Studies on the Interaction of Surface Films with Solute in Solution. I. Potentiometric Titration of Aqueous Dye Solution and Calculation of Ionization Constant of Dye

By Mitsuo MURAMATSU

(Received April 30, 1958)

Up to the present, work has been accumulated on the interaction of substances in aqueous solution with surface films of amphipathic compounds spread upon it[1]. Among these, the effect of solute in a substrate solution on monolayers spread on it was extensively studied and many interesting results were obtained. For instance, a remarkable expansion and solidification have been reported for surface film such as stearic acid or octadecylamine due to such a substance cobalt, aluminum, thorium, or alginate ion dissolved in the substrate upon which the film was spread[2,3]. Marked increase in film thickness and wettability were also reported when a built-up film of stearic acid was immersed in solutions containing these ions[4].

All these phenomena seem to show that the nature of the film is profoundly affected by ions which interlink with each other and are taken up by the film. To confirm this, further contributions will be made from the study of interaction between mono- or multilayers of amphipathic compounds and aqueous solutions of dyes, since the latter compounds have a tendency to form micelles or aggregates in an aqueous medium[5] and, as a result, they behave sometimes as if they were macromolecular electrolyte. It will be presumed, however, that the association of molecules is dominantly affected by the degree of ionization of dissociating groups in the dye molecule, which can be calculated from their respective ionization constants and pH of the medium. In spite of such a significance of ionization constant, little was successfully attempted to determine it for usual dyes. This may be due to the failure of the application of simple method of pK determination[6], while a more rigorous method gives values of low reliability in spite of an elaborate calculation as in

---

[1] A general review, cf. M. Muramatsu, T. Sasaki and R. Matuura, *Reports, Kyūshū Univ., Chem. Sect.*, **2**, 47 (1955).

[2] T. Sasaki and R. Matuura, This Bulletin, **24**, 274 (1951); T. Sasaki and M.Muramatsu, ibid., **29**, 35 (1956); J. H. Schulman et al., *Trans. Faraday Soc.*, **46**, 475 (1950); **50**, 1128, 1131, 1139 (1954), etc.

[3] E. G. Cockbain and J. H. Schulman, *Trans. Faraday Soc.*, **35**, 716 (1939); T. Sasaki and M. Muramatsu, This Bulletin, **26**, 96 (1953).

[4] M. Muramatsu and T. Sasaki, This Bulletin, **25**, 21, 25 (1952); A. Inaba, ibid., **26**, 43 (1953).

[5] E. L. Valko, "Colloid Chemistry" edited by J. Alexander, Vol. 6, Reinhold Publ. Corp., New York, (1946), p. 594; see also W. Pauli and F. Lang, *Monath. Chem.*, **67**, 159 (1936).

[6] e. g., L. Michaelis, Physical Method of Organic Chemistry, Part II, in "Technique of Organic Chemistry", edited by A. Weissberger, Interscience Publ., Inc., New York, (1949), p. 1712.

the case of polybasic acid[7)].

The present paper describes an improved method of evaluating the dissociation constant of polybasic acid and polyacidic base, as well as the results obtained for several dyes.

Method of Calculation

The following three assumptions are made for calculating ionization constants of ionizable groups in the dye molecule.

(i) Dye, OH^-, Cl^-, Na^+, etc., in the titration mixture are so dilute that the concentration instead of the activity is used in calculation.

(ii) Volume of titration mixture is the sum of the volume of the solution of dye and of titrating acid or alkali.

(iii) As for the concentration of the carbonate ion, the effect due to the second ionization constant is small enough to be neglected in the pH region of the present experiment.

Now we show the case of titrating a solution of chrysoidine, one of the diacidic bases, with a solution of sodium hydroxide or hydrochloric acid. Ionization constants, K_1 and K_2, for this dye are defined by

$$\left.\begin{aligned} R^{2+} &\rightleftarrows R^+ + H^+ : \quad K_1 = [H^+][R^+]/[R^{2+}] \\ R^+ &\leftrightarrows R + H^+ : \quad K_2 = [H^+][R]/[R^+] \end{aligned}\right\} \quad (1)$$

where R, R^+, and R^{2+} are the dye molecules possessing zero, one, and two ionized amino groups, respectively, and [ ] denotes the concentration of inscribed species. Total concentration, C, of the dye is then expressed by

$$C = [R] + [R^+] + [R^{2+}] \quad (2)$$

We now introduce a parameter f different from Schwarzenbach's[7)], defined by

$$f = 2[R^{2+}] + [R^+] \quad (3)$$

Then, from the condition of electrical neutrality

$$f = [Cl^-] + [OH^-] + [HCO_3^-] - [Na^+] - [H^+] \quad (4)$$

Substituting 1 and 3 into 2 we obtain

$$\left(\frac{f}{C}\right) + \left(\frac{f}{C} - 1\right)\frac{[H^+]}{K_2} + \left(\frac{f}{C} - 2\right)\frac{[H^+]^2}{K_1K_2} = 0 \quad (5)$$

In the case of aluminon, one of the acidic dyes, the following relations result;

$$\left.\begin{aligned} K_1 &= [H^+][R^-]/[R] \\ K_2 &= [H^+][R^{2-}]/[R^-] \\ K_3 &= [H^+][R^{3-}]/[R^{2-}] \end{aligned}\right\} \quad (6)$$

$$C = [R] + [R^-] + [R^{2-}] + [R^{3-}] \quad (7)$$

The solution of this dye is titrated with hydrochloric acid, so the parameter f is given by

$$\begin{aligned} f &= -3[R^{3-}] - 2[R^{2-}] - [R^-] \\ &= [Cl^-] + [OH^-] + [HCO_3^-] - [NH_4^+] - [H^+] \end{aligned} \quad (8)$$

Substituting 6 and 8 into 7 we have

$$\left(\frac{f}{C} + 3\right) + \left(\frac{f}{C} + 2\right)\frac{[H^+]}{K_3} + \left(\frac{f}{C} + 1\right)\frac{[H^+]^2}{K_2K_3} + \left(\frac{f}{C}\right)\frac{[H^+]^3}{K_1K_2K_3} = 0 \quad (9)$$

For the titration of a solution of such an amphoteric dye as methyl orange or tropäolin OO with hydrochloric acid solution, we obtain eventually

$$\left(\frac{f}{C} + 1\right) + \left(\frac{f}{C}\right)\frac{[H^+]}{K_2} + \left(\frac{f}{C} - 1\right)\frac{[H^+]^2}{K_1K_2} = 0 \quad (10)$$

with f being given by the equation 4 and K_1 and K_2 by

$$\left.\begin{aligned} K_1 &= [H^+][R^\pm]/[R^+], \text{ for sulfonic group} \\ K_2 &= [H^+][R^-]/[R^\pm], \text{ for basic group} \end{aligned}\right\} \quad (11)$$

where $R^\pm$ denotes the zwitterion form of dye molecule.

Similar treatment applied to Congo red, possessing two amino and two sulfonic groups in a molecule, leads us to the expression

$$\left(\frac{f}{C} + 2\right) + \left(\frac{f}{C} + 1\right)\frac{[H^+]}{K_4} + \left(\frac{f}{C}\right)\frac{[H^+]^2}{K_3K_4} + \left(\frac{f}{C} - 1\right)\frac{[H^+]^3}{K_2K_3K_4} + \left(\frac{f}{C} - 2\right)\frac{[H^+]^4}{K_1K_2K_3K_4} = 0 \quad (12)$$

with the parameter f determined by 4 and K's by

$$\left.\begin{aligned} K_1 &= [H^+]]R^{\pm +}]/[R^{2+}], \\ &\quad \text{for first sulfonic group} \\ K_2 &= [H^+][R^{2\pm}]/[R^{\pm +}], \\ &\quad \text{for second sulfonic group} \\ K_3 &= [H^+][R^{\pm -}]/[R^{2\pm}], \\ &\quad \text{for first amino group} \\ K_4 &= [H^+][R^{2-}]/[R^{\pm -}], \\ &\quad \text{for second amino group} \end{aligned}\right\} \quad (13)$$

[7)] G. Schwarzenbach et al., *Helv. Chim. Acta*, **30**, 1303, 1798 (1947); **32**, 1175 (1949).

From the assumption (ii), $[Cl^-]$, $[Na^+]$ or $[NH_4^+]$ in equation 4 or 8 can be calculated from the initial concentration, C_0, and volume, V_0, of dye solution, as well as initial concentration, C_0', and the volume, V_t, of the solution of acid or alkali added. Further, from the assumption iii

$$[HCO_3^-]=(K_c+[H^+]_0)([H^+]_0-[OH^-]_0)/K_c$$

and we have also

$$[OH^-]=K_w/[H^+]$$

where K_w and K_c are the ionic product of water and first dissociation constant of carbonic acid, respectively, and $[H^+]_0$ and $[OH^-]_0$ are the concentration of H^+ and OH^-, respectively, in conductivity water into which dye is dissolved. Therefore we can calculate the parameter f from equations 4 or 8. C in equations 5, 9, 10 or 12 can also be calculated from the initial concentration of dye used. Thus, putting the numerical value of f/C for given $[H^+]$ into the equations 5, 9, 10 or 12 enables the evaluation of K's for each dye.

Experimental

Material.—Dyes used were of chemically pure grade and were further purified by a special method, e. g., salting-out⁸⁾ for Congo red and methyl orange and reduction-precipitation⁹⁾ for aluminon, as the case requires. Although dye suffered hydrolysis occasionally during purification, the purification was continued until the titration curve became unaltered by the subsequent recrystallization. Actually, the successive recrystallization proved able to shift the titration curve of aminazobenzene hydrochloride, as shown in Fig. 1. Color of the solution also changed gradually from red to yellowish-red with the repeated recrystallization. These facts clearly show a detachment of hydrogen chloride from dye base. Assuming no impurity contained in dye, the amount of the acid detached can be calculated from the elemental analysis of the dye. Table I

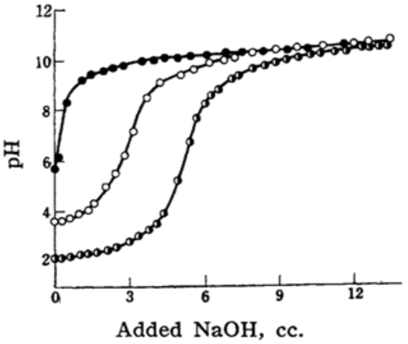
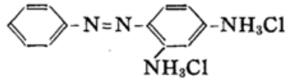
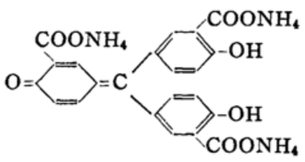
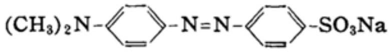
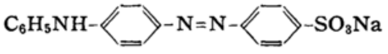
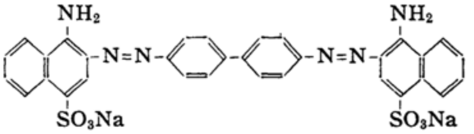


Fig. 1. Effect of recrystallization of aminazobenzene hydrochloride upon the titration curve: $[NaOH]=1.25\times10^{-3}$ mol./l.; $[dye]=2.0\times10^{-4}$ mol./l.; volume of dye solution=50.00 cc.

◑ recrystallized 3 times
○ recrystallized 6 times
● recrystallized 9 times

TABLE I

MOST PROBABLE COMPOSITION OF DYES USED

Name	Constitution	Type	Occurence, %	Type	Occurence, %
Chrysoidine		R^+Cl^-	98.06	$R^{2+}2Cl^-$	1.94
Aluminon		$R^{3-}3NH_4^+$	26.84	$R^{2-}2NH_4^+$	73.16
Methyl orange		R^-Na^+	80.97	$R^\pm$	19.03
Tropäolin OO		R^-Na^+	78.31	$R^\pm$	21.69
Congo red		$R^{2-}2Na^+$	46.03	$R^\pm$-Na^+	53.97

---

8) C. Robinson and H. A. T. Mills, *Proc. Roy. Soc.*, **A131**, 576 (1931).

9) N. Caro, *Ber.*, **25**, 939 (1892).

shows the most probable degree of detachment of such an acid or a base for samples used in the experiment. The calculation of composition in the table is based on the elemental analysis of carbon, hydrogen, nitrogen and sodium (for amphoteric dyes) or chlorine (for basic dye). The molar concentration of dye solution was calculated taking into account this detachment of acid or base.

Hydrochloric acid, twice distilled in an all-grand glass apparatus, and sodium hydroxide purified by alcohol were used as titratingagents and standardized with perchloric acid solution. Conductivity water to be used often suffered a slight lowering of pH presumably owing to the dissolution of carbon dioxide, the content of which was calculated as mentioned in the previous section.

Procedure. — Exactly 50 cc. of ca. 2×10^{-4} mol./l. of dye solution was titrated with hydrochloride acid or sodium hydroxide of ca. 1.25×10^{-3} mol./l. under mechanical stirring of 400 rpm and pH change was traced by means of pH meter (Shimadzu Model GU, using GL-6 glass electrode), which was calibrated with buffer solutions of two different pH values. The error introduced in the measurement of pH was estimated to be within ±0.02. Reading of pH was taken after equilibrium was attained for successive titration which was completed within 10 hrs. after the preparation of dye solution. It was confirmed in the preliminary experiment that the effect of aging of dye solution upon the titration curve could be eliminated by leaving it alone for at least 24 hrs.

All experiments were carried out at room temperature of 20±5°C.

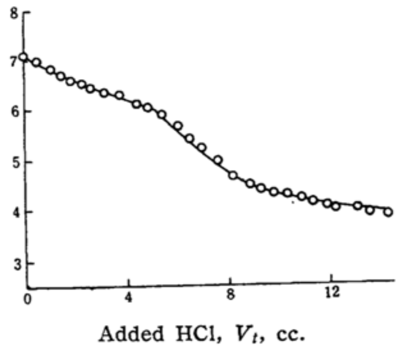


Fig. 2. $V_t\sim$pH relationship for methyl orange: $C_0=2.03\times10^{-4}$ mol./l.; $C_0'=1.25\times10^{-3}$ mol./l.; $V_0=50.00$ cc.; ○, observed; ——, calculated by Eq. 10 assuming $K_1=2.75\times10^{-4}$ and $K_2=3.22\times10^{-7}$.

Results

Fig. 2 shows the value of pH of the solution of methyl orange titrated with hydrochloride acid. The concentration of each ion species, except for dye ions, in the solution could be calculated from these pH values and from given conditions of $[Na^+]=1.64\times10^{-4}$ g. ion/l. at $V_t=0$, $[Cl^-]=1.25\times10^{-3}$ g.ion/l. for the initial concentration of titrating solution, $[H^+]_0=2.29\times10^{-7}$ ($pH_0=6.64$), $K_w=1.02\times10^{-14}$, and $K_c=3.5\times10^{-7}$. Table II shows the typical examples of these terms and f/C with varying V_t.

In applying these data to 10, we were hardly able to evaluate simultaneously K_1 and K_2 successfully from the graphical plotting of $\left(\frac{f}{C}\right)[H^+]\Big/\left(\frac{f}{C}+1\right)$ against $-\left(\frac{f}{C}-1\right)[H^+]^2\Big/\left(\frac{f}{C}+1\right)$. This was mainly due to the fact that $[H^+]$ changed widely from 10^{-7} to 10^{-4}, as V_t changed from 1 to 13 cc. Therefore a conventional approximation was made to determine K's. Since it was roughly estimated from Fig. 2 that K_2 was nearly of the order of 10^{-7} while K_1 was larger than 10^{-5}, the last term of left side of (10) was considered to be negligible in the region of $[H^+]\approx10^{-7}$. That is, we can safely ignore the reaction

TABLE II

CONCENTRATION OF VARIOUS ION SPECIES IN THE SOLUTION AND f/C FOR THE TITRATION OF METHYL ORANGE

V_t	C	$[H^+]$	$[Na^+]$	$[Cl^-]$	$[OH^-]$	$[HCO_3^-]$	f	f/C
1.0	1.99×10^{-4}	1.45×10^{-7}	1.61×10^{-4}	2.45×10^{-5}	0.69×10^{-7}	2.15×10^{-7}	-1.38×10^{-4}	−0.694
2.0	1.95 〃	2.63 〃	1.58 〃	4.81 〃	0.38 〃	1.73 〃	−1.10 〃	−0.565
3.0	1.91 〃	4.27 〃	1.55 〃	7.02 〃	0.23 〃	1.37 〃	−0.85 〃	−0.445
4.0	1.88 〃	6.61 〃	1.52 〃	9.62 〃	0.15 〃	1.06 〃	−0.56 〃	−0.298
5.0	1.85 〃	1.07×10^{-6}	1.49 〃	1.14×10^{-4}	0.10 〃	0.75 〃	−0.36 〃	−0.194
6.0	1.81 〃	1.95 〃	1.46 〃	1.34 〃	0.05 〃	0.46 〃	−0.14 〃	−0.0774
7.0	1.78 〃	6.03 〃	1.44 〃	1.55 〃	0.02 〃	0.17 〃	+0.05 〃	+0.0281
8.0	1.75 〃	1.66×10^{-5}	1.41 〃	1.72 〃	0.00 〃	0.06 〃	+0.14 〃	+0.0800
9.0	1.72 〃	3.47 〃	1.39 〃	1.91 〃	0.00 〃	0.00 〃	+0.17 〃	+0.0988
10.0	1.69 〃	4.90 〃	1.37 〃	2.08 〃	0.00 〃	0.00 〃	+0.22 〃	+0.130
11.0	1.66 〃	7.08 〃	1.34 〃	2.26 〃	0.00 〃	0.00 〃	+0.21 〃	+0.127

$R^{\pm}+H^+ \rightarrow R^+$ in this region, since $f=[R^+]-[R^-]$ is negative in this region. Thus we have a linear relationship between $-(f/C)[H^+]$ and $(f/C)+1$ in the region of $[H^+]\lesssim 5\times10^{-7}$ as shown in Fig. 3, from which we obtain $K_2=3.30\times10^{-7}$. Putting this value into 10 and plotting

$$-\left(\frac{f}{C}-1\right)\frac{[H^+]^2}{K_2} \text{ against } \left(\frac{f}{C}+1\right)+\left(\frac{f}{C}\right)\frac{[H^+]}{K_2},$$

as shown in Fig. 4, we obtain $K_1=2.73\times10^{-4}$. Successive approximation not neglecting the last term gave limiting values of $K_1=2.75\times10^{-4}$ and $K_2=3.22\times10^{-7}$. Substitutions of these values back into 10 give f/C for given $[H^+]$ which in turn gives V_t. $V_t\sim$pH relationship thus obtained is expressed as a full line in Fig. 2. A fairly good coincidence is seen between observed and calculated values in this figure.

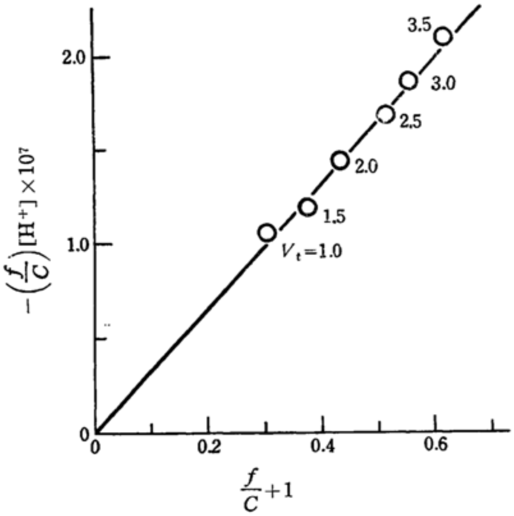


Fig. 3. $-\left(\frac{f}{C}\right)[H^+]$ vs. $\left(\frac{f}{C}+1\right)$ for methyl orange.

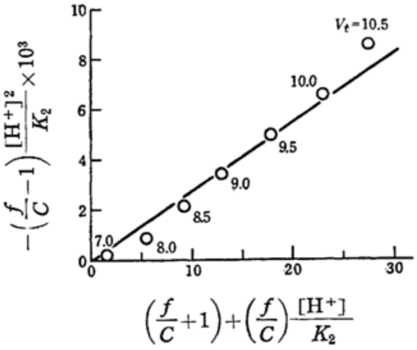


Fig. 4.
$-\frac{f}{C}-1\Big)\frac{[H^+]^2}{K_2}$ vs. $\left(\frac{f}{C}+1\right)+\left(\frac{f}{C}\right)\frac{[H^+]}{K_2}$
for methyl orange.

The open circles in Fig. 5 denote the observed values of pH of the solution of tropäolin OO titrated with hydrochloric acid. Similarly to the case of methyl orange, we obtained the dissociation constants, K_1 and K_2, defined by 11. The final values were $K_1=5.60\times10^{-4}$ and $K_2=2.98\times10^{-7}$. Again, the dependence of pH upon V_t is reproduced by putting these values into 10. The full curve in Fig. 5 represents the $V_t\sim$pH relationship thus obtained.

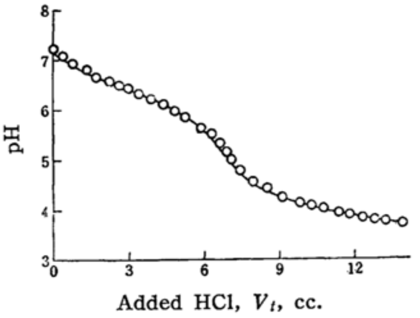


Fig. 5. $V_t\sim$pH relationship for tropäolin OO: $C_0=2.08\times10^{-4}$ mol./l., $C_0'=1.25\times10^{-3}$ mol./l., $V_0=50.00$ cc; ○, observed; ——, calculated by Eq. 10 assuming $K_1=5.60\times10^{-4}$ and $K_2=2.98\times10^{-7}$.

Solution of chrysoidine was titrated separately with the solutions of hydrochloric acid and sodium hydroxide, since the greater part of starting sample of dye is of R^+ form. The result is shown in Fig. 6. Putting the experimental data into equation 5, we obtained $K_1=4.84\times10^{-4}$ and $K_2=7.09\times10^{-6}$. $V_t\sim$pH relationship reproduced from these values of K's is shown as a full curve in Fig. 6.

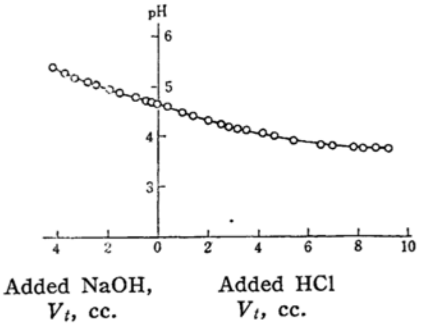


Fig. 6. Titration curve for chrysoidine: $C_0=2.01\times10^{-4}$ mol./l., C_0' of HCl$=1.25\times10^{-3}$ mol./l., C_0' of NaOH$=1.58\times10^{-3}$ mol./l., $V_0=50.00$ cc.; ○, observed; ——, calculated by Eq. 5 assuming $K_1=4.84\times10^{-4}$ and $K_2=7.09\times10^{-6}$.

Fig. 7 shows the titration curve of aluminon. When we followed the method of calculation mentioned above to equation 9, $K_3=6.08\times10^{-8}$ and $K_2=1.595\times10^{-5}$ were obtained. In calculation of K_1, however, plotting of (f/C) $[\mathrm{H}^+]^3/K_2K_3$ against

$$\left(\frac{f}{C}+3\right)+\left(\frac{f}{C}+2\right)\frac{[\mathrm{H}^+]}{K_3}+\left(\frac{f}{C}+1\right)\frac{[\mathrm{H}^+]^2}{K_2K_3}$$

was unsuccessful, owing to considerable fluctuation of the plot. If we reproduce the $V_t\sim$pH relationship assuming $K_2=1.595\times10^{-5}$, $K_3=6.08\times10^{-8}$ and K_1 being either of 1, 10^{-2} or 10^{-3}, we obtain three corresponding curves differing from one another in the tail parts of titration curves reproduced, as seen in the figure inserted in Fig. 7. Thus, when we take into account the experimental error in determining pH, we can say no more than $K_1=10^{-2}$ or larger.

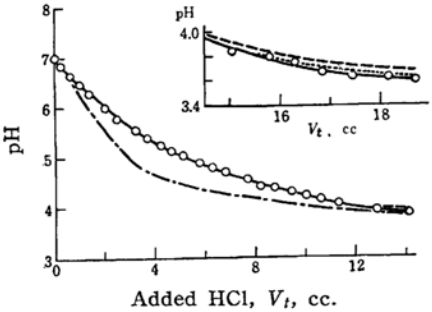


Fig. 7. Titration curve for aluminon: $C_0=2.06\times10^{-4}$mol./l., $C_0'=1.44\times10^{-3}$mol./l., $V_0=50.00$ cc.; ○, observed; curves, calculated by Eq. 9 assuming $K_2=1.595\times10^{-5}$, $K_3=6.08\times10^{-8}$ and $K_1\approx1$ (——), 10^{-2} (------) or 10^{-3} (– – –); semidotted curve, based on high-molecular electrolyte.

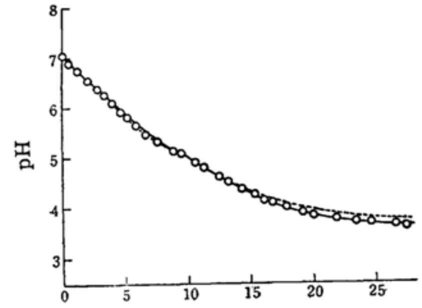


Fig. 8. Titration curve for Congo red: $C_0=2.03\times10^{-4}$ mol./l., $C_0'=1.25\times10^{-3}$ mol./l., $V_0=50.00$cc.; ○, observed; -----, calculated by Eq. 12; ——, calculated by Eq. 16.

Titration curve for Congo red is shown in Fig. 8. From these data we obtained the following values of K's using equation 12;

$$K_4=9.59\times10^{-8}$$
$$K_3=7.19\times10^{-6}$$
$$K_2=1.82\times10^{-4}$$

Again, we failed to plot and calculate the value of K_1, similar to the case of aluminon. Therefore we could merely evaluate K_1 to be 10^{-1} or larger. In Fig. 8 the dotted curve represents the calculated values of V_t for given pH using these experimental values for K's. We can see some deviations between calculated and observed values of pH for given V_t at the tail part of the titration curve.

Discussion

In Table III are summarized the values of pK's determined for each ionizable group in the dye used, except for Congo red. It should be noticed that the ionization constants are defined by 1, 6 or 11 and, therefore, that the stronger acid is of the smaller pK, while the stronger base is of the larger pK.

TABLE III

pK'S OF IONIZABLE GROUPS IN THE DYE

Dye	Acid group	Basic group
Chrysoidine	——	$pK_1=3.32$ $pK_2=5.21$
Aluminon	$pK_1\leq2$, $pK_2=4.80$ $pK_3=7.22$	——
Methyl orange	$pK_1=3.56$	$pK_2=6.49$
Tropäolin OO	$pK_1=3.25$	$pK_2=6.53$

It is well known that, when the second acid group of the same kind is introduced in the molecule having one acid group, the ionization constant of the former becomes smaller than that of the latter, while the value of the latter is slightly affected by the addition of the former. A typical example of this is seen in the case of dicarboxylic acids[10]. When we apply this principle to the dibasic dye, the pK values of chrysoidine are explained as those expected from the ionization constant, $pK=2.91$ as defined by 1, for aminazobenzene[11]. By means of the

---

[10] B. Adell, "Über die Elektrolytische Dissoziation von Dicarbonsäuren in Alkalichloridlösungen", Lund, (1938).

[11] R. C. Farmer and F. J. Warth, *J. Chem. Soc.*, **85**, 1726 (1904).

methods of titration and spectrophotometry, Woislawaski[12] has also reported $pK_2=5.3$ for an amino group in chrysoidine in aqueous solution.

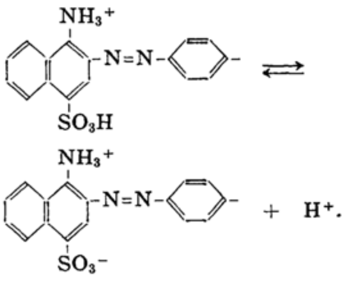
Substitution of amino group by sulfonic group makes little difference in pK_2 between chrysoidine and methyl orange or tropäolin OO. It is hardly believed that the ionization constant of an amino group in the dye is remarkably affected by dimethylation or phenylation, both of which show little effect upon the ionization constant of aniline[13]. It is further noted that pK_1 of methyl orange or tropäolin OO is of nearly the same value as that, $pK=3.28$ at 20°C, for sulfanilic acid[14].

It seems to be premature to ascribe the deviation of calculated pH value from the observed one at the tail part of the titration curve of Congo red, as seen in Fig. 8, to a mere experimental error. Actually the deviation is larger than that due to the pH measurement and exhibits a systematic tendency; namely, the calculated value is always larger than the observed one. Now, let us make a tentative explanation of this deviation which is ascribed to the special nature of Congo red in aqueous solution. If we assume two sulfonic groups, not distinguishable from each other with regard to their ionization, in the molecule, then we can treat Congo red similarly to a high-polymer electrolyte. We can safely assume this, since two sulfonic groups are both strongly ionizing and are far apart from each other. At least, such a consideration would be valid for the region where titrating hydrochloric acid reacts with these acid groups. The high-molecular or micellar nature of Congo red, suggested by the data of ultracentrifuge[15] and diffusion[5], in aqueous medium would also support this consideration.

From this standpoint we shall take the following K's, instead of those defined by 13, for Congo red as a high polymer-like substance;

$$\left.\begin{aligned} K_1=K_2&=[\mathrm{H}^+][\mathrm{R}^{2\pm}{}_{1/2}]/[\mathrm{R}^{2+}{}_{1/2}] \\ [\mathrm{R}^{\pm}{}_{1/2}]&=2[\mathrm{R}^{2\pm}] \\ K_3&=[\mathrm{H}^+][\mathrm{R}^{\pm-}]/[\mathrm{R}^{2\pm}] \\ K_4&=[\mathrm{H}^+][\mathrm{R}^{2-}]/[\mathrm{R}^{\pm-}] \end{aligned}\right\} \qquad (14)$$

where $\mathrm{R}^{2\pm}{}_{1/2}$ and $\mathrm{R}^{2+}{}_{1/2}$ express the unit segments in ionizing molecule, as appears in



Consequently

$$\left.\begin{aligned} C&=[\mathrm{R}^{2-}]+[\mathrm{R}^{\pm-}]+[\mathrm{R}^{2\pm}]+1/2[\mathrm{R}^{2+}{}_{1/2}] \\ f&=[\mathrm{R}^{2+}{}_{1/2}]-[\mathrm{R}^{\pm-}]-2[\mathrm{R}^{2-}] \\ &=[\mathrm{Cl}^-]+[\mathrm{OH}^-]+[\mathrm{HCO}_3{}^-] \\ &\quad-[\mathrm{Na}^+]-[\mathrm{H}^+] \end{aligned}\right\} \qquad (15)$$

Substituting 15 into 14 we obtain eventually,

$$\left(\frac{f}{C}+2\right)+\left(\frac{f}{C}+1\right)\frac{[\mathrm{H}^+]}{K_4}+\left(\frac{f}{C}\right)\frac{[\mathrm{H}^+]^2}{K_3K_4} +\left(\frac{f}{C}-2\right)\frac{[\mathrm{H}^+]^3}{K_2K_3K_4}=0 \qquad (16)$$

Application of the successive approximation to 16 leads us to the following result;

$$K_4=1.252\times10^{-7}$$

$$K_3=4.75\times10^{-6}$$

$$K_1=K_2=1.83\times10^{-3}$$

Table IV shows pK values of respective ionizing groups in Congo red for two equations on which the calculation is based.

TABLE IV

pK VALUES FOR CONGO RED

Equation used	Acid group	Basic group
(12)	$pK_1 \leq 1$ $pK_2=3.74$	$pK_3=5.14$ $pK_4=7.02$
(16)	$pK_1=pK_2=2.74$	$pK_3=5.32$ $pK_4=6.90$

In Fig. 8 the full and dotted curves express the $V_t \sim$pH relationship reproduced using equations 16 and 12, respectively. A better coincidence of equation 16 shows the validity of the above treatment. Applying a similar treatment to aluminon, we obtained $K_1=K_2=2.5\times10^{-4}$ and $K_3=6.18\times10^{-8}$ for this dye but we failed to confirm the coincidence between observed and calculated values in the range of $V_t >$

---

[12] S. Woislawski, *Proc. Soc. Exp. Biol. Med.*, **79**, 390 (1952); *J. Am. Chem. Soc.*, **75**, 5201 (1953).

[13] Landolt-Börnstein, "Physikalisch-Chemische Tabellen", 5th ed., **2**, 1159, second suppl., 1093 (1923).

[14] R. O. MacLaren and D. F. Swinehardt, *J. Am. Chem. Soc.*, **73**, 1822 (1951).

[15] T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," Clarendon press, Oxford, (1940), p. 310.

12 cc., as shown as semi-dotted curve in Fig. 7.

Various methods have been presented to determine the ionization constant. Of the methods, spectrophotometry seems hardly applicable for a polyionizing substance. In contrast with this, the potentiometric method is, in principle, applicable to any substance. However, we must solve a rather complicated equation which is liable to produce an appreciable error for a larger ionization constant appearing in the higher-order term of the equation[7]. In order to minimize the error and to facilitate the calculation, it is important to adopt a suitable parameter. The present method of successive approximation is convenient in evaluating the ionization constants of a polyionizing acid or base.

Summary

Change of pH of aqueous dye solution was traced by titrating with the solution of hydrochloric acid or sodium hydroxide. From these data, ionization constants for each ionizing group in chrysoidine, methyl orange, tropäolin OO and aluminon were calculated, making use of equations based on the law of mass action with a specially-selected parameter. The validity of the ionization constants thus determined were confirmed by reasonable coincidence of the titration curves obtained by calculation using these data with those observed, over the wide range of pH.

In the case of Congo red, however, it seemed better to treat it as a high-molecular electrolyte. Ionization constants calculated by an equation based on such a treatment explain the experimental result better than those based on the treatment similar to the case of other simple dyes.

In conclusion, the author wishes to express his sincere thanks to Professor T. Sasaki for his guidance and encouragement during this experiment. A part of the cost of this research has been defrayed from the Scientific Research Expenditure of the Ministry of Education.

Department of Chemistry, Faculty of Science
Tokyo Metropolitan University
Setagaya-ku, Tokyo