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STUDIES ON THE ELECTROCHEMICAL PROPERTIES OF COPOLYMERS OF MALEIC ACID, I Potentiometric Titration at Low Ionic Strength

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In this series, the polydibasic properties of some copolymers of maleic acid are studied from the viewpoint of the neighbor interaction. In the present paper, the potentiometric titrations of two copolymers, maleic acid-vinyl acetate and maleic acid-styrene copolymers, were studied at low ionic strength, with somewhat different experimental methods from Garrett and Ferry. The empirical equations to estimate the average dissociation constants were presented in comparison with that of the monomeric dibasic acids. The average dissociation constants in various polymer concentrations were obtained and the polydibasic properties were discussed.

Introduction

The copolymers of maleic acid are called the polydicarboxylic acid¹⁾ compared with the so-called polymonocarboxylic acid such as polyacrylic acid. The name is due to the analogy of monomeric acids; that is, the former undergoes two classes of dissociation although the latter does one class of dissociation, irrespective of the fact that both are polyacids. In spite of the apparent analogy, the dissociation equilibrium of polyacids is obviously different from that of all monomeric acids in the point that the counter-ions are subjected to the strong electrostatic force due to all ionized groups on a polymer chain²⁾.

Garrett and Guile³⁾ carried out the potentiometric titration on sodium salts of maleic acid-styrene copolymer. At the same time, the titration and viscosity studies on two copolymers of maleic acid were performed by Ferry and co-workers⁴⁾.

The author, in this series, attempts to compare the following two 1 : 1-copolymers; maleic acid-vinyl acetate (MA-VAc) copolymer and maleic acid-styrene (MA-S) copolymer, from the viewpoint of electrostatic neighbor interaction⁵⁾.

In Part I, the potentiometric titrations at low ionic strength are performed in various polymer concentrations and then the empirical equations to estimate the average dissociation constants are represented in comparison with that of the monomeric dibasic acids. In Part II, the dissociation

1) A. Katchalsky and P. Spitnik, *J. Polym. Sci.*, **2**, 432 (1947)

2) H. Eisenberg and R. M. Fuoss, *Modern Aspects of Electrochemistry*, Butterworths Sci. Pub., London (1954)

3) E. R. Garrett and R. L. Guile, *J. Am. Chem. Soc.*, **73**, 4533 (1951)

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

5) A. Katchalsky, J. Mazur and P. Spitnik, *J. Polym. Sci.*, **23**, 513 (1957), Discussion

constants, pK_1° and pK_2° , are estimated and are compared with the corresponding values of proper monomeric α , β -disubstituted succinic acids, from the potentiometric titrations at high ionic strength, where the effects of the polyion field may be fully eliminated. The results obtained in the two copolymers are discussed from the standpoint of the nearest neighbor interaction. In Part III, the polyion field effects at low ionic strength are estimated and compared between the two copolymers.

Experimentals

1 Preparation^{6,7)} of copolymers of maleic acid The copolymer samples were prepared by the copolymerization of maleic anhydride (1 mole) with vinyl acetate (1 mole) or styrene (1 mole) in thiophene free benzene (1.5 l) at $70^\circ \pm 0.2$ with 0.2% benzoyl peroxide as the initiator. These reactant monomers were purified by vacuum distillation before copolymerization. About 60% conversion products were separated and washed with benzene and ether repeatedly, then dried in vacuo for a week. The unfractionated samples were dissolved in acetone and then fractionated into eight fractions by addition of petroleum benzene. Since the titration curves for all of the fractionated and unfractionated samples at the same polymer concentration had coincided well (that will be shown in Part III), most of the titration experiments in Parts I and II were performed with the unfractionated samples dissolved in water.

Maleic anhydride-vinyl acetate copolymer was dissolved in pure water of $\text{pH}=6.88$ at room temperature (20°C) to avoid the saponification of acetyl group and successive lactonization. Maleic anhydride-styrene copolymer was dissolved in the same pure water at 90°C .

2 Potentiometric titration Potentiometric titrations were carried out with a Horiba pH-meter Model-P which can read with a sensitivity of 0.01 pH unit. The standard buffers were used to calibrate the instrument. Solutions of the copolymers were titrated with 0.5*N* NaOH by use of a microburette. All runs were performed in carbon dioxide free N_2 atmosphere at $20.0 \pm 0.1^\circ\text{C}$. To determine the neutralization points, the following methods were used at the same time.

For MA-VAc copolymer, the neutralization point is known to coincide with phenolphthalein end point in pyridine aqueous solution (1 : 1) by Minsk and co-workers⁸⁾, and also with that in 2*M* NaCl aqueous solution, in which the polymer concentrations used for titrations were more than 0.01 monomole per liter (*M*). For MA-S copolymer, the half neutralization point coincides with the phenolred end point in 0.01*M* aqueous solution. It was also confirmed that these points were in accord with the corresponding points of conductometric titration.

The copolymer composition was calculated from the titration results, taking account of free carboxyl content in copolymer anhydride based on anhydride analysis by the aniline method⁹⁾. The results

6) M. C. de Wilde and G. Smets, *J. Polym. Sci.*, **5**, 253 (1950)

7) T. Alfrey and E. Lavin, *J. Am. Chem. Soc.*, **67**, 2044 (1945)

8) L. M. Minsk, G. P. Waugh and W. O. Kenyon, *ibid.*, **72**, 2646 (1950)

9) K. Monobe, to be published in *This Journal*

for unfractionated samples were; $VAc/MA=1.11$ and $S/MA=1.10$. The values for fractionated samples will be shown in Part III. For MA-VAc copolymer, it was observed that the saponification of acetyl group and successive intramolecular lactonization did not occur under the given conditions. As for these reactions which would occur at high temperature, the results of conductometric titrations will be shown in a succeeding paper⁹⁾.

The Average Dissociation Constants

As is shown in Fig. 1, the titration curves of the copolymers of maleic acid exhibit marked

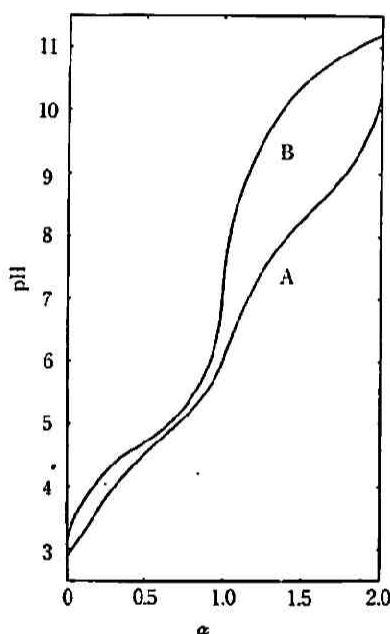


Fig. 1 Titration curves for MA-VAc and MA-S copolymers at 20°C

curve A : MA-VAc copolymer $0.986 \times 10^{-2} M$ aqueous solution
 curve B : MA-S copolymer $0.961 \times 10^{-2} M$ aqueous solution

inflection at the half neutralization point ($\alpha=1$) and the dissociation process can be divided into two classes. Each class corresponds to the dissociation of the primary carboxyl group and the secondary carboxyl group, respectively. The titration behavior apparently resembles that of the monomeric dibasic acids, having large difference between the first and second dissociation constants.

Thus, the following empirical equations were lead for polydicarboxylic acids to determine the average dissociation constants by the same treatment as Katchalsky and Spitnik's empirical equation¹⁾ for the weak polymonocarboxylic acids was obtained by the analogy of Henderson-Hasselbalch's equation.

The dissociation constants of a monomeric dibasic acid, H_2A , may be defined, assuming that the activity coefficients are unity, by the equations,

$$K_1 = [H^+][HA^-]/[H_2A], \quad K_2 = [H^+][A^-]/[HA^-],$$

where each bracket represents the concentration of the species, respectively. The degree of dis-

sociation, α' , may be defined by the equation¹⁰⁾,

$$\alpha' = \alpha + \frac{[\text{H}^+] - [\text{OH}^-]}{C} = \frac{K_1[\text{H}^+] + 2K_1K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}, \quad (1)$$

where α represents the degree of neutralization, $[\text{NaOH}]/C$, and C represents the total acid molar concentration. Equation (1) leads readily to Speakman's¹¹⁾ relation: $X = K_1Y + K_1K_2$. For $K_1 \gg K_2$, Equation (1) gives the following two equations,

$$\text{pH} = \text{p}K_1 + \log \frac{\alpha'}{1 - \alpha'} \quad (2)$$

and

$$\text{pH} = \text{p}K_2 + \log \frac{\alpha' - 1}{2 - \alpha'}. \quad (3)$$

Namely, Equations (2) and (3) correspond to the primary and secondary dissociation processes and

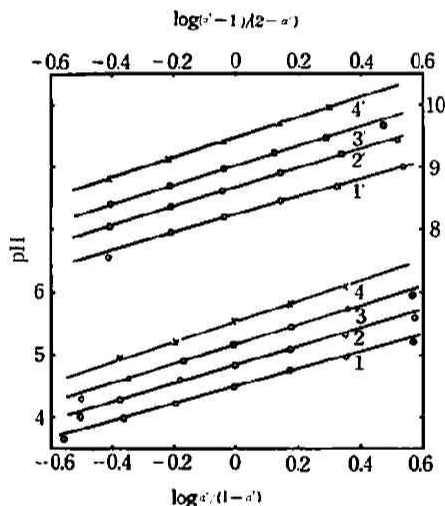


Fig. 2 Plots of pH against $\log \frac{\alpha'}{1 - \alpha'}$ or $\log \frac{\alpha' - 1}{2 - \alpha'}$ for MA-VAc copolymer

The scales for primary dissociation processes, 1, 2, 3 and 4 are the lower and left, and for secondary dissociation processes, 1', 2', 3' and 4' are the upper and right.

Polymer concentrations,

- 1, 1'— $0.986 \times 10^{-2} M$,
- 2, 2'— $0.329 \times 10^{-2} M$,
- 3, 3'— $0.123 \times 10^{-2} M$,
- 4, 4'—0.

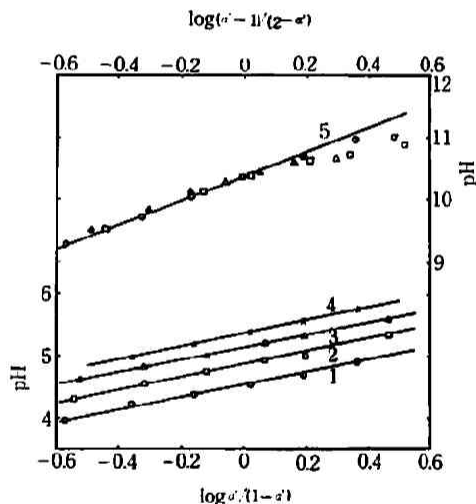


Fig. 3 Plots of pH against $\log \frac{\alpha'}{1 - \alpha'}$ or $\log \frac{\alpha' - 1}{2 - \alpha'}$ for MA-S copolymer

The scales for primary dissociation processes, 1, 2, 3 and 4, are the lower and left, and for secondary processes, 5, are the upper and right.

Polymer concentrations,

- 1, 5 (O)— $0.961 \times 10^{-2} M$,
- 2, 5 (□)— $0.320 \times 10^{-2} M$,
- 3, 5 (△)— $0.120 \times 10^{-2} M$,
- 4 (x)—0.

10) H. Yoshimura, *Theory and Measurements of pH*, Maruzen Co., Tokyo (1938)

11) J. C. Speakman, *J. Chem. Soc.*, 855 (1940)

are obtained by neglecting the term, K_2 and $[H^+]^2$ in Equation (1), respectively. The pK_1 and pK_2 denote the negative logarithm of K_1 and K_2 , respectively.

For the two dissociation processes of the copolymers of maleic acid, the plots of pH against $\log \frac{\alpha'}{1-\alpha'}$ or $\log \frac{\alpha'-1}{2-\alpha'}$ are shown in Figs. 2 and 3. The linear relationship within the range of $0.2 < \alpha < 0.8$ and $1.2 < \alpha < 1.8$, are obtained for the various polymer concentrations except the second dissociation range of the MA-S copolymer, but the slope n is always $n \geq 1$.

Thus, the empirical equations for polydicarboxylic acids ($pK_1 \ll pK_2$) are given by the equations,

$$\text{pH} = pK_1 + n_1 \log \frac{\alpha'}{1-\alpha'} \quad (4)$$

and

$$\text{pH} = pK_2 + n_2 \log \frac{\alpha'-1}{2-\alpha'}, \quad (5)$$

where pK_1 and pK_2 represent the average dissociation constants, and n_1 and n_2 are the empirical constants.

In general, the pH values of the solutions are independent of the degree of polymerization of the polyelectrolyte¹⁾, (that will be shown in Part III for the copolymers), but are markedly dependent on the polyelectrolyte concentrations as can be seen in Figs. 2 and 3 (0.01 M ~0.001 M).

The pK_1 and pK_2 values at $C=0$ were obtained, according to the method used by Oth and Doty¹²⁾, that is, the points of pH against $\sqrt{C}/(1+\sqrt{C})$ at the same α' gave the linear relationship and then the extrapolated pH values were plotted against $\log \frac{\alpha'}{1-\alpha'}$ or $\log \frac{\alpha'-1}{2-\alpha'}$ likewise the finite concentrations. The results were summarized in Table 1 with the results obtained by Ferry and co-workers⁴⁾.

Table 1 Average dissociation constants (20°C)

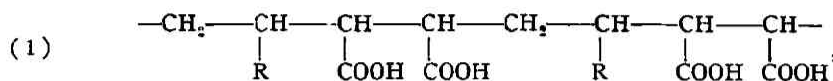
Copolymer	$M \times 10^2$	pK_1	n_1	pK_2	n_2
MA-VAc	0.986	4.50	1.41	8.25	1.46
MA-VAc	0.329	4.85	1.51	8.70	1.53
MA-VAc	0.123	5.17	1.55	9.05	1.55
MA-VAc	0	5.53	1.65	9.50	1.65
MA-S	0.961	4.55	1.0	10.37	2.0
MA-S	0.320	4.88	1.0	10.37	2.0
MA-S	0.120	5.14	1.0	10.37	2.0
MA-S	0	5.38	1.0	—	—
MA-S*	2.6	4.40	0.8	10.35	2.2
MA-VEE*	3.2	4.58	1.3	8.34	2.5

* Ferry and co-workers, Reference 4)

12) A. Oth and P. Doty, *J. Phys. Chem.*, 56, 43 (1952)

Discussion

Since it is known^{6,7)} that maleic anhydride reacts with vinyl acetate and styrene radicals much rapidly than with its own radical, the hydrolyzed copolymers have nearly the 1 : 1 alternative structure¹³⁾ as follows :



where $-\text{R}=-\text{OCOCH}_3$, MA-VAc copolymer; $-\text{R}=-\text{C}_6\text{H}_5$, MA-S copolymer. The titration data nearly agree with the required composition. From the results of Table 1 at low ionic strength, the following facts become clear.

The pK_1 values are nearly the same for the both copolymers and the values at highest concentration are also nearly equal to the value for maleic acid-vinyl ethyl ether (MA-VEE) copolymer obtained by Ferry⁴⁾. These pK_1 values apparently show that the primary carboxyl groups of these copolymers are relatively stronger acids than polyacrylic acid ($pK=6.79$ at $C=1.00 \times 10^{-2} M$)¹⁴⁾ and polymethacrylic acid ($pK=6.94$ at $C=1.243 \times 10^{-2} M$)¹⁵⁾. On the other hand, the pK_2 values for the both copolymers are markedly different, but the pK_2 value for MA-VAc copolymer at the highest concentration is nearly the same as that for MA-VEE copolymer obtained by Ferry⁴⁾. These pK_2 values show that the secondary carboxyl groups of these copolymers are considerably weak acids. In MA-S copolymer, particularly, the neutralizations do not perfectly proceed on actually by hydrolysis, so that the pK_2 values vary little with concentration owing to the resultant counter-ions effect.

As for the constants, n_1 and n_2 , there is generally the relation, $n_1 < n_2$. And the n_1 values are larger for MA-VAc copolymer than for MA-S copolymer and the n_2 values show the reverse relation.

Generally, the differences between both dissociation constants in monomeric-dibasic-acids are related with the electrostatic interaction energy $e^2/D_K r$ by the Bjerrum¹⁶⁾-Kirkwood¹⁶⁾ equation :

$$\Delta pK' = pK_2 - pK_1 = \log \sigma + 0.43 e^2 / D_K r k T. \quad (6)$$

where

- σ , statistical factor, ordinary takes the value 4
- r , distance between both carboxyls
- D_K , effective dielectric constant within distance r
- e , electronic charge
- k , Boltzmann constant
- T , absolute temperature.

While, in polydicarboxylic acids at low ionic strength, the difference between pK_1 and pK_2

13) See, for example, P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y. (1953)

14) H. P. Gregor and M. Fredrick, *J. Polym. Sci.*, **23**, 451 (1957)

15) N. Bjerrum, *Z. phys. Chem.*, **106**, 219 (1923)

16) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938)

may be larger than that shown by Equation (6), although the neighbor interaction energy is the same at the corresponding dibasic acids. The $\Delta pK'$ values for MA-VAc copolymer and MA-S copolymer are 3.8~4.0 and 5.5~5.8, respectively. Thus, these values are considerably larger than the $\Delta pK'$ values of α , β -diethyl succinic acid, 2.8~3.1¹⁷⁾. The obvious reason is that the $\Delta pK'$ values for copolymers contain, at the same time, the difference of the contribution of polyion potential between the first and second steps.

Ferry¹⁾ attributed the anomalous higher pK_2 value of MA-S copolymer to the more compact coil configuration due to the cohesive forces of hydrophobic phenyl group. Garrett²⁾ attributed it to the fact that the increased electrostatic interaction hurdles the barrier of phenyl alkyl group. Their interpretations will be more distinct by the results at high ionic strength in Part II. However, the distinction between the monobasic and dibasic titration behavior of polyacids may mainly depend on the magnitude of electrostatic interaction energy between the nearest neighbor ionized groups.

Table 2 Dissociation constants

	pK_1	pK_2
MA-VAc copolymer (0.01M)	4.50	8.25
MA-S copolymer (0.01M)	4.55	10.37
Phenolphthalein ¹⁸⁾	9.10	9.64

The pyridine method by Minsk⁶⁾ to determine the end point of neutralization for MA-VAc copolymer can not be applied to the MA-S copolymer. The distinction seems to be due to the difference of acid strength of the both secondary carboxylic group in comparison with phenolphthalein as acid. The comparison of the values, pK_1 and pK_2 is shown in Table 2. As can be seen in Table 2, there holds the following relation,

$$(pK_2)_{MA-S} > (pK_1)_{Ph} > (pK_2)_{MA-VAc}$$

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17) R. Gane and C. K. Ingold, *J. Chem. Soc.*, 2153 (1931)

18) *Beilsteins Handbuch der Org. Chem.*, Erg. II, 18, 119; the values at 18° C