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Group Interactions in Polyelectrolytes. III. The Electrostatic Effect of Neighboring Groups on the Ionization of Polyelectrolytes

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The two parameters in the modified Henderson-Hasselbach equation, $\mathrm{pH}=\mathrm{p}K_a-n'\log[(1-\alpha)/\alpha]$, where $\mathrm{p}K_a$ and n' are empirical constants and where α is a degree of the ionization of a polymeric acid, were evaluated on the assumption that the ionization of polyelectrolytes is electrostatically affected in the main by a few neighboring ionized groups and that the overall ionization is composed of only a few elementary ionization. The titration curves of various polyelectrolytes in the absence of salt could be classified into two types: $\Delta\mathrm{p}K'\gtrsim 2$ and $\Delta\mathrm{p}K'<2$, where $\Delta\mathrm{p}K'$ is the difference between the succeeding ionization constants. The maleic acid-styrene copolymer and polyvinyl amine belong to the former type, while polyacrylic acid and pectinic acid belong to the latter. In the former, a plot of pH against $\log[(1-\alpha)/\alpha]$ nearly falls on a line in only a limited range and n' is substantially equal to the number of elementary ionizations. In the latter, both $\mathrm{p}K_a$ and n' are related to the distance between the groups. The titration curve of polyacrylic acid, drawn by means of the above equation with the parameters calculated on the basis of the kinetic data of the alkaline hydrolysis of polymethyl acrylate, was in good agreement with the observed titration curve. The titration data of other polyelectrolytes also fall nearly on their calculated titration curves.

The potentiometric titration curves of polymeric acids (or polymeric bases) do not obey the Henderson equation for monomeric acids (or bases), and their apparent dissociation constant, K_{app}, decreases with an increase in the degree of ionization in the case of polymeric acids and increases in the cases of polymeric bases depending on the electrostatic effect of the ionized groups fixed on the macromolecule. Although it is difficult to eliminate the electrical effect entirely by adding neutral salt, Katchalsky *et al.*[1] showed that the titration data of some polyelectrolytes could be expressed by a single dissociation constant of their monomeric unit when the correction for an electric field was properly made.

On the other hand, Marcus[2] presented a theory of the potentiometric titrations of polymeric acids taking into account only electrical interaction between neighboring groups; he suggested that the polymeric acids under the conditions given in his theory would behave much like dibasic acid. Katchalsky *et al.*[3] found that the electrostatic interaction between neighboring ionized groups of polyvinylamine could not be eliminated by the addition of salt in a very high concentration or even by making a correction for electrostatic field, and showed that its behavior in the titration with hydrobromic acid in the presence of sodium chloride was also similar to that of diamine. It was also reported that the titration curve of the maleic acid-styrene copolymer resembled that of dibasic acid.[4,5]

The titration curves of polymeric acids in the absence of salt are difficult to analyze theoretically because of the intense electrostatic effect of neighboring ionized groups, and the Henderson-Hasselbach-Katchalsky equation[6] is the only empirical relation to describe their titration data. In the present study, the empirical constants in the equation have been evaluated by assuming that the ionization of polyelectrolytes is electrically affected mainly by a few neighboring charged groups; the titration curves of several polymeric acids and bases have been interpreted on this basis.

Experimental

Commercial anhydrous ethylenediamine of a reagent grade was distilled before use; it was proved to be pure by its refractive index. Crystalline 1,3-propanediamine dihydrochloride was dissolved in water, and the solution was passed through a column of Dowex-2 X-8 in the hydroxide form to remove the hydrogen chlo-

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[1] A. Katchalsky, N. Shavit and H.Eisenberg, *J. Polymer Sci.*, **13**, 69 (1954).

[2] R. A. Marcus, *J. Phys. Chem.*, **58**, 621 (1954).

[3] A. Katchalsky, J. Mazur, P. Spitnik, *J. Polymer Sci.*, **23**, 513 (1957).

[4] E. R. Garret and R. L. Guile, *J. Amer. Chem. Soc.*, **73**, 4533 (1951).

[5] J. D. Ferry, D. C. Udy, F. C. Wu, G. E. Heckler and D. B. Fordyce, *J. Colloid Sci.*, **6**, 429 (1951).

ride. Aqueous solutions of the amines (0.01 M) were titrated with 0.1 N hydrochloric acid at 25°C, and the pH of the solution was measured with a Beckman Model G pH meter.

Evaluation of the Parameters in the Henderson-Hasselbach-Katchalsky Equation

Katchalsky and spitnik[6] found that the potentiometric titration curves of some polymeric acids could be described by the generalized Henderson-Hasselbach relation:

$$\mathrm{pH} = \mathrm{p}K_a - n' \log \frac{1-\alpha}{\alpha} \tag{1}$$

where $\mathrm{p}K_a$ and n' are empirical constants and where α is a degree of ionization of an acid. For a monobasic acid, n' is unity.

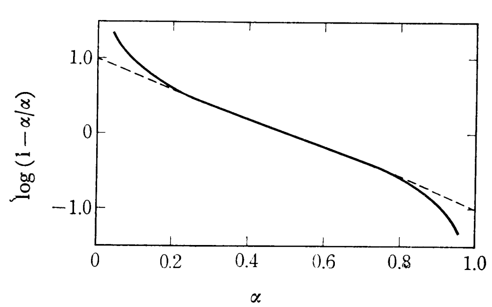

Fig. 1. Plot of log $[(1-\alpha)/\alpha]$ against α.

As is shown in Fig. 1, log $[(1-\alpha)/\alpha]$ is approximately proportiona to α over a wide range of α, 0.2—0.8:[*1]

$$\log \frac{1-\alpha}{\alpha} = 1 - 2\alpha \tag{2}$$

The introduction of Eq. (2) into Eq. (1) gives:

$$\mathrm{pH} = (\mathrm{p}K_a - n') + 2n'\alpha \tag{3}$$

Hence, n' may be estimated from the slope of a titration curve in its middle range at $(\Delta\mathrm{pH}/\Delta\alpha)/2$. Equation (3) also indicates that the main part of the titration curve of any monobasic acid ($n'=1$) is within 2 pH, and also suggests that in the titration curve of a dibasic acid or a mixture of two monobasic acids, two ionizable groups can be distinguished only when $\mathrm{p}K_2 - \mathrm{p}K_1 \gtrsim 2$.

In the titration of a polybasic acid with σ ionizable groups, the degree of ionization with respect to the nth ionized group, *i.e.*, the degree of the nth elementary ionization, α_n', is given by:

$$\mathrm{pH} = \mathrm{p}K_n' - \log \frac{1-\alpha_n'}{\alpha_n'} \tag{4}$$

or:

$$\alpha_n' = 1/[1+10^{(\mathrm{p}K_n' - \mathrm{pH})}] \tag{5}$$

where $\mathrm{p}K_n'$ is the negative logalithms of the nth elementary ionization constant.. If $\Delta\mathrm{p}K' \equiv \mathrm{p}K'_{n+1} - \mathrm{p}K'_n \gtrsim 2$, α'_n can be estimated over a wide range of α'_n by the following relation:

$$\alpha_n' = \sigma\alpha - (n-1) \qquad \Delta\mathrm{p}K' \geq 2 \tag{6}$$

Since the α'_n of a polybasic acid is calculated by Eq. (5) when $\mathrm{p}K_n'$ is known, the over-all degree of ionization of an acid with σ groups is given by:

$$\alpha = (\sum_{n=1}^{\sigma} \alpha_n')/\sigma \tag{7}$$

The titration curves of several imaginary polybasic acids with various $\Delta\mathrm{p}K'$ values have been drawn in this manner. The titration curves calculated by arbitrarily taking $\mathrm{p}K'_1$ as unity in the case $\sigma=4$ are shown in Fig. 2, in which the circles indicate the points where $\alpha'_n=0.5$ and in which the four vertical lines correspond to $\alpha=1/8$, 3/8, 5/8, and 7/8. In the figure, the calculated plots of pH against $\log[(1-\alpha)/\alpha]$ are also shown. It may be seen that the plots can be represented by a line over a wide range. Upon the examination of the case when $\sigma=2$, the plot was also found to be substantially linear over a wide range of α provided that $\Delta\mathrm{p}K'<2$. The values of n' thus determined are listed in Table 1. It was also found that the value of n' is closely equal to

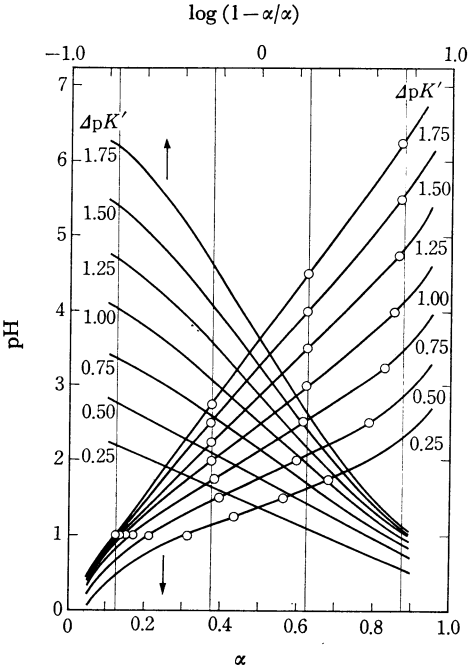

Fig. 2. Calculated titration curves of tetrabasic acids. ($\mathrm{p}K_1'=1$)

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6) A. Katchalsky and P. Spitnik, *J. Polymer Sci.*, **2**, 432 (1947).

[*1] Since the left term of Eq. (2) can be expanded as follows:

$$\log[(1-\alpha)/\alpha] = 2[(1-2\alpha) + (1-2\alpha)^3/3 + (1-2\alpha)^5/5 + \cdots]/2.303$$

this term is near to $(1-2\alpha)$.

TABLE 1. VALUES OF n' FOR SOME IMAGINARY POLYBASIC ACIDS

σ	$\Delta pK'$						
	0.25	0.50	0.75	1.00	1.25	1.50	1.75
2	1.02	1.12	1.16	1.28	1.45	1.66	1.87
4	1.09	1.32	1.69	2.10	2.58	3.06	3.58

the number of elementary ionization, σ, when $\Delta pK' \approx 2$. In the case when $\Delta pK' > 2$, it was found that the plots fall on σ parallel lines with the same slope, $n' = \sigma$, and that the distance between the lines is equal to $(\Delta pK' - 2)$ pH. Hence, when $\Delta pK' \gtrsim 2$, n' is an integer which represents the total number of elementary ionizations. However, some difficulties are encountered when a plot of pH against $\log[(1-\alpha)/\alpha]$, based on the experimental titration data, is expressed by a single line with n' closely equal to an integer, since, for instance, $n' \approx 2$ will be realized not only when $\sigma = 2$ and $\Delta pK' = 2$, but also when $\sigma = 4$ and $\Delta pK' < 2$. The criterion is that if the titration curve is divided into two equal parts at the middle ionization point, the data of each part will fit Eq. (4) in the former case, but not in the latter case.

On the basis of the above-mentioned nature of the titration curve, the parameters in Eq. (1) will be evaluated in the following two cases: $\Delta pK' \gtrsim 2$ and $\Delta pK' < 2$.

1) $\boldsymbol{\Delta pK' \gtrsim 2}$**.** On the basis of Eqs. (2) and (6), the following approximate relatoin is given for the case when $\Delta pK' \gtrsim 2$:

$$\log\frac{1-\alpha_n'}{\alpha_n'} = \sigma\log\frac{1-\alpha}{\alpha} - (\sigma+1-2n) \qquad (8)$$

The introduction of the relation to Eq. (4) gives:

$$\mathrm{pH} = [pK_n' + (\sigma+1-2n)] - \sigma\log\frac{1-\alpha}{\alpha} \qquad (9)$$

By comparing Eq. (9) with Eq. (1), we obtain:

$$\left.\begin{aligned} pK_a &= pK_n' + (\sigma+1-2n) \\ n' &= \sigma \end{aligned}\right\} \qquad (10)$$

Hence, the difference in pK_a between succeeding ionization steps, ΔpK_a, is:

$$\Delta pK_a = \Delta pK' - 2 \qquad (11)$$

If $\Delta pK' = 2$, pK_a takes a single value. Therfore, the plot of pH against $\log[(1-\alpha)/\alpha]$ may be represented by a line with a slope of $n' = \sigma$. If $\Delta pK' > 2$, the plot may be represented by σ parallel lines separated by a distance of $(\Delta pK' - 2)$. It can thus be concluded that when $\Delta pK' \gtrsim 2$ the constant n' does not correlate with the magnitude of the electrostatic effect, but is equal to the number of elementary ionizations. In this case, each ionization step is characterized substantially by a single ionizable group, and the electrostatic free energy of the nth elementary ionization, $(\Delta F^i{}_{\mathrm{el}})_n$, is given by:

$$(\Delta F^i{}_{\mathrm{el}})_n = 2.303\boldsymbol{R}T\left[pK_n' + \log\frac{\sigma-n+1}{n} - pK_0\right] \qquad (12)$$

where pK_0 is the intrinsic ionization constant.

2) $\boldsymbol{\Delta pK' < 2}$**.** When $\Delta pK' < 2$, each elementary ionization is no longer distinguishable in the titration curve, because the ionization of one kind of group is accompanied by that of certain number of other groups. When the ionizations of several kinds of groups overlap, the electrostatic free energy of ionization at a given α, $(\Delta F^i{}_{\mathrm{el}})_\alpha$, may be given by:[*2]

$$\begin{aligned} (\Delta F^i{}_{\mathrm{el}})_\alpha &= \sum_{n=1}^{\alpha} f_n (\Delta F^i{}_{\mathrm{el}})_n \\ &= 2.303\boldsymbol{R}T\left[\sum_{n=1}^{\sigma} f_n\left(pK_n' + \log\frac{\sigma-n+1}{n}\right)\right. \\ &\quad \left. - pK_0\sum_{n=1}^{\sigma} f_n\right] \end{aligned} \qquad (13)$$

where f_n is the mole fraction of the nth ionizable group at a given α. Since a differential amount of the nth elementary ionization is given, from Eq. (4), by $d\alpha'_n/d\mathrm{pH} = \alpha'_n(1-\alpha'_n)$, f_n is defined as follows:

$$\left.\begin{aligned} f_n &= \alpha_n'(1-\alpha_n')/\sum_{n=1}^{\sigma}\alpha_n'(1-\alpha_n') \\ \sum_{n=1}^{\sigma} f_n &= 1 \end{aligned}\right\} \qquad (14)$$

The second term of Eq. (13) is equal to pK_0 by the definition. The first term of Eq. (13) was computed for the imaginary acids given in Table 1 and then compared with the $\mathrm{pH} + \log[(1-\alpha)/\alpha]$ term. In Fig. 3, the numerical difference between the two terms is plotted against α for various

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[*2] Since pK_n' is given by Eq. (4), the first term of Eq. (13) is transformed as follows:

$$\begin{aligned} &\sum_{n=1}^{\sigma} f_n\left(\mathrm{pH} + \log\frac{(1-\alpha_n')(\sigma-n+1)}{\alpha_n' \times n}\right) \\ &= \sum_{n=1}^{\sigma} f_n\left(\mathrm{pH} + \log\frac{N_n(\sigma-n+1)}{N_n' \times n}\right) \\ &= \log\prod_{n=1}^{\sigma}\frac{(m_n)f_n}{(m_n')f_n \times m_{\mathrm{H}^+}} = -\log K_\alpha \end{aligned}$$

where N_n and N'_n are the numbers of the elements which concern the nth elementary ionization and which contain $(\sigma-n+1)$ unionized groups and n ionized groups respectively, where m_n and m'_n are the molarities of unionized and ionized groups of the respective elements, and where K_α is the ionization constant defined in the equation. Hence,

$$(\Delta F^i{}_{\mathrm{el}})_\alpha = 2.303\boldsymbol{R}T(pK_\alpha - pK_0)$$

By comparing this equation with Eq. (16), pK_α can be estimated by:

$$pK_\alpha = \mathrm{pH} + \log\frac{1-\alpha}{\alpha}$$

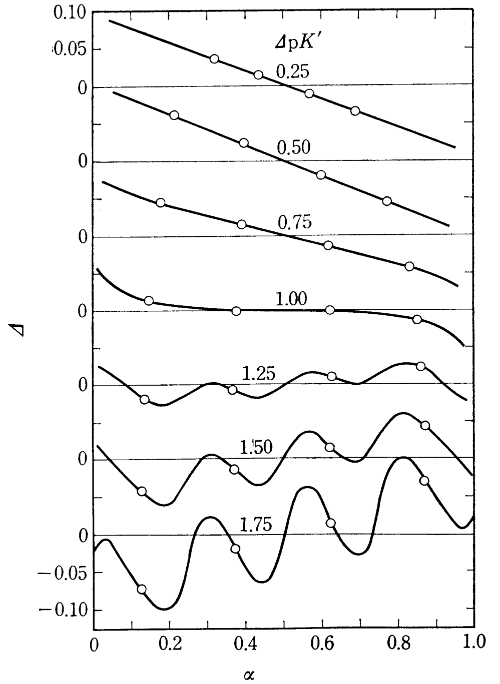

Fig. 3. Calculated difference $\Delta=\sum_{n=1}^{4}\left(\mathrm{p}K_n'+\log\frac{5-n}{n}\right)-\left(\mathrm{pH}+\log\frac{1-\alpha}{\alpha}\right)$ as a function of α.

$\Delta\mathrm{p}K'$ values when $\sigma=4$. In the figure, the circles indicate the points where $\alpha'_n=0.5$. For the case when $\Delta\mathrm{p}K'=2$, the difference amounts to about 0.2. Accordingly, the two terms may be equal within an error of ±0.1 when $\Delta\mathrm{p}K'<2$; therefore:

$$\sum_{n=1}^{\sigma} f_n\left(\mathrm{p}K_n'+\log\frac{\sigma-n+1}{n}\right)=\mathrm{pH}+\log\frac{1-\alpha}{\alpha} \quad (15)$$

Hence, in the case when $2>\Delta\mathrm{p}K'$, Eq. (13) may be transformed into the familiar equation:

$$\mathrm{pH}=\mathrm{p}K_0-\log\frac{1-\alpha}{\alpha}+\frac{(\Delta F^i{}_{\mathrm{el}})_\alpha}{2.303\boldsymbol{R}T} \quad (16)$$

This equation was derived by Katchalsky and Gillis[7] for polymeric acid and transcribed, in the neighborhood of the half-ionization point, in the form of Eq. (1).[1,7]

The first term of Eq. (13) was also numerically compared with the term, $\mathrm{p}K'+\log[(\sigma-n+1)/n]$, in Eq. (12) for the imaginary acids given in Figs. 2 and 3 ($\sigma=4$); the two terms were found to have almost the same value (within ±0.05) at $\alpha'_n=0.5$ when $n=2$ and 3. Hence, $(\Delta F^i{}_{\mathrm{el}})_\alpha$ can be replaced by $(\Delta F^i{}_{\mathrm{el}})_n$ at the points:

$$(\Delta F^i{}_{\mathrm{el}})_\alpha=(\Delta F^i{}_{\mathrm{el}})_n \qquad \alpha_n'=0.5\ (n=2 \text{ and } 3) \quad (17)$$

The fact that the titration curves of polyelectrolytes are independent of the chain length suggests that the electrical interaction between ionized groups which are situated close together compared with the over-all distance of the polyion contributes significantly to the electrostatic free energy of ionization.[8] Such an interaction was actually observed in the alkaline hydrolysis of polymethyl acrylate; the reaction in a 29% aqueous acetone solution proceeded in four distinct steps, and the rate constant of each step remained substantially unchanged.[9] This can be understood by assuming that the hydrolysis of an ester group is affected mainly by the electrical charges of the first and second neighboring groups. If the same assumption holds in the ionization of polyacrylic acid,[*3] the ionization of the acid may be considered to be composed of four elementary ionizations ($\sigma=4$) and the electrostatic free energy of the nth ionization may be given by:

$$(\Delta F^i{}_{\mathrm{el}})_n=(\boldsymbol{N}\boldsymbol{e}^2/D)\sum_i(z_i/\bar{r}_i) \quad (18)$$

where D is the effective dielectric constant, where z_i is the number of the electrical charge in the ith group apart from the ionizing group ($z_i=0,1$ or 2, and $i=1$ and 2), and where $\bar{r}_i$ is the average distance between the ionizing group and the ith group.

From Eqs. (12) and (18), it follows that:

$$\mathrm{p}K_0=\mathrm{p}K_n'+\log\frac{\sigma-n+1}{n}-\frac{\boldsymbol{N}\boldsymbol{e}^2}{2.303\boldsymbol{R}TD}\sum_i\frac{z_i}{\bar{r}_i} \quad (19)$$

Since $\sum_i(z_i/\bar{r}_i)$ is considered to be $2/\bar{r}_2$, $2/\bar{r}_1$, and $2(1/\bar{r}_1+1/\bar{r}_2)$ when $n=2$, 3, and 4 respectively, when $\sigma=4$, as has been illustrated in a previous paper,[9] this term can be represented by:

$$\sum_i(z_i/\bar{r}_i)=[2/k-1)\{(n-1)-2\}^2+(n-1)]/\bar{r}_1 \quad n\neq 1 \quad (20)$$

where $k=\bar{r}_2/\bar{r}_1$.

Although Eq. (6) has been found to be correct for the case when $\Delta\mathrm{p}K'\gtrsim 2$, the relation still

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[7] A. Katchalsky and J. Gillis, *Rec. Trav. Chim. Pays-Bas*, **68**, 879 (1949).

[8] H. Morawetz. "Macromolecules in solution," Interscience Publishers, New York (1965), p. 354; P. Doty and G. Ehrlich, *Ann. Rev. Phys. Chem.*, **3**, 81 (1952); See also Ref. 1.

[9] H. Kawabe and M. Yanagita, This Bulletin, **42**, 3109, (1969).

[*3] The reason why the four-step ionization does not appear in the titration curve of polyacrylic acid is that the $\Delta\mathrm{p}K'$ is proportional to the increase in $(\Delta F^i{}_{\mathrm{el}})_n$, whereas the rate constant of the alkaline hydrolysis of polymethyl acrylate, K_n, is an exponential function of $(\Delta F^{\ddagger}_{\mathrm{el}})_n$, the electrostatic free energy of activation. The succeeding step of ionization is distinguishable if $\Delta\mathrm{p}K'>2$, which corresponds to $\Delta(\Delta F^i{}_{\mathrm{el}})_n>2.8$ kcal. On the other hand, the succeeding steps of the chemical reaction are distinguishable if the ratio of the succeeding rate constants is more than 2, which corresponds to $\Delta(\Delta F^{\ddagger}_{\mathrm{el}})_n>0.5$ kcal.

holds at $\alpha' = 0.5$, at least when $n=2$ and 3 in the case when $\sigma=4$, even if $\Delta pK'<2$.
Hence:

$$\alpha = (2n-1)/8 \qquad \alpha_n' = 0.5 \ (n=2 \text{ and } 3) \tag{21}$$

It may be seen in Fig. 2 that the values of α at $\alpha'_n=0.5$ are almost equal to those given by Eq. (21) when $n=2$ and 3 (within an error of ± 0.05). It follows from Eqs. (2) and (21) that:

$$(n-1) = \frac{3}{2} - 2\log\frac{1-\alpha}{\alpha} \tag{22}$$

The combination of Eqs. (16), (17), (18), (20), and (22) yields the relation:

$$\mathrm{pH} = \mathrm{p}K_0 + \frac{\Phi}{\bar{r}_1}\left[\frac{3}{2} + \frac{1}{4}\left(\frac{2}{k}-1\right)\right] - \left\{1 + \frac{\Phi}{\bar{r}_1}\left[2-(6-8\alpha)\left(\frac{2}{k}-1\right)\right]\right\}\log\frac{1-\alpha}{\alpha} \tag{23}$$

where $\Phi = \boldsymbol{N}e^2/2.303\boldsymbol{R}TD$. This equation is derived under the conditions given by Eqs. (17) and (21). It has been shown that these conditions are well satisfied at the points where $\alpha'_n=0.5$ ($n=2$ and 3), whereas the equations yield larger errors if $n=1$ and 4. Additionally, Eqs. (2) and (15), which are also used in the derivation of Eq. (23), give a better approximation for the former points than the latter. Hence, the pH values at $\alpha'_n=0.5$ for $n=2$ and 3 are given, in good approximation, by Eq. (23). The values of α at the two points are estimated, according to Eq. (21), to be 3/8 and 5/8 respectively, and the corresponding pH values are given by Eq. (23). Provided that both the points are on a line represented by Eq. (1), $\mathrm{p}K_a$ and n' are given by:

$$\begin{aligned}\mathrm{p}K_a &= \mathrm{p}K_0 + \frac{\Phi}{\bar{r}_1}\left[\frac{3}{2} + \left(\frac{1}{4}+\log\frac{5}{3}\right)\left(\frac{2}{k}-1\right)\right] \\ &= \mathrm{p}K_0 + \frac{\boldsymbol{N}e^2}{2.303\boldsymbol{R}TD\bar{r}_1}\left(1.03+\frac{0.94}{k}\right)\end{aligned} \tag{24}$$

$$\begin{aligned}n' &= 1 + \frac{\Phi}{\bar{r}_1}\left[2-2\left(\frac{2}{k}-1\right)\right] \\ &= 1 + \frac{4\boldsymbol{N}e^2}{2.303\boldsymbol{R}TD\bar{r}_i}\left(1-\frac{1}{k}\right)\end{aligned} \tag{25}$$

From Eqs. (24) and (25) a parameter which is only a function of k is obtained:

$$\frac{\mathrm{p}K_a-\mathrm{p}K_0}{n'-1} = \frac{1}{4}\left(\frac{1.03k+0.94}{k-1}\right) \tag{26}$$

Since k is the relative distance concerning the first and second neighboring groups, the left term of Eq. (26) will be more or less sensitive to the stereoisomerism of polyelectrolytes.

Discussion

1) **$\Delta pK' \geqq 2$.** The plots of pH against log $[(1-\alpha)/\alpha]$ derived from some potentiometric titration data are shown in Fig. 4, where the solid lines are calculated on the basis of Eqs. (1) and (10) as below. Garret and Guile[4] and Ferry et al.[5] found that the titration curve of the maleic acid-styrene copolymer (MA–ST) was composed of two parts, which could be expressed by Eq. (1) with $n'=1$ and 2. If the second-half part ($n'=2$), which is plotted in Fig. 4 on the basis of Ferry's data,[4] is further divided into two parts, each of them can be represented by a line with a slope of unity. Hence, the corresponding dissociation constants can be determined on the basis of Eq. (4): $\mathrm{p}K'_2=9.4$ and $\mathrm{p}K'_3=11.4$. ($\mathrm{p}K'_1=4.4$ is given by Ferry for the first-half ionization). Upon substitution $\Delta \mathrm{p}K'=\mathrm{p}K'_3-\mathrm{p}K'_2=2.0$ in Eq. (11), we obtain $\Delta \mathrm{p}K_a=0$. Hence, the constants of Eq. (1) for the second-half ionization are given by Eq. (10). Since $\sigma=2$ in this case, the calculated values are $n'=2$ and $\mathrm{p}K_a=10.4$; these are close to the values observed by Ferry: $n'=2.2$ and $\mathrm{p}K_a=10.35$.

The behavior of MA–ST in the second-half ionization will be illustrated by the ionzation of 1,3-propanediamine (PDA), whose acidic dissociation constants are $\mathrm{p}K'_1=8.6$ and $\mathrm{p}K'_2=10.6$. The constants for PDA are calculated to be $n'=2$ and $\mathrm{p}K_a=9.6$. The line in Fig. 4, which is calculated by substituting these value in the parameters of Eq. (1), fits the titration data.

When $\Delta pK'>2$, the plot of pH *vs.* log $[(1-\alpha)/\alpha]$ will be represented by σ parallel lines separated

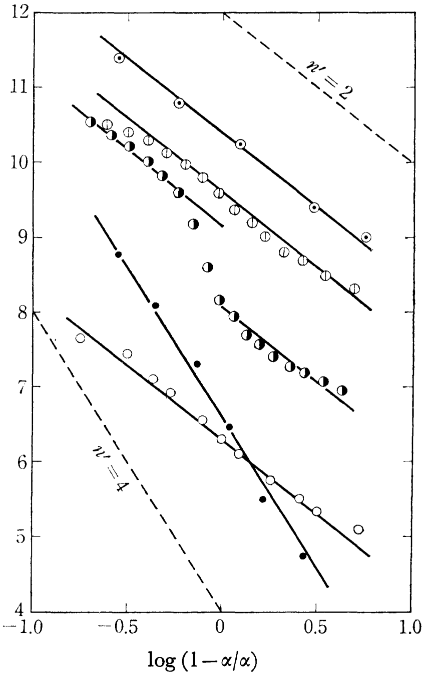

Fig. 4. Plot of pH *vs.* log $[(1-\alpha)/\alpha]$ from the potentiometric titration data in water.
⊙ MA-ST[5] (second-half ionization)
⦶ PDA ◑ EDA ● PVAM[3]
○ PVAM[3] (in 2 N NaCl, second-half ionization)
— calculated on the basis of Eqs. (1) and (10)

by a distance of (Δp$K'-2$), as was pointed out in the previous section. This situation will be illustrated by the ionization of ethylenediamine; p$K'_1=7.1$, p$K'_2=10.0$, and Δp$K'=3.0$. Actually, the titration data shown in Fig. 4 nearly all fall on two parallel lines with a slope of $n'=2$ and separated by a distance of 1.0 (Δp$K_a=3.0-2=1.0$).

It is interesting to note that polyvinylamine (PVAM) behaves similarly to MA-ST when it is titrated in the presence of salt. It is shown on the basis of the data in the 2N sodium chloride solution[3] that the titration curve can be divided into two parts. The plot of pH *vs.* log $[(1-\alpha)/\alpha]$ for the first-half ionization is represented by a line of $n'=1$, and the corresponding acidic dissociation constant is p$K'_3=9.6$. The plot for the second-half ionization shown in Fig. 4 has a slope of $n'=2$, and the data of this part can be expressed by Eq. (4) if they are further divided into two parts. Thus, the acidic dissociation constants in the second part can also be determined; they are p$K'_2=7.3$ and p$K'_1=5.3$. Here, it is seen again that Δp$K'=$pK'_2-p$K'_1=2.0$ and Δp$K_a=0$; hence, the parameters of Eq. (1) are given by Eq. (10). The line in Fig. 4 drawn with the calculated values, $n'=2$ and p$K_a=6.3$, can well represent the plot for the second ionization.

On the other hand, polyvinyl amine behaves differently in the absence of salt. The data[3] can be expressed by Eq. (1), with $n'=4$ and p$K_a=6.6$ in the middle range of the titration curve, as is shown in Fig. 4. If the titration curve is divided into four even parts and if Eq. (4) is applied to the data of each part, the corresponding four acidic dissociation constants can be determined: p$K'_1=4.1$, p$K'_2=5.6$, p$K'_3=7.6$, and p$K'_4=9.3$. The linearity of the plot in the middle ionization range shown in Fig. 4 can be explained by Δp$K'=$pK'_3-p$K'_2=2$. Since $\sigma=4$ in this case, the parameters are determined on the basis of Eq. (10) to be $n'=4$ and p$K_a=6.6$.

Since the ionization of all the acids and bases shown in Fig. 4 satisfies the condition Δp$K'\gtrsim 2$, their titration curves can be determined by the use of their pK'_n values on the basis of Eqs. (5) and (7). The observed values fall excellently on the calculated titration curves of MA-ST and PVAM, as is shown in Fig. 5, where β is the degree of the ionization of PVAM ($\beta=1-\alpha$).

2) **Δp$K'<2$.** polyacrylic acid was titrated with sodium hydroxide in the absence of salt;[9] the data are shown in Fig. 6, where the solid lines are calculated as below. The titration data are expressed by Eq. (1) with the parameters of p$K_a=6.9$ and $n'=2.4$; these values are in accordance with those given by Gregor and Frederic.[10]

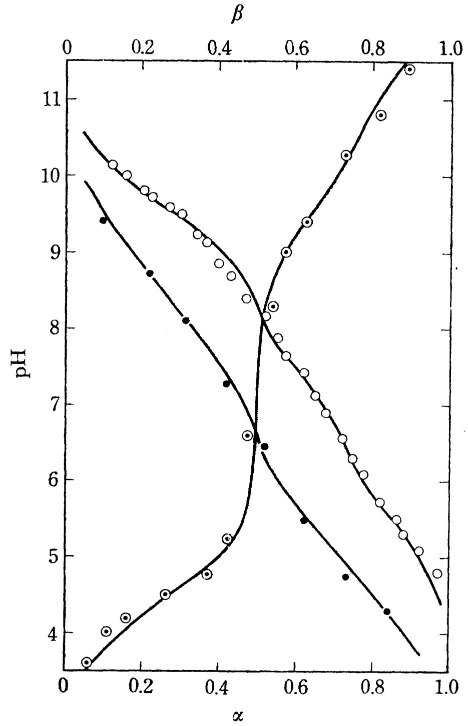

Fig. 5. Titration curves of the polyelectrolytes.
⊙ MA-ST[5] ● PVAM[3]
○ PVAM[3] (in 2N NaCl)
— calculated on the basis of Eqs. (5) and (7)

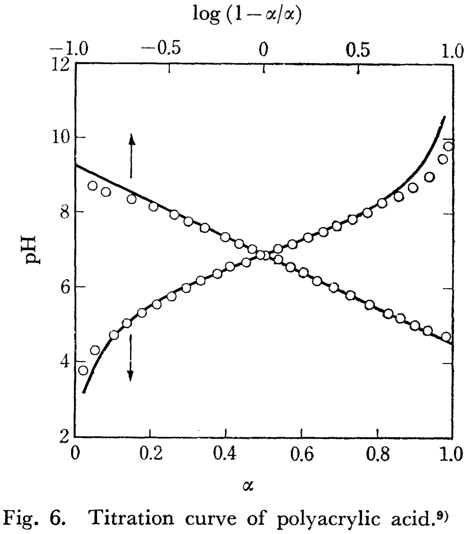

Fig. 6. Titration curve of polyacrylic acid.[9]
— calculated on the basis of Eq. (1) with pK_a $=6.89$ and $n'=2.35$.

The data do not fit Eq. (4) when they are divided into two equal parts. In the previous section, Eq. (23) was derived on the assumption that the ionization of polyacrylic acid is composed of four elementary ionizations, by analogy with the kinetic behavior in the alkaline hydrolysis of polymethyl acrylate. The distance between the groups

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[10] H. P. Gregor and M. Frederic, *J. Polymer Sci.*, **32**, 451 (1957).

TABLE 2. INTRINSIC IONIZATION CONSTANT OF POLYACRYLIC ACID

n	$\alpha(\alpha_n'=0.5)$	pH	$\sum z_i/\bar{r}_i$	pK_0	
2	3/8	6.40	$2/\bar{r}_2$	5.38	5.36
3	5/8	7.39	$2/\bar{r}_1$	5.34	

determined on the basis of the kinetic data are $\bar{r}_1=3.25$ and $\bar{r}_2=5.07$ Å.[9] The parameters in Eq. (23) are $k=1.56$ and $\Phi=3.04$ ($T=298$ and $D=80$). The intrinsic ionization constant, pK_0, can be determined on the basis of Eq. (19), in which pK'_n is given by pH at $\alpha'_n=0.5$. An approximate value of α corresponding to $\alpha'_n=0.5$ is given by Eq. (21); a better approximation is obtained when $n=2$ and 3 than when $n=1$ and 4, as has been discussed in the previous section. The calculated values of pK_0 are shown in Table 2; the average value is 5.36. This value is slightly higher than the dissociation constant of isobutylic acid, 4.86, but it is comparable with the value determined from the pH value of an aqueous solution of polyacrylic acid on the basis of the approximate relation, pK_0=2pH−log [COOH], where [COOH] represents the concentration of polyacrylic acid expressed by monomole/l. The value estimated from the present experimental data is 5.4 ([COOH]=0.019 and pH=3.57); the value of 5.2 is obtained from Gregor's data.[10] The empirical constants in Eq. (1) are calculated on the basis of Eqs. (24) and (25): $n'=2.35$ and pK =6.89. These values are in good agreement with the observed values of the parameter. The titration curve determined on the basis of the equation, pH=6.89 −2.35 log[(1−α)/α], fits the titration data in the middle range of the curve, as is shown in Fig. 6.

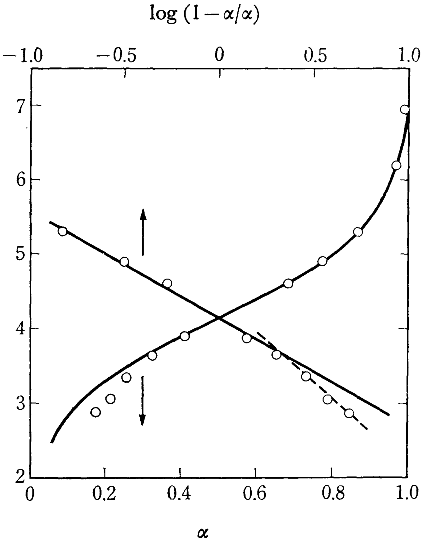

Fig. 7. Titration curve of pectinic acid.[11]
— calculated on the basis of Eq. (1) with pK_a=4.15 and n'=1.44.

Equation (23) is also applicable to the ionization of pectinic acid. The titration data of the acid[11] is shown in Fig. 7, in which the solid lines are drawn by means of Eq. (1) with the values of the parameter calculated as below. The plot of pH *vs.* log [(1−α)/α] is linear in the $\alpha>0.3$ range, and the empirical parameters determined from the titration data are $n'=1.5$ and p$K_a=4.1_5$. It may be presumed that pectinic acid has an elongated structure similar to cellulose when the ionization proceeds, for an intense repulsing force emerges among the charges formed on the macromolecule. It can thus be assumed that $r_2=10.3$ Å on the basis of the fiber period of cellulose.[12][*4] On the assumption of the elongated pectinic acid structure, $\bar{r}_1$ is estimated to be 7.5 Å on the basis of the length and angle of the bond. By assuming $\sigma=4$ for the ionization of pectinic acid, the pK_0 value is calculated on the basis of Eq. (19); the obtained values are shown in Table 3. The mean value, pK_0=3.45, is in good agreement with the pK=3.42 of D-garacturonic acid,[12] the monomeric homologue of pectinic acid. The parameters of Eq. (1) can now be calculated on the basis of Eqs. (24) ayd (25) to be $n'=1.44$ and pK_a=4.15; those values are in accordance with the observed values. All the titration data except for the extent $\alpha<0.3$ fall excellently on the titration curve drawn by means of pH=4.15 −1.44 log[(1−α)/α], which is shown in Fig. 7. The structural transformation of pectinic acid presumably occurs in this range on account of an increase in the repulsion force among the fixed charges.

TABLE 3. INTRINSIC IONIZATION CONSTANT OF PECTINIC ACID

n	$\alpha(\alpha_n'=0.5)$	pH	$\sum z_i/\bar{r}_i$	pK_0	
2	3/8	3.80	$2/\bar{r}_2$	3.45	3.45
3	5/8	4.45	$2/\bar{r}_1$	3.47	

It has been pointed out in the previous section that the left term of Eq. (26) may correlate with the steric arrangement of the groups; this seems

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11) R. Speicer, C. H. Hills and C. R. Eddy, *J. Phys. Colloid Chem.*, **49**, 328 (1945).

12) K. J. Palmer, M. B. Hartzog, *J. Amer. Chem. Soc.*, **67**, 1865 (1945). See also Katchalsky's paper.[13]

13) A. Katchalsky and J. Feitelson, *J. Polymer Sci.* **13**, 385 (1945).

[*4] By treating the kinetic data of the alkaline hydrolysis of pectin at 4°C in an aqueous solution[13] according to the procedure described in a previous paper,[9] the rate constans of k_3=6.6 and k_4=1.7 l/mol min are obtained; from them we obtain $\bar{r}_2$=11 Å.

really to be the case with polyacrylic acid and pectinic acid. The average distance from an ionizing group to the ith group, $\bar{r}_i$, is defined as follows:[9)]

$$1/\bar{r}_i = \sum_j (X_{i,j}/r_{i,j})$$

where j is related to the steric configuration, where r is the distance between two groups, and where X is the mole fraction ($\sum_j X_{i,j}=1$). If the planar zig-zag structure is assumed in the vicinity of an ionizing group of polyacrylic acid, the value of $(\mathrm{p}K_a-\mathrm{p}K_0)/(n'-1)$ for an atactic isomer, whose structure is completely random, is estimated to be 1.0. The value obtained from the titration data is 1.1, close to the calculated one. If it is assumed that pectinic acid has an elongated structure like cellulose and that carboxylic acid groups are situated alternatively on the opposite sides of the plane consisting of piranose rings, $(\mathrm{p}K_a-\mathrm{p}K_0)/(n'-1)$ will be 1.5; this is close to the value obtained from the titration data, 1.4.