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TITRATION OF POLYELECTROLYTES AT HIGHER IONIC STRENGTHS

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The titration behavior of polyelectrolytes at higher ionic strengths is treated on the basis of the nearest neighbor interaction between the fixed ions. This point of view suggests a quantitative comparison of the behavior of polymeric and dibasic acids. The application of these considerations to existing work on the correlation of viscosity and titration curves of polymeric acids is briefly discussed.

Introduction.—The correlation of various properties of polyelectrolytes, such as viscosity and titration behavior, has been the subject of a number of recent theoretical treatments.[1] These approaches have had varying degrees of success and while differing in a number of important respects, have in common the assumption that both the fixed and mobile ions in the polyelectrolyte system may be treated as a continuous charge distribution.

The purpose of the present note is to examine a different approach to the titration behavior of these systems, one which does not involve the latter assumption but instead assumes that the important interactions between the fixed ions on the polyelectrolyte are nearest neighbor interactions. It is expected that the repulsions between the immobile ions will vanish rapidly with distance, R, at the higher ionic strengths, in the first approximation as $e^{-\kappa R}/R$ where κ is the reciprocal Debye length. On this basis nearest neighbor interaction will begin to predominate when $\kappa R \sim 1$ where R is the distance between nearest neighbors. When $R \sim 5$ Å. this will occur when the salt concentration exceeds 0.4 M.

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[1] A. Katchalsky, O. Kunzle and W. Kuhn, *J. Polymer Sci.*, 5, 283 (1950); J. Hermans and J. T. G. Overbeek, *Rec. trav. chim.*, 67, 761 (1948); G. E. Kimball, M. Cutler and H. Samelson, This Journal, 56, 57 (1948).

If these considerations are valid a correlation between the titration behavior of a polymeric acid and of a suitable dibasic acid is to be anticipated. An examination of available data on polyacrylic and glutaric acids supports this. A treatment of the dependence of pK on the degree of neutralization is given in the following section using, at first, the Bragg–Williams approximation and later, the more exact Ising method.

Theory of Nearest Neighbor Interaction.—The polymer chain is considered to have N_a neutralized and N_b unneutralized acidic groups. We suppose that the free energy f_a of an immobile ion, A, and its counter ion atmosphere are modified by an amount $f_{aa}/2$ for each A nearest neighbor and by $f_{ab}/2$ for each B neighbor, there being only two neighbors in all. Additivity of these effects will be assumed. Corresponding quantities for the uncharged acidic group B will be denoted by f_b, $f_{ab}/2$ and $f_{bb}/2$, respectively. The total free energy of such an assembly depends on the number of pairs, N_{ab}, of nearest AB neighbors and may be written as

$$F_{ab} = f_aN_a + f_bN_b + f_{aa}N_{aa} + f_{bb}N_{bb} + f_{ab}N_{ab} - kT \ln g(N_a, N_b, N_{ab}) \quad (1)$$

where $g(N_a, N_b, N_{ab})$ is the number of ways of distributing, for a given N_a, N_b and N_{ab}, the A and B groups along the chain and where the number of AA pairs, N_{aa}, and of BB pairs, N_{bb}, is given by $2N_{aa} + N_{ab} = 2N_a$, $2N_{bb} + N_{ab} = 2N_b$. The free energy of this system, F, equals $-kT \ln (\text{P.F.}) = -kT \ln \Sigma(\text{P.F.})_{ab} = -kT \ln \Sigma_{\exp} (-F_{ab}/kT)$ where (P.F.) is the partition function for all configurations while $(\text{P.F.})_{ab}$ is the partition function for only those configurations corresponding to a given N_{ab}. The summation is over all N_{ab} consistent with the values of N_a and N_b. From equation 1 it then follows that

$$F = N_a(f_a + f_{aa}) + N_b(f_b + f_{bb}) - kT \ln \Sigma g(N_a, N_b, N_{ab}) \exp(-N_{ab}w/kT) \quad (2)$$

where

$$w = f_{ab} - f_{aa}/2 - f_{bb}/2$$

In the Bragg–Williams approximation N_{ab} in the exponential in the last term is replaced by $\bar{N}_{ab}$, the average value of N_{ab} when A and B are randomly distributed along the chain. The last term in equation 2 thus becomes $\exp(-w\bar{N}_{ab}/kT)\Sigma g$. The total number of ways of arranging the N_a A's and N_b B's along the chain, Σg, is $(N_a + N_b)!/N_a!N_b!$ $\bar{N}_{ab}$ is readily evaluated by observing that in this random case the probability of an adjacent pair of sites having an A on the first site and a B in the second is $N_a/(N_a + N_b) \times N_b/(N_a + N_b)$, so that the chance that this link is an AB link is twice this. Since there are $(N_a + N_b)$ such pairs of adjacent sites, $\overline{N_{ab}} = 2N_aN_b/(N_a + N_b)$. It then follows that $(\partial F/\partial N_a)$ is given by

$$\left(\frac{\partial F}{\partial N_a}\right)_{N_a + N_b} = f_a + f_{aa} - f_b - f_{bb} + 2w(1 - 2\alpha) \quad (3)$$

where

$$\alpha = N_a/(N_a + N_b)$$

Equating this to the partial molecular free energy, μ, of the hydrogen ions in a solution in which their activity is a_{H^+}, $\mu = f_H + kT \ln a_{H^+}$, it follows that

$$pK = pH - \log \frac{\alpha}{1 - \alpha} = \frac{\Delta f}{2.3kT} + \frac{2w}{2.3kT}(1 - 2\alpha) \quad (4)$$

where

$$f = f_a + f_{aa} + f_H - f_b - f_{bb}$$

Thus the pK is a linear function of α in this approximation and the change in pK, from $\alpha = 0$ to $\alpha = 1$ is $\Delta pK = -4w/2.3kT$. The major contribution to w is f_{aa}, the repulsion of the immobile ions, and it follows that f_{aa} is positive and w negative, as observed. Both Δf and w will depend on the counter ion atmosphere and hence upon the salt concentration.

If the repulsion of nearest neighbor ions is very pronounced, then the A and B groups are not distributed randomly along the chain. Using the approach employed by Ising in an analogous problem in ferromagnetism, an equation may be derived which takes into account in an exact manner such deviations from randomness. From such a treatment we find[2]

$$\left(\frac{\partial F}{\partial N_a}\right)_{N_a + N_b} = f_a + f_{aa} - f_b - f_{bb} + kT \ln \frac{\sqrt{4\alpha(1 - \alpha)(e^{2w/RT} - 1) + 1} + 2\alpha - 1}{\sqrt{(4\alpha(1 - \alpha)(e^{2w/RT} - 1) + 1)} + 1 - 2\alpha} \quad (5)$$

and from this, that

$$pK = \frac{\Delta f}{2.3kT} + \log \frac{(\sqrt{4\alpha(1 - \alpha)(e^{2w/RT} - 1) + 1} + 2\alpha - 1)(1 - \alpha)}{(\sqrt{4\alpha(1 - \alpha)(e^{2w/RT} - 1) + 1]} + 1 - 2\alpha)\alpha} \quad (6)$$

where w and Δf retain their previous significance. As before, the change in pK from $\alpha = 0$ to $\alpha = 1$, ΔpK, is $-\ 4w/2.3kT$. This is as expected since in both cases a dissociating acid group is in an environment of other undissociated groups when $\alpha = 0$ and in an environment of neutralized groups when $\alpha = 1$. When $-2w << kT$, equation 6 reduces to 4, as it should. A comparison between these equations is given in Fig. 1 for $\Delta pK = 1.0$. In this case $-2w/kT = 2.3/2$, which is not negligible compared with unity. When $\Delta pK = 0.5$ equations 4 and 6 are essentially equivalent.

Comparison with Experimental Data.—A survey of the titration behavior of polyelectrolytes[3,4] indicates three common types of pK–α curves: linear (as in Fig. 1), S-shaped (as in Fig. 1) with a maximum slope at $\alpha = {}^1/_2$, inverted S-shaped with a minimum slope at $\alpha = {}^1/_2$. Frequently the curvature in the latter cases is not particularly pronounced and its observance may well depend on the

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[2] An evaluation of the last term in equation 2 is given, for example, in Rushbrooke's "Statistical Mechanics," Oxford University Press, New York, N. Y., 1949, p. 304, equation 42. Denoting this term by ΔF, subsequent equations are also given there for $(\partial\Delta F/\partial N_a)_{N_b}$ and $(\partial\Delta F/\partial N_b)_{N_a}$. It is observed that

$$\left(\frac{\partial F}{\partial N_a}\right)_{N_a + N_b} = f_a + f_{aa} - f_b - f_{bb} + \left(\frac{\partial \Delta F}{\partial N_a}\right)_{N_b} - \left(\frac{\partial \Delta F}{\partial N_b}\right)_{N_a}$$

[3] *Cf.* P. Doty and G. Ehrlich, *Ann. Rev. Phys. Chem.*, 3, 81 (1952)

[4] H. P. Gregor and L. Luttinger, private communication.

number of experimental points recorded. In the various data examined the first two curves, and therefore equations 4 and 6, satisfy reasonably well the modified, empirical, Henderson–Hasselbach equation, $pH = pK_m + n \log \alpha/(1 - \alpha)$, proposed by Katchalsky and Spitnik,[5] if α is, say, between 0.1 and 0.9; while the third type generally obeys the equation over a somewhat larger region. However, when $\alpha > 0.9$ the experimental error is larger, while when $\alpha < 0.1$ the interpretation of the data may be more vague since here, the calculation of α depends on a knowledge of the self-ionization of the acid.

Of particular interest is the comparison of the titration behavior of glutaric and polyacrylic (PAA) acids. A comparison with α,γ-dimethylglutaric acid would, it is true, be more suitable, but data on that acid do not appear to be available. The ratio of the first and second dissociation constants K_1/K_2, of glutaric acid is about 12, of which a factor of 4 is statistical and the remaining factor of 3 may be attributed to the repulsions of the neighboring ionic groups and more specifically to the term, $-2w/kT$, discussed earlier. An examination of some approximate titration curves of glutaric acid[4] indicates that $pK_2 - pK_1$ is lowered by about 0.08 and 0.19 unit in the presence of 0.2 and 2 M $NaNO_3$, respectively. If nearest neighbor interaction predominates in PAA, then one might anticipate that ΔpK for PAA would be about 2 log 3, 2(log 3 − 0.08), 2(log 3 − 0.19); that is, 0.96, 0.80, 0.58 in the presence of no salt, 0.2 M $NaNO_3$ and 2M $NaNO_3$, since there are two nearest neighbors in the polymeric acid and only one in glutaric acid.

The pK–α curves for PAA,[4] in solutions dilute with respect to PAA, appear to be linear or slightly S-shaped, as in Fig. 1. ΔpK is approximately 2.5, 1.2, 0.8 in the presence of 0, 0.2 and 2 M $NaNO_3$, respectively. The agreement between the observed ΔpK's and those calculated from the behavior of glutaric acid improves with increasing salt concentration, as expected, and the agreement in the latter cases is reasonable, considering the extrapolation errors and assumptions employed.[6]

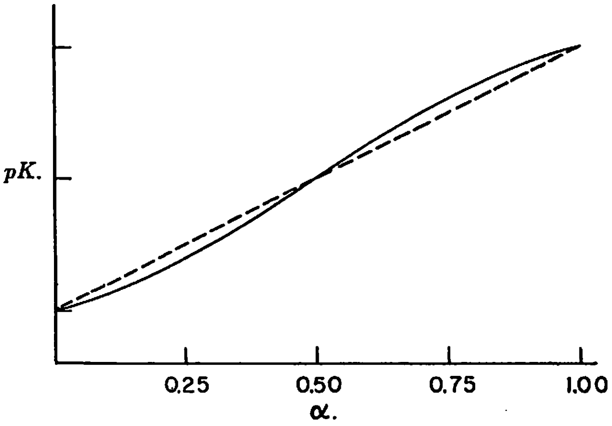

Fig. 1.—A plot of pK *versus* α when $\Delta pK = 1.0$ The dotted line is based on equation 4, and the full line on equation 6.

The titration behavior of dilute solutions of carboxylmethylcellulose[7] (CMC) is rather interesting. Extrapolating the linear curves of Hermans and Pals, one arrives at a rather rough value for ΔpK of about 1.8 in the absence of salt, a value somewhat less than that observed for PAA. This ΔpK decreases rapidly with increasing salt (NaCl) concentration so that at a salt concentration of 0.3 M, $\Delta pK \sim 0.2$, a value considerably smaller than that found for PAA. This CMC polymer differs from PAA in that the acid groups are, on the average, more widely spaced. In the presence of salt the nearest neighbor interaction will vary strongly with distance, R, approximately as $e^{-\kappa R}/R$, while at low salt concentration the interaction between all the immobile ions varies less strongly, as $1/R$. It is therefore expected that the former will be much more sensitive to change in nearest neighbor distance than the latter. This is consistent with the observed behavior of CMC and PAA.

In conclusion, it is observed that nearest neighbor interaction is expected to have a rather slight effect on viscosity. If such interaction is a large part of the total interaction, which in PAA it appears to be, then it must be taken into account in theories correlating viscosity and titration behavior. The neglect of this contribution to the interaction would tend to make ΔpK's calculated from viscosity behavior less than those observed experimentally.

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

(6) Two procedures are available for this calculation of ΔpK for PAA. The values cited in the text are based on a linear extrapolation of data given in the region $\alpha = 0.2$ and $\alpha = 0.8$. Another procedure, and one which is more self-consistent, calculates ΔpK from the slope of the pK–α curve in this region using equation 6 and the relation $\Delta pK = (-2w/2.3kT)$. The values of ΔpK calculated by the latter procedure are but slightly less, as expected, and are found to be 1.0 and 0.7 in the presence of 0.2 and 2 M $NaNO_3$, respectively.

(7) D. T. F. Pals and J. J. Hermans, *Rec. trav. chim.*, **71**, 513 (1952).