

Penetration of Water-Soluble Solutes into Cellulose Films

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Synopsis

Nonsolvent water determined in very dilute solutions of polymetaphosphate can be used as a measure of the true swelling of cellulose films. From these values and determinations of nonsolvent water under conditions permitting a penetration of the solute into the film, the average molality of trimetaphosphate, polymetaphosphate, and polyglycols inside the film has been determined under equilibrium conditions. With the electrolytes, the molality ratio (film:external solution) is strongly dependent upon the external concentration, which can at least partly be ascribed to the effect of the charged carboxyl groups inside the film. With polyglycols the molality ratio increases with decreasing molecular weight. With dense films there is no detectable penetration of high molecular weight polyglycols. A comparison between various films is made. It is shown that these contain areas of varying packing densities. The dialysis of trimetaphosphate and polymetaphosphate across the cellulose films has also been studied. In dialysis against water there is, within a wide range of concentration, a linear relationship between the rate of dialysis (flux) and the average internal concentration determined in equilibrium experiments. It is interesting to note that this simple relation holds true although the films are inhomogeneous.

Determinations of nonsolvent water in regenerated cellulose permit a reliable determination of the average concentration of various solutes inside the cellulose phase.¹ In dialysis experiments against water it was observed that the rate of dialysis (flux) of polymetaphosphate through a cellulose film is directly proportional to the inside concentration determined in equilibrium experiments.²

The aim of this work is to elucidate the factors which affect the equilibrium distribution of various solutes and to study further the correlation between the equilibrium concentration inside the membrane and the rate of dialysis across the membrane.

EXPERIMENTAL

Materials

The cellulose films used in the experiments were commercial samples made from viscose. Membrane D was a never-dried sausage casing with high milkiness (porous structure) manufactured by casting in acidified ammonium sulfate solution; membrane E was a sausage casing with low

milkiness (special manufacture); membrane G was a sausage casing of the same type as D (dried in the factory); membrane H was a sausage casing containing cotton fibers disposed inside the film; membrane I was never-dried cellophane.

The softening agents were removed by washing with large amounts of water.

Table I shows the thickness in water swollen state, the oven-dry weight of 1 cm.² swollen membrane sample, and the carboxyl number determined as described previously.³

TABLE I
Characterization of the Membranes

Membrane	Thickness (water-swollen), mm.	Weight (oven-dry), mg./cm. ²	Carboxyl number, meq./100 g.
D	0.25	6.5	3.2
E	0.16	7.2	2.9
G	0.18	8.6	2.9
H	0.14	6.8	2.5
I	0.09	2.7	4.4

The sample of radioactive sodium polymetaphosphate was prepared as described in an earlier paper.¹ The degree of polymerization was 85, which is a number-average value determined by endgroup titration.⁴ Trimetaphosphate was prepared by heating sodium dihydrogen phosphate for 2 hr. at 800°C. and then keeping the molten product at 550°C. for 24 hr.

Poly(ethylene glycol) samples were obtained from the British Drug Houses Ltd. and L. Light and Co. Ltd. The molecular weights given are those reported by the suppliers. In all experiments solutions containing 1% poly(ethylene glycol) have been used.

Procedure

The determination of nonsolvent water, δ , in the cellulose film was carried out as described in earlier papers.^{1,5} No centrifugation was performed in the experiments with the cellulose films. The true swelling, i.e., the total amount of solution inside the cellulose film, was determined by extrapolation to zero concentration of the δ values obtained with sodium polymetaphosphate as reference substance. This quantity is denoted by δ_0 . Figure 1 shows that the concentration has an influence upon the nonsolvent water both with trimetaphosphate and polymetaphosphate. As could be expected, the influence is more marked with trimetaphosphate than with the polyelectrolyte. In dilute solutions, however, the difference in the δ values determined with the two reference substances becomes rather small, and an extrapolation to zero concentration gives the same δ value. Table II shows the δ value at zero concentration (true swelling) for all membranes used in this work. This table also includes the average concentration of

TABLE II
True Swelling and the Average Concentration
of Carboxyl Groups in the Membranes

Membrane	True swelling, g. H ₂ O/g. cellulose	Carboxyl concentration, eq./1000 g. H ₂ O
D	3.21	0.010
E	1.62	0.018
G	1.40	0.021
H	1.10	0.023
I	3.03	0.015

the carboxyl groups (in equivalents/1000 g. H₂O) computed from the carboxyl numbers (Table I).

By using the value of the true swelling (δ_0) determined as described above and the δ values determined under conditions where exclusion of the solute is incomplete, the average molality or weight normality of the solute inside the cellulose phase can be calculated.¹ The molality ratio, m_r/m , defined as the ratio between the molality in the membrane and in the external solution, is calculated from the relation

$$m_r/m = 1 - \delta/\delta_0$$

The rate of dialysis was determined from experiments carried out in a dialysis cell described in an earlier paper.² One side of the membrane was in contact with the solution, the other with pure water. The dialysis time in all experiments was 15–30 min.

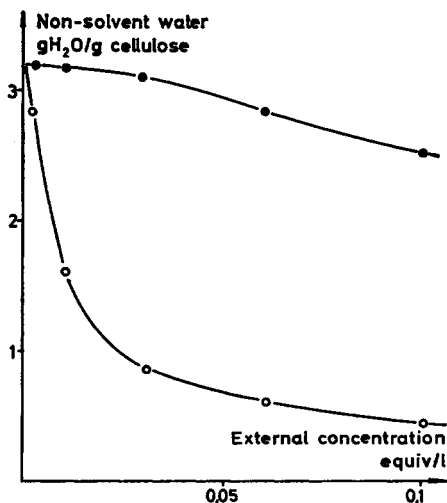


Fig. 1. Nonsolvent water with (●) sodium polymetaphosphate and (○) sodium trimetaphosphate as reference substances. Membrane D.

RESULTS AND DISCUSSION

Equilibrium Distribution of Glycols

As shown in an earlier paper,⁶ the distribution of glycols between cellulose and the external solution follows Henry's law, which means that the molality ratio is independent of the external concentration. The distribution of polyglycols of varying molecular weights between cellulose membranes and a 1% solution is illustrated in Figure 2. In agreement with the results reported earlier,⁶ the concentration of polyglycol inside the membrane is lower than the external concentration. At a low molecular weight the molality ratio is only slightly lower than unity, which means that the internal concentration is only slightly lower than the external concentration. A rise in the molecular weight results in lower values and for the membrane with the least swelling (membrane E) the molality ratio is, within the limits of experimental error, equal to zero with the polyglycol of the highest molecular weight. This means that the polyglycol is completely excluded from this membrane. Therefore, a polyglycol with a molecular weight of 20,000 can be used instead of polymetaphosphate for the determination of the true swelling in this type of membrane.

With the two never-dried films that exhibit the highest swelling there is an appreciable penetration of polyglycol into the cellulose phase within the whole range of molecular weight. As could be expected, the penetration is within the whole range higher than with the low-swelling membrane E.

A comparison of the results observed with the cellophane film (swelling 3.03) and the sausage casing (swelling 3.21) shows that the molality ratios for polyglycols of low molecular weight differ only slightly. With polyglycol of a molecular weight of 3600 the average internal polyglycol concentration is higher in the sausage casing than in the cellophane, whereas a

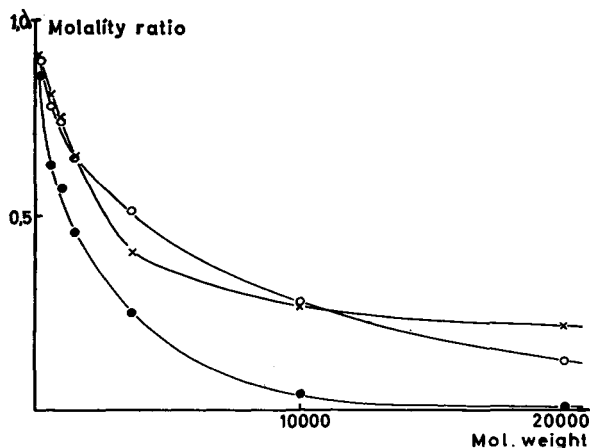


Fig. 2. Distribution of polyethylene glycols of different molecular weight: (O) membrane D; (●) membrane E; (X) membrane I. External concentration: 1%.

polyglycol of higher molecular weight is excluded more effectively from the sausage casing than from the cellophane. The shape of these curves can only be explained by the assumption that the membranes have a different spectra of packing density. The observation that at the highest molecular weight the molality ratio is higher with the cellophane film, which exhibits a lower average swelling than the sausage casing, indicates that the cellophane contains a larger amount of areas with a low packing density than the sausage casing.

Equilibrium Distribution of Trimetaphosphate

From the determination of nonsolvent water in trimetaphosphate the molality ratio of the salt between the two phases has been calculated. The results given in Figure 3 show that the molality ratio is less than unity and is dependent upon the external concentration. At low concentration the molality ratio approaches zero, which means that at low concentration the trimetaphosphate is excluded effectively from the membrane phase.

The fact that the electrolyte concentration inside the cellulose phase is lower than in the external solution has earlier been observed by a great number of authors.⁷⁻¹² The chief explanation for this is the presence of charged carboxyl groups inside the cellulose phase, but, as shown in an earlier paper, a lower electrolyte concentration can be observed even when this effect has been eliminated.¹ In neutral solutions of low concentration the charged carboxyl groups have, however, a predominant influence upon the exclusion of ions from the cellulose phase.

The data reproduced in Figure 3 show that great differences exist between various membranes. It is seen that at a given concentration in the external solution the molality ratio increases with a decrease in the average carboxyl concentration in the membrane. There is no direct correlation between the molality ratio and the average swelling of the membrane. These observations, as well as the strong influence of the external concentration, clearly demonstrate that the charge effect is the predominant one.

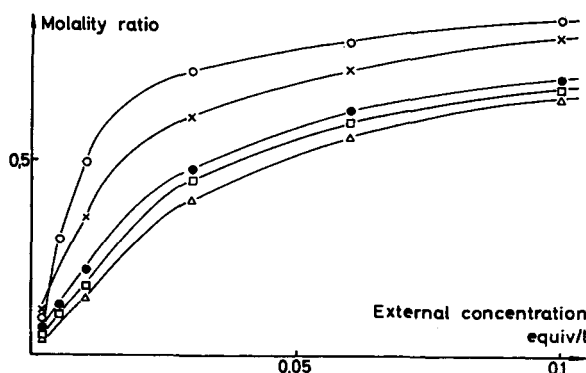


Fig. 3. Distribution of sodium trimetaphosphate (experimental values): (O) membrane D; (●) membrane E; (□) membrane G; (Δ) membrane H; (X) membrane I.

As shown in an earlier paper,¹ the swelling pressure in cellulose membranes is quite low. Hence, the equilibrium distribution for trimetaphosphate (Na_3P) between a homogeneous cellulose membrane and the external solution can be described by the Donnan equation written in the form

$$[\text{Na}]_r^3[\text{P}]_r / [\text{Na}]^3[\text{P}] = \Gamma \quad (1)$$

Brackets represent the concentrations in the solution and in the membrane phase (subscript r). In both phases the concentrations are expressed in moles/1000 g. H_2O . Γ is the activity coefficient quotient, which is equal to unity if the mean activity coefficient of trimetaphosphate is equal in both phases.

In addition, the concentrations of the ionic species in the two phases satisfy the electroneutrality requirements

$$[\text{Na}] = 3[\text{P}] = C \quad (2)$$

$$[\text{Na}]_r = [\text{COOH}]_r + 3[\text{P}]_r \quad (3)$$

where C is the concentration of the external solution (in equivalents/1000 g. H_2O) and $[\text{COOH}]_r$ is the average concentration of the ionized carboxylic groups.

Equations (1), (2), and (3) yield

$$C = [\text{COOH}]_r / [\Gamma^{1/3} (m_r/m)^{-1/3} - (m_r/m)] \quad (4)$$

where m_r/m is the molality ratio between the membrane and the solution, $[\text{P}]_r/[\text{P}]$.

By using eq. (4) the molality ratio was calculated as a function of the external concentration of trimetaphosphate. The results given in Figure 4 illustrate the influence of the concentration of charged groups as well as the

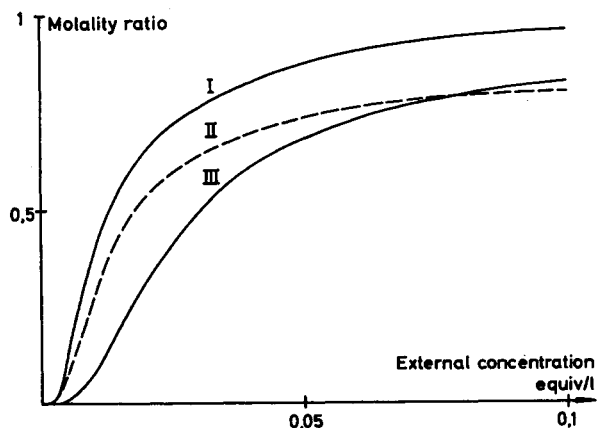


Fig. 4. Distribution of sodium trimetaphosphate between a homogeneous membrane and external solution calculated according to eq. (4): (I) $[\text{COOH}]_r = 0.01$, $\Gamma = 1$; (II) $[\text{COOH}]_r = 0.01$, $\Gamma = 0.6$; (III) $[\text{COOH}]_r = 0.023$, $\Gamma = 1$.

influence of the activity coefficient quotient in homogeneous membranes. It is seen that there exist obvious similarities between the shape of the calculated curves for homogeneous membranes and that of the observed curve (Fig. 3). Calculations based on various assumptions concerning the activity coefficient quotient reveal, however, that its variations cannot explain the deviation between the calculated and observed values. Instead, the explanation must be that the membranes are inhomogeneous, i.e., have varying carboxyl concentrations in different parts. In such systems eq. (4) is not valid.¹³⁻¹⁵ Hence, these results are in agreement with those obtained in the experiments with polyglycols, which show that the membranes are inhomogeneous.

Equilibrium Distribution of Polymetaphosphate

By using the δ determinations with membrane D in polymetaphosphate reproduced in Figure 1, the molality ratio for polymetaphosphate has been calculated. The results for this cellulose film as well as for the other films studied in this work are given in Table III. It is seen that with all membranes the values are much lower than those obtained with trimetaphosphate. This is explained by a combination of a molecular sieve effect and an increased effect of the charged groups in the cellulose owing to the highly charged polyelectrolyte anion.² With the never-dried films, which exhibit the highest swelling and the lowest average carboxyl concentration, the exclusion of polymetaphosphate is complete only at the lowest concentration, whereas with the other films the exclusion is complete even in 0.03*N* solution.

A comparison of the behavior of the two never-dried films (D and I) in polymetaphosphate and trimetaphosphate solution reveals some interesting features. The average swelling δ_0 of these membranes differs only slightly, and the average carboxyl concentration is higher in the cellophane than in the sausage casing. This latter fact explains the greater invasion of trimetaphosphate into the sausage casing (Fig. 3). With polymetaphosphate, however, the cellophane film (I) gives a higher molality ratio than the sausage casing (D), which means that at a given external concentration the invasion of polyelectrolyte is higher in the cellophane film.

TABLE III
Distribution of Sodium Polymetaphosphate

Polymeta- phosphate concentration, eq./l.	Molality ratio with various membranes				
	D	E	G	H	I
0.002	0	0	0	0	0
0.01	0.01	0	0	0	0.02
0.03	0.03	0	0	0	0.06
0.06	0.11	0.06	0.06	0.05	0.18
0.1	0.21	0.13	0.11	0.12	0.30

This result confirms that molecular sieve effects have a great influence with polyelectrolytes. Since the average swelling is about the same with both membranes, the differences must be ascribed to different packing densities in various areas of the films.

A prerequisite for the invasion of polymetaphosphate is that the fine structure does not prevent penetration for steric reasons, (which due to coiling effects depends upon the polyelectrolyte concentration). It can, therefore, be concluded that the cellophane film contains a larger number of areas with a low packing density than the sausage casing and, since the swelling is about the same, also contains a larger number of areas with high packing density. Expressed in other words it can be concluded that the cellophane film is less homogeneous than the sausage casing.

Rate of Dialysis of Polymetaphosphate and Trimetaphosphate

In dialysis experiments with effective stirring of the solutions on both sides of the membrane the diffusion inside the membrane is the rate-determining step. Even if the dialysis of an electrolyte is carried out against pure water the rate of dialysis is a complicated function of the concentration of the solution being dialyzed. This is explained by the fact (cf. section on equilibrium distribution of trimetaphosphate) that the concentration inside the membrane is a complicated function of the external concentration, which cannot be calculated with any accuracy from available data.

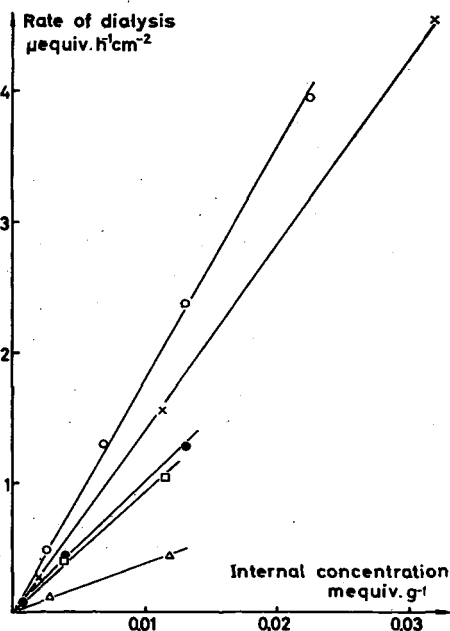


Fig. 5. Rate of dialysis as a function of the polymetaphosphate concentration inside the cellulose film: (O) membrane D; (●) membrane E; (□) membrane G; (Δ) membrane H; (X) membrane I.

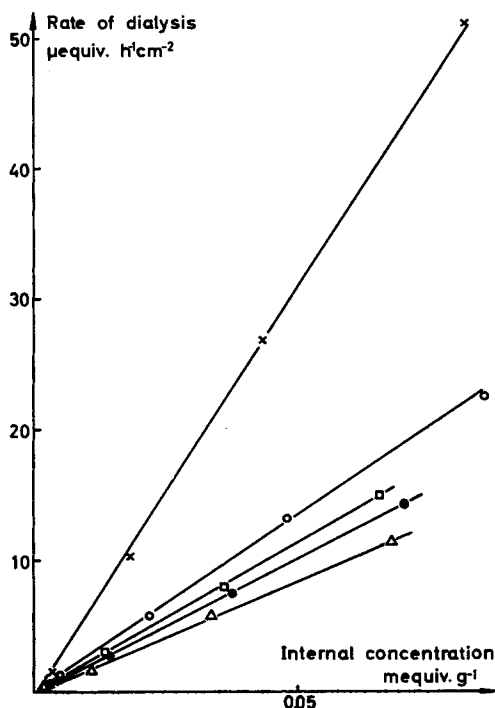


Fig. 6. Rate of dialysis as a function of the trimetaphosphate concentration inside the cellulose film: (O) membrane D; (●) membrane E; (□) membrane G; (Δ) membrane H; (X) membrane I.

As demonstrated in previous sections, the average equilibrium concentration inside the film can be determined experimentally with high accuracy by using the technique applied in this laboratory. The rate of dialysis should be expected to be a simpler function of the internal concentration than of the external concentration. Experiments with polymetaphosphate carried out in a previous piece of work² showed that the rate of dialysis (flux) is directly proportional to the internal concentration determined in equilibrium distribution experiments. This study has been extended to solutions with trimetaphosphate. Some additional experiments with polymetaphosphate have been carried out to elucidate the behavior of the membranes used in this work.

The results presented in Figure 5 confirm that over a wide range of concentration there is a linear relationship between the rate of dialysis and the internal equilibrium concentration. The validity of this simple correlation means that the inhomogeneities discussed in previous sections should not be thought of as pores or areas of low packing density from one surface of the membrane to the other. Instead, it should be assumed that different layers of the swollen film have varying packing densities ("skin and core effects"¹⁶).

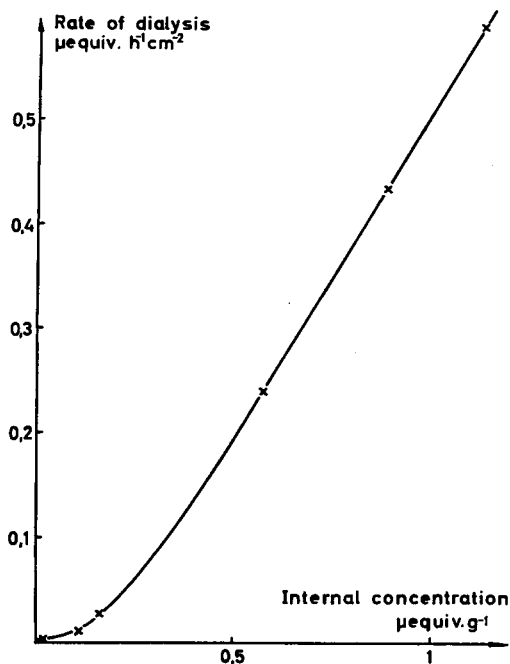


Fig. 7. Rate of dialysis as a function of the trimetaphosphate concentration at low internal concentration. Membrane I. External concentration of trimetaphosphate: 0.001 eq./l. Varying concentration of polymetaphosphate.

The results given in Figure 6 show that even with trimetaphosphate there is a linear correlation between the rate of dialysis and the internal equilibrium concentration. A close inspection of the results shows that the straight lines drawn in the figure do not pass through the origin. The intercept on the abscissa gives a positive value. Since the rate of diffusion cannot be zero unless the internal concentration is equal to zero, the line must be curved in a very low concentration interval (at concentrations <0.001). Accurate determinations of the internal concentration can hardly be made within this interval since the distribution coefficients are very low.

In solutions which besides trimetaphosphate contain a second electrolyte, the Donnan theory requires that the difference in concentration between the two phases be leveled out, i.e., that the molality ratio increase. In the presence of a polyelectrolyte the internal concentration of trimetaphosphate can be even higher than in the external solution, provided that the polyelectrolyte concentration is sufficiently high. This was confirmed experimentally with polymetaphosphate as the second electrolyte. By use of solutions containing inactive polymetaphosphate and radioactive trimetaphosphate, experiments can be carried out quite conveniently, even at very low trimetaphosphate concentrations. The results presented in Figure 7 show that a plot of the rate of dialysis against the internal equilib-

rium concentration gives a curved line at very low trimetaphosphate concentrations. The slope of the straight part of the curve is the same as that of the straight line obtained in experiments with the same membrane in the absence of polymetaphosphate (Fig. 6).

A comparison of the slopes of the straight lines given in Figures 5 and 6 indicates that with all membranes the rate of diffusion inside the membrane is much lower with polymetaphosphate than with trimetaphosphate. It is noteworthy that the order between some of the membranes is changed, i.e., that a membrane which exhibits a greater resistance to polymetaphosphate than another membrane does not necessarily exhibit a greater resistance to trimetaphosphate. This could hardly be explained if the membranes were homogeneous. If there were a spectrum of layers with varying packing densities, the closely packed areas would offer a greater resistance to the large polymetaphosphate ions than to the smaller trimetaphosphate ions.

A very striking difference exists between the never-dried cellophane film (I) and the never-dried sausage casing (D). The swelling of these films differs only slightly. With trimetaphosphate the rate of dialysis across the thin cellophane film is much higher than across the thicker sausage casing. With polymetaphosphate the situation is reversed. Despite its thinness the cellophane membrane offers a greater resistance to the polyelectrolyte. This observation lends additional support to the results given in earlier sections, which also indicate that the cellophane membrane is more heterogeneous than the sausage casing.

The experiments presented in this work have not been carried out in order to study the fundamental factors which govern the diffusion inside membranes. Firstly, the thickness of the membranes has not been determined with high accuracy. Secondly, the membranes have not been chosen with this aim in sight. No further comments about the differences in structure between the membranes will, therefore, be made.

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Résumé

L'eau non-solvant déterminée dans des solutions très diluées de polymétaphosphate peut constituer une mesure du gonflement vrai de films de cellulose. De ces valeurs et de la détermination de l'eau non-solvant dans des conditions permettant la pénétration du solvant, dans le film, on a tiré la molalité à l'équilibre du trimétaphosphate, du polymétaphosphate et des polyglycols dans le film. Dans le cas des électrolytes, le rapport de molalité (film/solution externe) dépend fortement de la concentration externe qui peut être partiellement attribuée à l'effet des groupes carboxyliques chargés à l'intérieur du film. Le rapport de molalité augmente avec une diminution du poids moléculaire dans le cas des polyglycols. Des films denses ne permettent pas la pénétration détectable des polyglycols de haut poids moléculaire. On compare plusieurs films et on montre que ceux-ci comprennent des sites de compacité variable. La dialyse du trimétaphosphate et du polymétaphosphate au travers des films de cellulose a également été étudiée. Dans la dialyse avec l'eau il existe, sur une large gamme de concentrations, une relation linéaire entre la vitesse de dialyse (flux) et la concentration moyenne interne déterminée dans des expériences à l'équilibre. Il est intéressant de noter que cette relation simple reste valable même si les films sont inhomogènes.

Zusammenfassung

Die Bestimmung des Nichtlösungsmittel-Wassers in sehr verdünnten Lösungen von Polymetaphosphat kann als ein Mass für das wahre Quellen von Zellulosefilmen verwendet werden. Aus diesen Werten und Bestimmungen von Nichtlösungsmittel-Wasser unter Bedingungen, die ein Eindringen des Gelösten in den Film erlauben, wurde die mittlere Molalität von Trimetaphosphat, Polymetaphosphat und Polyglycolen innerhalb des Films unter Gleichgewichtsbedingungen bestimmt. Bei Elektrolyten hängt das Molalitätsverhältnis (Film zu äusserer Lösung) sehr von der äusseren Konzentration ab, was zumindest teilweise dem Einfluss der geladenen Carboxylgruppen im Film zugeschrieben werden kann. Bei Polyglycolen nimmt das Molalitätsverhältnis mit abnehmendem Molekulargewicht zu. In dichten Filmen konnte keine Eindringung von hochmolekularen Polyglycolen festgestellt werden. Ein Vergleich zwischen verschiedenen Filmen wird angestellt. Es zeigt sich, dass sie Bereiche verschiedener Packungsdichte enthalten. Die Dialyse von Trimetaphosphat und Polymetaphosphat durch den Zellulosefilm wurde ebenfalls untersucht. Bei der Dialyse gegen Wasser besteht in einem weiten Konzentrationsbereich ein linearer Zusammenhang zwischen der Dialysegeschwindigkeit (Flux) und der mittleren inneren, durch Gleichgewichtsversuche bestimmten, Konzentration. Es ist interessant, dass trotz der Inhomogenität der Filme eine so einfache Beziehung besteht.

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