

Moisture and Ion Sorption in Cellulose Acetate

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Introduction

As a result of the biological importance and widespread industrial use of cellulose compounds and other hydrophilic polymers there have been many studies of their moisture sorption and permeation.¹⁻⁴ Aside from purely academic curiosity there is considerable interest in the mobility of ions in polymers because of their usefulness as electrical insulators. This interest extends to cellulose compounds, for which the large water absorption may lead to millionfold increases in electrical conductivity. Experiments to elucidate various aspects of the process of ion movement in cellulose compounds have been undertaken by many workers.⁴⁻²¹ In all of the studies dealing with cellulose acetate and related compounds, ion concentrations were either undetermined or estimated in relative terms.

The present work was done in conjunction with a study (to be described in a subsequent paper) of ionic conductivity in cellulose acetate (C.A.) impregnated with alkali-halide salts. The purposes are to report the effect of silver paste electrodes on the moisture permeation rate of cellulose acetate and to discuss some x-ray emission data which provide a quantitative estimate of the salt uptake (after 48 hrs.) from aqueous steeping solutions of concentrations ranging up to 1 mole/l.

Materials

The polymer used in this investigation was 4650 cellulose acetate (acetyl 40%, ASTM viscosity 25) made by Eastman Organic Chemicals. At 25°C. the intrinsic viscosity $[\eta]$ was 1.36 in acetone and 1.46 in methyl acetate, which correspond to a viscosity-average molecular weight M of about 53,000. This estimate is based on an evaluation due to Moore and Tidswell²² of the parameters in the Staudinger equation:

$$\text{Acetone } [\eta] = 2.8 \times 10^{-4} M^{0.78}$$

$$\text{Methyl acetate } [\eta] = 2.7 \times 10^{-4} M^{0.79}$$

Cellulose acetate disks of $\frac{3}{4}$ -in. diameter and 10.5-mil thickness were prepared as follows. For each sample 0.21 g. of C.A. powder was first cold-pressed at 600 psi and then placed between two platens at 210°C. and preheated for 10 min. After preheating, a pressure of 268 psi was maintained for 2 min., followed by 2150 psi for 3 min. The samples were

then cooled slowly at 4700 psi until they reached 180°C., after which water cooling was used. At 60°C. the pressure was removed and, after cooling to 40°C., the samples were taken out of the mold. This process provided a reasonable yield of unplasticized samples which did not fracture during the measurements.

Permeation Measurements

To determine the effect of silver paste electrodes on moisture permeation in C.A., two samples were painted with a coat of du Pont Silver Preparation 4817. After drying, these samples were attached, painted side out, to the ends of a permeation cell of a type which has been used by Norton²³ and which consists of a glass cylinder with a small sidearm which was sealed off after injecting a few drops of water. A similar cell with unpainted C.A. disks was assembled. The cells are indicated in Figure 1. The mass loss $-\Delta m$ of each cell was determined to ± 0.1 mg. on an analytical balance while they were stored in a room at 25°C. and 45% r.h. After initial transients of about 2-3 hr. duration, steady-state permeation is established for both the coated and uncoated films. Permeation coefficients P may be calculated from the steady-state data which are indicated in Figure 2 and the definition

$$P = -J / \langle \partial p / \partial x \rangle = -Jb / \Delta p \quad (1)$$

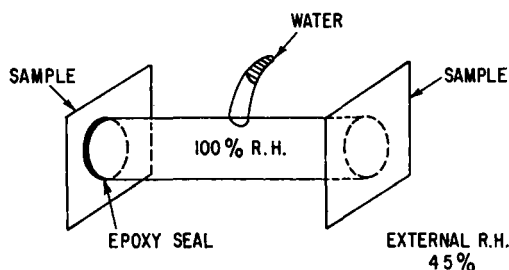


Fig. 1. Schematic diagram of the permeation cell: length = 2 cm., inside diameter = 1.6 cm., C.A. film thickness = 0.267 mm., and paint thickness = 0.031 mm.

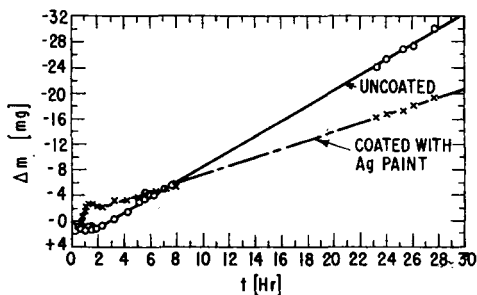


Fig. 2. Moisture permeation in cellulose acetate. Mass loss from the permeation cell vs. time. The linear portions allow one to calculate P , whereas the initial transients are related to D and K .

where $J = \dot{m}/A$ is the vapor flux density and $\langle \partial p / \partial x \rangle$ is the average vapor pressure gradient across the film of cross section A and thickness b . The unpainted and painted samples, respectively, have flux densities $J_1^\circ = 8.2 \times 10^{-8}$ g./cm.²-sec. = 10.2×10^{-6} cm.³(STP)/cm.²-sec. and $J = 4.8 \times 10^{-8}$ g./cm.²-sec. = 6.0×10^{-6} cm.³(STP)/cm.²-sec. Since the corresponding pressure gradients (100 to 45% r.h.) are $\Delta p^\circ/b_1 = 4.75$ cm. Hg/mm. and $\Delta p/b = 4.25$ cm. Hg/mm., the permeation coefficients based on eq. (1) are

$$P_1^\circ \equiv P_{CA} = 2.1 \times 10^{-5} \text{p.u.}$$

$$P \equiv P_{CA + \text{electrode}} = 1.4 \times 10^{-5} \text{p.u.} \quad (2)$$

where p.u. represents the conventional permeation unit cm.³(STP)/cm.²-sec. (cm Hg/mm.). From these results we conclude that the presence of the electrodes will have negligible influence on the moisture content of samples which have been conditioned for several hours.

In Fickian systems (P not dependent on concentration), $1/P$ is analogous to an electrical resistivity. Thus for a series of n membranes of thicknesses b_1, b_2, \dots, b_n , and permeation coefficients P_1, P_2, \dots, P_n , the equivalent flow impedance b/PA will be a sum of impedances:

$$b/PA = \sum_{i=1}^n (b_i/P_i A_i); \quad b = \sum_i b_i \quad (3)$$

In the present case $n = 2$ and $A_i = A$ so that the equivalent permeation coefficient of the silver paste electrode is

$$P_2 = [(b/b_2)(1/P) - (b_1/b_2)(1/P_1)]^{-1} \quad (4)$$

Since b, b_1 , and b_2 are respectively 0.298, 0.267, and 0.031 mm., it follows that $P_2 = [(9.51/P) - (8.50/P_1)]^{-1}$ and, with the values from eq. (2), $P_2 \approx 3.6 \times 10^{-6}$ p.u.

Within limitations to be indicated, the data of Figure 2 are suited for analysis by the Daynes²⁴ method (which has been discussed in detail by Barrer¹) to give order-of-magnitude values for the diffusion coefficients D and solubilities K of the samples. In its exact form, Daynes' analysis applies to one-dimensional Fickian diffusion through a slab of thickness b , with constant initial and surface concentrations: $c(x,0) = c_0$ and $c(0,t) = c_1$, $c(b,t) = c_2$, respectively. The result is that the linear portion of the mass transfer versus time curve (Δm vs. t) may be extrapolated to the point $\Delta m = 0, t = \tau_L$ where

$$\tau_L = b^2(c_2 + 2c_1 - 3c_0)/6D(c_2 - c_1) \quad (5)$$

is called the lag time (somewhat of a misnomer since it may be negative). Since the concentrations occur in a ratio, they may be replaced within the range of validity of Henry's law by appropriate pressures or humidities.

For the data shown in Figure 2, the relatively complicated transients indicate that the boundary conditions used in the Daynes analysis do not

apply. This is not surprising since slight heating of the samples occurred (at $t = 0$) when the sidearms were sealed off and, in the case of the painted C.A., a solution of $D\nabla^2c = \partial c/\partial t$ for a two-layer structure should be used. Furthermore, it is well known that water diffusion in C.A. is concentration-dependent.¹ Since the actual initial conditions are not known, a rigorous analysis of the transients will not be attempted; however, one can argue on an intuitive basis that an expression analogous to eq. (5) should result and that $|\tau_L|$ is of the order of one-half the duration of the transient. (Complications arise if $3c_0 \approx (c_2 + 2c_1)$.) On this basis, the transients of 2–3 hrs. for C.A. at 25°C. correspond to values $D \approx 5 \times 10^{-8}$ cm.²/sec. and $K \approx 7.6$ cm.-cm. Hg/atm.-mm. $P/D \approx 3 \times 10^3$ cm.³(STP)/cm.³-atm.

Direct measurements of moisture sorption (at 25°C. and 100% r.h.) also were made and the results are indicated in Table I. The equilibrium solubility was found to be 9.5% by weight or, in the units used previously, $K = 4.8 \times 10^3$ cm.³/cm.³-atm. This solubility corresponds to about 1.5 molecules of H₂O per cellulose unit, and is thus in agreement with the widely known hypothesis that H₂O attaches with two hydrogen bonds to the cellulose unit. Considering the anticipated limitations of the methods, the agreement is satisfactory. The values of D and P are in agreement with the range of values given by Barrer¹ and by Sheppard and Newsome.² The decreasing calculated values of D in Table I are indicative of the non-Fickian character of the sorption process in C.A.¹

TABLE I
Moisture Sorption by 0.267-mm. Cellulose Acetate Film (40% Acetyl) at 100% r.h. and 25°C.

t , min.	0	50	100	200	400	600	1400
Δm , %	0	6.0	6.9	8.1	8.7	9.0	9.5
$10^3 D$, cm. ² /sec.	—	1.87 ^a	1.35 ^a	1.0 ^a	— ^b	—	—

^a Computed by the "parabolic diffusion law" $D \approx b^2\theta/(\pi^2t) \approx 7.26 \times 10^{-6}$ cm.² \times θ/t , where θ was determined graphically from Sheppard's² plot of $m(t)/m(\infty) = (8/\pi^2)(e^{-\theta} + e^{-9\theta}/9 + e^{-25\theta}/25 + \dots)$.

^b Even for Fickian systems the approximation is poor when $\theta > 1.1$ or when $m/m(\infty) > 0.6$.

Sorption of Salt Solutions

Subsequent to the molding process, which has been described, each of a set of samples was steeped for 48 hrs. in one of the following salt solutions: 0.1M of the chlorides of Li, Na, K, Rb, and Cs; 0.1M of KF, KBr, and KI; 0.2, 0.3, 0.4, 0.7, 1.0M KCl. After removal from the solutions, the samples were washed in distilled water to reduce possible surface deposits.

The alkali halide content was determined by x-ray emission spectrography. A General Electric XRD-5 x-ray spectrograph and S.P.G. #4 gas flow proportional counter tube were used for the determinations. The G. E. Machlette tube had a chromium target and was operated at 50 kv. and 40 ma. The spectrogoniometer was used with a flat reflecting NaCl crystal in a helium atmosphere and with a collimator 20 mils in diameter. Chlo-

TABLE II
Alkali-Halide Content of Cellulose Acetate (40% Acetyl) Films after 48 hr. in 0.1M Steeping Solutions: X-Ray Emission Data

Solution	Concentration of salt in polymer			Radii of variable ions, A. ^c		
	ppm ^a	$\mu\text{mole/g.}$ C.A.	$\mu\text{mole/}$ mole Cellul. units, ^b	r_{ion}	r_{Stokes}	$r_{\text{hyd.}}$
Unsteeped	<10	<0.3	<80	—	—	—
LiCl	66	1.9	520	0.60	2.38	3.82
NaCl	87	2.4	680	0.95	1.84	3.58
KCl	20	0.56	160	1.33	1.25	3.31
RbCl	210	5.9	1650	1.48	1.18	3.29
CsCl	124	3.5	970	1.69	1.19	3.29
Unsteeped	38	1.0	260	—	—	—
KF	72	1.8	500	1.36	1.66	3.52
KCl	61	1.6	420	1.81	1.21	3.32
KBr	91	2.3	630	1.95	1.18	3.30
KI	207	5.3	1430	2.16	1.19	3.31

^a Determined by comparison of x-ray emission with a series of Carbowax reference samples having known amounts ($\mu\text{g./g.}$) of either Cl or K: Alkali chlorides by K_{α} emission of chlorine, and potassium halides by K_{α} emission of potassium.

^b Multiply numbers in this column by 10^{-4} to get approx. mol. salt/polymer molecule; e.g., there is one RbCl molecule for about six polymer molecules.

^c Data of Nightingale.²⁸

rine contents between 10 and 2000 ppm could be determined with a relative error of 2.0% at 1000 ppm and about 10% at 100 ppm.

Typical results for salt contents as determined by x-ray emission are given in Table II. The K_{α} emissions of chlorine and potassium were used to obtain the alkali chloride and potassium halide data, respectively. These results are based on the assumption that there is a 1:1 ratio between the alkali and chlorine ions, and between the halide and potassium ions. On comparison of the Cl and K data it appears that this assumption is not valid for the determination of [KCl] using the chlorine- K_{α} emission, because the presence of $\lesssim 40$ ppm of undetected potassium in the unimpregnated samples. Figure 3 illustrates the effect of varying the steeping solution concentration in the case of KCl.

The data of Table II and Figure 3 were reproducible to within 20%. In addition to the uncertainties due to the x-ray technique, there may be errors due to variations in sample microstructure resulting from the molding process (examination between crossed polaroids indicated residual stresses, but the patterns were similar on the different samples).

The sorption by C.A. of ions from the steeping solution involves ion exchange mechanisms where the ions in solution possibly exchange with the hydrogen at unacetylated sites or on free acetic acid which may be present in small concentrations. For ion exchange resins under ideal circumstances

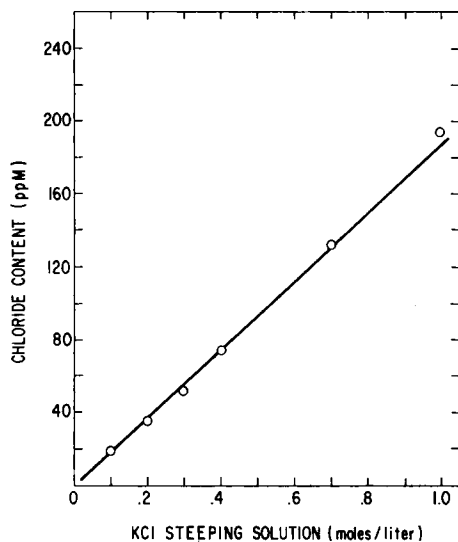


Fig. 3. Chlorine content of 40% acetylated cellulose acetate as determined by x-ray emission of the $\text{Cl } K_{\alpha}$ line vs. concentration of KCl solution.

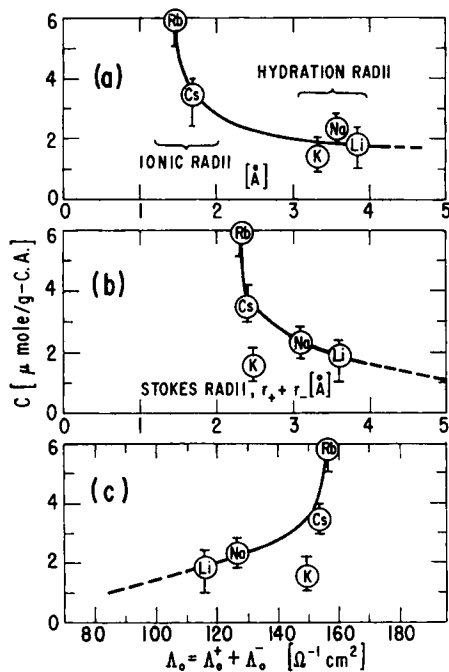


Fig. 4. Alkali chloride salt concentration in 10.5-mil films of 40% acetylated C.A. after 48 hrs. in 0.1M steeping solutions: (a) vs. effective radii adduced from Samoilov's differential hydration hypothesis; (b) vs. the Stokes' radii of the ions; (c) vs. the equivalent conductances of the same ion pairs in aqueous solution.

the order of exchange affinities is usually that of the lyotropic series, i.e., $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ and $\text{F} < \text{Cl} < \text{Br} < \text{I}$.^{25,26} For nondilute solutions and for a number of other reasons the series may not be followed.²⁶ With the exceptions of CsCl and KCl the data of Table II follow the lyotropic series.

The low value for KCl uptake is believed to be due to some type of interference with impurity potassium which is present in the unsteeped samples. Comparison of the concentrations determined by chlorine and potassium $K\alpha$ emission, respectively, indicates that about 1.0 μmole of K per g. of C.A. is undetected in the former case. A possible explanation of the low value for CsCl relative to RbCl is that Samoilov's²⁷ theory of differential hydration applies. If so, Li^+ and Na^+ can be considered to have rather rigid spheres of hydrated water molecules, whereas Rb^+ and Cs^+ will allow flexibility of their more fluid envelopes. Thus the mobilities of Li^+ and Na^+ are functions of their radii of hydration, but the ionic radii tend to become limiting factors for Rb^+ and Cs^+ . Electrical measurements which will be discussed in a subsequent paper add support to this hypothesis. Its plausibility is illustrated by Figure 4(a) which plots salt concentrations versus the effective radii suggested above.

Conclusions and Discussion

The silver paste electrodes had a fairly small influence on the rate of water permeation in C.A. films. This result probably is rather general and, in fact, the influence on permeation would be less for materials having a smaller permeation coefficient than C.A.

Alkali halide ions are absorbed at concentrations of 50–500 ppm from dilute aqueous solutions when thin (ca. 10-mil) C.A. films are steeped for 1–2 days. Since the ions, on a macroscopic average, enter as positive-negative pairs, there will be some tendency of the smaller of the ions to enter first and then pull the larger ones into the host material. For this reason an average radius of some type should be used in the comparison of the salt sorption data. We assume that generalized forms of the Stokes-Einstein and the Nernst-Einstein relations apply, i.e.,

$$K\eta rD = kT \quad (6)$$

$$qD = kT\mu \quad (7)$$

where r , μ , D , and K are the effective ion radius, mobility, diffusivity and shape factor, respectively, and η is the viscosity of the solvent or host material in the immediate neighborhood of the ion of charge q . For ions i and j (in dilute solution) it follows from eqs. (6) and (7) that

$$r = q/(K\eta\mu) \quad (8)$$

and that, for $q_i = q_j$,

$$r_i/r_j \approx \eta_j\mu_j/\eta_i\mu_i = \eta_j\Delta_j/\eta_i\Delta_i \quad (9)$$

where the lambdas are equivalent conductances. To the extent that the local viscosity can be considered a property of the solvent, independent of the specific ion, the equivalent conductances should serve as an inverse measure of effective ion sizes in the same medium; i.e., $r_i/r_j \approx \Lambda_j/\Lambda_i$. Figure 3(c) is a plot of alkali chloride concentrations (in C.A.) versus the equivalent conductances (in aqueous solution) of the pairs of ions involved. Figure 4(b) is a similar plot in which the Stokes' radii given by Nightingale²⁸ are used. These radii were computed from a relation similar to eq. (8) and differences in local solvent viscosities were neglected. However, as Nightingale mentions, certain ions including Cl^- , Br^- , I^- , K^+ , Rb^+ , and Cs^+ tend to decrease viscosity by disordering the local solvent structure, whereas other ions including Li^+ , Na^+ , and F^- tend to order the solvent structure and increase the viscosity of the solution. These empirical results, pointed out by Nightingale, are in general accord with the differential hydration idea discussed by Samoilov.²⁷ They also appear to agree, at least qualitatively, with the theoretical treatment of Boyd,²⁹ which accounts for the added frictional drag on an ion due to energy dissipation via dielectric relaxation in the solvent. It follows from Boyd's model that

$$r_{\text{Stokes}} \approx r_{\text{ion}} + (2e^2/27\pi)\tau/r_{\text{ion}}^3\eta\epsilon_s \quad (10)$$

where $e = 4.8 \times 10^{-10}$ statcoul, τ = dielectric relaxation time, and ϵ_s = static dielectric coefficient. In qualitative agreement with Nightingale, r_{Stokes} vs. r_{ion} will exhibit a minimum (at $r_{\text{ion}} \approx 0.516 (\tau/\eta\epsilon_s)^{1/3}$).

All three of the plots of Figure 4 behave in a qualitatively reasonable way. The larger ions tend to be restrained from entering the polymer, but below a critical size the ions are relatively free to enter. Figure 4(b) and (c), which basically are different presentations of the same data (since the radii of eq. (9) are Stokes' radii), probably are more satisfactory approximations than Figure 4(a), as they account for both members of the ion pairs whereas 4(a) does not. One can argue on the basis of Kohlrausch's law (of independent migration of ions) that the equivalent conductances should be additive and therefore, by eq. (8) or (9), that the Stokes' radii should add reciprocally so that the equivalent Stokes' radius is

$$r_s = 4r_s^+r_s^-/(r_s^+ + r_s^-) \quad (11)$$

where the 4 enters because the effective charge is $2e$. In view of the idea that very large ions will not enter the C.A. matrix it seems better to take $r_s = r_s^+ + r_s^-$ as the size variable. However, a plot of c versus r_s made with eq. (11) is only slightly different from Figure 4(b). Both plots indicate that the 48-hr. salt uptake might become vanishingly small for $r \sim 10 \text{ \AA}$., suggesting a maximum "channel size" in the C.A. One would not draw this conclusion from Figure 4(a). On the basis of the increase in concentration at smaller radii, Figure 4(a) and (b), it appears that the distribution of effective channel radii may be approaching a maximum in the vicinity of 1-2 \AA .

The potassium halide data of Table II do not fit onto the same curves of Figure 4 but, rather, drop off much more rapidly, resembling the corresponding solution viscosity data discussed by Nightingale.²⁸ One would not necessarily expect positive and negative ions to behave in the same way and, furthermore, the difference suggests that an unequal weighting of Stokes' radii should be used in a comparison like Figure 4(b). On this point, large charge carriers should probably also be weighted heavier in the averaging process.

The similarities of our ion sorption data in C.A. to the types of variations obtained in studies of hydration radii, solvation, and electrolytic conduction rather strongly suggest that ions move in moisture-swollen C.A. in much the same way as in aqueous solution.

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Synopsis

Measurements described in this paper show that the effective water permeation coefficients of silver paste electrodes on polymers such as cellulose acetate are of about the same magnitude as those of the polymer itself and, therefore, that such electrodes will have negligible effect on moisture penetration when conditioning periods of several hours or longer are used. X-ray emission spectrography with $K\alpha$ radiation from chlorine and potassium was employed to determine the salt content of 0.267-mm. cellulose acetate films (about 100 acetyl groups per polymer molecule = 40% acetyl), which were soaked for 48 hr. in aqueous solutions ranging up to 1M in concentration of the alkali chlorides or potassium halides. Typically, the salt contents are about 100 ppm or 3 μ mole/g. of cellulose acetate. The actual salt contents are discussed in relation to ionic hydration, and Stokes' radii via the differential hydration energy concept of Samoilov and the phenomenological developments of Nightingale. The evidence suggests that ionic motion in moisture-swollen cellulose acetate is quite similar to that in aqueous solution.

Résumé

Les mesures décrites dans ce article montrent que les coefficients effectifs de perméation d'eau d'électrodes en pâte d'argent sur des polymères comme l'acétate de cellulose, ont environ la même grandeur que ceux du polymère même, et que par conséquent l'effet de ces électrodes sur la pénétration d'eau sera négligeable quand on emploie des périodes de conditionnement de plusieurs heures ou davantage. On a employé les spectrographies d'émission aux rayons-X (la radiation $K\alpha$ du chlore et de potassium) afin de déterminer la teneur en sel de films d'acétate de cellulose (environ 100 groupes acétyles par molécule de polymère = 40 % acétyl) dont l'épaisseur est 0.267 mm et qui ont été trempés pendant 48 heures dans des solutions aqueuses dont la concentration en chlorure alcalin ou en halogénure de potassium atteignait jusqu'à 1M. Typiquement les teneurs en sel sont environ 100 pp ou 3 μ mole/g C.A. Les teneurs effectives en sel sont discutées en relation avec les rayons des ions, de l'hydratation et des rayons de Stokes, au moyen de la notion d'énergie différentielle d'hydratation de Samoilov et des développements phénoménologiques de Nightingale. L'évidence suggère que le mouvement ionique dans l'acétate de cellulose gonflé d'humidité est semblable à celui dans une solution aqueuse.

Zusammenfassung

Die in der vorliegenden Arbeit beschriebenen Messungen zeigen, dass die effektiven Permeationskoeffizienten für Wasser von Silberpastenelektroden auf Polymeren wie Celluloseacetat etwa die gleiche Grösse besitzen wie diejenigen des Polymeren selbst und dass daher der Einfluss solcher Elektroden auf das Eindringen von Feuchtigkeit bei einer Konditionierungsdauer von einigen Stunden oder länger vernachlässigt werden kann. Röntgenemissionsspektroskopie mit $K\alpha$ -Strahlung von Chlor und Kalium wurde zur Bestimmung des Salzgehaltes von 0,267 mm-Celluloseacetatfilmen (etwa 100 Acetylgruppen pro Polymermolekül = 40% Acetyl) herangezogen. Diese waren durch 48 Stunden der Einwirkung von bis zu 1M Alkalichlorid- oder Kaliumhalogenidlösungen ausgesetzt worden. Typische Salzgehalte liegen bei etwa 100 ppM oder 3 μ Mol/g C.A. Der Salzgehalte wird in seiner Beziehung zu den Ionen-, Hydrations- und Stokes' schen Radien anhand des Konzepts der differentiellen Hydratationsenergie von Samoilov und der phänomenologischen Betrachtungen von Nightingale diskutiert. Man kommt zu dem Schluss, dass die Ionenbewegung in feuchtigkeits-gequollenem Cellulose-acetat derjenigen in wässriger Lösung sehr ähnlich ist.

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