

## Acid-Base Properties of Fibers. Part II. A Polyelectrolyte Theory of the Combination of Fibers with Acids and Bases

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### Synopsis

A new theory for the acid-base properties of fibers is presented, resembling those for polyelectrolytes, and based on the normal titration of the charged groups of the fibers and the energy needed to remove the protons from the fiber to the solution, against the electrostatic, osmotic, and affinity differences. The acid titration equation for a polyampholyte fiber is:

$$\text{pH} = \text{p}K_0' - \log [(1 - \alpha)/\alpha] - (0.4343/RT)[\chi F + \pi \bar{V}_H + \Delta\mu_H^\circ]$$

where  $\text{p}K_0'$  is the intrinsic dissociation constant of the titrating groups in the fiber,  $\alpha$  is the degree of dissociation,  $\chi$  is the electrostatic potential of the fiber,  $\pi$  the osmotic pressure,  $\bar{V}_H$  the partial molar volume of the hydrogen ion, and  $\Delta\mu_H^\circ$  the difference of standard chemical potential in the fiber and the solution. In all cases examined, the osmotic term proved to be negligible. The electrostatic potential was calculated assuming it to be uniform over the fiber. For wool,  $\text{p}K_0'$  is independent of salt concentration but varies linearly with degree of dissociation, indicating that two  $\text{p}K$ 's are operating,  $\text{p}K_q = 3.58_5$  for paired groups and  $\text{p}K_p = 4.85_5$  for nonpaired groups at  $0^\circ\text{C}$ ., present in equal proportions. Titrations of wool with sulfuric acid and a wide range of strong monobasic acids also obey the theory, and values of the anion affinities in general agreement with those given by Gilbert and Rideal are found. The acid titration of native ox-hide collagen gave a constant value of  $\text{p}K_0' = 4.0$ . For nylon, the value of  $\text{p}K_0'$  is, to a first approximation, independent of degree of dissociation and salt concentration, in agreement with the theory.

### INTRODUCTION

Fibers such as wool and nylon combine with acids and bases from aqueous solution, and pH-titration curves may be determined. Several theories have been proposed to interpret this behavior for wool. Steinhardt and Harris<sup>1</sup> considered that wool combines with protons and anions according to mass-action equilibria, Gilbert and Rideal<sup>2</sup> used the equation of Fowler and Guggenheim<sup>3</sup> (with an additional electrostatic term) for sorption at random among a limited number of sites and applied it to the independent adsorption of protons and anions in equal numbers, while Peters and Speakman<sup>4,5</sup> treated the system in terms of the Donnan membrane equilibrium and calculated an "internal pH" within the fiber. For nylon, the theory of Wall et al.<sup>6-8</sup> is similar to that of Gilbert and Rideal,

while Myagkov and Pakshver<sup>9</sup> used an ion-exchange approach; these theories have been considered in Part I.<sup>10</sup>

Since these fibers carry dissociating groups, they can be considered to be related to the polyelectrolytes, both soluble and crosslinked, for the acid-base properties of which different theories have been proposed.<sup>11-13</sup> These theories, in contrast to those for fibers, have generally been based on the electrostatic potential of the polymer. A simple monobasic acid at infinite dilution obeys the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_0 - \log [(1 - \alpha)/\alpha] \quad (1)$$

where  $\alpha$  is the degree of dissociation and  $\text{p}K_0$  the dissociation constant of the acid. It seems reasonable to approach the titration of polyacids from this standpoint, and for the titration of a polybasic acid, Bjerrum<sup>14</sup> suggested that the free energy, ( $\Delta F_\nu$ ), accompanying the removal of a proton from a carboxyl group of a molecule carrying  $(\nu - 1)$  negative charges, in addition to the carboxyl group considered, is the sum of the energy required to dissociate the proton from the group, ( $\Delta F_0$ ), and that needed to remove it then to infinity against the field, ( $\Delta F_i$ ). Hence,

$$\Delta F_\nu = -RT \ln K = \Delta F_0 + \Delta F_i = -RT \ln K_0 + \Delta F_i \quad (2)$$

and

$$K = K_0 \exp \{ -\Delta F_i/RT \} \quad (3)$$

where  $K_0$  is the dissociation constant which the carboxyl group would show if it were the only ionizing group of a molecule corresponding to the basic unit of the polymer. The Henderson-Hasselbalch equation therefore becomes, for such a polybasic acid,

$$\text{pH} = \text{p}K_0 - \log [(1 - \alpha)/\alpha] + (0.4343 \Delta F_i/RT) \quad (4)$$

In the equation due to Hartley and Roe<sup>15</sup>

$$\text{pH} = \text{p}K_0 - \log [(1 - \alpha)/\alpha] + (0.4343 \chi F/RT) \quad (5)$$

the electrostatic energy  $\chi F$  was identified with  $\Delta F_i$  by Arnold and Overbeek<sup>16,17</sup> and Katchalsky and Gillis,<sup>18</sup> assuming that this was the only significant contribution to  $\Delta F_i$ . Equation (5) has been shown to apply to solutions of spherical proteins, poly(acrylic acid), and poly(methacrylic acid)<sup>18,19</sup> by calculating  $\chi$  from experimental determinations of the electrophoretic mobility. The direct calculation of  $\chi$  from the charge and dimensions of the polymer molecules is difficult, except for proteins of relatively low charge and fixed dimensions,<sup>20</sup> but recently a solution for flexible polyelectrolytes has been given by Lifson<sup>21</sup> which agrees with a numerical solution<sup>22</sup> and shows that the Debye-Hückel approximation is invalid for these systems. The Donnan approximation as employed by Kimball, Cutler, and Samelson<sup>23</sup> is more nearly correct.

This approach has been extended, with some success, to the acid-base properties and the swelling of crosslinked polyelectrolytes. Katchalsky,

Lifson, and Eisenberg<sup>24</sup> calculated the electrostatic potential by treating the polymeric component of the gel as if it consisted of isolated polymer molecules. The more detailed theory of Lazare, Sundheim, and Gregor<sup>25</sup> makes allowance for the rigidity of the structure due to the crosslinks and considers the segments of the polymer chains as being surrounded by a solution phase in the gel itself, with a different potential on the polymer and in the gel solution. This type of theory is necessary for highly swollen systems in which the degree of swelling depends markedly on the pH and in which a high concentration of uncombined acid or base exists in the gel, but for fibers which swell relatively little as compared with gels, a much simpler treatment can be given. It is simpler to consider the fiber as a whole, rather than to treat separately the polymer molecules and the small amount of solvent within the fiber. The degree of swelling needed to invalidate this approximation is not known, but experiments are being made using crosslinked systems to answer this question.

It seems likely that a single theory would describe successfully the acid-base properties of all these materials, provided its character was sufficiently general so that allowance could be made for the wide differences of structure and reactivity and for the different types of experimental data which are available for the different materials.

## THEORETICAL

Two derivatives will be given for an equation to describe the acid-base properties of fibers, one a simple extension of the theory for soluble poly-electrolytes, the other based on the equations of Donnan and Guggenheim<sup>3</sup> but making no assumptions concerning either membranes or selective adsorption at sites. The electrostatic potential is the key term in the titration equation, and simple calculations of  $\chi$  for fibers will be given.

### The Titration Equations

Equation (4) for the titration of a polybasic acid can be applied directly to the titration of a fiber. Then,  $K_0$  represents the dissociation constant of a particular dissociating group of the fiber, and  $\Delta F_i$  the energy required to transfer a proton from the neighborhood of the dissociating group to the solution surrounding the fiber. There can be three contributions to  $\Delta F_i$ , i.e., (1) an electrostatic contribution  $\chi F$  already considered, as the proton adjacent to the dissociating group in the fiber is in a region of potential  $\chi$ , and is to be transferred to the solution where the net potential is zero; (2) an osmotic contribution  $\pi \bar{V}_H$ , where  $\pi$  is the osmotic pressure between the fiber and the solution and  $\bar{V}_H$  is the partial molar volume of the hydrogen ion (supposed independent of pressure over the range considered); and (3) an "affinity" contribution  $\Delta\mu_H$ , the difference in standard chemical potential of the hydrogen ion in the fiber and in the solution, this difference arising for acids which have anions showing selective adsorption in the fiber

or which dissociate to different extents in the fiber and in the solution. The complete titration equation is therefore, for a polyacid fiber,

$$\text{pH} = \text{p}K_0' - \log [(1 - \alpha)/\alpha] + (0.4343/RT)[\chi^F - \pi\bar{V}_H - \Delta\mu_H^\circ] \quad (6)$$

and for the acid titration of a polyampholyte fiber like wool and nylon,

$$\text{pH} = \text{p}K_0' - \log [(1 - \alpha)/\alpha] - (0.4343/RT)[\chi^F + \pi\bar{V}_H + \Delta\mu_H^\circ] \quad (7)$$

where  $\text{p}K_0'$  refers to finite concentrations.

An alternative, more rigorous approach to the equation regards the system as having two phases, fiber (considered as a single phase) and solution, represented by subscripts 1 and 2. For a positive ion  $i$ , with a net positively charged polyampholyte fiber, the chemical potentials at equilibrium are:

$$\begin{aligned} \mu_{i,2} &= \mu_{i,2}^\circ + RT \ln a_{i,2} + P_2\bar{V}_{i,2} + \chi_2^F \\ \mu_{i,1} &= \mu_{i,1}^\circ + RT \ln a_{i,1} + P_1\bar{V}_{i,1} + \chi_1^F \end{aligned} \quad (8)$$

being the same in both phases. Assuming that

$$\bar{V}_{i,1} = \bar{V}_{i,2} = \bar{V}_i$$

i.e., that the partial molar volume of the ions is independent of  $P$  over the required range,

$$(\chi_1 - \chi_2)^F = RT \ln (a_{i,2}/a_{i,1}) + (P_2 - P_1)\bar{V}_i + \mu_{i,2}^\circ - \mu_{i,1}^\circ \quad (9)$$

Putting

$$\pi = P_1 - P_2$$

$$\chi = \chi_1 - \chi_2$$

$$\Delta\mu_i^\circ = \mu_{i,1}^\circ - \mu_{i,2}^\circ$$

then

$$RT \ln (a_{i,1}/a_{i,2}) = -\chi^F - \pi\bar{V}_i - \Delta\mu_i^\circ \quad (10)$$

Applying this equation to hydrogen ions yields

$$\text{pH}_2 = \text{pH}_1 - (0.4343/RT)[\chi^F + \pi\bar{V}_H + \Delta\mu_H^\circ] \quad (11)$$

where  $\text{pH}_1$  and  $\text{pH}_2$  refer to the fiber phase ("internal" pH) and to the solution, respectively.

Regarding the titration as taking place inside the fiber, considered to be uniform and of constant volume, no electrostatic, osmotic, or "affinity" work is involved, and so

$$\text{pH}_1 = \text{p}K_0' - \log [(1 - \alpha)/\alpha]$$

Hence,

$$\text{pH}_2 = \text{p}K_0' - \log [(1 - \alpha)/\alpha] - (0.4343/RT)[\chi^F + \pi\bar{V}_H + \Delta\mu_H^\circ] \quad (7)$$

For the negative ions,  $j$ , again supposing the partial molar volume to be independent of pressure,

$$RT \ln (a_{j,1}/a_{j,2}) = \chi^F - \pi\bar{V}_j - \Delta\mu_j^\circ \quad (12)$$

or

$$pJ_2 = pJ_1 + (0.4343/RT)[\chi^F - \pi\bar{V}_j - \Delta\mu_j^\circ] \quad (13)$$

where  $pJ = -\log a_j$ . Katchalsky, Lifson, and Eisenberg,<sup>24</sup> who treated highly swollen gels, included a term to allow for the free energy of the gel due to changes in the gel volume with  $\alpha$  and inserted the electrostatic and elastic energies of the polymer molecules in this term. This is appropriate for a highly swollen gel, while the method given here is more appropriate for a fiber or a gel which swells little.

After  $\chi$  has been calculated, eq. (7) can be tested by using experimental values of  $pH_2$  and  $\alpha$  to calculate the term

$$pK_0' - (0.4343/RT)[\pi\bar{V}_H + \Delta\mu_H^\circ] = pK_e \quad (14)$$

If this term is constant, independent of the salt concentration, then evidently the term  $\pi\bar{V}_H$  can be neglected. Further, if this term has a value close to the expected intrinsic  $pK_0$  of the acid group of the fiber (about 4.8 for a carboxylic acid), then  $\Delta\mu_H^\circ$  is negligible also, and the acid anion has no specific affinity. This might be expected to hold for hydrochloric acid.

The relation of this theory to those of Gilbert and Rideal<sup>2</sup> and Peters and Speakman<sup>4</sup> should be made plain. Gilbert and Rideal suppose that all anions in the fiber are specifically adsorbed at sites, while the present theory allows for a proportion only to be so adsorbed. Peters and Speakman treat the fiber as possessing a solid phase, analogous to the Donnan membrane, and a liquid phase consisting of the swelling fluid, and calculate an internal pH, not measurable, relating to this fluid phase. This makes it necessary to find the volume of this fluid, which is not easy. The present theory considers the fiber and swelling fluid as a single phase of known volume, and lays stress on the external pH of the surrounding solution as the theoretically important, as well as the measurable parameter. The internal pH is used here ( $pH_1$ ) only in the process of the second derivation of the titration equation and refers to the whole fiber.

### Different Acids used for Titration

If no salt is present, the usual approximation for individual ionic activities gives  $pH_2 = pJ_2$ , and combining eqs. (7) and (13) yields

$$2pH_2 = pK_0' - \log \frac{1 - \alpha}{\alpha} + pJ_1 - \frac{0.4343}{RT} \times [\pi_j(\bar{V}_H + \bar{V}_j) + \Delta\mu_{H(j)}^\circ + \Delta\mu_j^\circ] \quad (15)$$

Writing this equation for two different acids with anions  $j$  and  $L$  respectively, and subtracting for constant  $\alpha$ ,

$$2(pH_{2,L} - pH_{2,j}) = pL_1 - pJ_1 - \frac{0.4343}{RT} [\pi_L\bar{V}_{HL} - \pi_j\bar{V}_j + \Delta\mu_{HL}^\circ - \Delta\mu_{Hj}^\circ] \quad (16)$$

where  $\bar{V}_{HL}$  has been written for  $\bar{V}_H + \bar{V}_L$ , and  $\Delta\mu_{HL}^\circ$  for  $\Delta\mu_H^\circ(L) + \Delta\mu_L^\circ$ , and similarly for  $H_j$ . Equation (16) can only be used if something is known about  $pL_1 - pJ_1$ . Gilbert and Rideal supposed that  $pL_1 = pJ_1$ , since, for net electrical neutrality in the fiber,

$$C_{j,1} = C_f + C_{H,1} = C_{L,1}$$

where the  $C$ 's are concentrations and  $C_f$  is the net concentration of fixed charge in the fiber. This involves equating concentrations with activities, and assuming that  $C_{j,1}$  refers to all the anions in the fiber. Equation (7) can be used directly to calculate affinity values without this assumption.

### Calculation of the Electrostatic Potential

The equations given are quite general, and make no assumptions concerning the chemical structure of the fiber. Unfortunately, some structural assumptions must be made for the calculation of  $\chi$ , and it is most logical to begin with the simplest. Suppose the fiber has a structure sufficiently uniform so that the electrostatic potential is constant over the whole fiber, and that the fiber is sufficiently extensive so that surface and end effects may be neglected. Clearly the first of these is a gross approximation. Poisson's equation should apply here,

$$\nabla^2\chi = -4\pi\rho/D \quad (17)$$

where  $\rho$  is the net charge on the fiber and  $D$  the dielectric constant. Using  $C_f$  for the concentration of net positive charges in the fiber due to the fixed charges themselves, for a polyampholyte fiber with excess of positive fixed charges,

$$\rho = \epsilon(C_f + C_{i,1} - C_{j,1}) \quad (18)$$

where  $C_{i,1}$  and  $C_{j,1}$  are the concentrations of positive and negative small ions in the fiber and  $\epsilon$  is the electronic charge. Considering that  $C_{i,1}$  and  $C_{j,1}$  are related to the concentrations in the external solution by the Boltzmann relations

$$\begin{aligned} C_{i,1} &= C_{i,2} \exp \left\{ -\epsilon\chi/kT \right\} \\ C_{j,1} &= C_{j,2} \exp \left\{ \epsilon\chi/kT \right\} \end{aligned} \quad (19)$$

and considering now only a 1:1 electrolyte,

$$C_{i,2} = C_{j,2} = C_s$$

where  $C_s$  is the molar concentration of electrolyte in the external solution. Hence,

$$\rho = \epsilon \left[ C_f + C_s (\exp \left\{ -\epsilon\chi/kT \right\} - \exp \left\{ \epsilon\chi/kT \right\}) \right]$$

and so,

$$\nabla^2\chi = (-4\pi\epsilon C_f/D) + (8\pi\epsilon C_s/D) \sinh (\epsilon\chi/kT) \quad (20)$$

If the electrostatic potential is uniform over the fiber,  $\Delta^2\chi = 0$  and so,

$$\epsilon\chi/kT = \sinh^{-1} C_t/2C_s \quad (21)$$

allowing  $\chi$  to be calculated easily.

For titration by a polybasic acid in the presence of its salt, e.g., sulfuric acid in the presence of sodium sulfate, the corresponding result is,

$$\epsilon\chi/kT = \sinh^{-1} C_t/2ZC_s \quad (22)$$

where  $Z$  is the valency of the anion, and for an acid in the presence of excess of any multivalent salt,

$$\epsilon\chi/kT = \sinh^{-1} C_t/2Z_iZ_jC_s \quad (23)$$

where  $Z_i, Z_j$ , are the valencies of the ions of the salt.

Equation (21) may be compared with previous calculations of the electrostatic potential of polyelectrolytes. It represents certain limiting cases of the calculations of Kimball, Cutler, and Samelson<sup>23</sup> and Lifson<sup>21</sup> for soluble polyelectrolytes, and of Hill<sup>26</sup> for cylindrical gels. Peters<sup>5</sup> has also obtained the equation in a less rigorous manner by making use of the conditions of overall fiber neutrality. If agreement with experiment were found by use of eq. (7) with  $\chi$  calculated from eq. (21), it would not be necessary to consider any more complicated cases.

It can be shown that eq. (21) is inconsistent with the assumption that  $pL_1 = pJ_1$ .

### Nonuniform Potential Distributions

Although the simple calculation of  $\chi$  already given might be expected to apply to a fiber having a random distribution of a single type of charged group, where there is a preference for fixed charges to be grouped together in pairs of oppositely charged groups, as for example in the salt links of wool, the approximation of a uniform potential distribution will be too crude. For such a paired or salt-linked group, the local potential will exceed the average potential by an amount  $\chi_s$ . The system can be treated by considering this extra potential to be superimposed on the average potential still itself considered to be uniformly distributed. This is similar to the procedure suggested by Harris and Rice<sup>27</sup> for ion binding in polyelectrolyte solutions and gels, in which an overall electrostatic potential is superimposed on that due to nearest-neighbor interactions. Nagasawa and Rice<sup>28</sup> have shown that the local charge density dominates the behavior of dissociating carboxyl groups in copolymers of maleic acid with vinylpyrrolidone and vinyl acetate. Thus for the titration of a paired carboxyl group, an extra term,  $-0.4343 F\chi_s Q/RT$ , can be included in eq. (7), where  $Q$  is the fraction of charged groups involved in such pairs. This term is difficult to calculate *a priori* since  $Q$  will vary with  $\alpha$ , but if  $Q$  were known, an estimate of the term might be made by using the  $\text{COO}^- \dots \text{H}_3\text{N}^+$  distance in the pair and the distance of closest approach of the carboxyl and hydrogen ions before recombination.

However, it is easier to regard the carboxyl groups, with and without pairing, as being two different dissociating groups with different values of  $pK_0$ . Suppose  $pK_p$  and  $pK_q$  represent the intrinsic dissociation constants of nonpaired and of paired carboxyl groups, respectively.  $pK_p$  and  $pK_q$  are likely to be quite different, the difference between them completely overshadowing any small difference of dissociation constants between the carboxyl groups for different amino acids. This device allows the use of a uniform potential  $\chi$  which can still be calculated by eq. (21), together with a superimposed potential for the paired group only, represented by the change of  $pK$ . If  $p$  and  $q$  are the degrees of dissociation of these two kinds of groups, eq. (7) becomes:

$$pH = pK_p' - \log [(1 - p)/p] - (0.4343/RT)[\chi^F + \pi\bar{V}_H + \Delta\mu_H^\circ]$$

and

$$pH = pK_q' - \log [(1 - q)/q] - (0.4343/RT)[\chi^F + \pi\bar{V}_H + \Delta\mu_H^\circ] \quad (24)$$

Application of eq. (7) to such a system, if  $\pi\bar{V}_H$  were negligible, would result in a value of  $pK_0'$  which varied with  $\alpha$  between extreme values of  $pK_q'$  and  $pK_p'$ , but the same value of  $pK_0'$  would be found for a given value of  $\alpha$  for all concentrations of salt. Thus  $pK_p'$  and  $pK_q'$  could be found, as the extreme values of  $pK_0'$  when  $\alpha = 0$  and 1.0. If  $P$  and  $Q$  are, respectively, the fractions of the nonpaired and paired groups,

$$1 - \alpha = P(1 - p) + Q(1 - q) \quad (25)$$

and

$$\begin{aligned} pK_0' - \log [(1 - \alpha)/\alpha] &= pK_p' - \log [(1 - p)/p] \\ &= pK_q' - \log [(1 - q)/q] \end{aligned} \quad (26)$$

$P$  and  $Q$  can be found as well as  $pK_p'$  and  $pK_q'$ . The values of  $P$  and  $Q$  would be confirmed if the same values were obtained using different acids for titration, when only  $\Delta\mu_H^\circ$  would have been changed.

Since

$$K_q' = K_p' \exp \{ \epsilon\chi_s/kT \} \quad (27)$$

$pK_q'$  will be less than  $pK_p'$ , and eq. (27) allows  $\chi_s$  to be calculated and compared with the estimate already mentioned.

### Effect of Molecular Weight

For a polymer in which only the endgroups dissociate, the molecular weight affects the titration. The concentration of titratable groups is inversely proportional to the degree of polymerization, and so also is the net concentration of fixed charged,  $C_i$ , provided the degree of accessibility of the groups to acid and base is not appreciably affected by the degree of polymerization. The terms  $pK_0'$  and  $\Delta\mu_H^\circ$  will be almost if not completely independent of the degree of polymerization, and so for a series of polymers



of different degrees of polymerization at the same degree of dissociation, by combining eqs. (7) and (21)

$$\text{pH} = \text{Const.} - 0.4343 \sinh^{-1} C_t/2C_s$$

if the osmotic term is negligible. Provided  $C_t/C_s$  is large (greater than 200), which holds generally if the concentration of added salt is very low,

$$\sinh^{-1} C_t/2C_s = \ln C_t/C_s$$

and so

$$\text{pH} = \text{Const.} - \log (C_t/C_s) \quad (28)$$

For such systems, plots of pH against  $\log C_t$  at constant  $\alpha$  and  $C_s$  should be linear with a slope of  $-1$ .

### Advantages of the Theory

This theory can be applied directly to the titration data, as it makes no assumptions regarding the mechanism of adsorption or about the activity coefficients or standard chemical potentials and it brings the theory for fibers into line with that for soluble and crosslinked polyelectrolytes. In particular, however, it allows values to be obtained for  $\text{p}K'_0$ , and this makes the direct correlation of the theory with elastic and structural properties of the fibers possible, as will be seen when the results for wool, nylon, and modified wools are discussed.

## APPLICATION OF THE THEORY TO THE TITRATION OF NYLON

### Titration of Nylon 66 Fibers by Hydrochloric Acid

The results given in Part I<sup>10</sup> for the titration of nylon 66 fibers by hydrochloric acid in the presence of potassium chloride were considered suitable for testing the theory. The net concentration of fixed charges,  $C_t$ , in gram-ions per liter, was calculated by neglecting the very small extent of swelling. Values of the pH of the solutions were interpolated from the titration curves at intervals of  $1 - \alpha$  of 0.1, the electrostatic term calculated from equation (21), and  $\text{p}K_e$  calculated from eq. (7). The results are shown in Table I.

The values of  $\text{p}K_e$  calculated in this way are, to a first approximation, independent of both the degree of dissociation and the salt concentration, within the experimental error. This supports the use of the theory in this case, and implies that the osmotic term in eq. (7) is negligible. The values of  $\text{p}K_e$  for  $1 - \alpha = 0.1$  are lower than the average values, but this may be an experimental error connected with the difficulty of defining accurately the position of the titration curve at its extremes for nylon, which takes up comparatively little acid. The average value of  $\text{p}K_e$  observed, 5.30, is greater than the values usually found for carboxylic acid groups. This

means either that  $\Delta\mu_{\text{H}}^{\circ}$  is not negligible, implying perhaps some affinity of the chloride ion for nylon, whereas it has none for wool (*q.v.*), or that very powerful inductive effects are operating. The second possibility seems unlikely, since adipamic acid,  $\text{H}_2\text{NCO}(\text{CH}_2)_4\text{CO}_2\text{H}$ , which represents a reasonably close approximation to the monomeric unit concerned in the nylon 66 chain, has  $\text{pH} = 4.63$ .<sup>29</sup> Since a tendency toward pairing of positive and negative fixed charges, such as occurs in salt links, would result in a lowering of the  $\text{pK}$  of the carboxyl group as it does for wool (*q.v.*), this possibility can be excluded too. This indication of the absence of salt-linking in nylon 66 is in agreement with the results on the effect of  $\text{pH}$  on the elastic properties of the fibers (*q.v.*). The salt concentrations studied

TABLE I  
Titration of Nylon 66 Fibers by Hydrochloric Acid in the Presence of Potassium Chloride at 21.5°C.;  $C_f = 0.0362(1 - \alpha)$  1.14

1 - $\alpha$	0.02M KCl			0.04M KCl			0.10M KCl		
	pH	$C_t/2C_s$	$\text{pK}_e$	pH	$C_t/2C_s$	$\text{pK}_e$	pH	$C_t/2C_s$	$\text{pK}_e$
0.1	5.94	0.103	(5.02)	6.03	0.052	(5.09)	6.12	0.0207	5.17
0.2	5.72	0.207	5.20	5.82	0.104	5.26	5.95	0.0413	5.37
0.3	5.49	0.310	5.25	5.61	0.155	5.30	5.77	0.062	5.43
0.4	5.27	0.413	5.26	5.40	0.207	5.31	5.60	0.083	5.45
0.5	5.04	0.518	5.25	5.20	0.259	5.31	5.43	0.103	5.47
0.6	4.82	0.620	5.26	4.99	0.310	5.30	5.26	0.124	5.49
0.7	4.58	0.725	5.24	4.78	0.363	5.30	5.07	0.145	5.50
0.8	4.30	0.827	5.23	4.53	0.414	5.30	4.84	0.166	5.52
0.9	3.80	0.930	5.12	3.96	0.465	5.12	—	—	—

were all rather high for nylon, which should show a large effect on the titration curve even at very low salt concentrations. New results are at present being obtained by Mr. S. P. Barve for salt concentrations of 0.0001, 0.001, and 0.01M, and these also agree with the theory. They will be published in due course. They strengthen the view, also indicated by the results given here (Table I) that the exact values of  $\text{pK}_e$  are not completely independent of salt concentration over the whole range, but rather increase slowly with increased salt concentration. This could be due to the nature of the gross approximation involved in the calculation of  $\chi$  to some small influence of the osmotic term  $\pi \bar{V}_{\text{H}}$ , or to a specific binding of the metal ions by the nylon.

#### Titration of Nylon 6 by Hydrochloric Acid

The results given in Part I<sup>10</sup> for nylons 6 and 66 in the absence of added salt were not considered suitable for testing the theory, since extreme precautions against the presence of adventitious salt had not been taken. The form of eq. (21) is such that very small amounts of added salt make very large differences in the value of  $\chi^F/RT$ , especially for nylon, the term  $C_s$  for titrations in the absence of salt referring to the acid only. Thus for  $\text{pH}$

$= 4.75$ ,  $C_s$  (no salt)  $= 1.77 \times 10^{-5}$ , but  $C_s$  (0.001M salt)  $= 102 \times 10^{-5}$ . Particularly in the experiments on nylon 6, adventitious salt was probably present, the preparation of the polymer having involved precipitation using calcium chloride, and the complete removal of such a salt from the polymer is extremely difficult. On the assumption that adventitious salt equivalent to a concentration of 0.002M of a 1:1 salt was present, the titration curves for the four nylon 6 polymers of different degrees of polymerization give good agreement with the theory, average values of  $pK_e$  of 5.41, 5.34, 5.45, and 5.44 being obtained for polymers B to E, respectively. Although this cannot be regarded as experimental evidence in favor of the theory, it is not inconsistent with it. New preliminary results have been obtained by S. P. Barve for nylon 6 in the presence of small concentrations of added salt, which agree with the theory. These results will be published later.

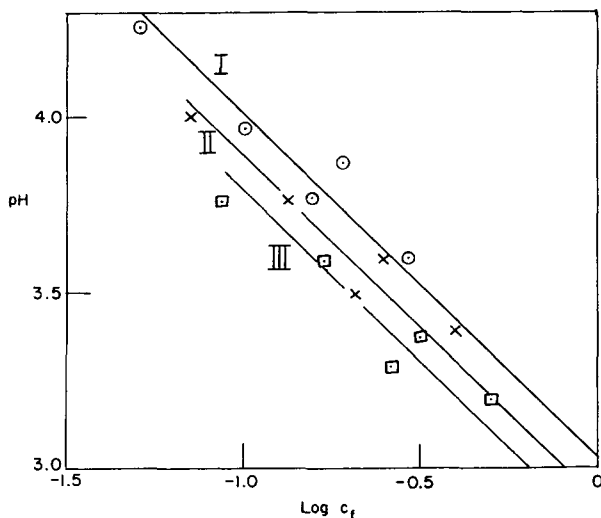


Fig. 1. Effect of degree of polymerization on the acid titration of nylon 6: (I)  $1 - \alpha = 0.3$ ; (II)  $1 - \alpha = 0.4$ ; (III)  $1 - \alpha = 0.5$ . Straight lines are drawn to the theoretical slope.

The degree of polymerization of the nylon affects the titration curves, as only endgroups are involved. As it seems that the whole material is not accessible to acid (Part I),<sup>10</sup> the values of  $C_f$  obtained from the two-phase titration with hydrochloric acid, rather than those calculated from the degrees of polymerization, should be used. Equation (28) should be applicable, and this is tested in Figure 1, for values of  $(1 - \alpha)$  from 0.3 to 0.5, above which the acid contributes significantly to  $C_s$ , invalidating the argument. Considering the experimental difficulties and the uncertainties about the salt present, the results lie reasonably well on the theoretical straight lines.

TABLE II  
 Values of  $pK_e$  for the Titration of Wool by Hydrochloric Acid at 0°C.

Ionic strength	$pK_e$									
	$1 - \alpha = 0.1$	$1 - \alpha = 0.2$	$1 - \alpha = 0.3$	$1 - \alpha = 0.4$	$1 - \alpha = 0.5$	$1 - \alpha = 0.6$	$1 - \alpha = 0.7$	$1 - \alpha = 0.8$	$1 - \alpha = 0.9$	$1 - \alpha = 0.9$
No salt added	4.72	4.65	4.49	4.33	4.27	4.22	4.06	3.85	4.01	4.01
0.005	4.77	4.64	4.49	4.34	—	—	—	—	—	—
0.01	4.80	4.58	4.45	4.32	4.22	4.10	—	—	—	—
0.02	4.69	4.62	4.44	4.31	4.21	4.08	3.96	—	—	—
0.04	4.74	4.61	4.41	4.24	4.12	4.04	3.94	3.85	—	—
0.10	4.63	4.48	4.37	4.24	4.12	4.00	3.91	3.86	3.77	3.77
0.20	4.74	4.62	4.44	4.26	4.14	4.05	3.96	3.90	3.73	3.73
0.50	4.75	4.71	4.56	4.36	4.27	4.12	3.99	3.88	3.82	3.82
1.00	—	4.91	4.75	4.51	4.22	4.01	3.90	3.73	3.67	3.67
Average values	4.73	4.65	4.49	4.32	4.20	4.08	3.96	3.85	3.75	3.75

## APPLICATION OF THE THEORY TO THE TITRATION OF WOOL

## Titration of Wool by Hydrochloric Acid

The excellent results of Steinhardt and Harris<sup>30</sup> at 0°C. will be used to test the theory. For calculating the net concentration of fixed charges, the swelling of the wool has to be taken into account. As the effect of the acid on the degree of swelling is very small,<sup>31</sup> the swelling in water was used throughout, which, together with the density of wool and the maximum uptake of acid by the titrating groups, gave  $C_f = 0.93(1 - \alpha)$ . The experimental results were obtained for various constant ionic strengths with potassium chloride and are presented in Table II as values of  $pK_e$  calculated from eqs. (7) and (21). For titration curves in the absence of added salt,  $C_s$  was calculated from the final pH of the solution by using the activity coefficient of hydrochloric acid tabulated by Harned and Owen.<sup>32</sup>

The results show that  $pK_e$  varies with  $1 - \alpha$ , but is independent of the ionic strength. This indicates that the theory is obeyed and that the osmotic term is negligible. The variation of  $pK_e$  with  $1 - \alpha$  is linear (Fig. 2), obeying the relation,

$$pK_e = 3.58_5 + 1.27 \alpha = 4.85_5 - 1.27(1 - \alpha) \quad (29)$$

obtained by use of least squares. Here the interpretation already given for a paired system holds, with two values of  $pK$  of 4.85<sub>5</sub> and 3.58<sub>5</sub>. The first of these is the value to be expected for a simple carboxylic acid, and it is reasonable to conclude therefore that  $\Delta\mu_H^0$  is effectively zero and that 4.85<sub>5</sub> is the intrinsic dissociation constant of the nonpaired groups in wool, and 3.58<sub>5</sub> that of the paired groups. Thus for wool at 0°C.,  $pK_p' = 4.85_5$  and  $pK_q' = 3.58_5$ .  $pK_p'$  may be compared with the dissociation constants ( $pK_0$ ) of acetic acid (4.76), of propionic acid (4.88), and of butyric acid (4.82) at 0°C.  $pK_q'$  may be compared with the dissociation constants ( $pK_0'$ ) of the  $\alpha$ -carboxyl groups of glutamic and aspartic acids (2.01 and 1.88) and of the  $\beta$ -carboxyl groups of these acids (4.25 and 3.65), respectively. Tanford and Hauenstein<sup>33</sup> found two kinds of carboxyl groups for ribonuclease with  $pK$ 's of 4.6 and 3.75 and suggested that the low  $pK$  was due to close contact with a center of positive charge, though another explanation has been suggested by Scheraga.<sup>34</sup> Acetyl glycine has  $pK' = 3.60$ , so the very small proportion of C-terminal amino acids will be included with the paired groups in  $pK_q$ .

The relationship between  $pK_p'$  and  $pK_q'$  can be examined crudely by using eq. (27), considering the amino group as a point charge distant  $r$  from the proton when this is just about to combine with the carboxyl group. The excess potential  $\chi_s$  is then just  $\epsilon/Dr$  and eq. (27) becomes,

$$pK_q' = pK_p' - 0.4343 \epsilon^2/DrkT$$

For values of  $T = 273$ , and  $D = 80$  (admittedly a dubious value),  $r = 2.6$  A. is obtained, a reasonable minimum value for this distance, as  $D$  is likely to be much less than 80.

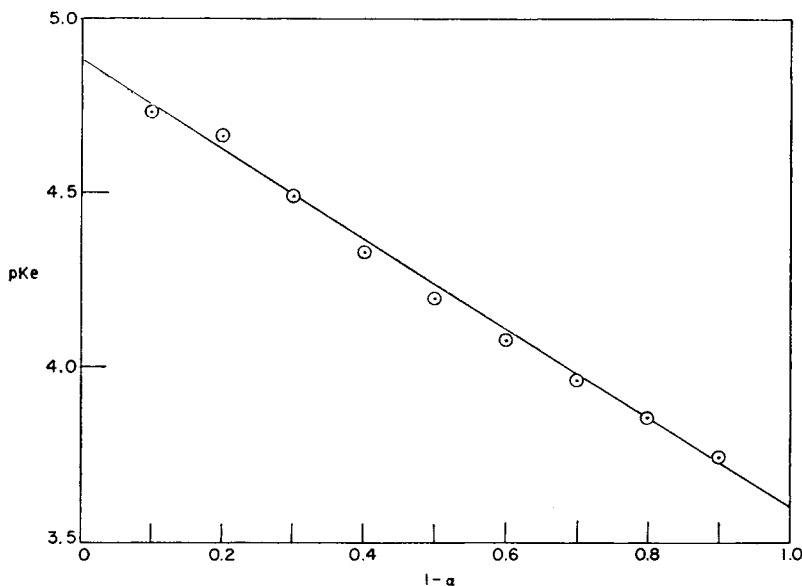


Fig. 2. Values of  $pK_0'$  at various degrees of dissociation for wool at  $0^\circ\text{C}$ . Points represent average values for titrations with hydrochloric acid at a large number of different ionic strengths.

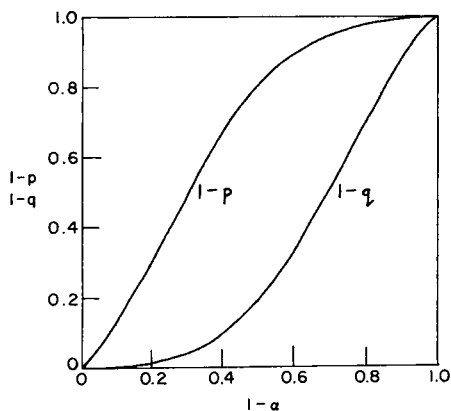


Fig. 3. The degree of dissociation of paired ( $1 - q$ ) and unpaired ( $1 - p$ ) carboxyl groups of wool, at various overall degrees of dissociation,  $0^\circ\text{C}$ .

The proportion of carboxyl groups involved in pairs can be calculated from eqs. (25) and (26), and it is found that  $P = Q = 0.5$ ; i.e., just half the carboxyl groups are involved in pairs. This conclusion will be examined further in the light of the data on work to stretch in a later paper. The way in which the degrees of dissociation of the non-paired and the paired carboxyl groups, ( $1 - p$ ) and ( $1 - q$ ), respectively, varies with  $1 - \alpha$ , is shown in Figure 3. At the midpoint of the titration 80% of the

nonpaired groups have titrated, and only 20% of the paired groups. A feasible alternative interpretation to that of 50% pairing would be that carboxyl groups were present in all conditions between completely paired and completely unpaired groups, giving a smooth change of  $pK'_o$  with degree of dissociation. This possibility seems less likely and will not be considered further.

### Titration of Wool by Sulfuric Acid

Results obtained by da Silva<sup>35</sup> and which will be discussed in a subsequent paper in this series for the titration of wool by sulfuric acid can also be used to test the theory. For the titration by sulfuric acid, eq. (22) was used to calculate the electrostatic term since at the concentrations employed, sulfuric acid is almost completely dissociated.<sup>32</sup> The results are in general agreement with the present theory (Table III). For the titration in the

TABLE III  
Values of  $pK_e$  for the Titration of Wool by Sulfuric Acid at 22.2°C.

$1 - \alpha$	$pK_e$	
	H <sub>2</sub> SO <sub>4</sub> , no salt	H <sub>2</sub> SO <sub>4</sub> -0.0025M Na <sub>2</sub> SO <sub>4</sub>
0.1	5.80	—
0.2	5.65	—
0.3	5.47	5.45
0.4	5.28	5.08
0.5	5.03	4.85
0.6	4.85	4.61
0.7	4.67	4.53
0.8	4.51	4.36
0.9	4.28	4.28

absence of added salt, the means of the present results and those of Speakman and Stott<sup>36</sup> have been used. The values of  $pK_e$  are substantially independent of salt concentration and the plot of  $pK_e$  against  $1 - \alpha$  is linear for value of  $1 - \alpha$  of 0.4–1.0, with the same slope as for hydrochloric acid titration (Fig. 4). This means that the theory is confirmed for titration by a 1:2 acid and its salt, with the same values of  $pK'_p$  and  $pK'_q$  and with the same proportion of paired groups, but with a finite value for  $\Delta\mu_H^\circ$ .

### Titration of Wool by Different Monobasic Acids

The results of Steinhardt, Fugitt, and Harris<sup>37</sup> for the titration of wool at 0°C. by a wide range of strong monobasic acids have been interpreted by using eqs. (7) and (21), and the values of  $pK_e$  found are shown graphically in Figure 4 as a function of  $1 - \alpha$ . For all the acids except picric acid,  $pK_e$  is almost a linear function of  $1 - \alpha$ , with the same overall slope as for

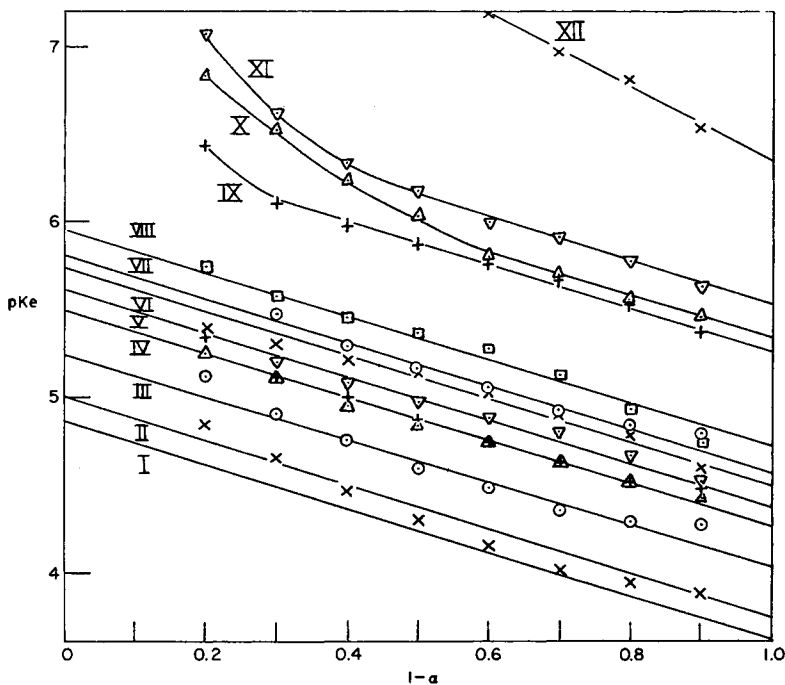


Fig. 4. Titration of wool by strong monobasic acids at 0°C.,  $pK_e$  versus degree of dissociation: (I) HCl; (II) ethylsulfuric acid; (III) HBr; (IV)  $\text{HNO}_3$  + benzenesulfonic acid; (V) *p*-toluenesulfonic acid; (VI) *o*-xylene-*p*-sulfonic acid; (VII) trichloroacetic acid; (VIII) *o*-nitrobenzenesulfonic acid; (IX) 2,5-dichloro- and 4-nitrochlorobenzenesulfonic acids; (X) 2,4-dinitrobenzenesulfonic acid; (XI) naphthalene-2-sulfonic acid; (XII) picric acid.

hydrochloric acid titrations. Thus for all the strong acids examined, the  $pK_e$  values obey the equation

$$pK_e = 4.87 - 1.27(1 - \alpha) + A \quad (30)$$

where  $A$  represents the constant affinity term,  $-0.4343 \Delta\mu_H^\circ/RT$ . This lends strong support to the theory. The results are more scattered than for hydrochloric acid titrations, due in part to reliance in most cases on a single titration curve, instead of the average of many as for hydrochloric acid, and also to the increased experimental difficulty of titration over the neutral region. It is noteworthy, however, that all the results for  $1 - \alpha = 0.1$  are higher than predicted (to avoid confusion they are not plotted on the graph), and that this tendency extends to higher values of  $1 - \alpha$  to a lesser degree. This effect is associated with a definite trend in the results and although the increasingly large value and sensitivity of the electrostatic term, as the neutral region of pH is approached, increases the uncertainty of the  $pK_e$  values, it may be a real effect due to anion binding on different sites in the fiber. It is hoped to consider this aspect later. The results for picric acid are different, a greater slope being obtained.



Values of the affinity for the different acids are given in Table IV. Column 4 of the table shows the results calculated by Gilbert and Rideal from the midpoints of the titration, with the value for hydrochloric acid subtracted. Reasonable agreement is found between the two methods for calculating the affinities, all but one of the new values being slightly lower.

TABLE IV  
Affinities of the Acid Anions for Wool at 0°C.

Acid	$-0.4343\Delta\mu_{\text{H}}^{\circ}$		$-\Delta\mu_{\text{H}}^{\circ}$ , cal./mole	
	$RT$			
	Present theory	Present theory	Gilbert and Rideal	
Hydrochloric	0	0	0	
Ethylsulfuric	0.13	160	200	
Hydrobromic	0.42	510	—	
Sulfuric	0.57	710	760	
Benzenesulfonic	0.65	810	900	
Nitric	0.66	830	—	
<i>p</i> -Toluenesulfonic	0.75	940	1000	
<i>o</i> -Xylenesulfonic	0.86	1070	1200	
Trichloroacetic	0.97	1210	1200	
<i>o</i> -Nitrobenzenesulfonic	1.12	1400	1450	
2,5-Dichlorobenzenesulfonic	1.65	2060	2100	
4-Nitrochlorobenzene-2-sulfonic	1.65	2040	2250	
2,4-Dinitrobenzenesulfonic	1.72	2150	2250	
Naphthalene- $\beta$ -sulfonic	1.96	2450	—	

### APPLICATION OF THE THEORY TO THE TITRATION OF COLLAGEN

Bowes and Kenten<sup>38</sup> have published titration curves and swelling data for native ox-hide collagen which had been subjected only to mild treatments with water, sodium chloride, petroleum ether, and acetone and was studied in the form of approximate centimeter cubes. The equations developed here should be applicable to this material, and Table V shows values of  $pK_e$  calculated by use of eqs. (7) and (21) from the titrations with hydrochloric acid. The maximum uptake of acid was taken as 0.875 mmole/g., and  $C_f$  was calculated by using the swelling data for various pH values for the titration in the absence of added salt. No swelling data are available for the titrations in the presence of 0.5*M* sodium chloride, and it was assumed here that there was no swelling. This assumption makes little difference to the results, as the contribution of the electrostatic term here is in any case small. Also, the amount of swelling to be expected is small, since alkali-treated collagen at pH 3 shows only 5% swelling in 2*M* sodium chloride as against 60% in the absence of salt.<sup>39</sup>

A sensibly constant value of  $pK_e$  is found, average values being 4.03 and 3.98 for the absence and presence of salt respectively. Values of  $\text{pH} + \log$

TABLE V  
Titration of Native Ox-Hide Collagen by Hydrochloric Acid at 20°C.

1 - $\alpha$	No added salt			0.5M sodium chloride		
	pH + log		pK <sub>e</sub>	pH + log		pK <sub>e</sub>
	$\frac{1 - \alpha}{\alpha}$	0.4343 sinh <sup>-1</sup> C <sub>t</sub> /2C <sub>e</sub>		$\frac{1 - \alpha}{\alpha}$	0.4343 sinh <sup>-1</sup> C <sub>t</sub> /2C <sub>e</sub>	
0.1	2.12	1.87	(4.20)	3.86	0.05	3.91
0.2	2.33	1.75	4.08	3.85	0.10	3.95
0.3	2.36	1.69	4.05	3.83	0.14	3.97
0.4	2.41	1.64	4.05	3.79	0.19	3.98
0.5	2.46	1.58	4.04	3.75	0.23	3.98
0.6	2.52	1.50	4.02	3.70	0.27	3.97
0.7	2.60	1.44	4.04	3.66	0.31	3.97
0.8	2.68	1.33	4.01	3.66	0.34	4.00
0.9	2.81	1.14	3.97	3.68	0.38	4.06

(1 -  $\alpha$ )/ $\alpha$  are included in Table IV to show that they are not constant. The value of pK<sub>e</sub> = 4.0 can be identified with the pK<sub>0'</sub> of the carboxyl group in collagen. Its independence of the degree of dissociation implies that there is only one type of carboxyl group, but its values suggests that this is intermediate in character between the paired and nonpaired types of group found for wool.

*Note:* Subsequent to the preparation of this paper a similar theory has been proposed by A. Chattenjee and J. A. Marinsky (*J. Phys. Chem.*, **67**, 41, 1963). These workers, however, confined their attention solely to the combination of acids and bases with ion exchange resins and they calculated the electrostatic term by the method of Katchalsky, Shavit, and Eisenberg<sup>9</sup> which refers to isolated randomly linked molecules. They also showed that the "osmotic term" was virtually zero in the system they considered.

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## Résumé

On présente une nouvelle théorie pour les propriétés acide-base des fibres, théorie qui ressemble à celle des polyélectrolytes et qui est basée sur la titration normale des groupements chargés des fibres et l'énergie nécessaire à déplacer les protons des fibres malgré les différences électrostatique, osmotique, et différences d'affinité. L'équation de la titration de l'acide pour une fibre polyampholyte est:

$$\text{pH} = \text{p}K'_0 - \log[1 - \alpha/\alpha] - (0,4343/RT)[\chi F + \pi \bar{V}_H + \Delta\mu_H^\circ]$$

$\text{p}K'_0$  est la constante de dissociation intrinsèque des groupements à titrer dans la fibre,  $\alpha$  est le degré de dissociation,  $\chi$  est le potentiel électrostatique de la fibre,  $\pi$  la pression osmotique,  $\bar{V}_H$  le volume molaire partiel de l'ion hydrogène et  $\Delta\mu_H^\circ$  la différence du potentiel Standard chimique dans la fibre et la solution. Dans tous les cas examinés, on a trouvé que le terme osmotique est négligeable. On calcule le potentiel électrostatique en admettant qu'il est uniforme pour toute la fibre. Dans le cas de la laine  $\text{p}K'_0$  est indépendant de la concentration en sel, mais varie d'une façon linéaire avec le degré de dissociation, ce que indique que deux  $\text{p}K'$  jouent un rôle.  $\text{p}K_q = 3,58_6$  pour les groupes associés et  $\text{p}K = 4,85_6$  pour des groupes dissociés à  $0^\circ\text{C}$ , présents en proportions égales. La titration de la laine avec de l'acide sulfurique et plusieurs sortes d'acides forts monobasiques obéit à la théorie, et les valeurs des affinités des anions correspondent en général avec celles trouvées par Gilbert et Rideal. La titration acide du collagène de la peau de boeuf donne une valeur constante de  $\text{p}K'_0 = 4,0$ . Dans le cas du nylon, la valeur de  $\text{p}K'_0$  est, en première approximation indépendante du degré de dissociation et de la concentration en sel, en accord avec la théorie.

### Zusammenfassung

Eine neue Theorie der Säure-Baseneigenschaften von Fasern, ähnlich der Polyelektrolyttheorie, wird vorgelegt, die auf einer normalen Titration der geladenen Gruppen der Fasern und auf der zur Übertragung der Protonen von der Faser in die Lösung gegen die elektrostatischen, osmotischen und Affinitätsunterschiede notwendigen Energie beruht. Die Säuretitrationsgleichung für eine Polyampholytfaser lautet:

$$\text{pH} = \text{p}K_0' - \log_{10} (1 - \alpha)/\alpha - (0,4343/RT) [\chi^F + \pi \bar{V}_H + \Delta\mu_H^\circ]$$

wo  $\text{p}K_0'$  die für die titrierte Gruppe in der Faser charakteristische Dissoziationskonstante,  $\alpha$  der Dissoziationsgrad,  $\chi$  das elektrostatische Potential der Faser,  $\pi$  der osmotische Druck,  $\bar{V}_H$  das partielle Molvolumen des Wasserstoffions und  $\Delta\mu_H^\circ$  der Unterschied zwischen dem chemischen Standardpotential in der Faser und Lösung ist. In allen untersuchten Fällen kann der osmotische Term vernachlässigt werden. Das elektrostatische Potential wurde unter der Annahme eines einheitlichen Wertes für die Faser berechnet. Bei Wolle ist  $Kp'$  unabhängig von der Salzkonzentration, besitzt aber eine lineare Abhängigkeit vom Dissoziationsgrad, was für zwei wirksame  $\text{p}K$ -Werte spricht,  $\text{p}K_q = 3,58_5$  für gepaarte Gruppen und  $\text{p}K_p = 4,85_5$  für nicht gepaarte Gruppen bei  $0^\circ\text{C}$ , die in gleichem Verhältnis vorhanden sind. Titration von Wolle mit Schwefelsäure und einer grossen Zahl starker einbasischer Säuren gehorcht ebenfalls der Theorie und die gefundenen Werte für die Anionenaffinität stimmen im allgemeinen mit den von Gilbert und Rideal angegebenen überein. Die Säuretitration von nativem Ochsenhautkollagen lieferte einen konstanten Wert  $\text{p}K_0' = 4,0$ . Bei Nylon ist der  $\text{p}K_0'$ -Wert in erster Annäherung in Übereinstimmung mit der Theorie von Dissoziationsgrad und Salzkonzentration unabhängig.

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