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A Chain Model for Polyelectrolytes. V. A Study of the Effects of Local Charge Density[1]

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A series of copolymers of a difunctional acid and a neutral monomer have been synthesized. By determination of the titration curve and extent of counter ion association it is shown that the local charge density dominates the behavior of the dissociating carboxyl group, but the over-all charge density appears more important for ion-binding. On the other hand the experimental results indicate that the mean electrostatic field acting on a fixed charge is dominated by neither the over-all charge distribution nor the nearest neighbor charge but that both effects are of comparable importance. A derivation of the Kern equation for the titration curve of a polyacid is given without any assumption about uniformity of charge distribution.

I. Introduction

From the extensive research on polyelectrolytes in recent years three sets of facts emerge.

(1) As the ionic strength of the medium in which a polyion is dissolved is lowered, the polyion expands.

(2) In any process involving the translational or rotational motion of the polyion, a large fraction of the counterions to the polyion are intimately associated with it.

(3) The activity of the counterions to a polyion is markedly lower than the concentration, whereas the activity of the byions is relatively unaffected. For the case of Na^+ as the counterion, the activity coefficient increases as the ionic strength is increased.

A number of theories have been proposed to account for the observations cited. The various theories differ chiefly in two respects: the retention or omission of the connectivity of the polymer skeleton and the method of handling ion association. In previous papers[1b] a chain model for polyelectrolytes has been proposed which has had moderate success in semiquantitatively interpreting both the thermodynamic and configurational properties of the polyion. In dealing with the phenomenon of counterion association it has been suggested that the major part of the binding mechanism consists of the formation of ion-pairs, similar to but not necessarily identical with the ion pairs originally suggested by Bjerrum. The phenomenology of the binding was handled through an assumed dissociation constant, a representation of our ignorance of the true interactions at the molecular level. It is our opinion that there are still many unsettled aspects of the nature of the ion binding, particularly questions related to the difference between ion-binding and the dissociation of weak acid groups. Although all current theories compute the electrostatic free energy of the polyion as if the charge distribution were uniform, it is the local charge distribution which may be expected to affect the dissociation of carboxyl groups and the possible formation of ion pairs. Studies of polyelectrolytes with non-uniform charge distributions are therefore pertinent to the understanding of ion association and proton dissociation.

It is the purpose of this paper to discuss the properties of copolymers of maleic acid and non-ionizable monomers. Although a few studies of 1:1 copolymers have been reported,[2-4] this is the first systematic study of copolymers of variable ratio.

II. Preparation of Copolymers

The copolymer samples were made by the polymerization of maleic anhydride or diethyl maleate with vinyl acetate or vinylpyrrolidone. As is well known, maleic anhydride and/or diethyl maleate will not polymerize with themselves and thereby a copolymer containing more than 50 mole % maleic acid cannot be made. It should be noted however, that a 50 mole % copolymer of maleic acid and neutral monomer has the same linear charge density as polyacrylic acid. Copolymers of less than 50 mole % maleic acid content can be made by proper choice of initial conditions and the resultant polymers will never have adjacent maleic acid monomers. All monomers were purified by vacuum distillation: maleic anhydride b.p. 89–90° (~15 mm.); diethyl maleate b.p. 100° (~11 mm.); vinylpyrrolidone b.p. 97° (~15 mm.); vinyl acetate b.p. 72°. Solution polymerization methods were employed, with the polymerizations terminated at about 20% conversion to insure polymer uniformity.

1. Maleic Anhydride–Vinylpyrrolidone.—The polymerization was carried out in thiophene free benzene in an atmosphere of N_2 at temperatures between 70 and 80° with 0.2% benzoyl peroxide as initiator. The polymer precipitates from the benzene solution, is separated from the supernatant and purified by precipitation with ethanol from acetone solution. The purified polymer is a white powder. All the copolymers were dissolved in water and heated at 80–90° for 48 hr. before use. The copolymer composition was determined by potentiometric titration with the first break taken to correspond to the neutralization of the primary carboxyl group (see subsequent discussion). The reactant ratios and resultant copolymer compositions are shown in Table I.

As can be seen, the composition of the copolymer

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[1] (a) This research was supported by a grant from the National Science Foundation, NSF G5117. (b) F. E. Harris and S. A. Rice, *J. Phys. Chem.*, **58**, 725, 733 (1954).

[2] E. R. Garrett and R. L. Guile, THIS JOURNAL, **73**, 4533 (1951).

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

[4] J. D. Ferry, L. D. Grandine, Jr., and D. C. Udy, *ibid.*, **8**, 529 (1953).

is sensibly independent of the reactant ratio. This may be due to the formation of a molecular complex between the monomers, an explanation which is suggested by a yellow color in the monomer mixture and the marked increase in the solubility of maleic anhydride in the presence of vinylpyrrolidone.

TABLE I

MALEIC ANHYDRIDE–VINYLPYRROLIDONE

Sample	Reactant ratio, MA/VP	Copolymer, composition MA/VP
B1	3/1	1/1.29
2	2/1	1/1.11
3	1/1	1/1.36
4	1/2	1/1.23
5	1/3	1/1.22

2. **Maleic Anhydride–Vinyl Acetate.**—For these polymerizations we used as the solvent benzene and as the initiator α,α'-azodiisobutyronitrile at temperatures between 70 and 80°. During the course of the polymerization the product precipitates from solution. The polymer was dissolved in acetone and hydrolyzed with NaOH. As the hydrolysis proceeds the polymer precipitates. The precipitation was completed after 24 hr. of hydrolysis by the addition of ethanol. The sample was then again dissolved in aqueous NaOH to complete hydrolysis and again purified by precipitation with ethanol. The solution of purified polymer was deionized by passage through ion-exchange columns (Amberlite IR-120, IR-4B). The samples were stored in the refrigerator in solution. Combustion of sample polymer with H_2SO_4 on a platinum plate verified the absence of excess small ions. The reactant ratios and copolymer compositions are listed in Table II.

TABLE II

MALEIC ANHYDRIDE–VINYL ACETATE

Sample	Reactant ratio, MA/VA	Copolymer composition, MA/VA
C	1/32	1/2.35
D	1/1	1/2.77
E	1/35	1/3.13

3. **Diethyl Maleate–Vinyl Acetate.**—This system was suggested to us by Professor A. E. Woodward of Pennsylvania State University. The procedures were similar to those cited for the case of maleic anhydride plus vinyl acetate except that a sun lamp was used to accelerate polymerization, and the temperature was only 60°. The polymer is soluble in benzene from which it may be precipitated by petroleum ether. It was then dissolved in ethanol and hydrolyzed with NaOH in a manner analogous to that already described. It was found that 5–7 days were necessary to carry the hydrolysis to completion. The hydrolyzed polymer was purified by precipitation with ethanol and finally deionized with ion exchange resins. The reactant ratios and resultant copolymer compositions are shown in Table III.

TABLE III

DIETHYL MALEATE–VINYL ACETATE

Sample	Reactant ratio, DM/VA	Copolymer composition, DM/VA
F	1/10	1/4.84
G	1/20	1/16.3
H	1/40	1/14.0

III. Properties of the Copolymers

1. **General Comments.**—The polymers described in Section II are almost colorless, except for occasional samples hydrolyzed at higher temperatures. These latter samples had a yellow color, but there was no detectible difference in properties between these and the colorless polymers. While polyvinyl alcohol is soluble in water, copolymers of vinyl alcohol and maleic acid are not always soluble in water when not neutralized. In fact, copolymers which have an acid content of less than about 3 mole % are insoluble, probably because these polymers salt themselves out of solution. The degree of neutralization at which the polymer becomes soluble in water is shown in Fig. 1. As the content of maleic acid decreases the polymer becomes less soluble. All solutions of copolymers exhibited some viscoelasticity.

2. **Potentiometric Titrations.**—Potentiometric titrations were carried out with a Beckman GS *p*H meter. Typical curves are shown in Fig. 1. Sample B has a titration curve similar to that of a maleic acid–styrene copolymer, as reported by Garrett and Guile[2] and Ferry and co-workers.[3] The neutralization point of the secondary carboxyl group is smeared out and lies in a very alkaline region. The composition of copolymer B was determined by assuming that the break at *p*H 8 corresponded to the dissociation of the primary carboxyl group. Since the equivalence point of the second carboxyl could not be determined, the question arose as to whether this point is indeed correctly identified. Garrett and Guile have demonstrated for the case of maleic acid–styrene copolymers that this point coincides with the phenolphthalein endpoint of the primary carboxyl group as determined in a non-aqueous solvent by the volumetric titration method of Morgan and Siegel.[5]

The titration curves of the other copolymers are very unusual. The neutralization point of the primary carboxyl group is not at the center of the titration curve but is displaced toward the neutralization point of the secondary carboxyl group. In particular, it is interesting to note that the titration curve approaches the titration curve of a polymonobasic acid and the characteristic features of a dibasic acid disappear as the content of maleic acid decreases. This is in contradiction with the naive expectation that the titration curve should approach that of the maleic acid monomer as the content of maleic acid decreases. As can be seen by examination of Fig. 1, the experimental results

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[5] M. K. Morgan and E. F. Siegel, THIS JOURNAL, 69, 1457 (1947).

are just the opposite. It is easy to verify that the break at $\alpha = 1$ is the stoichiometric equivalence point of the secondary carboxyl group because it occurs at an almost constant pH for all the copolymers and this pH is the equivalence point of the secondary carboxyl of the monomer.

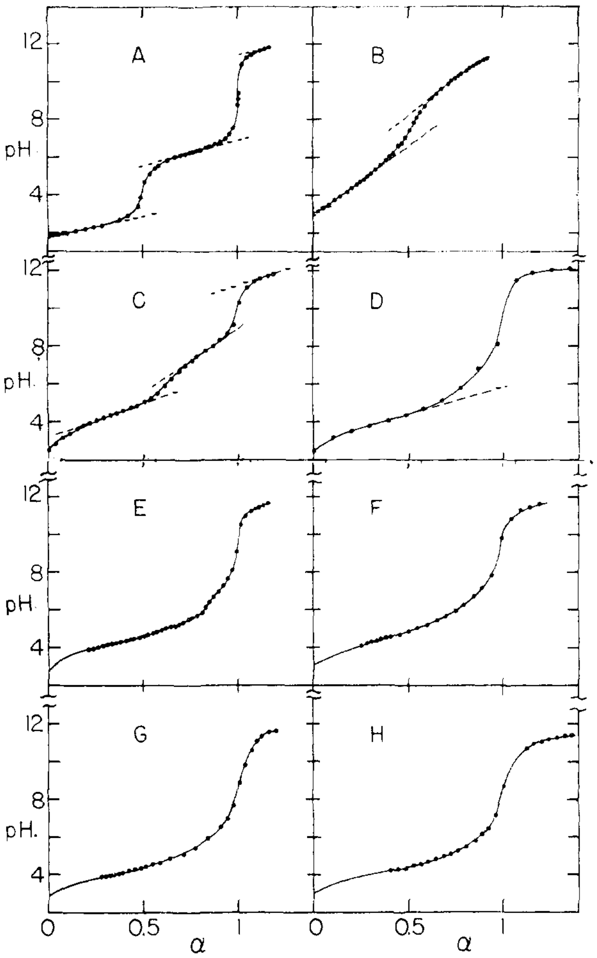

Fig. 1.—Potentiometric titration of copolymers (25°):

Code	Sample	Copolymer mole ratio (M.A.: other monomer)	Initial soln., eq. –COOH	NaOH, N
A	Monomer	...	0.05	0.0981
B	B-1	1:1.29	.0199	.0802
C	C	1:2.35	.111	.0802
D	D	1:2.77	.130	1.00
E	E	1:3.13	.0103	0.0967
F	F	1:4.84	.0652	.967
G	G	1:14.0	.0749	.967
H	H	1:16.3	.0161	.967

To explain the phenomena described it seems necessary to invoke changes of molecular configuration accompanying the changes of composition. That is, the dissociation constant of a carboxyl group in a polyelectrolyte molecule is determined by the local electrostatic potential, the relationship between pH, α and $K_a{}^0$ being[6,7]

$$pH = pK_a{}^0 - \log \frac{1-\alpha}{\alpha} + 0.434\,\frac{q\psi}{kT} \qquad (1)$$

with ψ the mean electrostatic potential. If the content of maleic acid is small, the molecule will be highly coiled even when $\alpha = 1$. In this case a model with all charged groups uniformly smeared throughout the polymeric domain, such as that of Hermans and Overbeek,[8] leads to the expectation that the electrostatic potential is approximately constant throughout the molecule. Thus, with many of the charged groups much closer together than anticipated from the linear charge density and a mean electrostatic potential essentially independent of charge location, the net effect is the suppression of the influence of the nearest ionized group relative to the influence of other charges in the polymeric domain. Although the equivalence point of the primary carboxyl group of maleic acid is at the center of the titration curve (essentially all primary groups are titrated before the secondary groups start to titrate), in the coiled copolymer the electrostatic field keeps some primary carboxyl groups undissociated even after the initiation of the titration of the secondary carboxyl groups.

As an extension of the preceding argument, when the maleic acid content is large and the polyion extended it is to be expected that the characteristic features of the dibasic acid titration curve will be recovered. Of course, when the maleic acid content is large, interactions between colinear difunctional groups will tend to smear the titration curve, but the field of the first neighbor should remain dominant so long as there are few internal long range polymer–polymer interactions. This expectation is confirmed as is the predicted spreading of the primary carboxyl end-point when salt is added. Typical data are represented in Fig. 2 (sample C).

We must conclude that a non-uniform charge distribution has an important influence on the dissociation of carboxyl groups, especially when the polymer is extended.

Finally, it is interesting to examine the empirical relationships between the apparent dissociation constant and the pH or the degree of dissociation originally suggested for polymonobasic acids. If the apparent dissociation constant K is defined by the relation

$$\frac{a_{H^+}[COO^-]}{[COOH]} = K \qquad (2)$$

then for a polyelectrolyte K is not a constant but becomes a function of the pH or α. The empirical equations reported are

$$(\text{Kern}[9]) \quad pK = pK_0 + BpH \qquad (3)$$

$$(\text{Kagawa, } \textit{et al.}[10]) \quad pK = pK_s - m \log\left(\frac{1-\alpha}{\alpha}\right) \qquad (4)$$

$$(\text{Katchalsky, } \textit{et al.}[11]) \quad pH = pK_a + n \log\left(\frac{1-\alpha}{\alpha}\right) \qquad (5)$$

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[6] J. Th. G. Overbeek, *Bull. Soc. Chim. Belges*, **57**, 252 (1948).

[7] A. Katchalsky, N. Shavit and H. Eisenberg, *J. Polymer Sci.*, **13**, 69 (1956).

[8] J. J. Hermans and J. Th. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948).

[9] W. Kern, *Z. physik. Chem. (Leipzig)*, **A181**, 269 (1938).

where pK_0, pK_s, pK_a, B, m, n are constants. These equations are equivalent, the relationships amongst the constants being

$$m = \frac{B}{1 - B}, n = \frac{1}{1 - B} \tag{6}$$

In Fig. 3 we have compared Kern's equation 3 with our experimental results. The over-all agreement suggests that it is likely that the empirical equation of Kern holds for all polyacids and is independent of the distribution of fixed charges. The extrapolated value of pK_0 is in good agreement with the primary dissociation constant of maleic acid (pK_1 = 1.921). On the other hand, equations 4 and 5 do not represent our data satisfactorily. In view of the equivalence of eqs. 3, 4 and 5, this suggests that B is not exactly constant, and a variation in B is exaggerated in m and n because B is not far from unity.

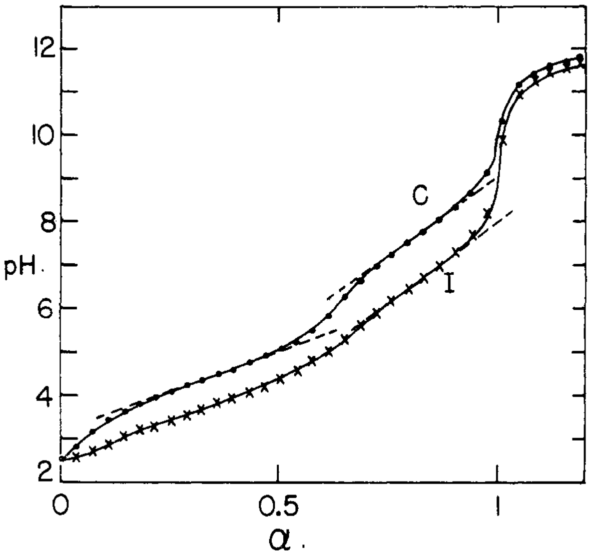

Fig. 2.—Effect of added salt:

	Sample	Initial soln., N	NaCl, N	NaOH, N
C	C	0.130	0	0.0802
I	C	0.065	0.5	0.0802

3. Counterion Mobility.—The mobility of the counterions to a polyion is conveniently determined by measurement of the tracer diffusion coefficient, a method first used by Huizenga, Grieger and Wall.[12] If the observed decrease of the mobility of the counterions due to the presence of the polyelectrolyte is attributed to ionic association, a measurement of counterion mobility is equivalent to a determination of the extent of counterion binding. If f is the fraction of ionized groups occupied by ion pairs, then

$$1 - f = \frac{D}{D^*} \tag{7}$$

where D^* is the self diffusion coefficient of the counterion in an ordinary electrolyte solution having the same ionic strength as the polyelectrolyte solution. As always, the contribution of the polyion to the ionic strength is neglected. Previous experiments have shown that $1 - f$ is almost independent of polymer concentration.

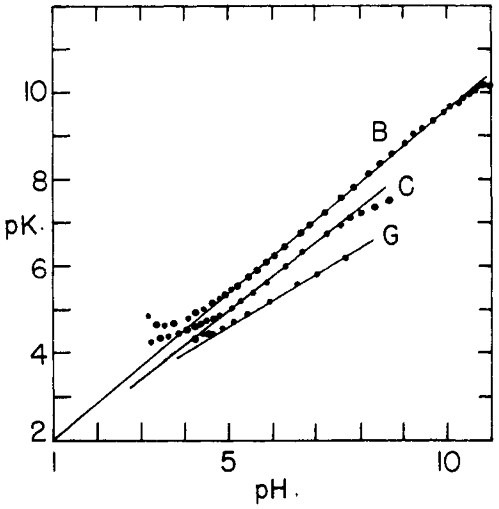

Fig. 3.—Examination of the empirical relationship of Kern between pK and pH: B, calcd. from B in Fig. 1, $n \approx 0.95$; C, calcd. from C in Fig. 1, $n \approx 0.80$; G, calcd. from G in Fig. 1, $n \approx 0.58$.

In our experiments a sodium salt solution of a copolymer with Na^{22} labeling of the counterions is placed in contact through a fine glass frit with the same sample solution without Na^{22}. The self diffusion coefficient of Na then is calculated easily from the rate of exchange of Na between the two solutions. We have used eq. 6 in the paper of Huizenga, Grieger and Wall[12] for the purposes of calculation. After evaporation of an aliquot of the sample solution, the activity of the isotope is determined in a proportional counter. All diffusion experiments were conducted by tumbling the cell in a large 25° water thermostat. The reproducibility of our measurements was good but over-all slightly poorer than that reported by Huizenga, Grieger and Wall. This we attribute to the use of several different cells rather than only one cell.

The results of the experiments are shown in Figs. 4 and 5. Also plotted are the data points of Huizenga, *et al.*, for sodium polyacrylate. In Fig. 4, f is plotted *versus* α and in Fig. 5 f for several copolymers, all at a stoichiometric degree of neutralization of 0.95, is plotted *versus* the reciprocal average distance between neighboring charged groups. It is seen readily that there is no marked difference between the effects of primary and secondary carboxyl groups. We may therefore conclude that the non-uniform local distribution of fixed charges does not uniquely affect the mobility of the counterions but that the total charge density of the polyion is a factor of primary importance.

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(10) I. Kagawa and K. Tsumura, *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*) **67**, 437 (1946).

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

(12) J. R. Huizenga, P. H. Grieger and F. T. Wall, THIS JOURNAL, **72**, 4228 (1950).

IV. Discussion

Let the polymer chain be composed of Z acidic groups. We divide the free energy, A, of the polyelectrolyte solution into three parts, one of which, A_1, describes the free energy of the free hydrogen ion and counter ions eligible to take part in binding and neutralization phenomena. (Note that the free energy is expressed as energy per polyelectrolyte molecule.) The remainder of the free energy will then be the contribution of the polyion itself. The first portion of this free energy, A_2, will be the electrical interaction free energy of the net charge of the polyion, regarding the ion-pairs as uncharged sites completely equivalent to un-ionized groups. The remainder, A_3, includes the chemical free energy of dissociated, undissociated and counter ion paired acid groups, which are assumed to behave independently. In A_2, two kinds of electrostatic interactions must be taken into account; one is the interaction amongst the fixed charges of the polymer in equilibrium with the "outer" solution only through the exchange of hydrogen ions and counter ions. The other is the electrostatic effect on the polymer molecule of other polyions and the small ions (ionic atmospheres). If the former is denoted A_4 and the latter A_5

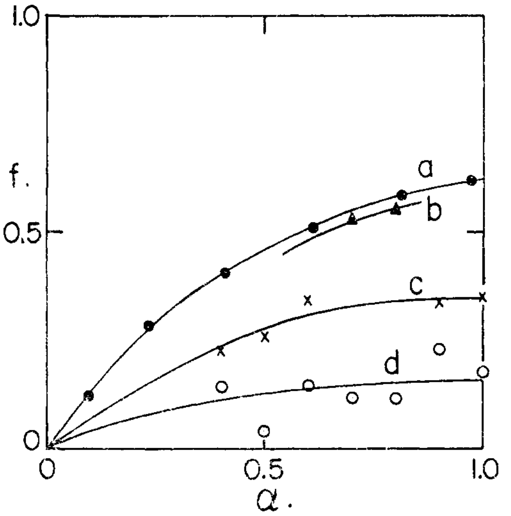

Fig. 4.—Relationship of ion-binding of copolymers to the degree of neutralization:

Code	Sample	Equivalent concn. polymer (N)
a	Polyacrylate	0.0378
b	B	.0168
c	C	.0106
d	G	.0110

$$A = A_1 + A_2 + A_3 = A_1 + A_4 + A_5 + A_3 \quad (8)$$

Let α be the stoichiometric degree of neutralization of the polyacid, $\Delta\alpha$ the degree of dissociation of carboxyl groups and f the fraction of the dissociated sites occupied by bound ion pairs. The net fractional charge of the polyion, α', will thus be $(\alpha + \Delta\alpha)(1 - f)$ and the fraction of bound sites, β, referred to the total number of sites of the polymer will be $(\alpha' + \Delta\alpha)f$. Thus

$$\alpha' = \alpha + \Delta\alpha - \beta \quad (9)$$

A_1 can be expressed easily in terms of the chemical potentials of the free hydrogen ions and counter ions

$$A_1 = Z\Delta\alpha\mu_{\mathrm{H}^+} + Z(\alpha - \beta)\mu_{\mathrm{C}^+} \quad (10)$$

A_4 is a function of the net charge, $Z\alpha'$, of the polymer only, and A_5 is a function of α, $\Delta\alpha$, β and the polymer concentration. Corresponding to eq. 10 A_3 may be written

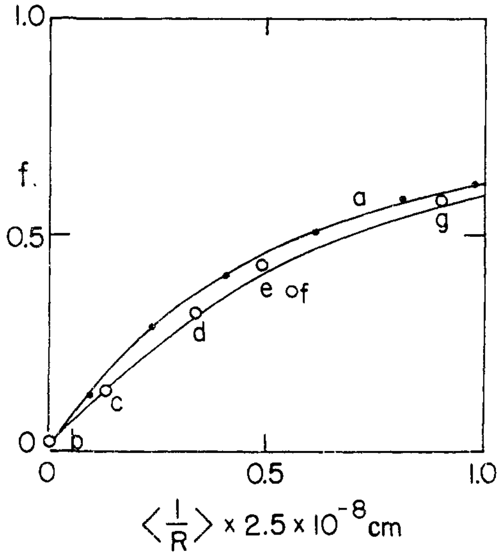

Fig. 5.—Relationship of ion-binding of copolymers to the reciprocal average distance between two neighboring charges:

Code	Sample	Concn., N	Degree neutraliz.
a	Polyacrylate	0.0378	. . .
b	Maleic acid	.0300	0.95
c	G	.0300	.95
d	F	.0300	.95
e	E	.0300	.95
f	C	.0106	.95 extrap. from
g	B	.0148	.95 Fig. 4.

$$A_3 = Z(1 - \alpha - \Delta\alpha)\mu_{\mathrm{COOH}} + Z(\alpha + \Delta\alpha - \beta)\mu_{\mathrm{COO}^-} + Z\beta\mu_{\mathrm{COO}^-\mathrm{C}^+} \quad (11)$$

where μ_{COOH}, μ_{COO^-} and $\mu_{\mathrm{COO}^-\mathrm{C}^+}$ are the chemical potentials of COOH, COO^- and $\mathrm{COO}^-\mathrm{C}^+$ groups, respectively. Substitution of the above into eq. 8 gives

$$A = A_1(\alpha, \Delta\alpha, \beta) + A_4(\alpha') + A_5(\alpha, \Delta\alpha, \beta, C_p) + A_3(\alpha, \Delta\alpha, \beta) \quad (12)$$

The equilibrium hydrogen ion activity can be determined by minimizing A with respect to $\Delta\alpha$, holding α and β constant

$$\left(\frac{\partial A}{\partial \Delta\alpha}\right)_{\alpha,\beta} = 0 \tag{13}$$

Performing the indicated operation we find

$$Z\mu_{\mathrm{H^+}} - Z\mu_{\mathrm{COOH}} + Z\mu_{\mathrm{COO^-}} + \frac{\partial A_4}{\partial \Delta\alpha} + \frac{\partial A_5}{\partial \Delta\alpha} = 0 \tag{14}$$

from which

$$\frac{a_{\mathrm{H^+}}[\mathrm{COO^-}]}{[\mathrm{COOH}]} = K_0 e^{-\frac{1}{Zkt}\frac{\partial}{\partial\Delta\alpha}(A_4 + A_5)} \tag{15}$$

or

$$pH = pK_0 - \log\frac{1-\alpha}{\alpha} + \frac{1}{ZkT}\frac{\partial(A_4 + A_5)}{\partial\Delta\alpha} \tag{16}$$

if $\alpha >> \Delta\alpha$. The third term on the right side of eq. 16 has been calculated by several investigators for the case of a uniform charge distribution. Herein we shall evaluate $\partial A_4/\partial\Delta\alpha$ by a method different from that discussed in ref. 1. Our intention is to obtain a relation similar to the empirical eq. 3 without the assumption of a uniform charge distribution. To proceed, let the absolute activities of the hydrogen ions and the counter ions be $\lambda_{\mathrm{H^+}}$ and $\lambda_{\mathrm{C^+}}$. Then the grand partition function for the system may be written

$$\Xi = \sum_{N_{\mathrm{H^+}}}\sum_{N_{\mathrm{C^+}}} Q(N_{\mathrm{H^+}}, N_{\mathrm{C^+}})\lambda_{\mathrm{H^+}}^{N_{\mathrm{H^+}}}\lambda_{\mathrm{C^+}}^{N_{\mathrm{C^+}}} \tag{17}$$

with $N_{\mathrm{H^+}}$, $N_{\mathrm{C^+}}$ the numbers of hydrogen ions and counter ions, and $Q(N_{\mathrm{H^+}}, N_{\mathrm{C^+}})$ the canonical partition function. For our purposes it is convenient to evaluate the double sum of eq. 8 by replacing the sum by its maximum term, Ξ_{m}, determined by

$$\left(\frac{\partial \ln}{\partial N_{\mathrm{H^+}}}\Xi_{\mathrm{m}}\right)_{N_{\mathrm{C^+}}} = 0,\ \left(\frac{\partial \ln}{\partial N_{\mathrm{C^+}}}\Xi_{\mathrm{m}}\right)_{N_{\mathrm{H^+}}} = 0 \tag{18}$$

By definition $N_{\mathrm{H^+}}$ and $N_{\mathrm{C^+}}$ are

$$\begin{aligned} N_{\mathrm{H^+}} &= Z(1 - \alpha - \Delta\alpha) \\ N_{\mathrm{C^+}} &= Z\beta \end{aligned} \tag{19}$$

whereupon

$$\left(\frac{\partial \ln}{\partial \Delta\alpha}\Xi_{\mathrm{m}}\right)_{\alpha,\beta} = 0,\ \left(\frac{\partial \ln}{\partial \beta}\Xi_{\mathrm{m}}\right)_{\alpha,\Delta\alpha} = 0 \tag{20}$$

and

$$-kT\ln Q(N_{\mathrm{H^+}}, N_{\mathrm{C^+}}) = A_4(\alpha') \tag{21}$$

Substitution of Ξ into eq. 17 with eq. 20 and 21 gives

$$-\frac{1}{ZkT}\frac{\partial A_4}{\partial\Delta\alpha} = \ln\lambda_{\mathrm{H^+}} \tag{22}$$

from which it follows that

$$\frac{a_{\mathrm{H^+}}[\mathrm{COO^-}]}{[\mathrm{COOH}]} = K_0\lambda_{\mathrm{H^+}}\, e^{-\frac{1}{ZkT}\frac{\partial A_5}{\partial\Delta\alpha}} \tag{23}$$

or

$$pK = pK_0' + pH + \frac{1}{ZkT}\frac{\partial A_5}{\partial\alpha} \tag{24}$$

since

$$(\partial A_5/\partial\Delta\alpha) = (\partial A_5/\partial\alpha)$$

The calculation of A_5 in salt free systems will not be discussed in this paper. However, the following qualitative deduction can be made from eq. 24. Since A_5 must be a smooth function of its arguments, the empirical equation of Kern, eq. 3, must be insensitive to the non-uniformity of the charge distribution with B probably near to unity, as suggested by the data plotted in Fig. 3.[13]

If we assume that the ion association can be described simply by a dissociation equilibrium, then

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[13] The previous statements may be verified in greater detail by consideration of a simple model. Consider a copolymer in which the doubly charged groups are dilute with respect to the non-ionizable groups. In this case, each difunctional group may be considered to be independent of other difunctional groups. If with each site we associate a state variable η_i, $i = 1,1',2,2', \ldots Z,Z'$ where the sites are numbered consecutively along the chain, and the η_i take on the two values 0 or 1 corresponding, respectively, to uncharged and charged sites, then the semi-grand partition function of the system becomes

$$\Xi' = \sum_{\{\eta\}} e^{-E/kT}\lambda^{\Sigma\eta_i} = \sum_{\{\eta_i\}} e^{-\Sigma\frac{\eta_i\eta_i'x}{kT}}\lambda^{\Sigma\eta_i}$$

whereupon

$$\Xi'(\lambda,T) = (1 + 2\lambda + \lambda^2 e^{-x/kT})^Z$$

and

$$\alpha' = \frac{1}{2Z}\left(\frac{\partial \ln \Xi'}{\partial \ln\lambda}\right)_T = \frac{\lambda(1 + \lambda e^{-x/kT})}{1 + 2\lambda + \lambda^2 e^{-x/kT}}$$

$$\frac{S(\alpha')}{2Zk} = \frac{1}{2}\ln[1 + 2\lambda + \lambda^2 e^{-x/kT}] - \alpha'\ln\lambda + \frac{x}{2kT}\frac{\lambda^2 e^{-x/kT}}{1 + 2\lambda + \lambda^2 e^{-x/kT}}$$

where λ is the absolute activity of the charged group, x the interaction energy between the two charged groups of the difunctional monomer and $S(\alpha')$ is the entropy associated with the distribution of charged and uncharged groups. When the free energy of expansion and of building ion atmospheres is negligible relative to the other contributions and the mixing of ion-pairs and un-ionized groups is taken to be random, it may be shown that these relations are approximately valid

$$-\ln\lambda + \ln K_s^0 - \ln a_{\mathrm{C^+}} + \frac{1}{2}\ln\frac{2\alpha f}{1 - \alpha + 2\alpha f} = 0$$

$$\ln\lambda - \ln K_a^0 + \ln a_{\mathrm{H^+}} - \frac{1}{2}\ln\frac{1-\alpha}{1 - \alpha + 2\alpha f} = 0$$

from which the degree of binding, f, may be computed, if the ion-pair dissociation constant K_s^0 is known. For the case of maleic acid some values of f are

λ	α	($K_s^0 = 10$)	($K_s^0 = 100$)	($K_s^0 = 1000$)
0.01	0.0098	....	....	......
.1	.0833	....	....	......
.5	.250	0.0005	....	......
1.0	.333	.003	....	......
5.0	.455	.030	0.0031	......
1000.0	.545	.48	0.099	......

Thus the simple model of this footnote predicts a vanishingly small amount of binding until $\alpha \geqslant 0.5$, as expected. When K_s^0 is as small as 10, complete ion pairing of one carboxyl group is predicted in the limit $\alpha \rightarrow 1$.

the maleic acid monomer should show considerable ion-bonding. For, for the case of maleic acid, $pK_1 = 1.921$, $pK_2 = 6.225$ and the calculated interaction energy between two charged groups, x, is $8.22RT$ after correction for the statistical factor. If it is further assumed that the mechanism of dissociation of a carboxyl group is the same as the mechanism of association of a counter ion, the ratio of the dissociation constants of the primary and secondary ion pairs would be

$$\frac{K_{s2}^0}{K_{s1}^0} = 2.5 \times 10^{-4} \qquad (25)$$

Therefore, even if the dissociation constant of the primary ion pair is large (as large as in the case of 1:1 electrolytes $\sim 10^2$–10^3), the dissociation constant of the secondary ion pair would be relatively small. If $K_{s_1}^0$ were 10^2, $K_{s_2}^0$ would be 0.025 and there would be appreciable ion pairing. However if K_{S1}^0 were 10^3, there would be negligible ion pairing. As shown in Fig. 5, the measured ion-binding of the maleic acid monomer at 95% neutralization is indeed negligible. It is, in any event, likely that the ion-pair in a simple electrolyte solution is entirely different from the "undissociated molecule" pictured in the dissociation equilibrium description. From the physical point of view the major characteristic of the ion pair lies in the assumption (or definition) that the ion-pair has no electrostatic influence on other ions. Therefore, the present experimental results which show that the effect of the non-uniform distribution of fixed charges (and in particular the effect of the nearest neighboring charge) is less important for ion-binding than for the dissociation of the carbonyl group is not unexpected. However, this result does not necessarily mean that there is no site-binding in polyelectrolyte solutions. Since the ions attracted to the neighborhood of the fixed charges by the strong electrostatic field shield the fixed charges and these shielded charges have little or at least lessened electrostatic effect on other charges, the notion of site-binding is useful for explaining many polyelectrolyte phenomena. In this context, the interpretation of site-binding is closely related to the interpretation of the depression of the counter ion activity coefficient. The difference in description is primarily a difference in language.

We believe the most important result of these experiments to be the demonstration of the comparable importance of the near neighbor electric field and the domain electric field. This result clearly calls for a re-examination of the current approximate polyelectrolyte theories, a problem we shall examine in a subsequent publication.

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[CONTRIBUTION FROM THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN, AND THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

Polarographic Behavior of Alkyl Phenyl Ketones with Nuclear and Side-chain Halogen Substituents

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Several alkyl phenyl ketones with chlorine and bromine substituted on the benzene ring and/or on the alkyl group have been examined polarographically to determine the effect of structure on the carbonyl group and carbon–halogen bond reductions and to obtain further information on the mechanism for the latter process. Nuclear halogen substitution facilitates carbonyl group reduction, although not in the manner expected from a consideration of inductive effects; it has no apparent effect on the fission of side-chain halogen. Addition of halogen on the side chain has no effect on carbonyl group reductions since the carbon–halogen bond is ruptured at a more positive potential. In the acidic region, *e.g.*, below *p*H 3.5, fission of the C–Cl bond is facilitated by increasing hydrogen ion concentration; this dependence probably is due to the role of hydrogen ion in a push-pull mechanism at the electrode, which is likely accentuated by the decreased dissociation of hydrogen chloride in the 9.5% ethanol solutions used.

Continuing the systematic investigation of electrochemical carbon–halogen bond fission in organic compounds,[1] a series of haloacetophenones, *i.e.*, phenacyl halides, and nuclear halogenated acetophenones and phenacyl halides, have been studied.

The following general characteristics of carbon–halogen bond fission can be deduced from the behavior of substituted aliphatic and aromatic carboxylic

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