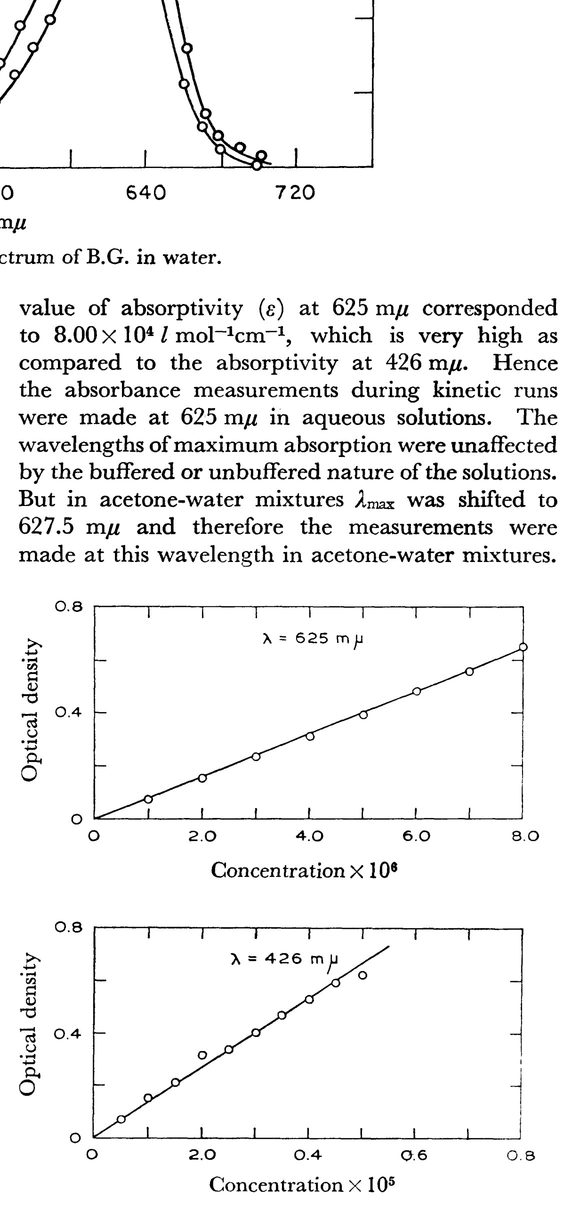

Fig. 2. Applicability of Beer's law.

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[11] B. P. Gyani, *J. Indian Chem. Soc., Ind. and News Ed.*, 13, No. 1 (1950).

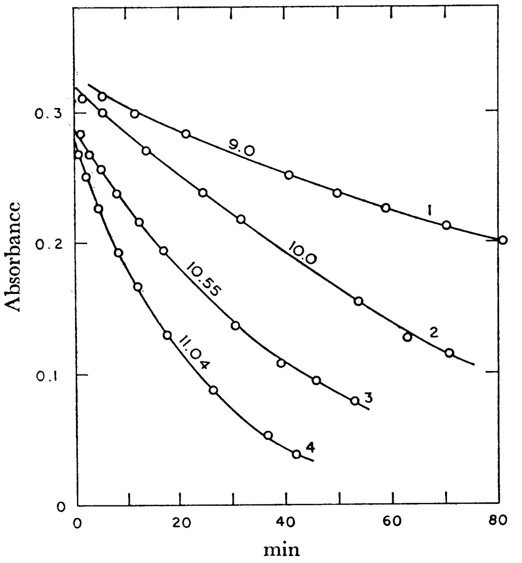

Fig. 3. Typical kinetic runs for the reaction of B.G. in different buffers.

Kinetic studies for the reaction of B.G. and sodium hydroxide could not be carried out at concentrations greater than 5×10^{-5}M of the dye and also at $\lambda=426$ mμ for the following reasons. At concentrations greater than 5×10^{-5}M, turbidity appeared. This was due to the low solubility of the reaction product. At concentrations below 5×10^{-6}M, the absorbance at $\lambda=426$ mμ was so small that spectrophotometric measurements were not feasible.

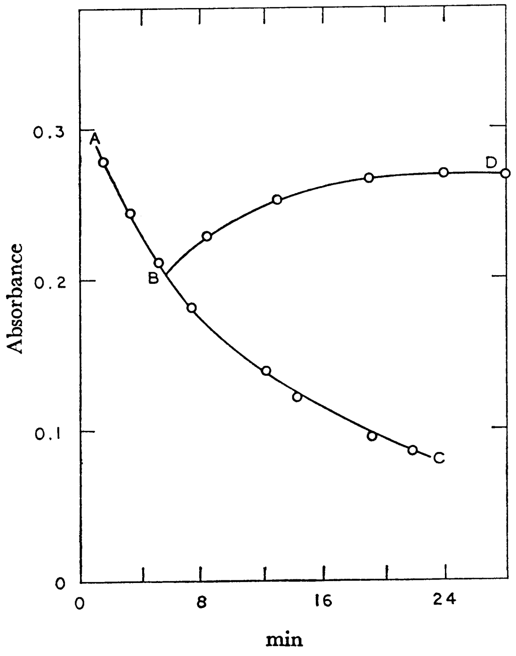

Fig. 4. Reversible nature of the reaction.

Nature of the Reaction. A typical set of kinetic data for the reaction of B.G. in alkaline medium is given in Fig. 3. Here curves 1, 2, 3 and 4 refer to the kinetic runs obtained at pH 9.0, 10.0, 10.35 and 11.04 respectively, the concentration of B.G. being 4×10^{-6}M in all the experiments. In the presence of sufficient hydroxyl ions, the absorbance of the solutions progressively decreased to zero and the solutions became colorless; the color however reappeared gradually with time when the alkali was neutralized by addition of acid. This suggests that the reaction of B.G. with the alkali is reversible in nature, an observation in conformity with that made by Sidgwick and Moore.[8] The reversibility of the reaction was further confirmed by the data presented in Fig. 4. In this figure the portion AB represents the process of fading of color of 4.5×10^{-6}M B.G. solution containing 1.0×10^{-3}M sodium hydroxide. This reaction would have normally proceeded along the curve BC, but as a result of addition of pre-determined quantity of the acid (HCl), which exactly neutralized the alkali present without causing any significant change in volume, the reaction followed the course shown by BD. This portion represents a process in which there is a gradual formation of B.G. This experiment, besides proving the reversibility of the reaction also exposes the complete dependence of the reaction on hydroxyl ion concentration.

In order to make the reaction kinetically simple, sufficient alkali was employed to make the back reaction negligible. Under this condition the equilibrium point of the reaction was shifted to the

TABLE 1. ORDER OF REACTION BY EQUIFRACTIONAL PARTS METHOD

Concentration of B.G. $=4\times10^{-6}$M
Temperature $=25$°C

pH	Initial absorbance a_1	Initial absorbance a_2	Fraction reacted	Time taken t_1 min	Time taken t_2 min	Order of reaction
10.00	0.325	0.260	0.66	26.75	27.00	1.04
	0.325	0.260	0.50	46.00	46.50	1.05
	0.325	0.260	0.40	58.50	58.50	1.00
10.55	0.280	0.200	0.66	18.00	17.50	0.91
	0.280	0.200	0.50	29.00	28.00	0.90
	0.280	0.200	0.40	37.50	37.00	0.96
	0.280	0.200	0.33	46.00	45.50	0.97
11.04	0.264	0.180	0.66	9.00	9.30	1.09
	0.264	0.180	0.50	16.50	16.00	0.92
	0.264	0.180	0.40	21.00	20.50	0.94
	0.264	0.180	0.33	24.50	24.50	1.00
11.20	0.270	0.180	0.66	2.70	2.90	1.18
	0.270	0.180	0.50	4.35	4.85	1.00
	0.270	0.180	0.40	6.35	6.35	1.00
	0.270	0.180	0.33	8.25	8.20	0.98

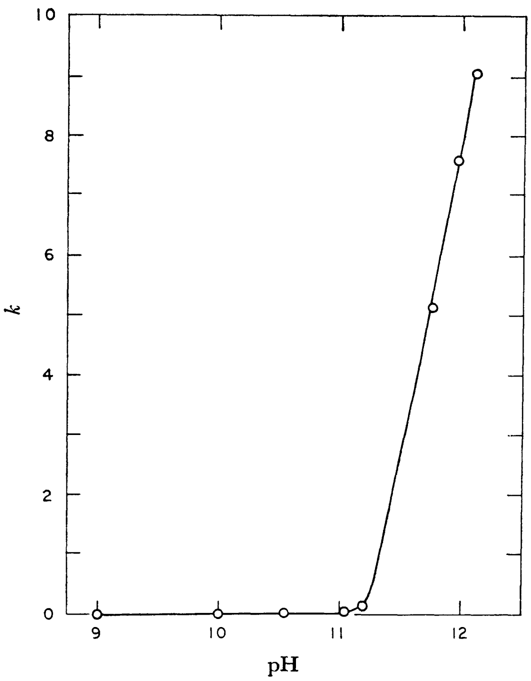

Fig. 5. Variation of velocity constant with pH.

side of the products. Further, less alkali could not be used since spurious rate constants were obtained when the reaction proceeded slowly ($t_{2/1}>1$ hr). The order of the reaction (n) was determined by various methods,[12] *viz.* integration method, graphical method, equifractional parts method, differential method and Guggenheim's method.[13] A typical set of values of n calculated from the data of Fig. 3 by equifractional parts method are given in Table 1. The last column of this table shows that the order of reaction responsible for the decolorization of B.G. corresponds to 1.04 ± 0.14, which indicates that the reaction is first order with respect to B.G. concentration. The values of velocity constant (k) were determined in a number of alkaline buffers in the pH range 9—12. The variation of k with pH is shown in Fig. 5. It is of interest to note from this figure that the value of velocity constant increases slowly up to pH 10.5 but the increase becomes very steep at pH values greater than 10.5. This confirms the marked dependence of the reaction on the OH^- ion concentration.

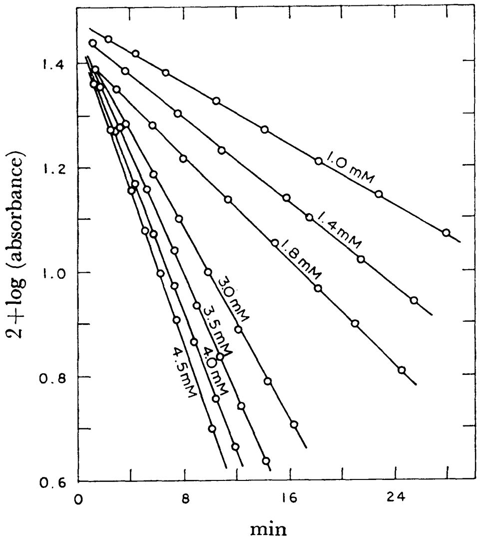

Fig. 6. Kinetic runs at varying sodium hydroxide concentration.

Dependence of Rate on Hydroxyl Ion Concentration. The dependence of the rate of reaction on the hydroxyl ion concentration was investigated by running the reaction at different concentrations of sodium hydroxide. The data obtained are reported in Fig. 6. In all these experiments the initial concentration of B.G. was 4×10^{-6}M while that of sodium hydroxide was varied in the range 1.0—4.5×10^{-3}M. The linear variation of logarithm of absorbance of B.G. with time indicates the applicability of the first order law. The values of the apparent velocity constant (k) obtained from the data of Fig. 6 at different concentrations of hydroxyl ion are given in Fig. 7. It is of interest to note that a linear plot is obtained, which shows that the experimental condition employed in the experiments, *viz.* the excess of OH^- ion concentration, is an important factor responsible for the above observations. This is not an uncommon observation and similar behavior was noticed by Turgeon

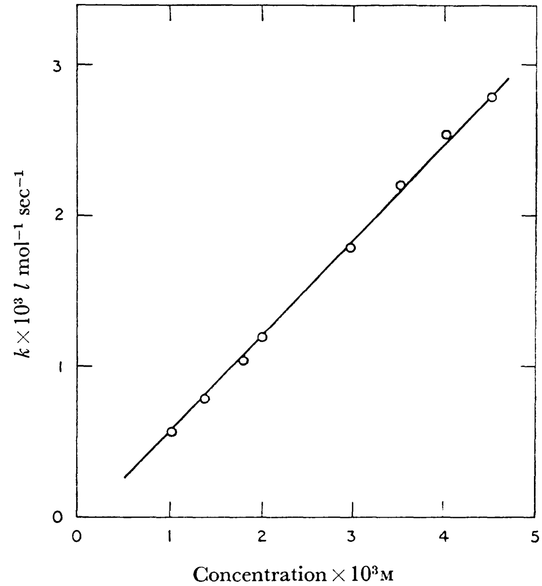

Fig. 7. Dependence of k on sodium hydroxide concentration.

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[12] See for example, A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York (1953), p. 40.

[13] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

and LaMer[14] and Amis and Lamer.[15] The reaction under study is in fact bimolecular but since OH^- present is in much excess, change in its concentration is negligible. The real or true velocity constant was therefore computed by dividing the apparent velocity constant k by the hydroxyl ion concentrations:

$$k' = \frac{2.303(\Delta \log C_{\mathrm{B.G.}})\ l}{(\Delta t)(C_{\mathrm{OH^-}})\ \mathrm{mol \cdot sec}} \quad \text{(i)}$$

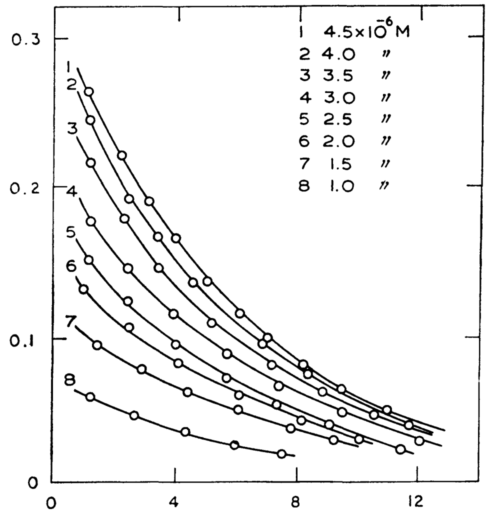

Fig. 8. Dependence of k on B.G. concentration.

Table 2. Effect of concentration of B.G. on k

pH=11.2, Temperature=25°C

Concentration of B.G. $\times 10^{-6}$M	Velocity constant $k \times 10^2$ sec^{-1}
4.5	0.274
4.0	0.274
3.5	0.273
3.0	0.262
2.5	0.260
2.0	0.240
1.5	0.240
1.0	0.211

Dependence of Rate Constant on B.G. Concentration. The effect of concentration of B.G. on the rate constant of the reaction was examined by carrying out the reaction at varying concentrations of B.G. and fixed concentration of hydroxyl ions. The data obtained are given in Fig. 8. It is noted that k is independent of the conecntration of B.G. in the range $(1.0—5.0)\times 10^{-6}$M, as the values of k obtained from Fig. 8 and shown in Table 2 are constant. Similar observations were made earlier for the reaction of murexide[16] and crystal violet[14] with alkali where the value of k' was independent of the initial concentration of murexide and crystal violet. Studies at higher concentrations of B.G. could not be carried out due to low solubility of the reaction product and inapplicability of Beer's Law.

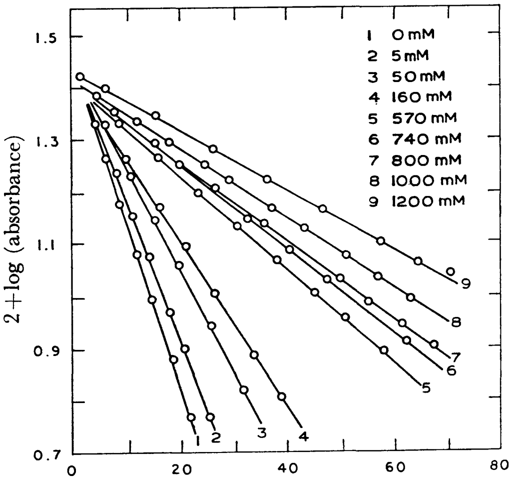

Fig. 9. Kinetic runs at varying ionic strength in aqueous medium.

Table 3. Velocity constants at varying ionic strength in water

Concentration of B.G.$=4\times 10^{-6}$M
Concentration of NaOH$=2\times 10^{-3}$M
Temperature=25°C

Ionic strength μ	$\frac{\sqrt{\mu}}{1+\beta a_i\sqrt{\mu}}$ where $a=0.49$	Apparent velocity constant $k\times 10^3$ sec^{-1}	Real velocity constant k' l mol^{-1}sec^{-1}
0.002	0.043	1.180	0.588
0.0036	0.059	1.070	0.537
0.007	0.081	1.020	0.510
0.052	0.205	0.768	0.384
0.162	0.336	0.561	0.281
0.572	0.552	0.341	0.170
0.742	0.605	0.307	0.153
0.802	0.623	0.288	0.144
1.002	0.671	0.258	0.129
1.202	0.713	0.230	0.115

Dependence of the Rate on the Ionic Strength. Figure 9 gives a typical set of kinetic data obtained at varying ionic strength (μ). The

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[14] J. C. Turgeon and V. K. LaMer, *J. Amer. Chem. Soc.*, **74**, 5988 (1952).

[15] E. S. Amis and V. K. LaMer, *ibid.*, **61**, 905 (1939).

[16] R. K. Chaturvedi, Doctoral dessertation, Agra Univ., 1960.

concentrations of B.G. and NaOH were kept constant, while the ionic strength was varied in the range 0.002—1.2. In the calculation of μ of the reaction system, the concentration of B.G. (4×10^{-6}M) was not taken into account due to its extreme low value as compared to the added neutral electrolyte. Prior to carrying out investigations on the influence of μ on k', it appeared necessary to examine the effect of the neutral salt, potassium nitrate, on the absorption spectrum of B.G. Experiments indicated that potassium nitrate exerts no influence on the absorption spectrum of B.G. which shows the same characteristic absoprtion maxima at $\lambda=625$ and 426 mμ. It may be seen from the data of Fig. 9 that increase in ionic strength of the system decreases the rate of reaction of B.G. The value of k' at different ionic strengths are summarized in Table 3. These data were analyzed by the Brϕnsted equation, which gives the following relation between k' and μ at 25°C.

$$\log k' = \log k_0' + 1.02 Z_A Z_B \sqrt{\mu} \qquad \text{(ii)}$$

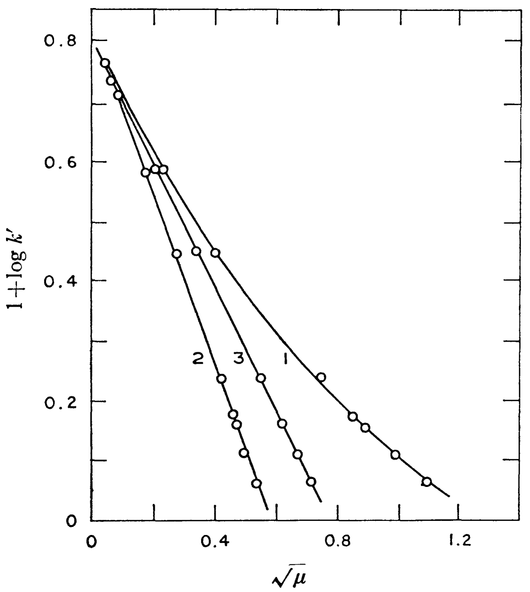

Fig. 10. Variation of velocity constant with ionic strength in water.

where Z_A and Z_B are the charges on the reacting species. According to this equation a plot of log k' *vs.* $\sqrt{\mu}$ should be a straight line with a slope equal to 1.02 $Z_A Z_B$. The variation of log k' *vs.* $\sqrt{\mu}$ is shown in Fig. 10 (curve 1). It may be noted from this plot that at higher values of μ, the points do not lie on a straight line suggesting thereby the non-applicability of Brϕnsted's equation at higher values of μ. However, if a straight line is drawn by taking into consideration the data below 0.09 μ, the slope of it gives a value of -0.82 for $Z_A Z_B$. The non-applicability of the above equation at higher ionic strengths has been attributed to the inaccurate values of activity coefficients computed from the Debye-Hückel equation, and has been observed by numerous workers. Guntelberg suggested the use of modified form of the Debye-Hückel equation which is as follows:

$$\log k' = \log k_0' + \frac{1.02 Z_A Z_B \sqrt{\mu}}{1+\sqrt{\mu}} \qquad \text{(iii)}$$

Plot 2 of Fig. 10 represents the variation of log k' *vs.* $\sqrt{\mu}/(1+\sqrt{\mu})$. It is instructive to find that the plot is linear over a wide range of μ and the $Z_A Z_B$ as computed from the slope of this plot is -1.36 which is higher than unity. Scatchard[17] made a further modification of the Debye-Hückel equation and this modification when introduced into the Brϕnsted-Christiansen equation gave the relation

$$\log k' = \log k_0' + \frac{2A Z_A Z_B \sqrt{\mu}}{1+\beta a_i \sqrt{\mu}} \qquad \text{(iv)}$$

A and β are Debye-Hückel constants and a_i is an ionic interaction parameter.[18] The computation of a_i was done by observing the influence of different values of a_i on the constancy of Eq. (iv). The value of a_i which gives a constant value of log k_0' for all the observed values of k' at different μ, over the whole range of ionic strength investigated, was calculated by the method of successive trials. The effect of varying ionic parameter on the constancy of Eq. (iv) is shown in Fig. 11. The calculations were made by taking the values of $2A$ and β as 1.02 and 0.329×10^8 in water at 25°C respectively. According to Eq. (iv) for a correct value of a_i the plot of log k_0' and $\sqrt{\mu}$ will be a straight line parallel to $\sqrt{\mu}$ axis. Interesting enough is to note that curves 1 and 3 of Fig. 11, which give the variation of log k_0' with $\sqrt{\mu}$ at ionic parameter values equal to 0.5 and 4 Å respectively, are not straight lines parallel to x-axis, but are rather diverging lines. This suggests that the correct value for a_i for B.G. in water lies between 0.5 and 4 Å. Plot 2 in Fig. 11 which represents a linear variation of log k_0' *vs.* $\sqrt{\mu}$ was obtained by putting a_i equal to 1.5 Å, suggesting thereby that 1.5 Å is the correct value of interionic attraction parameter for B.G. in water.

Now putting this value of a_i in Eq. (iv) the variation of log k' *vs.* $\sqrt{\mu}/(1+\beta a_i\sqrt{\mu})$ was examined. The plot thus obtained is shown in Fig. 10 (plot 2). From the slope of this plot the value of $Z_A Z_B$ corresponds to -1.01. It is instructive to compare this value with other values of $Z_A Z_B$ computed earlier which corresponded to -0.82 and -1.36. It may, therefore, be concluded that the Brϕnsted-Christiansen-Scatchard equation gives a value of $Z_A Z_B$ which is nearest to unity. This value suggests that the reaction is taking place between oppositely

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17) G. Scatchard, *J. Amer. Chem. Soc.*, **52**, 52 (1930).
18) V. K. LaMer, *J. Franklin Inst.*, **225**, 709 (1938).

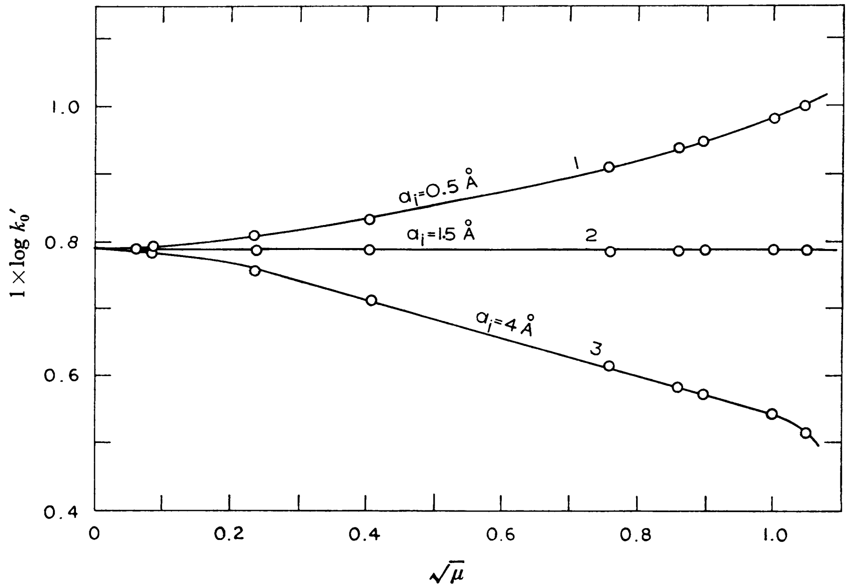

Fig. 11. Effect of varying ionic parameter on the constancy of Eq. (iv) in water.

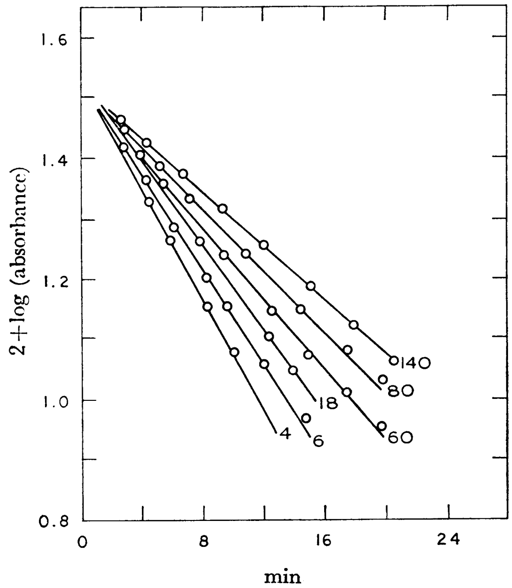

Fig. 12. Kinetic runs at varying ionic strength in 40% acetone-water medium.

charged species of unit charges.

Salt Effect in 40% Acetone-Water Mixtures. The studies of salt effects were extended to 40% acetone-water mixtures, to determine the value of interionic attraction parameter and hence indirectly the extent of solvation of B.G. in mixed media. To investigate this, kinetic runs were made in 40% acetone-water at varying ionic strength but with fixed concentration of B.G. (4×10^{-6}M) and NaOH (2×10^{-3}M). A typical set of data obtained are given in Fig. 12. The linearity of plots indicates the first order nature of the reaction in this medium. The velocity constant k' was found to decrease with increase in the ionic strength, an observation similar to that obtained in aqueous medium. Analysis of the data for Eqs. (ii) and (iii) yielded the results shown in Fig. 13. Curves 1 and 2 of this figure give the variation of log k' *vs.* $\sqrt{\mu}$ and $\sqrt{\mu}/1+\sqrt{\mu}$ respectively. It is quite evident that plot 1 is a

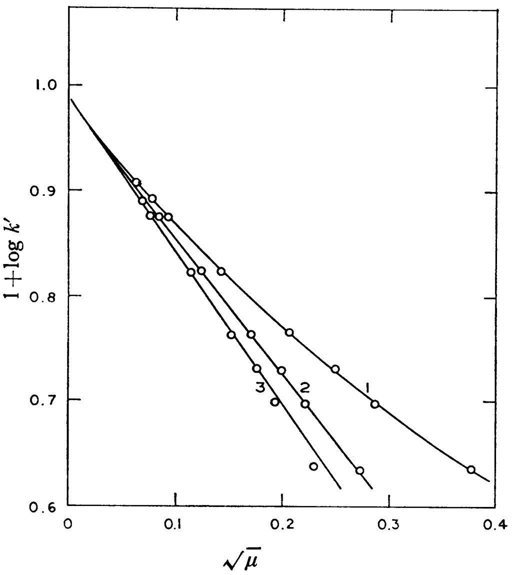

Fig. 13. Variation of k' with ionic strength in 40% acetone-water.

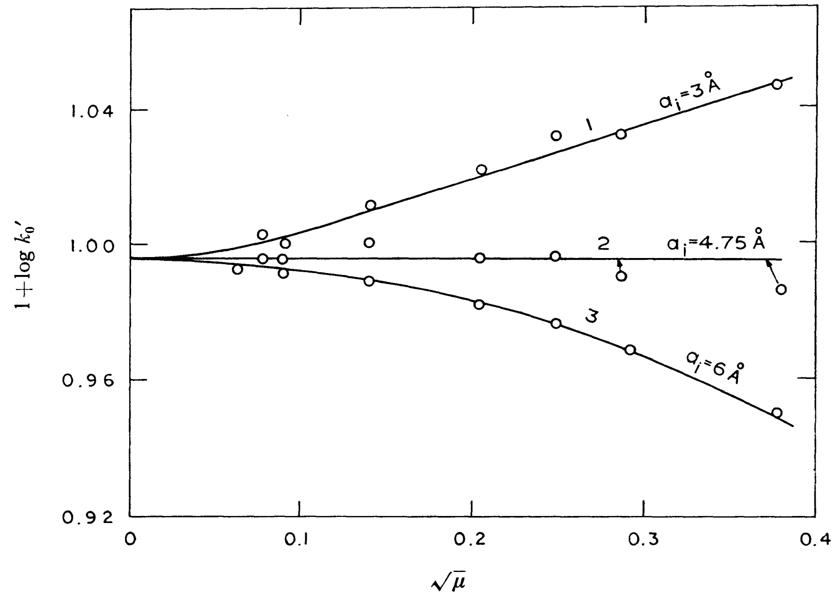

Fig. 14. Effect of varying ionic parameter on the constancy of Eq. (iv) in 40% acetone-water.

curved line and not a straight line, which indicates the non-applicability of Eq. (ii) at higher μ, while plot 2 is linear over a wide range of μ. The slopes of plots 1 and 2 gave a value of Z_AZ_B equal to -0.89 and -1.25 respectively.

For the application of Eq. (iii) the value of a_i of B.G. in acetone-water medium was determined as described earlier. The results obtained are summarized in Fig. 14, which gives the effect of varying ionic parameter on the constancy of Eq. (iv) in 40% acetone-water medium. For the calculations β was taken to be equal to 0.38×10^8 at 25°C. It is of interest to note from Fig. 14 that plots 1 and 3 obtained by putting a_i equal to 3 and 6 Å are non-linear, while plot 2 obtained by putting a_i equal to 4.75 Å is linear. Thus the value of ionic attraction parameter corresponds to 4.75 Å in 40% acetone-water, which is substantially larger than its value in aqueous medium (1.5 Å). Utilizing the value of $a_i=4.75$ Å in 40% acetone-water, the plot of log k' *vs.* $\sqrt{\mu}/(1+\beta a_i\sqrt{\mu})$ (Fig. 13, plot 3) gave a value of -1.30 for Z_AZ_B, which indicates that the reaction is taking place between oppositely charged species of unit charge. In a ternary system a too precise physical meaning cannot be attached to the parameter a_i. Hence from its larger value in the acetone-water mixture it can be presumed that B.G. ion is solvated to a greater extent in this solvent than in water. In agreement with Sheppard and Geddes[19] it can be suggested that in the B.G. ion the hydrophilic groups at the end of benzene ring are preferentially surrounded by water molecules whereas acetone molecules are probably bound to the hydrophobic parts. These bound acetone molecules will make the B.G. ion appear larger during its reaction in alkaline medium with OH^- ion, as indicated by the larger value of a_i. It appears therefore that it approaches the central carbon atom from a direction perpendicular to the plane of B.G. ion. A similar type of behavior was observed by Turgeon and LaMer[14] in the reaction of crystal violet.

The author is indebted to Professor N. A. Ramaiah of National Sugar Institute, Kanpur for valuable and helpful discussions during the progress of this work.

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[19] S. E. Sheppard and A. L. Geddes, *J. Amer. Chem. Soc.*, **66**, 1995 (1944).