# STUDIES ON THE ELECTROCHEMICAL PROPERTIES

# OF COPOLYMERS OF MALEIC ACID, III

## On the Difference of Titration Behaviors

## due to Comonomer Species

By Kazuo Monobe

The sharp difference of titration behaviors between maleic acid–vinyl acetate copolymer and maleic acid–styrene copolymer was briefly considered according to the Kirkwood model for organic ions. On the other hand, the electrostatic potential of polyion with which the coil configuration was related, was estimated from the potentiometric data at low ionic strength and the comparison between two copolymers in various polymer concentrations was done. During the dissociation of the primary carboxyl group, the potential curves as the function of $\alpha'$ markedly differed between two copolymers. In particular, the anomalous behavior of the styrene copolymer was considered to come from its tighter coiling.

In addition, the independency of titration curves of the degree of polymerization was ascertained in two copolymers.

## Introduction

It was shown in the previous paper[1] that the titration behaviors of the copolymers of maleic acid (I) exhibited a remarkable difference according to the kind of substituent R at high ionic strength as well as at low ionic strength;

(I)

$$-CH_2-CH-CH-CH-CH_2-CH-CH-CH-$$
$$\quad\quad\quad R \quad\quad COOH\;COOH \quad\quad R \quad\quad COOH\;COOH,$$
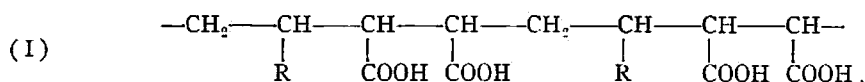
where     $-R=-OCOCH_3$; maleic acid–vinyl acetate (MA–VAc) copolymer

$-R=-C_6H_5$; maleic acid–styrene (MA–S) copolymer.

The difference was examined with the titration data at high ionic strength, and was attributed to the difference in the type of the nearest neighbor interaction. Another respect of the difference was that of coil configuration by the presence of the nonpolar comonomer group, as was pointed out by Ferry and co-workers[2].

The coil configuration is related with the contribution of a polyion potential to the titration curve. Thus, the polyion potential is estimated here and a comparison between two copolymers,

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1) K. Monobe, *This Journal*, **30**, 145 (1960)
2) J. D. Ferry, D. C. Udy, F. C. Wu, G. E. Heckler and D. F. Fordyee, *J. Colloid Sci.*, **6**, 429 (1951)

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MA–VAc and MA–S copolymers, is shown.

In general, the titration curves of polyelectrolytes are independent of the degree of polymeri-zation[3]. To ascertain it for the copolymers of maleic acid, the titration experiments were carried out with the samples of different molecular weight.

## Experimentals

The copolymers used here are mainly the fractionated samples described in Part I in this series. The molecular weights and compositions were given in Table 1. The molecular weights were determined from osmotic pressure measurements[4] in tetrahydrofuran solutions of the corres-ponding copolymer anhydrides. The compositions were measured from the titration curves, taking into account the free carboxyl content in copolymer anhydride obtained by the anhydride analysis with the aniline method[5]. There is a little variation in the composition of each sample. The titrations were carried out at 20°C and the details were given in Part I in this series.

Table 1   Molecular weights and compositions of MA–VAc copolymers and MA–S copolymers

| Copolymer fractions | | Mol. wt. $M_n \times 10^4$ | Composition comonomer/MA |
|---|---|---|---|
| MA–VAc | $F_0$ | — | 1.11 |
| MA–VAc | $F_3$ | 12 | 1.19 |
| MA–S | $F_0$ | — | 1.10 |
| MA–S | $F_2$ | 24 | 1.12 |
| MA–S | $F_4$ | 20 | 1.12 |
| MA–S | $F_5$ | 17 | 1.15 |
| MA–S | $F_7$ | 10 | 1.19 |

$F_0$ represents the unfractionated sample

## Influence of the Degree of Polymerization

The copolymer samples with different molecular weights were titrated and the plots of pH against $\log \dfrac{\alpha'}{1-\alpha'}$ or $\log \dfrac{\alpha'-1}{2-\alpha'}$ were illustrated in Fig. 1, where $\alpha'$ represented the degree of dis-sociation.

As is shown in Fig. 1, there is no influence of the molecular weight change (100,000~240,000) except the discrepancy (about 0.2 pH unit) of the unfractionated MA–S copolymer in the secondary dissociation process. The discrepancy for the unfractionated MA–S copolymer may presumably be considered as due to the low molecular weight diene products[6], which may not be removed. In MA–VAc copolymer, such discrepancy between the titration data for fractionated

3)  A. Katchalsky and P. Spitnik, *J. Polym. Sci.*, **2**, 432 (1947)
4)  K. Monobe, *to be published in This Journal*
5)  L. M. Minsk, G. P. Waugh and W. O. Kenyon, *J. Am. Chem. Soc.*, **72**, 2646 (1950)
6)  K. Alder and R. Schmitz-Josten, *Ann. der Chem.*, **595**, 1 (1955)
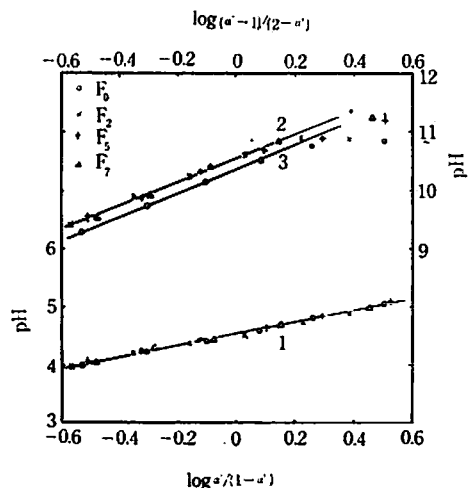
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Fig. 1  Titration results of MA–S copolymer with different molecular weights

Primary dissociation process, 1: the lower and left scales.  Secondary dissociation processes, 2 and 3; the upper and right scales. Polymer concentrations are $0.96 \times 10^{-2} M$. $F_0(\bigcirc)$, $F_2(\times)$, $F_5(+)$, $F_7(\triangle)$.  Molecular weights of these fractions are given in Table 1.

sample ($F_n$) and that for unfractionated sample ($F_0$) was not found at the same polymer concentration.

In other words, the fact that the titration data are independent of the molecular weights of the copolymers means that there is no great change in composition among these fractionated samples.

## Localization[7] of the Nearest Neighbor Electrostatic Interaction[10, 11, 12]

In the previous paper, the results of the copolymers at high ionic strength were considered in comparison with the corresponding $\alpha$, $\beta$–disubstituted succinic acids.  The abnormality of MA–S copolymer was pointed out from the completely localized type of the interaction between neighbor charges on a copolymer chain.   On the contrary, MA–VAc copolymer gave rather reasonable result.

If the Kirkwood model[8, 9] for organic ions is extended to the chain polyelectrolyte, it may be said that the domain of each segment in the solvent may be regarded as the cavity of low dielectric constant in which the charges are imbedded.  Using this model, one can show the free energy of the interaction between a pair of charges $\epsilon_1$ and $\epsilon_2$ by the equation,

$$E = \epsilon_1 \epsilon_2 / D_K r \quad , \tag{1}$$

where                    $D_K$,   effective dielectric constant of cavity

        $r$,   distance between $\epsilon_1$ and $\epsilon_2$   .

If the cavity in the neighborhood of a comonomer may be designated as follows:

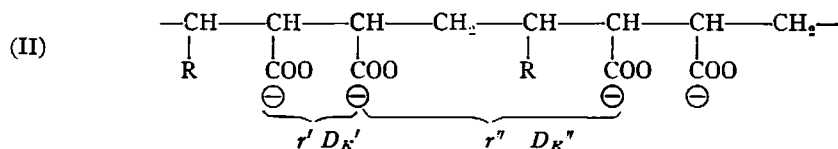7)  A. Katchalsky, J. Mazur and P. Spitnik, *J. Polym. Sci.*, 23, 513 (1957), Discussion
8)  J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 6, 506, 513 (1938)
9)  C. Tanford, *J. Am. Chem. Soc.*, 79, 5348 (1957)
10)  R. A. Marcus, *J. Phys. Chem.*, 58, 621 (1954)
11)  F. E. Harris and S. A. Rice, *ibid.*, 58, 725, 733 (1954); *J. Chem. Phys.*, 24, 326 (1956); 25, 955 (1956)
12)  S. Lifson, *J. Chem. Phys.*, 26, 727 (1957)

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(II)  $-CH-CH-CH-CH_2-CH-CH-CH-CH_2-$
         |    |    |         |    |    |
         R   COO  COO        R   COO  COO
             $\ominus$  $\ominus$           $\ominus$   $\ominus$

         $\underbrace{\quad}_{r'\ D_K{}'}$   $\underbrace{\quad}_{r''\ D_K{}''}$

when $r''D_K{}'' \gg r'D_K{}'$, the interactions are localized, but when $r''D_K{}'' \simeq r'D_K{}'$, the interactions are unlocalized.

The idealized type of localization corresponds to the monomeric dibasic acids. Therefore, the first and second dissociation constants, $pK_1°$ and $pK_2°$, when the contribution of a polyion potential is fully eliminated, are related with the intrinsic dissociation parameter $pK_0$ by the equations :

$$pK_1° = pK_0 - \log 2 \qquad (2)$$

and

$$pK_2° = pK_0 + \Delta pK + \log 2 , \qquad (3)$$

where $\Delta pK = 0.43 \epsilon^2/D_K r kT$, the interaction constant within carboxyl pair of maleic acid group in the copolymers.

The similar relation for the idealized unlocalized type is given by applying Katchalsky's treatment[3,13] (Appendix) to the polyacids in which the neighbor interaction energy is large :

$$pK_1° = pK_0 - \log \frac{4}{3} \qquad (4)$$

and

$$pK_2° = pK_0 + 2\Delta pK + \log \frac{4}{3}. \qquad (5)$$

Using the proper values of $pK_0$ and $\Delta pK$, the calculated values of $pK_2°$ for localized and unlocalized types were compared with the observed values of the copolymers at high ionic strength. The calculated values are given in Table 2.

Table  2     The calculated values of $pK_2°$

| $pK_0$ | $\Delta pK$ | $pK_2°$ localized | unlocalized |
|--------|-------------|-------------------|-------------|
| 3.6    | 2.2         | 6.1               | 8.1         |
| 3.8    | 2.5         | 6.6               | 8.9         |
| 3.2    | 3.0         | 6.5               | 9.3         |

The values, $pK_0 = 3.8$ and $\Delta pK = 2.5$, correspond to the values in $\alpha$, $\beta$–diethyl succinic acid (lower melting point). If the $\Delta pK$, the interaction constant between carboxyls in maleic acid group in the copolymers, takes the value shown in Table 2, the observed value, 5.97, for MA–VAc copolymer is approximately the localized value, and the 7.52, for MA–S copolymer is the inter-

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13) J. Mazur, A. Silberg and A. Katchalsky, *J. Polym. Sci.*, **35**, 43 (1959)

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mediate value between the localized and unlocalized types.

## Electrostatic Potential

The general potentiometric equation[14] for the primary dissociation process of the copolymers of maleic acid (I) at low ionic strength, is given by the following equation, neglecting the dissociation of the secondary carboxyl,

$$\mathrm{pH} = pK_1^\circ + \log \frac{\alpha'}{1-\alpha'} + \frac{0.43\,\epsilon\phi_1}{kT} \quad , \tag{6}$$

where
$\alpha'$ , degree of dissociation

$pK_1^\circ$ , dissociation parameter

$\phi_1$ , electrostatic potential of a polyion

$\epsilon$ , unit charge

$k$ , Boltzmann constant

$T$ , absolute temperature.

Using the values of $pK_1^\circ$, estimated at high ionic strength, the contribution of a polyion potential at low ionic strength, $\epsilon\phi_1/kT$, can be evaluated[15] from potentiometric titration, according to Equation (6). The results obtained for copolymers, MA–VAc and MA–S, in polymer concentrations ranging from $10^{-3}$ to $10^{-2}$, are shown as the function of $\alpha'$ in Fig. 2.
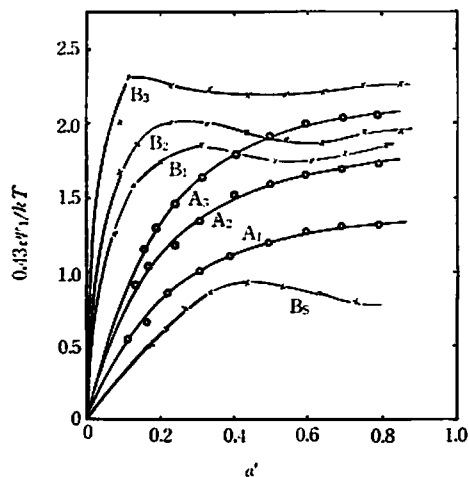


Fig. 2  The potentials as the function of $\alpha'$ (20°C)

It is shown as plots of $0.43\,\epsilon\phi_1/kT$ against $\alpha'$. Polymer concentrations, $A_1$ ($0.99\times10^{-2}\,M$), $A_2$ ($0.33\times10^{-2}\,M$), $A_3$ ($0.12\times10^{-2}\,M$) for MA–VAc copolymer aqueous solutions respectively. $B_1$ ($0.96\times10^{-2}\,M$), $B_2$ ($0.32\times10^{-2}\,M$), $B_3$ ($0.12\times10^{-2}$ $M$) for MA–S copolymer aqueous solutions respectively. Bs ($0.79\times10^{-2}\,M$) for MA–S copolymer $0.2\,M$ NaCl solution.

In Fig. 2, upper three curves, $B_1$, $B_2$ and $B_3$ were obtained from the titration curves for MA–S copolymer. Polymer concentrations are $B_1=0.96\times10^{-2}\,M$, $B_2=0.32\times10^{-2}\,M$, and $B_3=0.12\times10^{-2}\,M$, respectively. The curves, $A_1$, $A_2$ and $A_3$ were obtained from the titration curves for

14) G. S. Hartley and J. W. Roe, *Trans. Faraday Soc.*, 36, 101 (1940)
15) A. Katchalsky, N. Shavit and H. Eisenberg, *J. Polym. Sci.*, 13, 69 (1954)

MA–VAc copolymer. Polymer concentrations are $A_1 = 0.99 \times 10^{-2} M$, $A_2 = 0.33 \times 10^{-2} M$, and $A_3 = 0.12 \times 10^{-2} M$, respectively. The curve Bs was obtained from the titration curve for MA–S copolymer in $0.2 M$ NaCl aqueous solution, in which polymer concentration is $0.79 \times 10^{-2} M$.

It is readily noticed that the form of three curves for MA–S are markedly different from that for three MA–VAc. In MA–VAc copolymer, the potential increases with $\alpha'$ with relatively small slope. In MA–S copolymer, the potential increases very sharply and exhibits the maximum at lower degree of dissociation and then slightly changes. The maximum point shifts to the lower degree of dissociation, as the ionic strength of the solution becomes lower.

The change of potential as the function of $\alpha'$ shows the counter-ions binding behavior. The tendency for MA–S copolymer is considered as due to tighter coiling[16], as was pointed out by Ferry[2]. On the other hand, the tendency corresponds to that the $n_1$ value of the empirical equation describing the titration curves at low ionic strength nearly equals unity.

Katchalsky and co-workers[15] have shown that the electrostatic potential $\psi$ may be identified with the electrokinetic potential $\zeta$ obtained from the electrophoretic data. Consequently, it is desirable to check the potentiometric results by the electrophoretic experiments. For the present purpose, it has not been done here.

## Appendix

The application of Katchalsky's treatment[3] to an ideal polyacid model which carries the ionizable groups at the same intervals on a polymer chain and in which the nearest neighbor electrostatic interaction energy $\Delta pK$ is considerably large, leads to the following potentiometoric equations, when the influence of polyion potential is fully eliminated,

$$\text{pH} = pK_0 - \log \frac{\alpha'(1 - 2\alpha' + x)^2}{(1 - \alpha')(\alpha' - x)^2} \tag{A1}$$

and

$$\Delta pK = \log \frac{(\alpha' - x)^2}{x(1 - 2\alpha' + x)} \quad , \tag{A2}$$

where $\alpha'$ is the degree of ionization, and $x$ is the fraction of nearest neighbor $(-, -)$ doublets and is unity, when $\alpha' = 1$. $x$ is negligible at low $\alpha'$ value $(\alpha' < 0.5)$. Hence, the pH value at $\alpha' = \frac{1}{4}$ (corresponds to $pK_1^\circ$) is given from Equation (A1) as follows:

$$\text{pH}_{\frac{1}{4}} = pK_0 - \log \frac{4}{3} \quad . \tag{A3}$$

When $\alpha'$ is large $(\alpha' > 0.5)$, Equations (A1) and (A2) reduce to

$$\text{pH} = pK_0 + 2\Delta pK + \log \frac{(1 - \alpha')x^2}{\alpha'(\alpha' - x)^2} \quad , \tag{A4}$$

where $x$ is given from Equation (A2);

16)  W. Dannhauser, W. H. Glaze, R. L. Dueltgen and K. Ninomiya, *J. Phys. Chem.*, **64**, 954 (1960)

$$x = \frac{A(2\alpha'-1) - 2\alpha' + [A^2(2\alpha'-1)^2 + 4A\alpha'(1-\alpha')]^{\frac{1}{2}}}{2(A-1)} \quad , \qquad \text{(A5)}$$

where      $A = 10^{\Delta pK} = \exp(\epsilon^2/D_K r kT)$.

Hence, the pH value at $\alpha' = \dfrac{3}{4}$ (corresponds to $pK_2^\circ$) is given from Equations (A4) and (A5).
For large value of $A$, it is given as

$$\mathrm{pH}_{\frac{3}{4}} = pK_0 + 2\Delta pK + \log\frac{4}{3}. \qquad \text{(A6)}$$

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