Studies of the Electrolytic Conductance of a Dye Solution. I. Complex Formation in an Aqueous Solution of the Mixture of Chlorazol Sky Blue FF and Chrysophenine G

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As is commonly known, the McBain effect[1] caused by the aggregation of dye ions is observed in most direct dyes in an aqueous solution[2]. A typical McBain effect has been found in Methylene Blue[3], the basic dye, and later it was confirmed by a change in the absorption spectrum that this dye forms an aggregate with an increase of its own concentration[4].

Recently, studies have come to be made, by means of spectrophotometry, of the complex formation of unlike dye molecules in mixtures in an aqueous solution[5-7]. These studies have discovered the important fact that Chlorazol Sky Blue FF and Chrysophenine G form complexes in definite mole ratios[6,7]. In the case of Methylene Blue in water mentioned above, the evidence of its aggregation was found in the measurements of conductance[2] as well as in those of the absorpsion spectrum[8]. In the same way, it may be expected that a proof of complex formation between Chlorazol Sky Blue FF and Chrysophenine G will also be derived from the conductance measurement.

In the present paper, the authors will investigate the complex formation of a two-component dye mixture in an aqueous solution from the view point of electrolytic conductance. Unfortunately, however, in the field of conductance study, there is no rule such as Beer's law in the field of light absorption. Though a theoretical treatment of the conductance of a mixed electrolyte solution has been attempted by Onsager and his co-workers[9], no application of the theory to experimental results has yet been made. Considering that we can not yet analyze quantitatively the conductance of dyes, even in a single solution, much less can we expect to perform a satisfactory analysis of dye mixtures. Accordingly, as a first step towards a preliminary investigation, attention is directed to the examination of how the complex formation of Chlorazol Sky Blue FF and Chrysophenine G is reflected in the conductance of a mixed system. Also, we will examine how the complex formation is to be understood in relation both to the conductance characters of the mixture and to those of its components.

Experimental

The dye samples used were Chlorazol Sky Blue FF and Chrysophenine G, both of which had already been used in other reports by the present authors[7]. Potassium chloride (the extra pure grade of the Japan Pharmacopeia) was once recrystallized from distilled water. Sodium chloride (the extra pure grade of the Japan Pharmacopeia) was purified once by recrystallization from a water-alcohol solution. Conductance water was prepared from a specially-designed distilling apparatus; its specific conductance upon measurement was $(5\sim10)\times10^{-7}$ mho/cm. at 30°C.

Conductance measurement was carried out by means of the usual Wheatstone bridge. The frequency of the oscillator was 800 cycle/sec. A null point was determined with a cathode ray oscilloscope. Waves on the oscilloscope vanished in the cases of resistance under 10^5 ohm. In the other cases, however, the minimum point was regarded as a null point. The volumes of the four conductance cells employed were from 15 to 20 ml. The electrodes of two of the cells were square platinum plates $19\times13\times0.3$ mm³, while those of the other two were $15\times13\times0.3$ mm³; all of them had been platinized beforehand. The cell constants were determined by measuring the conductance of a 0.01 D aqueous potassium chloride solution[10] at 30°C. All the cell constants were redetermined every one or two months.

During the preparation and measurement of solutions, attention was paid to avoid the effect of the carbon dioxide in air. For this purpose,

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[1] J. W. McBain, *Kolloid Z.*, **12**, 256 (1913).

[2] N. Ando, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaisi*), **64**, 1305, 1431 (1943); F. H. Holmes and H. A. Standing, *Trans. Faraday Soc.*, **41**, 568 (1945).

[3] C. Robinson, ibid., **31**, 245 (1935).

[4] E. Rabinowitch and L. F. Epstein, *J. Am. Chem. Soc.*, **63**, 69 (1941); D. R. Lenin and R. Vickerstaff, *Trans. Faraday Soc.*, **43**, 491 (1947).

[5] S. M. Neale and W. A. Stringfellow, *J. Soc. Dyers Colourists*, **59**, 241 (1943); Y. Tanizaki T. Kobayashi and N. Ando, This Bulletin, **32**, 119 (1959); T. Kobayashi, Y. Tanizaki and N. Ando, ibid., **32**, 675, 680 (1959).

[6] A. N. Derbyshire and R. H. Peters, *J. Soc. Dyers Colourists*, **72**, 268 (1956).

[7] T. Kobayashi Y. Tanizaki and N. Ando, This Bulletin, **33**, 661 (1960).

[8] Y. Tanizaki and N. Ando, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 343 (1957).

[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 3rd. Ed., Reinhold, New York (1958), pp. 105-117.

[10] International Critical Tables, **6**, 230, Table 2, Parker Solution.

desired volumes of distilled water or solutions were measured out in flasks through burettes under the carbon dioxide-free conditions by the use of a particular device; thus, the sample liquids were prepared without being exposed directly to the open air. The mother solution and distilled water were stored once in each stock bottle, and then sample solutions were prepared from them within 24 hr. All of the concentrations were determined by weight. Each series of solutions in concentrations was prepared by diluting a mother solution. All solution measurements prepared were carried out within two days. The three thermostated water bath were adjusted at 30, 40 and 60°C and were constant within ±0.02°C. The resistance of a cell containing a solution became constant over 10 min. after it had been soaked in a bath. In this report, the observed values are of 20 min. after. The resistance of water as a solvent approached a constant value in about 10 min., but it did not give a stationary value, showing an inclination to decrease slightly with the lapse of time. However, in this case the resistance after 20 min. was employed as an observed value of the water used.

Results and Discussion

Concerning the two series of binary mixtures at the respective constant ratios of Blue (Chlorazol Sky Blue FF) and Yellow (Chrysophenine G), the values of the observed specific conductance, κ_{obs}, divided by the total equivalent concentration of the dyes involved have been plotted against the square root of the total concentration. This provides the white and the half black circles in Fig. 1. A black circle in this figure represents the value, $\kappa_{sum}/(C_F+C_G)$, calculated by the following expressions, using the specific conductances of the components in a single solution:

$$\kappa_{sum}=k_F+\kappa_G=(C_F\Lambda_F+C_G\Lambda_G)\times 1/1000 \qquad (1)$$

$$\kappa_{sum}/(C_F+C_G)=(f_F\Lambda_F+f_G\Lambda_G)\times 1/1000 \qquad (2)$$

Here, C_F and C_G are the equivalent concentrations, Λ_F and Λ_G, the equivalent conductances, and $f_F=C_F/(C_F+C_G)$ and $f_G=C_G/(C_F+C_G)$, the equivalent fractions of Blue and Yellow respectively. The "sum" value defined here may give a standard for deciding whether or not the observed conductance is abnormally increased in a mixed system. This is because the value of κ_{sum} implies the conductance of mixture when no interaction is produced by mixing between ion species; therefore, κ_{sum} should be larger than κ_{obs}, according to the general tendency of electrolyte solutions for the mobility to decrease with an increase in the concentration. In the comparison of "sum" and "obs" conductances in the mixture, it may be convenient to express the conductance in the very form of κ divided by the total equivalent concentration at which κ was observed (Eq. 2). This form is considered to have the physical meaning that it is the mean conductance applied to a one-gram equivalent of the cations and anions in the solution.

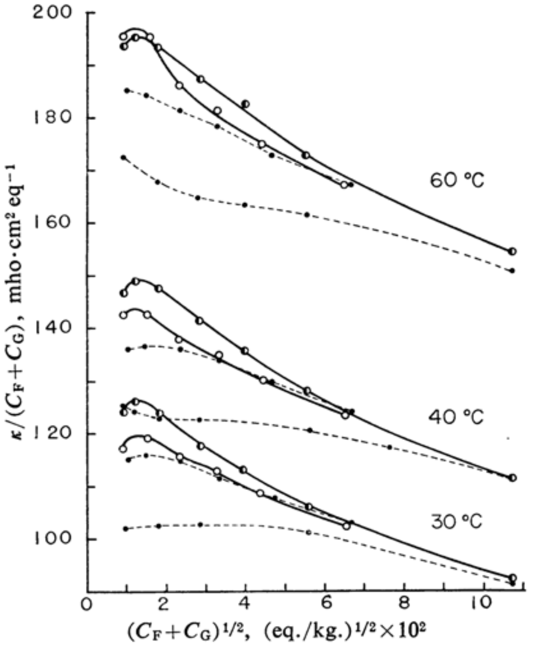

Fig. 1. Relation of conductance of the mixture of Blue and Yellow to square root of its total equivalent concentration.
In each series the concentration ratio of Blue and Yellow is constant.
○: $C_G/C_F=0.1034$ ◐: $C_G/C_F=1.1716$
●: sum

The conductance curves in Fig. 1 indicate the relation,

$$\kappa_{obs}/\sum C \geqq \kappa_{sum}/\sum C \qquad (3)$$

in the greater part in the concentration region observed here. In Eq. 3, $\sum C$ means (C_F+C_G). This fact indicates that new ion species having a larger mobility per charge than any respective component are produced in this system. Considering the fact, already clarified by absorption spectra, that in such a system Blue (F) and Yellow (G) form the (FG and FG_2) complexes[6,7], the new ion species mentioned above may be regarded as such complexes.

In the two series of constant mixing ratios shown in Fig. 1, the differences between the corresponding conductances, $\kappa/\sum C$, of "obs" and "sum" are greater at the lower concentrations and decrease with an increase in the concentration. This tendency appears more remarkably in the case of $C_G/C_F=1.716$ than when the values is 0.1034. The correlations of "obs" and "sum" in the other series, which are not illustrated here, showed a similar tendency, but only in the case of the especially large ratio of $C_G/C_F=4.811$ did the correlation at higher concentration go into the reverse tendency, i. e. $(\kappa_{obs}/\sum C)<(\kappa_{sum}/\sum C)$. In a series of constant ratios of mixing, the concentration ratio of the complexes formed to the respective residual components is considered to be nearly constant. Consequently, it may be said that the above fact indicates that the decreasing conductance rate of the complexes with its increasing concentration is greater than those of components. Moreover, this can easily be accepted because the ionic charges of complexs FG and FG_2 are 6 and 8 respectively.

Thus, in the series of constant mixing ratios, the correlation between $\kappa_{obs}/\sum C$ and $\kappa_{sum}/\sum C$ varied with the total concentration, even when the concentration ratio of the complex to the residual components is constant. However, the system in which the total equivalent concentration is kept constant will be give rise to the following advantage over the above system: the changes in the respective equivalent conductances of the complexes formed and in the residual dye components with the mixing ratio may be considered to be not very large[*1]. If the $\kappa_{obs}/\sum C$ curve agaist f reveals a marked bend point, with a system involving ion species of respective constant equivalent conductances, the fraction value for this point could be closely related to the composition of a complex formed (see Appendix). In the present case, it can be considered that each conductance value is constant in the neighborhood of the central part of f, so that a conclusion will be derived in the way just mentioned.

The $\kappa_{obs}/\sum C$ values for the total concentration of 2.25×10^{-4} eq./kg. in several mixture-compositions, obtained from Fig. 1 and from other, unshown ones, against the equivalent fraction of the component are expressed by white circles in Fig. 2. Here, black circles represent $\kappa_{sum}/\sum C$ values. The $\kappa_{obs}/\sum C$ and $\kappa_{sum}/\sum C$ values are connected by broad lines and broken ones respectively. This figure shows that $(\kappa_{obs}/\sum C)>(\kappa_{sum}/\sum C)$ in the whole region and that the differences between them are largest at about $f_G=0.5$. Inspecting in more detail, $\kappa_{obs}/\sum C$ at first increases rapidly, forms a shoulder, and then comes to a maximum value with an increase in f_G from 0.

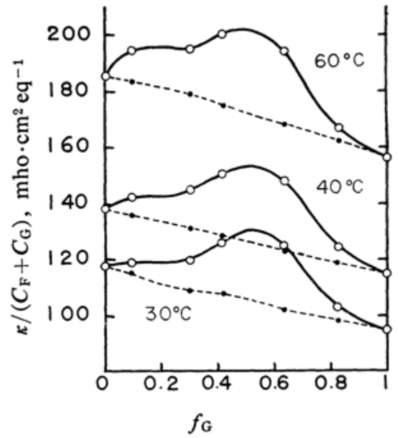

Fig. 2. Relation of conductance of the mixture of Blue and Yellow to equivalent fraction of its components.
The total equivalent concentration is kept at 2.25×10^{-4} eq./kg.
○: obs. ●: sum

This tendency appears more clearly at higher temperatures.

The same relation at six different concentrations of $(1\sim25)\times10^{-4}$ eq./kg. are shown in Fig. 3. Roughly speaking, the $\kappa_{obs}/\sum C$ curves at the several concentrations are similar

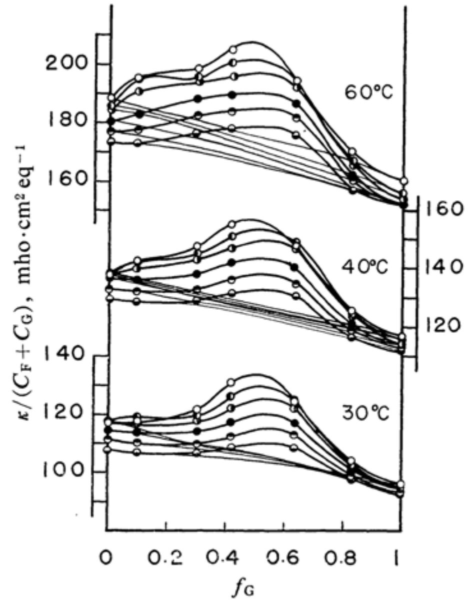

Fig. 3. Relation of conductance of the mixture of Blue and Yellow in six different total equivalent concentrations to equivalent fraction of its components.
The total equivalent concentrations are as follows; ($\times10^{-4}$ eq./kg.)
○: 1 ◐: 2.25 ◑: 4, ●: 9
◓: 16 ◒: 25 —: sum

[*1] This concept is based on the fact that, in this series, the equivalent concentration of sodium ions and the sum of those of dye ions are constant. That the electrical effect on an ion due tothe other ions in a solution is constant, however, can be said of the systm in which the constant is not the total concentration but the ionic strength Γ, i. e., $\sum n_i z_i^2$ (n_i and z_i: the number and the charge of the i-th ion respectively). Since the value in this series changes because of the different charges of the two dye anions, the above assumption can not be exactly true. (See Ref. 9, p.117, Eq. 4-3-69).

to one another and show that $(\kappa_{\text{obs}}/\sum C) > (\kappa_{\text{sum}}/\sum C)$. However, the maximum points of the curves show a slight tendency to deviate from 0.5 to a large value in f_G with an increase in the total concentration. The shoulders of the curves observed at about $f_G=0.15$ in Fig. 2 disappear with an increase in the concentration.

On the other hand, as is well known, the aggregation of many dye anions is promoted by the presence of another electrolyte[8]. Thus, in this case each Blue or Yellow anion might be promoted in its aggregation by the effect of the partner dye. Consequently, the McBain effect caused by this effect must be taken into account. The promotion effect of the self-aggregation of the dye anion will be produced mainly by the co-existing electrolyte. Therefore, the magnitude of this effect is supposed to be estimated from that produced by the equivalent amount of sodium chloride. From this viewpoint, measurements of the binary system of Blue and sodium chloride were carried out in the first place. In Fig. 4 are shown the $\kappa/\sum C$ values, where $\sum C$ means (C_F+C_{NaCl}), versus the square roots of the total equivalent concentrations of two cases in these results. The solid and broken lines represent $\kappa_{\text{obs}}/\sum C$ and $\kappa_{\text{sum}}/\sum C$ respectively. This figure indicates that $(\kappa_{\text{obs}}/\sum C) < (\kappa_{\text{sum}}/\sum C)$ in the greater part, but that at a very low concentration a slight inverse relation appears. This would suggest that the aggregation of Blue anions is promoted more or less by the effect of sodium chloride. The $\kappa/\sum C$ values versus equivalent fractions for the binary mixture of Blue and sodium chloride, corresponding to the dye mixture in Fig. 3, are shown in Fig. 5. The circles represent the observed values and are connected by broad lines. In order to avoid superposition of plots, the $\kappa/\sum C$ axes for respective concentrations are shifted from one another. This figure shows that the "obs" value is larger than the "sum" value when the total concentration is below 4×10^{-4} eq./kg. This tendency is clearer at a larger f_{NaCl} (or at a smaller f_F) value. On the other hand, when the total concentration is above 4×10^{-4} eq./kg., the "obs" value is smaller than the "sum" value over the whole region. A similar tendency appears for three different temperatures, though slightly clearer for higher temperatures. In short, the promotion of the self-aggregation of Blue anions in mixture with sodium chloride is certainly recognized by the increase of $\kappa_{\text{obs}}/\sum C$ in low concentrations, as has been shown above, but its increase is too

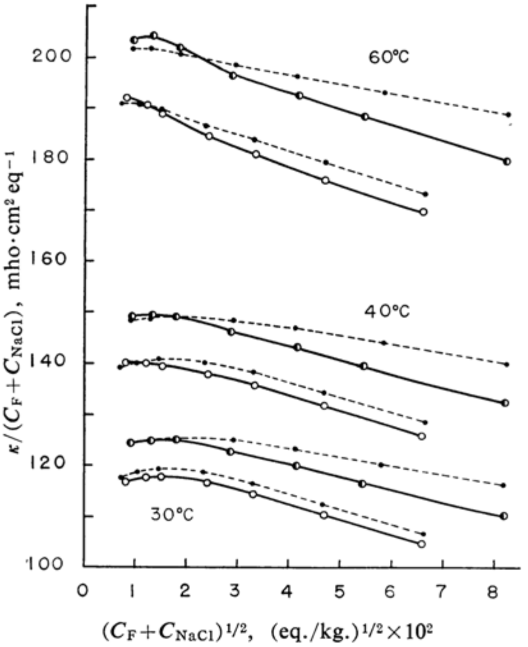

Fig. 4. Relation of conductance of the mixture of Blue and sodium chloride to square root of its total equivalent concentration.
In each series the concentration ratio of Blue and sodium chloride is constant.
◐: $C_{NaCl}/C_F=0.6970$
○: $C_{NaCl}/C_F=0.1015$ ●: sum

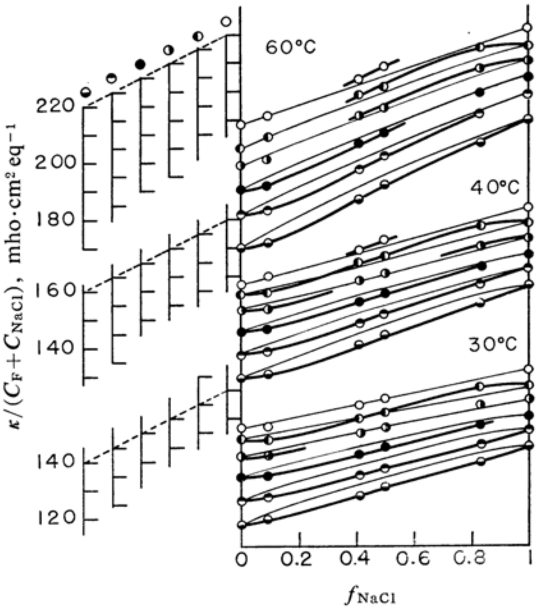

Fig. 5. Relation of conductance of the mixture of Blue and sodium chloride in six different equivalent concentrations to equivalent fraction of its components.
The total equivalent concentrations are as follows; $(\times10^{-4}$ eq./kg.)
○: 1 ◐: 2.25 ◑: 4 ●: 9
◓: 16 ◒: 25 —: sum

small to be compared with that in mixture with Yellow; further, the $\kappa_{obs}/\sum C$ curves in Fig. 5 do not show a tendency to have their maxima at $f=0.5$ as do these in Fig. 3.

Next, the results obtained in the same way with the binary mixture of sodium chloride and Yellow are shown in Fig. 6. From Fig. 6 it is clear that, in the region where the total concentration is below 9×10^{-4} eq./kg., the relation $(\kappa_{obs}/\sum C)>(\kappa_{sum}/\sum C)$, where $\sum C$ indicates $(C_{NaCl}+C_G)$, appears for all equivalent fractions more clearly in the case of smaller f, and that in the region above this concentration the relation is reversed. As a whole, the results of this figure are similar to those of Blue and sodium chloride.

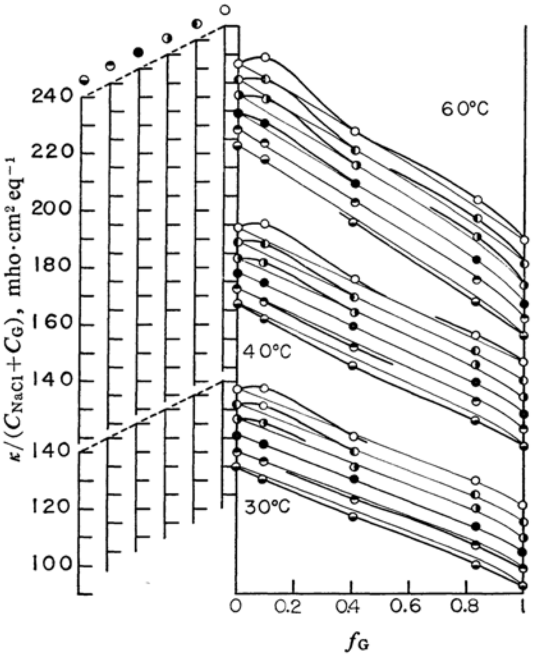

Fig. 6. Relation of conductance of the mixture of Yellow and sodium chloride in six different equivalent concentrations to equivalent fraction of its components.
The total equivalent concentrations are as follows; ($\times10^{-4}$ eq./kg.)
○: 1 ◐: 2.25 ◑: 4 ●: 9
◓: 16 ◒: 25 —: sum

To sum up these results, we can certainly say that the conductance of Blue or Yellow is affected by sodium chloride, and also that the difference in "obs" and "sum" values in a mixture of the dye and sodium chloride is not so large as that in the combination of Blue and Yellow. Accordingly, it may probably be considered that the largest difference in "obs" and "sum" at about the same equivalent fraction of Blue and Yellow in Fig. 3 is due to the complex formation of FG_2. Thus, the formation of FG_2 is concluded from the above discussion, while the formation of another complex, namely FG, is found spectrophotometrically. According to the above argument, an abnormal feature responsible for FG is to appear at $f_G=1/3$, but Fig. 3 does not show any distinctive peak or shoulder at this part of the curve. Comparing the two parts into which a curve of Fig. 3 is divided at a maximum, the difference between $\kappa_{obs}/\sum C$ and $\kappa_{sum}/\sum C$ is greater in the region richer in F than in G. This seems to correspond to the formation of FG.

The shoulder of the $\kappa_{obs}/(C_F+C_G)$ curve at about $f_G=0.15$ in Fig. 3 may be explained by the fact that Yellow is accelerated in its aggregation by the presence of Blue, since the shoulder corresponds to the abnormal increase of $\kappa_{obs}/(C_{NaCl}+C_G)$ obtained with the same fraction of a mixture of sodium chloride and Yellow (Fig. 6).

In Figs. 2 and 3, it must be noticed that the relative increase in conductance due to the complex formation becomes larger with the temperature. If the complex formation is only considered in the system, this does not agree

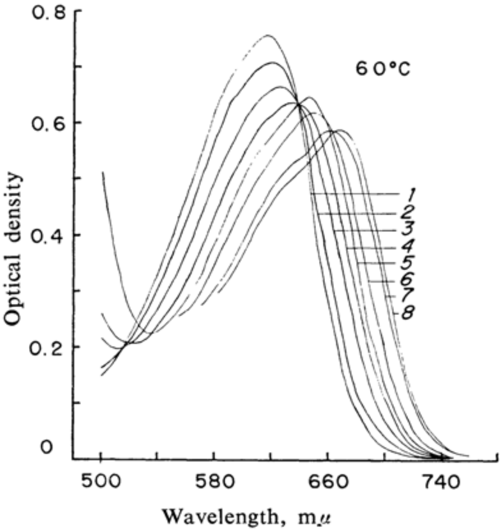

Fig. 7. The visible absorption spectra of Chrysophenine G-Sky Blue FF aqueous solution: temperature, 60°C; cell, 2 cm.

	Chrysophenine G mol./l.	Sky Blue FF mol./l.
1	0	4.000×10^{-6}
2	1.016×10^{-6}	4.000×10^{-6}
3	4.000×10^{-6}	4.000×10^{-6}
4	8.072×10^{-6}	4.000×10^{-6}
5	3.412×10^{-5}	4.000×10^{-6}
6	1.211×10^{-4}	4.000×10^{-6}
7	3.998×10^{-4}	4.000×10^{-6}
8	8.023×10^{-4}	4.000×10^{-6}

with the general rule that the amount of complex formed should decrease with the temperature. This will be understood by taking into account the self-aggregation which competes with the complex in decomposing by raising the temperature. In this case the self-aggregation should be considered to be more unstable than the complex. However, at the present stage, thermodynamic values of the self-aggregation which can be compared with those of the complex have not yet been obtained.

Some results, however, may support the above consideration. It has been reported that Blue and Yellow in an aqueous solution form a 1 : 1 and a 1 : 2 complex at room temperature[7]. According to further investigation[11], it may be concluded that even at 60°C the same complexes are formed, as is shown by the well-defined isosbestic points illustrated in Fig. 7. The estimated enthalpy changes show in this case -24 kcal./mol. for $F + G \rightarrow FG$ and -20 kcal./mol. for $FG + G \rightarrow FG_2$. These values are larger than the adsoption energies obtained for the respective components of the cellulose.

Next, the conductance curve of Blue in the single aqueous solution is shown in Fig. 8. It indicates that the McBain effect, which is due to the aggregation considered, comes to disappear with an increase in the temperature; the curve becomes nearly a straight line at 60°C, and then at 80°C it is bent conversely[*2]. In this case it must be said that at 80°C, the highest temperature observed, the dye anion is closest to the single and that at 30°C the aggregation number is largest.

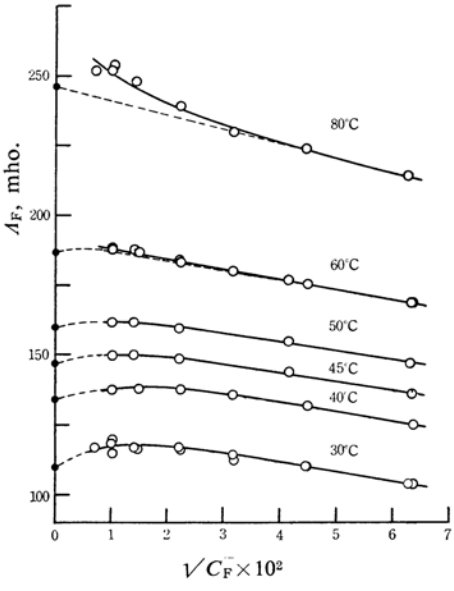

Fig. 8. Conductance of Chlorazol Sky Blue FF in aqueous solution. C_F stands for the equivalent concentration.

Assuming that the straight line of the higher concentration region at 80°C is due to the single dye ion species, the line is extraporated to obtain Λ_0. The Walden product, $\Lambda_0\eta_0$ (η_0: viscosity coefficient of water), is evaluated; then the correspoding Λ_0's at the respective temperatures are estimated by the Walden rule. The results are indicated in black circles in Fig. 8. When the black circles are connected with the corresponding observed curves, the broken lines shown in Fig. 8 are obtained. These curves evidently reveal the change in aggregation against the temperature. It may be supposed from the above discussion that Blue is nearly a single-dye ion species, though not quite a single one.

From the above interpretation, it is proper to consider that the compactness of the complexes in the system under consideration is stronger than that of the self-aggregates and that, for this reason, the higher the temperature, the larger the difference between the $\kappa_{obs}/(C_F+C_G)$ value and the corresponding $\kappa_{sum}/(C_F+C_G)$ value.

Summary

The conductances of aqueous solutions of Chlorazol Sky Blue FF (Blue), Chrysophenine G (Yellow), sodium chloride and their binary mixtures at various constant ratios have been measured. The conductance observed with a mixture of Blue and Yellow increased abnormally compared with that obtained by the sum of individual dye conductances; the difference between the observed and the sum values reached a maximum at about the same fraction of the equivalent concentration of component dyes. A similar relation of the conductance against the fraction of the equivalent concentration of components, obtained with mixtures in which component dye was substituted by sodium chloride, did not always show a coincidence between the observed value and the sum one. The difference, however, was much smaller than that obtained with dye mixtures. Thus, the abnormal increase described above may be attributed to the formation of complexes of Blue and Yellow;

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[11] T. Hoshi, Y. Tanizaki and N. Ando, to be published.

[*2] The increase of conductance at the very low concentration is interpreted as due to the dissociation of the OH group. (cf. C. Robinson and H. E. Garrett, *Trans. Faraday Soc.*, 35, 771 (1939).) Because, comparing the Walden products for the low concentration region at 80 and 60°C, that of the former is considerably larger than that of the latter, indicating the iecrease of charge per species.

a 1 : 1 complex and a 1 : 2 complex, consisting of Blue and Yellow already known, were sufficiently reflected in the conductance curve, especially in a 1 : 2 complex.

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Appendix

A general theory of the relationship between the composition of the complex and that of the solution has been set forth by Eaton[12]. This theory will be applied to conductance as follows. Here we assume that the conductance of an electrolyte is linear to its concentration, C, with a gradient $\Lambda/1000$. For a binary mixture of A and B, whose total equivalent concentration is fixed, the Λ curve against the equivalent fraction f_A (or f_B) becomes a line connecting Λ_A and Λ_B, provided that no interaction exists between A and B, as follows:

$$\Lambda \equiv 1000\kappa_{\mathrm{sum}}/(C_A+C_B)=\{f_A\Lambda_A+(1-f_A)\Lambda_B\}$$

When p mol. of A react with q mol. of B to form r mol. of complex AB: $p\mathrm{A}+q\mathrm{B}=r\mathrm{AB}$, then

$$1000\kappa_{\mathrm{obs}}/(C_A+C_B)=\{f_A\Lambda_A+(1-f_A)\Lambda_B\}$$
$$+\{\Lambda_C-ap\Lambda_A/(ap+bq)-bq\Lambda_B/(ap+bq)\}f_C$$

where f_C is the equivalent fraction of the complex formed and a and b the charges of A and B respectively. Therefore, $\kappa_{\mathrm{obs}}/(C_A+C_B)$ is linear to f_C. f_C reaches its maximum at $f_A=ap/(ap+pq)$ in the case of $a=b$. Accordingly, we can calculate p/q from the f_A value of $\kappa_{\mathrm{obs}}/(C_A+C_B)$ at its maximum. However, when $a\neq b$, $f_{A(f_C=\max)}$ is dependent on the equilibrium constant, K, and $f_{A(f_C=\max)}=ap/(ap+bq)$ only when $K=\infty$. Though in the present case of the combination of Blue and Yellow, the charges are 4 and 2 respectively, namely $a\neq b$, it may safely be said that the above relation is applicable to this combination, as, for instance, the equilibrium constant of $\mathrm{F}+2\mathrm{G}=\mathrm{FG}_2$ is 3×10^{10}.

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[12] J. C. Eaton, Appendix to F. M. Arshid et al., *J. Chem. Soc.*, **1955**, 67.