under certain conditions. It appears that there is a shift of the maximum near 750 mμ toward the "red" as the ratio $(SCN^-)/(VO^{++})$ increases; this is borne out by the spectrum, also shown in Fig. 8, obtained when $(SCN^-)/(VO^{++}) = 400$. The extinction coefficients appearing in Figs. 7 and 8 are based on formal concentrations of vanadium in order to facilitate comparisons of spectra obtained in solutions of different thiocyanate ion concentrations.

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[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Potentiometric Titrations of a Polydicarboxylic Acid: Maleic Acid–Styrene Copolymer

BY EDWARD R. GARRETT[1] AND RALPH L. GUILE

The polydicarboxylic nature of saponified maleic anhydride–styrene copolymers is demonstrated and generalized Henderson–Hasselbalch equations presented for both carboxyls. Quantitative procedures for copolymer analyses by aqueous and anhydrous titrations are given. Certain copolymer properties are discussed.

Katchalsky and Spitnik[2] have mentioned that dibasic group copolymers such as polyallyl acetate–maleic acid may be assigned two different dissociation constants and these copolymers may be considered as polydibasic acids but have presented no data pertaining thereto. They have applied potentiometric titration techniques to polymonobasic acids such as polyacrylic and polymethacrylic acids and have found that their resultant curves can be described by a generalized form of the Henderson–Hasselbalch equation

$$pH = pK - n \log \frac{1-\alpha}{\alpha} \qquad (1)$$

Alfrey and Lavin[3] as well as Wilde and Smets[4] have stated that they have used potentiometric methods for maleic anhydride composition of such or similar copolymers but they have not asserted its polydicarboxylic nature or provided sufficient data for its use as an analytical technique.

In view of the fact that no conclusive evidence has been heretofore provided as to the polydicarboxylic nature of such copolymers, it is our belief that such evidence is worthy of presentation.

Aqueous potentiometric titrations have been applied to three copolymers of maleic anhydride–styrene, the dibasic character of such polymers have been substantiated and the distal parts of the resulting potentiometric curves analyzed in relation to equation (1) to provide the constants for this copolymer. The potentiometric curve provides a valid method of analysis of the maleic anhydride composition of the copolymer.

Anhydrous potentiometric titrations of the polymeric mono-ester in acetone media have also been shown to be practical. The rate constant of copolymerizations has been evaluated.

Experimental

A. Copolymerizations of Maleic Anhydride and Styrene.—Dow styrene was vacuum distilled and the fraction distilling at 41–43°, 14–16 mm., $n^{20}D$ 1.5446 was used immediately after distillation.

Eastman Kodak Co. maleic anhydride was redistilled at 135° at 80 mm. The polymerizations[5] were carried out in thiophene-free benzene, while nitrogen gas, washed by alkaline pyrogallol, was bubbled under the surface of the solvent. The mixture was agitated.

A 1:1 molar ratio of reactants of 0.233 mole of anhydride to 0.233 mole of styrene, a 1:3 ratio of 0.116 mole of anhydride to 0.349 mole of styrene and a 3:1 ratio of 0.349 mole of anhydride to 0.116 mole of styrene were copolymerized in 615.2 g. of benzene in the presence of 0.2333 g. of benzoyl peroxide.

The rate of appearance of copolymer in refluxing benzene is first order with $k = 5.3 \times 10^{-4}$ sec.$^{-1}$. This was determined by filtering weighed aliquots of the reaction mixture through tared gooch crucibles and washing several times with hot benzene; the crucibles were vacuum dried at 3 mm. pressure at 140° for three weeks and then cooled and reweighed. The copolymerizations can be duplicated.

B. Preparation of Copolymer for Titration.—The reaction mixture was filtered after practical stoichiometric completion of the reaction as based on the evaluated rate constant and the concentration of the lesser reactant. The solid polymer was washed several times with hot benzene. The polymer was then extracted by benzene in Soxhlet extractors for three weeks and vacuum dried at 140° at 3 mm. for three weeks.

For the aqueous titrations, 1 g. of copolymer was dissolved in acetone and standard excess of 0.1 *N* NaOH added very slowly with constant stirring. The acetone was boiled off on a hot-plate until the solutions became water clear and no odor of acetone remained. The total volume of the solution was measured. This solution was titrated with 0.1 *N* HCl followed by alternate titrations with standard alkali and acid.

For the anhydrous titrations 1 g. of the anhydride copolymer dissolved in acetone was titrated with 0.1 *N* methanolic NaOH.

A Beckman *p*H meter equipped with out-side glass electrodes was used at the usual room temperature of 25°.

C. Properties of the Copolymer.—The copolymer as prepared is soluble in alkali and acetone. It is also soluble in small chain primary alcohols. The acid copolymer is soluble in acetone and water mixtures while the anhydride copolymer is insoluble in water. The anhydride and acid copolymer are insoluble in benzene. The monosodium salt of the acid copolymer is insoluble in acetone. The acid copolymer provides good buffering action in the acid range 3.5–4.5 *p*H, lathers well and possesses dispersive properties which are unusual properties for an acidic soap. In alkaline regions where the disodium salt is partially present, the dispersive properties are considerably decreased, probably due to a decrease in the non-polar length of molecule which is available for contact with the oil phase.

The acid copolymer will start precipitating at an approximate *p*H of 2.2 but will not be completely precipitated until the *p*H has been considerably lowered. This property may possibly be correlated with chain length and the number of free anionic groups still on the molecule.

I. Determination of Maleic Anhydride Content of Copolymers. A. Aqueous Titrations.—The copolymers prepared from three differing molar ratios of the reactants, maleic anhydride and styrene, were potentiometrically titrated. Curves that are typical of many titrations are shown in Fig. 1. The stoichiometric titer for one-half the total car-

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[1] The Upjohn Co., Kalamazoo, Michigan.

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

[3] T. Alfrey and E. Lavin, THIS JOURNAL, **67**, 2044 (1945).

[4] M. C. de Wilde and G. Smets, *J. Polymer Sci.*, **5**, 253 (1950).

[5] G. F. D'Alelio, "Experimental Plastics and Synthetic Resins," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 113.

boxyls in the copolymer molecule (*i.e.*, one carboxyl per maleic anhydride unit) was taken from the potentiometric titration curves as the amount of titer between the inflection point at pH 6.25 and the point below a pH of 3 which corresponded to the complete neutralization of the standard alkali in which the copolymer anhydride was originally dissolved. This point is equivalent to the 0.0 ml. of 0.1 N NaOH in Fig. 1. Calculations show that for a 1:1 molar ratio of reactants the molar ratio of monomers (maleic anhydride:styrene) in the copolymer is 0.890:1; for a 1:3 molar ratio of reactants it is 0.845:1; and for a 3:1 molar ratio it is 0.975:1.

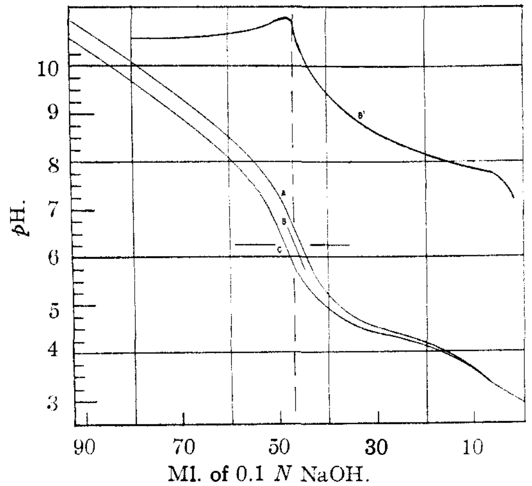

Fig. 1.—Typical potentiometric titration curves of 1 g. of maleic anhydride–styrene copolymer prepared from different molar ratios of reactants.

Aqueous titration curve	Reactant ratio M. H.:styrene	Ml. of 0.1 N NaOH to pH 6.25
A	1:3	45.5
B	1:1	46.5
C	3:1	48.5
Anhydrous titration in acetone		Ml. of 0.1 N alc. NaOH to max. d pH/d ml.
B'	1:1	46.5

It is apparent from Fig. 1 that either brom thymol blue or phenol red (not phenolphthalein) could be used as an indicator to approximate the stoichiometric pH on acid titration of the alkali dissolved copolymer and give information relative to its maleic acid content.

B. Anhydrous Titrations.—Moran and Siegel[6] have shown that in anhydrous solutions organic dibasic acid anhydrides form the monoester with primary alcohols on base catalysis and that titration of the anhydrides to phenolphthalein end-point with alcoholic alkali in acetone solvent gives the stoichiometric value for one carboxyl. The adsorption of the phenolphthalein indicator on the precipitated copolymer (the monosodium salt of the polymonoester) made a color change difficult to ascertain. However it will be seen from Fig. 1 that in titration of acetone dissolved maleic anhydride–styrene copolymer with 0.1 N methanolic NaOH the maximum of d pH/d ml. exactly coincides with the stoichiometric point for the aqueous neutralization of one-half the total potentially available carboxyls. Thus a potentiometric technique may be applied to a polymeric anhydride.

II. Dissociation Constants

A plot based on the data of pH *vs.* log $\frac{1-\alpha}{\alpha}$ from aqueous titrations is given in Fig. 2 for the stronger primary carboxyls and in Fig. 3 for the weaker secondary carboxyls of the copolymer molecule where α is the degree of dissociation for one kind of carboxyl.

A. Primary Carboxyls.—The plot in Fig. 2 is linear conforming to equation (1). The slope of the curve (n) is unity well within experimental error and the apparent pK_1' for the three copolymers prepared from different molar ratios of re-

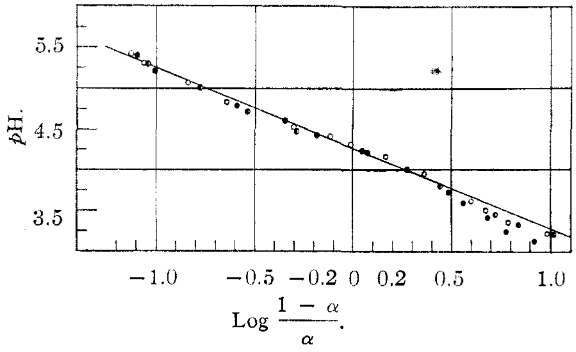

Fig. 2.—Plot of pH *vs.* log $\frac{1-\alpha}{\alpha}$ for primary carboxyls from the potentiometric titrations of 1 g. of maleic anhydride–styrene copolymer prepared from different molar ratios of reactants, based on the equation: $pH = pK_1' - n \log \frac{1-\alpha}{\alpha}$ from which pK_1' equals 4.25, $n = 1$.

Legend	Molar ratio of reactants M. A.:styrene	
○	1	1
◐	3	1
●	1	3

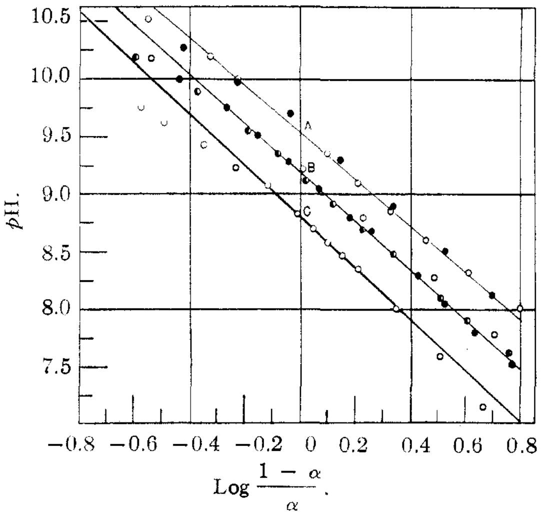

Fig. 3.—Plot of pH *vs.* log $\frac{1-\alpha}{\alpha}$ for secondary carboxyls from the potentiometric titrations of 1 g. of maleic anhydride–styrene copolymer prepared from different molar ratios of reactants based on the equation: $pH = pK_2' - n \log \frac{1-\alpha}{\alpha}$.

Line	A	B	C
Approx. ionic strength at α = 0.5	0.24	0.265	0.29

Legend	Molar ratio of reactants M. A.:styrene	
○	1	1
◐	3	1
●	1	3

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(6) M. K. Moran and E. F. Siegel, THIS JOURNAL, **69**, 1457 (1947).

actants is 4.25. Variations of ionic strength from 0.038 to 0.05, in the region of pH 4.25, show no significant experimental effect on the slope or on the intercept.

The degree of copolymerization of maleic anhydride in the range studied for the three copolymers apparently has little effect on the titration curves.

B. Secondary Carboxyls.—In Fig. 3, the linear displacement of the curves is not dependent on the maleic acid:styrene ratio in the copolymer. These curves approximate straight lines, although they are actually slightly parabolic.

In dilute solution of polyampholytes, the well known relationship[7] is

$$\partial pH/\partial \sqrt{\mu} = 0.5\,(2z + 1) \qquad (2)$$

where z is the net charge on the molecule and in this case is negative. Thus, comparative titration pH's may be expected to decrease with increasing ionic strength, a fact which accounts for the vertical displacement of the curves for different titrations in Fig. 3. Also since the copolymer dissolved in a known amount of standard alkali was titrated by acid, the ionic strength decreased during the course of a given titration and the pH tended to be relatively lower than a linear extrapolation for a constant ionic strength. This fact could also account for the parabolic trend of a given curve, *i.e.* tendency for the slope (n) to increase during acidic titration.

Representative straight lines are drawn through the three different approximate ionic strengths in Fig. 3. For a true comparison of the displaced curves, it is necessary to choose a slope of the linear plot of a given titration at the same degree of ionization, and then account for the variations in ionic strength.

The slope (n), pK'_2, and existing ionic strengths for 50% dissociations ($\alpha = 0.5$; $\log \frac{1-\alpha}{\alpha} = 0$) are presented in Table I.

TABLE I

TABULATION OF IONIC STRENGTHS CORRESPONDING TO THE CONSTANTS OF THE TITRATION CURVES FOR THE SECONDARY CARBOXYLS OF COPOLYMERS PREPARED FROM DIFFERENT MOLAR RATIO OF REACTANTS

Data obtained from the curves of Fig. 3: $pH + n \log \frac{1-\alpha}{\alpha} = pK'_2 = pK_2 - n\,\lambda\sqrt{\mu}$

Initial molar ratio of copolymer reactants (M.A.:Styrene)	Slope n	Apparent pK_2 or pK'_2	u
1:1	1.97	9.55	0.475
1:1	2.26	8.80	.650
1:3	2.14	9.19	.565
1:3	1.92	9.60	.460
3:1	2.14	9.16	.595
3:1	2.02	9.22	.550

If correction for activity is made by a procedure similar to that of Katchalsky and Spitnik[2] equation (1) is transformed to

$$H = K_2 \left[\frac{HMA^-}{MA^=}\right]^n \times 10^{0.5n\, z_1 z_2 \sqrt{\mu}} \qquad (3)$$

where the monomaleate unit ionizes

$$HMA^- \rightleftarrows MA^= + H^+ \qquad (4)$$

and $z_1 = 1$, $z_2 = 2$ and $\mu = {}^1/_2\Sigma c_i z_i^2$

Because of the acid back titration technique

$$\mu = {}^1/_2\{2^2\,(MA^=) + 1^2\,(Na^+) + 1^2\,(HMA^-) + 1^2\,(Cl^-)\} \qquad (5)$$

and since ${}^1/_2(Na^+) = {}^1/_2(Cl^-) + {}^1/_2(HMA^-) + (MA^=)$, the value for μ is given by

$$\mu = (Na^+) + (MA^=) \qquad (6)$$

where $(Na^+) = (NaOH)$, the molar concentration of alkali and where $(MA^=)$ is the molar concentration of dimaleate ion. This is calculated from the amount of standard alkali consumed between the stoichiometric point of neutralization (pH 6.25) of the primary carboxyl and the chosen point on the upper portion of neutralization curve (Fig. 1) representing the extent of titration of the secondary carboxyl.

Equation (3) can be transformed by the appropriate substitutions to

$$pH + n \log \frac{(HMA^-)}{(MA^=)} = pK'_2 = pK_2 - n\,\lambda\sqrt{(NaOH) + (MA^=)} \qquad (7)$$

where $(HMA^-)/(MA^=) = (1 - \alpha)/\alpha$.

pK_2 is the value of the intercept at zero ionic strength from the straight line plot of pK'_2 *vs.* $n\sqrt{\mu}$ as given in Table I. The slope (λ) is a measure of the size of a single carboxyl.[2] Thus, in the case of the secondary carboxyl of the copolymer, equation (7) becomes

$$pH + n \log \frac{1-\alpha}{\alpha} = pK'_2 = 11.3 - 3.7n\sqrt{\mu} \qquad (8)$$

where $n \cong 2$.

Since titration curves of the primary carboxyls show no deviation in slope and are similar to univalent acid titrations,[8] pK'_1 is a measure of the "fundamental" as well as the "practical" dissociation constant and each of the primary carboxylic groups dissociates independently of the ionization of the others. The nature of the secondary titration curves and their varying slopes indicate that the successive dissociation constants for secondary carboxyl ionizations are not the same; that there is no same fundamental constant here; that one ionization affects the ability of other similar groups on the macromolecule to dissociate.

The recurrent units of the macromolecule tend to act independently during the dissociation of one carboxyl in the unit; the increased electrostatic interaction during the dissociation of the second carboxyl hurdles the heretofore effective barrier of the phenyl alkyl group.

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(7) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943, p. 472.

(8) L. Michaelis, "Advances in Enzymology," Vol. IX, Interscience Publishing, Inc., New York, N. Y., 1949.