

Sorption of Simple Ions by Nylon 6

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Synopsis

The sorption isotherms of Na^+ and Cl^- ions by nylon 6 from aqueous solutions at pH = 2.2, 4.0, and 6.0 are reported. Detailed analysis of the results showed that they could not be interpreted satisfactorily by the classical Gilbert–Rideal or Donnan equilibrium treatments usually applied to nylon and/or wool. On a qualitative basis, the former model may be considered more successful, but, even so, the behavior of the partition coefficient of Na^+ cannot be explained. This difficulty persists even when some important restrictions imposed by the simple Donnan equilibrium treatment are relaxed, as in the models of Glueckauf and of McGregor and Harris. A different theoretical viewpoint is put forward here, which explains the observed behavior qualitatively and shows how it fits into the general pattern of ion sorption by polyelectrolytes in general and by amphoteric polyelectrolytes in particular. The conclusions drawn also have important implications concerning previous interpretations of ion sorption by wool.

INTRODUCTION

Study of the sorption of simple ions by polyamides is of considerable importance in relation to the mechanism of dyeing by anionic dyes and, more generally, in connection with the mechanism of ion sorption and transport in both artificial and biological membranes.

The sorption of simple acids and acid dyes by wool has been treated theoretically principally on the basis of either the Gilbert–Rideal or simple Donnan models with similar degrees of success.^{1,2} In analogous studies on polyamides, the former model has been employed preferentially,^{1,2} although McGregor and Harris³ applied a more sophisticated Donnan model to the sorption of acid dyes with considerable success. Nevertheless, the validity of the basic Donnan equilibrium relation has not, so far, been tested. This is best done by studying the sorption of simple ions that possess little or no affinity for the polymer, as demonstrated by previous work on wool⁴ and cellulose.⁵

In the present paper, we report the results of a study of the sorption of Na^+ and Cl^- by nylon 6 at various pH, which throw considerable light on the above question.

EXPERIMENTAL

Materials. Biaxially drawn nylon 6 film ($15 \pm 1 \mu\text{m}$ in thickness) was supplied by Unitika Co., Ltd. The films were immersed in water at 95°C for 24 h and then at 70°C for a further 24 h before the experiments. The amounts of terminal

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carboxyl and amine groups were estimated as 5.04×10^{-5} and 4.07×10^{-5} eq/g of dry film, respectively. Sodium chloride of analytical grade was used without further purification. Water was distilled and passed through a mixed bed ion exchange column immediately afterwards. The water regain of the film was 0.0572 g/g.

Procedures. The amounts of sorbed ions were determined by a desorption method. After equilibration with the appropriate salt concentration, the film was removed from the solution, carefully blotted with filter paper (Toyō Roshi Co. quantitative grade) and immersed in distilled water for 24 h at 40°C. The concentrations of the desorbed ions were measured by means of a Microprocessor Ionanalyser (Model 901, Orion Research) with appropriate ion electrodes. The amounts of sorbed ions remaining in the films after desorption were estimated to be less than 2% of the values so determined. Corrections were applied for the amounts of ions contained in the thin solution layers remaining on the film surfaces after blotting, by the method described by Glueckauf and Watts.⁶

All glass vessels employed were of "Pyrex" grade and were steamed before use. Care was taken to remove dissolved CO₂ (by passing N₂ through the solution) in the experiments at pH 6.0.

RESULTS AND DISCUSSION

General Considerations

The sorption data for NaCl are shown in Figures 1 and 2. Plots of the amounts of sorbed Na⁺ and Cl⁻ at 40°C and 30°C from 0.1M salts solutions gave isoelectric points of ~6.2 and ~6.5, respectively (cf. Fig. 3), which may be compared with the values of 5.35–5.5 for nylon 6 fiber reported by Suzawa⁷ (the difference being justifiable by the different nylon 6 samples and methods of determination used in each case).

The uptake of Cl⁻ at low pH is considerably in excess of that of Na⁺, as is expected in view of the concurrent sorption of H⁺. The uptake of H⁺ at given pH is enhanced with increasing salt concentration C_{Na} (see Fig. 4). This is shown most clearly by the data at pH 4.0 and agrees with what has previously been observed in the case of keratin.⁸

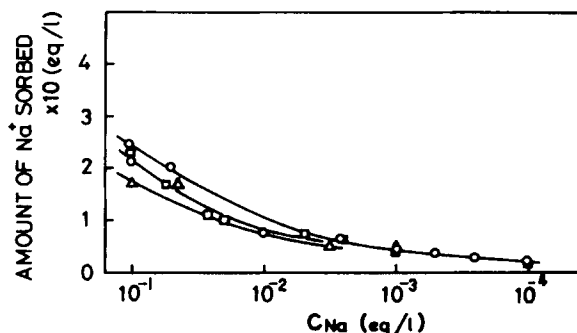


Fig. 1. Sorption of sodium ion from NaCl solution at 40°C. pH: (○) 6.0; (□) 4.0; (△) 2.2.

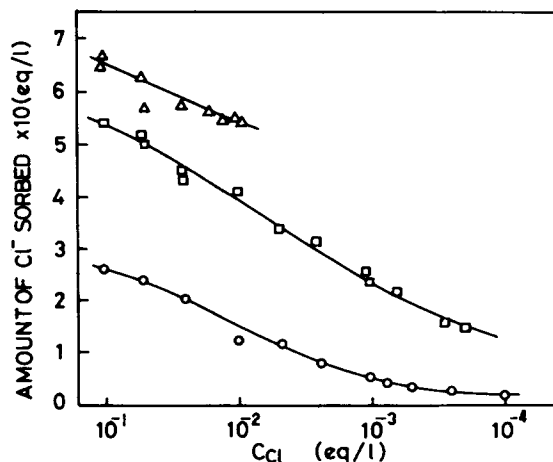


Fig. 2. Sorption of chloride ion from NaCl solution at 40°C. pH: (O) 6.0; (□) 4.0; (Δ) 2.2.

Applicability of the Gilbert-Rideal Model

The Gilbert-Rideal model^{1,2} assumes that the sorbed ions are bound at sites provided by the appropriate end groups of the polyamide and yields

$$\frac{\bar{C}_{\text{Na}}}{S_{\text{NH}_2} - \bar{C}_{\text{H}} - \bar{C}_{\text{Na}}} \cdot \frac{\bar{C}_{\text{Cl}}}{S_{\text{NH}_2} - \bar{C}_{\text{Cl}}} = K C_{\text{Na}} C_{\text{Cl}} \quad (1)$$

where C denotes ionic concentration in the bath (eq/L water) and \bar{C} the concentration of sorbed ion (eq/L imbibed water); S_{NH_2} is the concentration of terminal amino groups in the polymer (in the same units as \bar{C}) considered as being in the form of $-\text{NH}_3^+$; and K is a constant. Bearing in mind that $\bar{C}_{\text{H}} + \bar{C}_{\text{Na}} = \bar{C}_{\text{Cl}}$ and defining the partition coefficient of ion i as $\Lambda_i = \bar{C}_i / C_i$, eq. (1) may be written as

$$\Lambda_{\text{Na}} \Lambda_{\text{Cl}} = K (S_{\text{NH}_2} - \bar{C}_{\text{Cl}})^2 \quad (1')$$

The plots of $\log \Lambda_{\text{Na}} \Lambda_{\text{Cl}}$ vs. $\log (S_{\text{NH}_2} - \bar{C}_{\text{Cl}})$, at constant pH, were found to deviate markedly from the theoretical line of slope 2, especially at higher pH, as

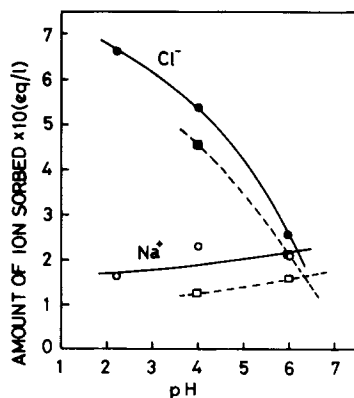


Fig. 3. Sorption of sodium and chloride ions from 0.1M NaCl: (—) 40°C; (---) 30°C.

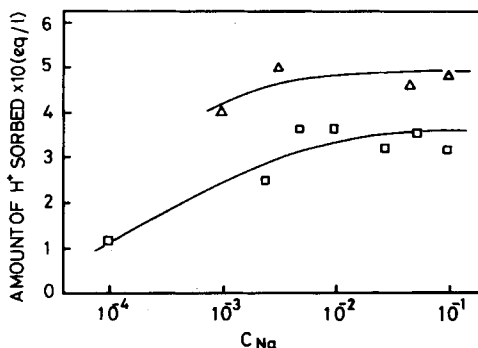


Fig. 4. Hydrogen ion sorption at 40°C from NaCl solutions at pH = 4.0 (□) or 2.2 (Δ).

illustrated in Figure 5. Hence, the Gilbert-Rideal model does not fit the data satisfactorily. A greater measure of success has been observed in connection with the sorption of NaBr by keratin.⁸

The H⁺ uptake data can be examined similarly. We have

$$\frac{\bar{C}_H}{S_{\text{NH}_2} - \bar{C}_H - \bar{C}_{\text{Na}}} \cdot \frac{\bar{C}_{\text{Cl}}}{S_{\text{NH}_2} - \bar{C}_{\text{Cl}}} = K C_H C_{\text{Cl}} \quad (2)$$

and, since $C_H \cong \text{const}$,

$$\bar{C}_H \Delta_{\text{Cl}} = K' (S_{\text{NH}_2} - \bar{C}_{\text{Cl}})^2 \quad (2')$$

Equation (2') was tested using the data for pH 4.0, which covered a reasonably wide range in \bar{C}_H values. The plot of $\log \bar{C}_H \Delta_{\text{Cl}}$ vs. $\log (S_{\text{NH}_2} - \bar{C}_{\text{Cl}})$ was reasonably linear, but even so the slope was ~ 3.4 as compared with the theoretical value of 2 (cf. Fig. 6). Alternatively,^{1,2} if the sites for H⁺ in the polymer include all terminal carboxyl groups, S_{NH_2} and \bar{C}_H in eqs. (2) and (2') should be replaced by S_{COOH} (the concentration of terminal carboxyl groups) and $\bar{C}'_H = \bar{C}_H + S_{\text{COOH}} - S_{\text{NH}_2}$, respectively. As shown in Figure 6, however, this modification does not yield better results. Hence, the H⁺ uptake data also are not fitted satisfactorily by the Gilbert-Rideal model.

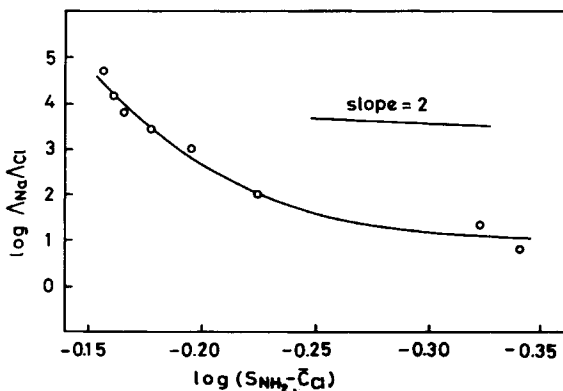


Fig. 5. Test of applicability of the Gilbert-Rideal treatment for Na⁺ and Cl⁻ sorption (mol/L) at 40°C; pH = 6.0 by means of eq. (1').

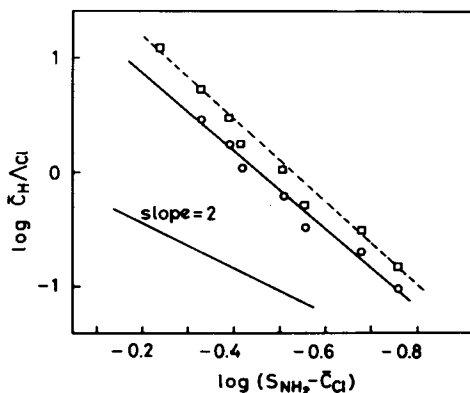


Fig. 6. Test of applicability of the Gilbert-Rideal treatment for H^+ and Cl^- sorption (mol/L) at $40^\circ C$ by means of eq. (2'), using $\log \bar{C}_H \Delta_{Cl}$ (O) or $\log \bar{C}'_H \Delta_{Cl}$ (□).

Nevertheless, the qualitative predictions of the model in question are in accord with the observed behavior. Thus, eqs. (1') and (2) correctly predict that $\Lambda_{Na} \Delta_{Cl}$ should increase as C_{Cl} (and hence \bar{C}_{Cl}) is lowered (cf. Fig. 7). Also, it is found that, at constant pH, $(S_{NH_2} - \bar{C}_{Cl})^2 / \Delta_{Cl}$ increases with rising C_{Cl} ; hence the increase of \bar{C}_H with salt concentration noted in Figure 4 is in qualitative accord with eq. (2).

Applicability of the Donnan Equilibrium

Models based on the Donnan equilibrium principle^{1,2} consider that there are no specific adsorption sites for the sorbed ions other than H^+ . Simple sorbed ions are assumed to be "dissolved" in the polymer phase, which is treated as an equipotential volume. Thus, eqs. (1') and (2') simplify, respectively, to

$$\Lambda_{Na} \Delta_{Cl} = K \quad (3)$$

$$\bar{C}_H \Delta_{Cl} = K(S_{NH_2} - \bar{C}_H) \quad (4)$$

Equation (3) was shown to be of limited applicability to the sorption of NaBr

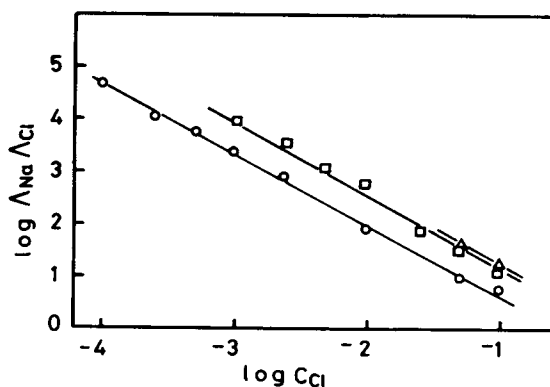


Fig. 7. Test of applicability of the Donnan approach for Na^+ and Cl^- sorption at $40^\circ C$; pH = 6.0 (O), 4.0 (□), and 2.2 (Δ) by means of eq. (5).

by horn keratin.⁸ Much larger deviations from eq. (3) are found here (cf. Fig. 7). Similarly, the plots of $\log \bar{C}_H \Lambda_{Cl}$ vs. $\log (S_{NH_2} - \bar{C}_H)$, at constant pH (and the analogous plots with \bar{C}_H replaced by \bar{C}_H), are not very different from those of Figure 6. Hence, eq. (4) is also not successful. In this connection, it is worth pointing out that the model advanced by Mathieson and Whewell⁹ is also based on the Donnan equilibrium and would, therefore, be expected to be subject to the same limitations. This has been confirmed by checking the equation derived by these authors by combining eqs. (7) and (10) of Ref. 9 against their data (as given in Table 1 of Ref. 9) concerning the effect of KCl on the uptake of HCl by nylon 66.

At the qualitative level, the Donnan equilibrium treatment predicts the observed dependence of \bar{C}_H on salt concentration at given pH, but not the increase of $\Lambda_{Na} \Lambda_{Cl}$ with diminishing C_{Cl} . Hence, it is inferior to the Gilbert-Rideal model in this respect.

The dependence of $\Lambda_{Na} \Lambda_{Cl}$ on C_{Cl} noted above is also encountered in other cases, notably in the case of cellulose,⁵ where it has been attributed to the breakdown of the equipotential volume hypothesis. This leads to a tendency of $\Lambda_{Na} \Lambda_{Cl}$ to increase with diminishing C_{Cl} , as shown, e.g., by the treatment of Glueckauf,¹⁰ which for constant charge on the polymer and sufficiently low C_{Cl} yields

$$\Lambda_{Na} \Lambda_{Cl} = K C_{Cl}^{-z} \quad (5)$$

where $0 \leq z \leq 1$ and $z = 0$ corresponds to eq. (3). Plots of $\log \Lambda_{Na} \Lambda_{Cl}$ vs $\log C_{Cl}$ appear to be consistent with eq. (5), as shown by the examples of Figure 7. More detailed examination shows, however, that this similarity of the behavior of the polyamide and cellulose substrates is superficial and even misleading. Thus, as the net charge carried by the polymer is reduced, the variability of $\Lambda_{Na} \Lambda_{Cl}$ with C_{Cl} is progressively suppressed in cellulose, but little affected in the case of nylon (cf. Fig. 7).

Sorption Behavior of Individual Ions

Consideration of the behavior of Λ_{Na} and Λ_{Cl} individually provides further insight into the above question. In this connection, it should be borne in mind that Na^+ is the counterion and Cl^- the co-ion for cellulose (which contains carboxyl groups only), whereas the reverse is true for nylon 6 (which always possesses a net positive charge under our experimental conditions). Comparison of Figure 8 here with Figure 1 of Ref. 5 shows that the dependence of Λ for the counterion on electrolyte concentration and amount of charge carried by the polymer is similar. Λ for the co-ion, however, tends to decrease with diminishing salt concentration and increasing charge on the polymer (ion exclusion effect) in the case of cellulose; but in nylon the effect of salt concentration is in the opposite direction and that of the polymer charge is hardly discernible (cf. also Fig. 1). The latter type of behavior is qualitatively inconsistent with the basic Donnan equilibrium concept.

This important point was investigated further with the aid of the more elaborate model of McGregor and Harris,³ where we included the possibilities of "binding" of the sorbed Na^+ to the terminal $-CO_2^-$ groups,¹¹ and of sorbed Cl^- to the terminal $-NH_3^+$ groups, of the polyamide. The latter possibility was

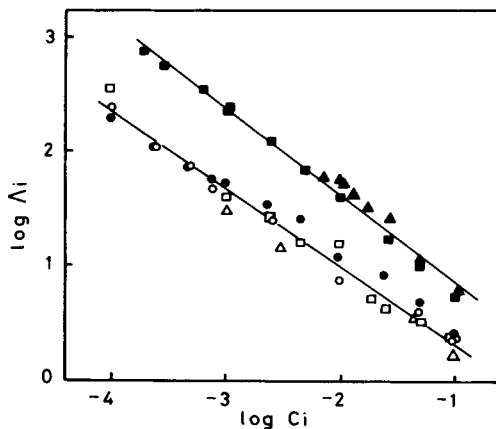


Fig. 8. Dependence of the partition coefficient of Na^+ (open points) and Cl^- (filled points) on electrolyte concentration at pH = 6.0 (O), 4.0 (□), and 2.2 (Δ), at 40°C.

made use of by Delmenico and Peters⁴ to fit a model of this type to their data on the sorption of Na^+ and Cl^- by wool (with reasonable success at least in the neutral to acid pH range). Computations covering a large number of combinations of dissociation constants of the $-\text{CO}_2\text{H}$ and $-\text{NH}_3^+$ groups, ionic distribution coefficients and binding constants (where relevant), consistently predicted much stronger exclusion of Na^+ from the polymer phase, as the salt concentration and the pH were lowered, than was actually observed. The assumption of strong binding of Na^+ to $-\text{CO}_2^-$ tended to correct the discrepancy between the calculated and experimental Na^+ uptake, but the improvement was substantial only at pH = 6.0. On the other hand, the uptake of Cl^- could be reproduced without difficulty except at pH = 6.0. The fact that the McGregor-Harris model is shown here to fail mainly where the behavior of the co-ion is concerned explains perhaps why this model has proved reasonably successful in describing the sorption of anionic dyes (cf. introduction).

It is important to add that substitution of the experimental values of \bar{C}_{Cl} , Λ_{Cl} in eqs. (1') and (5) shows that both these equations predict diminution of Λ_{Na} with decreasing C_{Cl} at a given pH, though to a smaller extent than that required by eq. (3). The Glueckauf model¹⁰ under conditions of constant charge on the polymer and sufficiently low C_{Cl} yield

$$\Lambda_{\text{Na}} = K' C_{\text{Cl}}^{1-z} \quad (6)$$

where z is the same constant as in eq. (5). Equation (6) was deduced on the premise that the charge carried by the polymer is not uniformly distributed [as required by the equipotential volume hypothesis inherent in eq. (3)], but varies locally from one microregion of the polymer to another. The plots of $\log \Lambda_{\text{Na}}$ vs. $\log C_{\text{Cl}}$ are reasonably linear (similar to those given in Fig. 8); but eq. (6) is of strictly empirical significance, because the resulting values of z are well beyond the upper limit of unity, which is imposed by theory.

However, the observed behavior of Λ_{Na} can be understood, at least qualitatively, by an extension of Glueckauf's concept, which in the above model is restricted to polymer phases containing only one kind (positive or negative) of charged group. In such cases, the ion which happens to be, say, the co-ion with

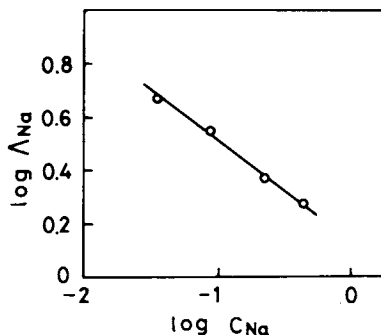


Fig. 9. Replot of Fig. 3 of Ref. 13 on a log-log scale.

respect to the overall polymer phase will also be the co-ion for every individual microregion. In an amphoteric polyelectrolyte, on the other hand, some microregions may be positively, and others negatively, charged. Consequently, the same ion may be the co-ion for some of the microregions and the counterion for others. Hence, it is understandable that the dependence of Λ_{Na} and Λ_{Cl} on salt concentration should be similar.

Although no physically meaningful quantitative interpretation of the linear $\log \Lambda_{\text{Na}}$ vs. $\log C_{\text{Na}}$ plots of Figure 8 can be offered at present, it is noteworthy that the same type of relation is obeyed by the data reported by Hatch et al.¹² on the sorption of NaCl from neutral solutions by a polyacrylate-Dowex 2 "snake cage" ion exchange resin containing $-\text{NR}_3^+$ and $-\text{CO}_2^-$ groups (see Fig. 9). The corresponding data on wool⁴ are insufficient for a similar test. On the other hand, a strong tendency of Λ_{Na} to drop rapidly with increasing net positive charge on the polymer is evident in both Refs. 4 and 12. This may be interpreted in terms of the physical picture proposed above, as implying a rapid increase of the number of positively charged microregions at the expense of the negatively charged ones. At the point where few or no microregions of the latter type remain, Λ_{Na} would be expected to exhibit typical "co-ion exclusion" behavior. In the polyacrylate-Dowex 2 resin, this point is attained when the concentration of $-\text{NR}_3^+$ is in excess of ca. twice that of the $-\text{CO}_2^-$ groups (as far as can be seen from Fig. 6 of Ref. 12). The behavior of wool appears to be similar.⁴ By contrast the insensitivity (already noted above) of Λ_{Na} in nylon 6 to the net charge of the polymer must, by the same argument, imply that the negatively charged microregions largely preserve their identity even in the presence of a large excess of $-\text{NH}_3^+$ groups. This is presumably made possible by the much wider separation of the charges (resulting from the much lower charged group content) in this polymer coupled with its low dielectric constant.

The above interpretation clarifies the basic qualitative similarities and differences in the behavior of wool and nylon which have emerged here. At the same time, it throws doubt on the fundamental applicability of the Donnan equilibrium to wool near its isoelectric point. In this connection, it is worth recalling that interpretation of the sorption of NaCl by the fiber in question on this basis⁴ had to include the assumption of binding of Cl^- to the $-\text{NH}_3^+$ groups and, even so, was reasonably successful only in the acid pH range. Clearly, a satisfactory model for the description of ion sorption by wool, polyamides, and other amphoteric polyelectrolytes is yet to be developed. Application of a dual Langmuir

+ Nernst sorption isotherm to the sorption of NaCl by an amphoteric ion exchange resin¹³ may be noted, but this is, so far, only an empirical representation.

CONCLUSION

We conclude that none of the main models applied to the sorption of dye and other ionic species by polyamides can yield a satisfactory interpretation of the present results.

Comparison of the qualitative predictions of the Gilbert–Rideal model and the simple Donnan equilibrium approach, as usually applied, shows that the former model may be considered more successful in that it predicts the increase of both \bar{C}_H and of $\Lambda_{Na} \Delta_{Cl}$ with diminishing electrolyte concentration at constant pH, whereas the latter approach predicts correctly only the former effect.

Examination of the sorption behavior of Na^+ and Cl^- individually affords a more stringent test of the theoretical treatments. Here, it is found that both the aforementioned models fail with respect to Na^+ . The failure of the Donnan equilibrium approach extends to more elaborate models related to, or based on, it. In particular, neither the Glueckauf nor the McGregor–Harris (even including the possibility of ion binding by the charged groups) model appear to be capable of correcting the situation. Nevertheless, it has proved possible to interpret the behavior observed qualitatively and to show how it fits into the general pattern of ion sorption by polyelectrolytes in general and by amphoteric polyelectrolytes in particular. Apart from the well-known similarity of wool and nylon, important differences have also been shown to exist. These differences can be understood in terms of the qualitative theoretical framework established here. They explain why the failure of the classical models is more pronounced in the case of nylon. The results of the aforementioned comparative analysis are also important from the point of view of the proper interpretation of the sorption of ions by wool.

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