

Semipermeable Membranes of Cellulose Acetate for Desalination in the Process of Reverse Osmosis. I. Lyotropic Swelling of Secondary Cellulose Acetate*

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Synopsis

The role of certain inorganic salts in increasing the flux of water through semipermeable membranes of cellulose acetate is related to the capacity of the component ions to swell the cellulosic substrate. The mechanism whereby ions which are high on the Hofmeister lyotropic series swell and dissolve secondary cellulose acetate has been investigated. Swelling is effected by the formation of metastable complexes involving the highly hydrated cationic fraction of the salt and both the hydroxyl and acetate groups of the cellulose acetate. Whereas effective anions possess large ionic radii and cause a breakdown in the structure of water which results in increased hydration of the cation, ineffective anions possess higher charge densities and tend to pair with the cation and decrease the latter's electrophilicity and hence hydratability. Ionic charge density is the factor of prime importance both with respect to the hydratability of the cation and the tendencies toward water disaggregation and ion association of the anion. The mechanism involved in the swelling of secondary cellulose acetate is related to swelling phenomena in many other polymers containing polar groups.

I. INTRODUCTION

There is a strong current interest in the use of semipermeable membranes of secondary cellulose acetate for desalination in the process of reverse osmosis. Biget¹ prepared cellulose acetate membranes from aqueous solutions containing metallic perchlorates, specifically those of magnesium and beryllium and observed that 97% of the dissolved salt was removed from solutions. Dobry² had earlier attributed to perchlorates the capability of solubilizing cellulose acetate but had not elucidated the mechanism whereby solution was effected. Reid and Spencer³ studied semipermeable polymeric membranes and observed that cellulose acetate was unique among the systems which were investigated in the extent to which it could effect the

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separation of salt from water. Loeb⁴ added small quantities of inorganic salt additives to the casting solutions from which membranes were fabricated; the resulting films exhibited fluxes which were much greater than those obtained by Reid. Loeb reported that the concentration of membrane salt in the finished membranes was extremely low and concluded that it played no part in the process of desalination. This agreed with the findings of Dobry and Biget that sufficient washing could remove even the last traces of salt from the gel structure. In attempting to explain the function of the membrane salt, Loeb postulated that the important portion thereof was the anion which usually, but not always, possessed a tetrahedral structure, thus enabling it to fit into the tetrahedral structure of water.

Another school of thought, subscribed to by Gilman et al.,⁵ stated that magnesium perchlorate was actually laid down in the film, presumably as fine crystals. Gregor⁶ postulated that the divalent magnesium ion participated in the desalination process and that membrane collapse (decrease in desalination performance) occurred as a result of a leaching process which removed the salt from the membrane.

Clearly then, there has been much divergence of opinion as to the role of the membrane salt in casting solutions from which semipermeable membranes of cellulose acetate are fabricated. The present study shows that the effect of adding certain salts to the casting solutions is to swell the resultant membranes and the mechanism whereby swelling occurs is established. The hypotheses that the role of the membrane salt is to effect chemical modification of the cellulose acetate or to participate in desalination by virtue of physical inclusion in the membrane have also been investigated and discarded.

Although the mechanism whereby secondary cellulose acetate is swollen by solution of inorganic salts is the immediate subject of the present study, its ramifications are quite extensive and include the mechanism of the solvent action of aqueous solutions of lyotropic salts not only upon cellulose derivatives,⁷ but also upon other polar polymers such as starch,⁸ polyacrylonitrile,⁹ and the polypeptides.¹⁰

II. EXPERIMENTAL

A. Materials

Cellulose acetate (Eastman Organic E-398-3, Lot 60), degree of substitution 2.4 (intrinsic viscosity at 25°C. in acetone 0.85; in acetone-water, 66.7–10.0 parts by weight 0.92) was employed throughout this study. The solvents employed as model compounds for the polymer substrates for studies in the near infrared were spectroscopic grade. The salts: KF, KCl, KBr, KI, KSCN, KMnO₄, NaIO₄, MgCl₂·6H₂O, MgBr₂·6H₂O, Mg(ClO₄)₂, and ZnCl₂ were Baker analyzed reagents. MgF₂, MgI₂·8H₂O, and Mg(SCN)₂·4H₂O were obtained from British Drug Houses and BF₃ etherate from Baker and Adamson.

B. Experimental Techniques

1. Gel Fabrication Procedure

The composition of the casting solutions was as follows: cellulose acetate, 22.0 parts; acetone, 66.7 parts; water, 10.0 parts; membrane salt, varied.

Gel samples were prepared in the form of membranes by pouring casting solution onto a doctor blade, drawing the blade across a glass plate, allowing the ripples to dissipate (drying), and immersing the plate together with the solution into water.

The temperatures at which casting, drying, and immersion of the membranes in water were effected were -11 , -11 (3 min.), and 0°C ., respectively. Those membranes which were employed for swelling studies were about 3 mm. thick when cast and about 1 mm. thick after separation from the glass plate in the water immersion process. Measurements in the infrared necessitated the fabrication of thinner membranes with a dry thickness of approximately 0.1 mm. Cellulose films were prepared from cellulose acetate by hydrolysis with 0.4*M* ethanolic NaOH.¹¹

2. Volume Measurements

The volume of the swollen gel samples was calculated after measuring the thickness of the circular samples with a micrometer and the diameter with a centimeter tape. The data are presented in Table VII.

3. Water Contents

The water contents of the swollen gel samples were obtained after removing surface water and weighing in closed weighing bottles. The dry weights were determined after the wet samples had been allowed to stand in a vacuum desiccator for two days over P_2O_5 . The data are summarized in Tables V and VI and Figures 4 and 5.

4. Conductance Measurements

Conductance measurements were made utilizing an Industrial Instruments, Inc. conductance bridge, Model RC-16B1. The cell constant of the glass dip cell was experimentally determined by calibration against 0.01*N* KCl to be 0.091 at 0°C . The magnesium salts were dissolved in acetone-water (66.7–10.0 parts by weight) at 0°C . Resistance values were converted to conductance figures and a correction was made for a small conductance (5×10^5 mho) of the acetone-water solvent system. Extrapolation was made to infinite dilution to obtain comparative values of limiting equivalent conductance. Solubilities have been determined independently by titration of the magnesium ion in the saturated salt solutions with ethylenediaminetetraacetic acid¹² (Table VI).

5. Infrared and Near Infrared Spectra

The Beckman IR-4 (LiF optics) and IR-5 (NaCl optics) instruments were employed for obtaining infrared spectra of cellulose and acetate

films and the Beckman DK-2 for studies with water and alcohol in the near infrared (Figs. 1-3, 6-8).

6. Viscometry

Samples (1 g.) of carefully dried cellulose acetate were dissolved with varying amounts of magnesium perchlorate in 100 ml. acetone (Eastman Organic Spectro Grade). A 10-ml. aliquot of each solution (taken after the sample had been allowed to equilibrate in a thermostat bath at $25 \pm 0.1^\circ\text{C}.$) was pipetted into a 50-ml. Cannon Ubbelohde dilution viscometer, which was also placed in the thermostat. After the efflux time of the solution was measured, the solution was diluted by the addition of a measured quantity of acetone and another efflux time was obtained. The process was repeated several times, after which specific viscosities were calculated. The results were plotted as η_{sp}/c versus c (where η_{sp} is the specific viscosity and c is the concentration of polymer in grams/100 cc.) and extrapolated to infinite dilution. A similar series of experiments was carried out with each of several different $\text{Mg}(\text{ClO}_4)_2$ concentrations in the original solution, so as to enable the calculation of specific viscosities.

In order to determine the influence of water upon the solution viscosity of cellulose acetate and to approximate more closely the actual casting solutions, measurements were also made in acetone-water solvent systems of varying compositions. The procedure was the same as for measurements in acetone solution, with the exception that successive dilutions were made with acetone-water of the same ratio as employed in effecting the original solution. The data are summarized in Table III.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Salt Concentration in Finished Membranes

The concentration of magnesium ion in the cellulose acetate gel both subsequent to gelation and following the heat treatment clearly indicate that only residual amounts of magnesium ion remain in the finished membrane (Table I). These results agree with those of Biget¹ and Dobry,² who have stated that sufficient washing will remove even the last traces of

TABLE I
Concentration of Mg^{+2} in Cellulose Acetate Gels
after Exhaustive Extraction

Source	Mg^{+2} in dried film, %	Extraction procedure
Biget ¹	0.0	Prolonged washing
Loeb ¹³	0.027	1 hr. ice water, 16 hr. at $80^\circ\text{C}.$
Gilman, ⁵ Gregor ⁶	Significant amounts postulated	Not extracted
Present study	0.002	2 weeks in distilled water at $25^\circ\text{C}.$, water changed daily

salt from such gels. Loeb¹³ has determined the concentrations of salt in semipermeable membranes of the same type and (although reporting somewhat higher values than are reported in this paper) is of the opinion that the presence of salt in the finished membrane is not related to the process of desalination by reverse osmosis. Since the ratio in the polymer structure of glucose units, acetyl groups, and hydroxyl groups to magnesium ions is at least of the order of $10^5:1$, it is unlikely either that these magnesium ions are present in any stoichiometric relationship to polymer groups or that it participates in any way in the desalination process. Even were the residual membrane salt concentrated completely in the active* layer, stoichiometric relationships to other functional groups would be 1000:1 or greater. It was, therefore, concluded that the salt in some way affected the structure of the membrane without becoming an integral part thereof.

B. Chemical Modification of Membranes by Membrane Salts

If the salt in the casting solution altered the membrane chemically, then the membrane structure would be affected in either or both of two ways: directly, by changing the hydrophilicity of the polymer through oxidation or saponification and indirectly, by changing properties of the polymer in solution prior to the act of gelation.

Both hydrolysis and oxidation were examined by the technique of infrared spectrophotometry. Studies were made with cellulose as well as with cellulose acetate because the former does not *per se* possess carbonyl groups and consequently the appearance of a small amount of carbonyl absorption would not go unnoticed as might well have been the case in the presence of the strong carbonyl band of cellulose acetate. The salt concentrations, temperatures of reaction, etc. were varied within wide limits (Table II).

The only salt which was capable of oxidizing cellulose acetate to any significant degree was KMnO_4 , the inclusion of which (either in the casting solution or in the aqueous heating bath) caused extensive degradation of the cellulose acetate molecules. The oxidative effect of NaIO_4 on the cellulose acetate was minimal because of the small number of 1,2-glycol structures in the cellulose acetate molecule.¹⁴ BF_3 etherate and $\text{Mg}(\text{ClO}_4)_2$ gave no indication of oxidation; however, large amounts (5–10 wt.-%) of BF_3 etherate in the casting solutions caused the cellulose acetate to gel after 12 hr. (even if held at -11°C .). No complete explanation for this phenomenon can be offered, but infrared evidence clearly indicates a broadening of both the hydroxyl and carbonyl stretching bands for cellulose acetate in the presence of BF_3 . This broadening may be attributed to the formation of complexes between BF_3 molecules and both hydroxyl and ester groups. Furthermore, infrared studies of BF_3 and diacetin (a model com-

* Semipermeable membranes of cellulose acetate are unidirectional; i.e., desalination will occur only if the "active" or "tight" layer is positioned against the salt water reservoir and the "substructure" or "open" layer against the fresh water reservoir. The origin and extent of this layer will be treated in the second paper of this series.

TABLE II
Chemical Modification of Cellulose and Cellulose Acetate by Membrane Salts*

Mem- brane salt	Exposure conditions							
	Mild ^b				Rigorous ^c			
	Cellulose acetate		Cellulose		Cellulose acetate		Cellulose	
	Hyd.	Oxid.	Hyd.	Oxid.	Hyd.	Oxid.	Hyd.	Oxid.
NaIO ₄	—	—	—	CHO	—	—	—	CHO + COOH
KMO ₄	—	CHO + COOH	—	COOH + CHO	—	COOH	—	COOH
BF ₃	—	—	—	—	—	—	—	—
Mg(ClO ₄) ₂	—	—	—	—	—	—	—	—

* A dash (—) denotes the absence of any discernible oxidative or hydrolytic effect.

^b 1% salt solution at ambient temperature.

^c 10% salt solutions at 50–100°C.

pound for secondary cellulose acetate) shows the complete removal of the OH stretching band characteristic of dehydration. It may, therefore, be inferred that complex formation is followed by dehydration and subsequent crosslinking of the modified polymer structure.

None of the four salts which were intensively studied effected any hydrolysis of the cellulose acetate. The concentration of acetate groups was identical at the end of each hydrolysis experiment to that which was measured before.

The results of this study are in agreement with those of Dobry² and Biget,¹ who found that no chemical modification of cellulose acetate occurred as a result of its having been treated with magnesium perchlorate. The basis for their statement was the fact that no decrease in the solution viscosity of the polymer could be ascertained subsequent to such treatment. It may be assumed that the mechanism whereby a particular salt functions to increase the flux of water through a desalination membrane bears no relation to any oxidative or hydrolytic effect which these salts may have on the cellulose acetate molecules. This statement can be made in spite of the small chemical changes which were effected by some of the salts, because Mg(ClO₄)₂ effected no change whatsoever, and nevertheless, produced dramatic increases in the flux of water through the membranes.

C. Effect of Membrane Salts upon the Viscosity of Solutions of Cellulose Acetate

It is well known that the viscosity of a polymer solution may greatly affect the properties of films which are cast therefrom. The viscosity of such solutions may be influenced in a number of ways in addition to varying the degree of polymerization or the extent of branching of the polymer substrate. Other possibilities include: bridge formation between polymer molecules, plasticization, which may influence the viscosity just prior to the

TABLE III
Effect of a Membrane Salt upon the Viscosities of Cellulose Acetate Solutions

Composition of 100 ml. of stock solution				Efflux times for given stock/solvent dilutions, sec.				Intrinsic viscosity $[\eta]$	
Cellulose acetate, g. ^a	Mg(ClO ₄) ₂ , g.	H ₂ O, g.	Acetone to mark	1:0	2:1	1:1	2:3		1:2
1.0	0.0	0.0		289.9	230.5	200.3	184.3	173.9	0.85
1.0	0.1	0.0		302.9	231.7	201.5	185.7	174.6	0.85
1.0	0.5	0.0		310.1	235.1	204.1	186.7	176.1	0.85
1.0	1.0	0.0		316.4	238.2	205.4	188.8	177.1	0.85
1.0	0.0	10.0	Acetone-water ^b to mark	406.5	316.1	276.3	255.3	241.8	0.92
1.0	0.1	10.0	Acetone-water to mark	407.6	318.6	278.8	257.5	243.8	0.92

^a Eastman Organic E-398-3 Lot 60.

^b Acetone: Water 6.67:1.

point of incipient gelation, and solvation of the salt by the solvent system.

The viscosity of solutions of cellulose acetate (as measured by efflux times) were determined experimentally for a variety of $\text{Mg}(\text{ClO}_4)_2$ concentrations and found to increase with increasing salt concentration (Table III). Since it had been demonstrated that no chemical effects such as oxidation or hydrolysis which would influence either the degree of polymerization or extent of branching of the polymer substrate have occurred, the reasons for the observed viscosity increases were sought elsewhere. The presence of even a small number of carboxyl groups has been shown to increase the effect of a salt upon the viscosity of cellulose acetate solutions because of the formation of intermolecular salt bridges involving divalent salt cations and carboxyl anions of adjacent cellulose acetate molecules.¹⁵ Such an explanation for the viscosity increase is not probable in the present instance, since water, which tends to associate with the carboxyl groups and thus to inhibit such bridge formation, is present in the casting solution. Nevertheless, the intrinsic viscosities of cellulose acetate in both acetone and acetone-water solutions were determined and found to remain constant as the salt concentration was increased. The increase in the absolute viscosity of acetone-water solutions of cellulose acetate, therefore, is attributable to ion-solvent rather than ion-polymer interaction. The results of the viscometric studies of casting solutions of cellulose acetate indicated that ion-solvent interactions might be related to the function of a given salt to increase the flux of water through the desalination membranes. Accordingly, experiments were undertaken which had as their objective the elucidation of the effects of the cationic and anionic portions of both effective and ineffective salts upon the structure of water.

D. The Nature of Ion-Water Interactions

In any consideration of ion-solvent interactions, it must be remembered that inorganic salts consist of cations and anions which have various effects upon the structure of the solvent. The most common solvent for inorganic salts, water, exists as a low molecular weight polymer species (average degree of polymerization at ambient temperatures of approximately 5 in equilibrium with monomolecular water.¹⁶ The nature and extent of polymeric water may be greatly influenced by the nature of solute salt. The rather dramatic effects which the various salt ions have on the structure of water have been studied by a variety of techniques among which viscometry, calorimetry, and infrared spectroscopy have been outstanding. The ability of an ion to be hydrated (i.e., to associate closely to itself molecules of water) varies markedly. The order-producing effects of an inorganic ion on the structure of water are limited largely to the cationic portion of the salt, which increases in effectiveness with increased charge density.^{17a} Charge density is a function both of the ionic radius and of the ionic charge. The high positive charge density of the cations strongly attracts the nucleophilic oxygen atoms of water and causes a rearrangement of the water structure about the cation because of ion-dipole interaction

forces. Those ions which possess a high charge density will cause a rearrangement of the water structure in their vicinity owing to ion-dipole interaction forces.

1. Viscosity Measurements

An increase in viscosity of aqueous solutions (compared to the viscosity of pure water) should be noticed if the hydration effect of the cation is not offset by any opposing effect of the anion to degrade the polymeric structure of water. Two series of salts were studied in which the cation was held constant while the anion was varied (Table IV). In the first series, potassium was chosen as the cation because its low charge density would permit a minimum of hydration, not obscuring the extent of hydration of the various anions. The viscosities of molar and saturated solutions of this salt series indicate that the chloride, bromide, and iodide ions serve to break down the structure of water and decrease its viscosity to varying degrees in a manner qualitatively related to their charge densities. The fluoride ion, on the other hand, actually effected an increase in viscosity, which is attributable to capacity of this ion for solvation by water molecules or aggregates thereof. The second series of salts comprised the magnesium ion in combination with various anions. It is apparent that rather significant increases in viscosity are observed and that these are attributable to the hydration of the magnesium ion. The various anions, in a manner dependent upon their charge densities, negate the structure-enhancing effects of the cation to varying extents. The smaller chloride ion is more highly hydrated and consequently decreases the viscosity of the water to a lesser extent than do the larger bromide and iodide ions. The extremely low solubility of magnesium fluoride is explicable on the basis of the high mutual attraction between cations and anions, both of which

TABLE IV
Viscosities of Aqueous Solutions of Inorganic Salts

Salt	Efflux times at 25°C. for given salt concentration, sec. ^a	
	Saturated	1M
KF	523.9	319.4
KCl	269.1	278.5
KBr	235.4	260.6
KI	193.9	245.9
KSCN	324.3	273.4
KClO ₄	296.7	^b
MgCl ₂	2102.3	401.0
MgBr ₂	768.8	390.9
MgI ₂	583.9	322.7
Mg(ClO ₄) ₂	899.5	352.5
Mg(SCN) ₂	798.2	390.9

^a The efflux time for water was 295.2 sec.

^b Not soluble to this extent.

possess an unusually high charge density. It is apparent, therefore, that cationic and anionic effects which tend to enhance the structure of water are not additive in any but the most dilute solutions owing to complications originating in ion-ion interactions. Such interactions can lead to ion pair formation and, in the limiting case, to complete insolubility of the salt. It may, of course, be assumed that solubility in the casting solution is a prerequisite of any membrane salt.

2. Spectrophotometry in the Near Infrared

It is evident that the polymeric structure of water which is under discussion refers to aggregation by hydrogen-bond formation between water molecules rather than to a static covalently bonded polymer. A study of the effects of the presence of inorganic salt ions upon the hydrogen-bonding behavior of water is of great assistance in understanding both the nature of water and the role of the various salts in increasing the flux of water through desalination membranes.

With respect to the relative importance of the cations and anions of membrane salts, it appears that anions play only an indirect role insofar as any influence upon the structure of water is concerned. The cation is the salt species of prime importance with respect to the acquisition of spheres of hydration. If the charge density of the cation is too low, hydration or even dissolution will not occur, as is witnessed by the relative insolubility of KClO_4 in both water and acetone-water. Anions do assist a particular cation by depolymerizing water and, as will be demonstrated, by failing to associate with the cation. The perchlorate ion permits the magnesium ion to acquire many spheres of hydration, whereas the fluoride ion prevents this because it is more nucleophilic than the oxygen atoms of water and can, therefore, lower the effective charge density of the cation by association therewith. Infrared spectroscopy has been one of the classic techniques for studying hydrogen-bonding phenomena. Although both the absorbance and band width of water at its fundamental OH stretch absorption are so great as to make such studies difficult, nevertheless, the overtones of this band in the near infrared have proven of great value in studying the effects of various inorganic salt ions on the structure of water. Early studies of the effect of temperature upon the absorption spectra of water in the near infrared showed a narrowing of the OH stretch band widths as well as increased absorption and a blue shift (shift of the maxima to shorter wavelengths) as the temperature was raised.¹⁸ The narrowing of the absorption bands and the increase in extinction coefficient are to be expected on the depolymerization of a polymeric species to a monomer, and the blue shift is indicative of a decrease in hydrogen bonding. Similar effects for aqueous solutions of a series of alkali halides has been observed and it was determined that the extent of blue shift increased as the anionic radius increased.¹⁹ It was also found that another phenomenon was superimposed upon this blue shift, viz., a red shift, which when coupled with the broadening of the OH bands was termed the hydration effect. Hydration un-

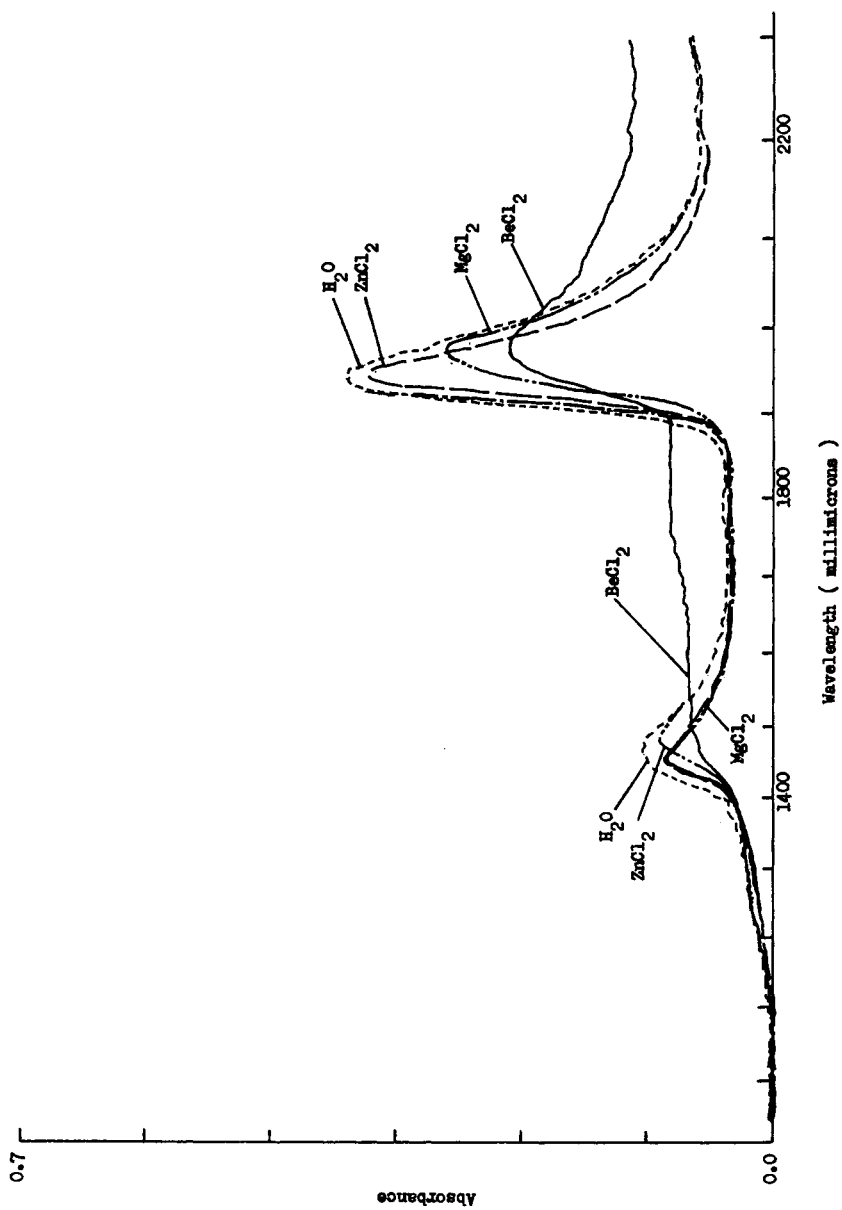


Fig. 1. Near infrared absorption spectra of aqueous solutions of metallic chlorides.

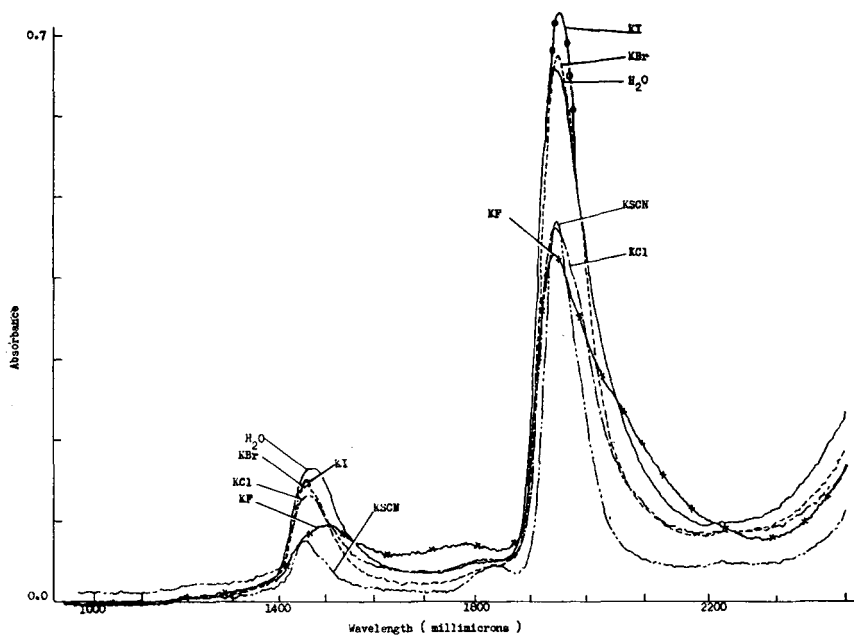


Fig. 2. Near infrared absorption spectra of aqueous solutions of potassium salts.

doubtedly opposes depolymerization, and since the former increases with increasing charge density of the cationic species, it may be attributable to increased hydrogen bonding as a result of a closer packing of water molecules about the cationic species. One consequence of the preceding considerations is that predictions as to viscosity effects in aqueous solutions of inorganic salts should be possible on the basis of spectroscopic data and vice versa. It should be possible, moreover, to eliminate various uncertainties as to the effects of particular ions upon the structure of water by the use of both techniques in conjunction with one another.

The near infrared absorption spectra at 25°C. of saturated solutions of several series of salts have been recorded (Figs. 1-3). The first of these depicts a series of chlorides with which cations of varying ionic radii and hence varying charge density have been paired (Fig. 1). The maximum of the OH stretching band at 1.94 μ undergoes a red shift to a degree proportional to the charge density of the cation involved. This is quite understandable on the basis of the greater influence of the stronger electrical fields of the more highly charged cations upon the water dipoles. Water molecules will be aligned along the ionic sphere such that the electron

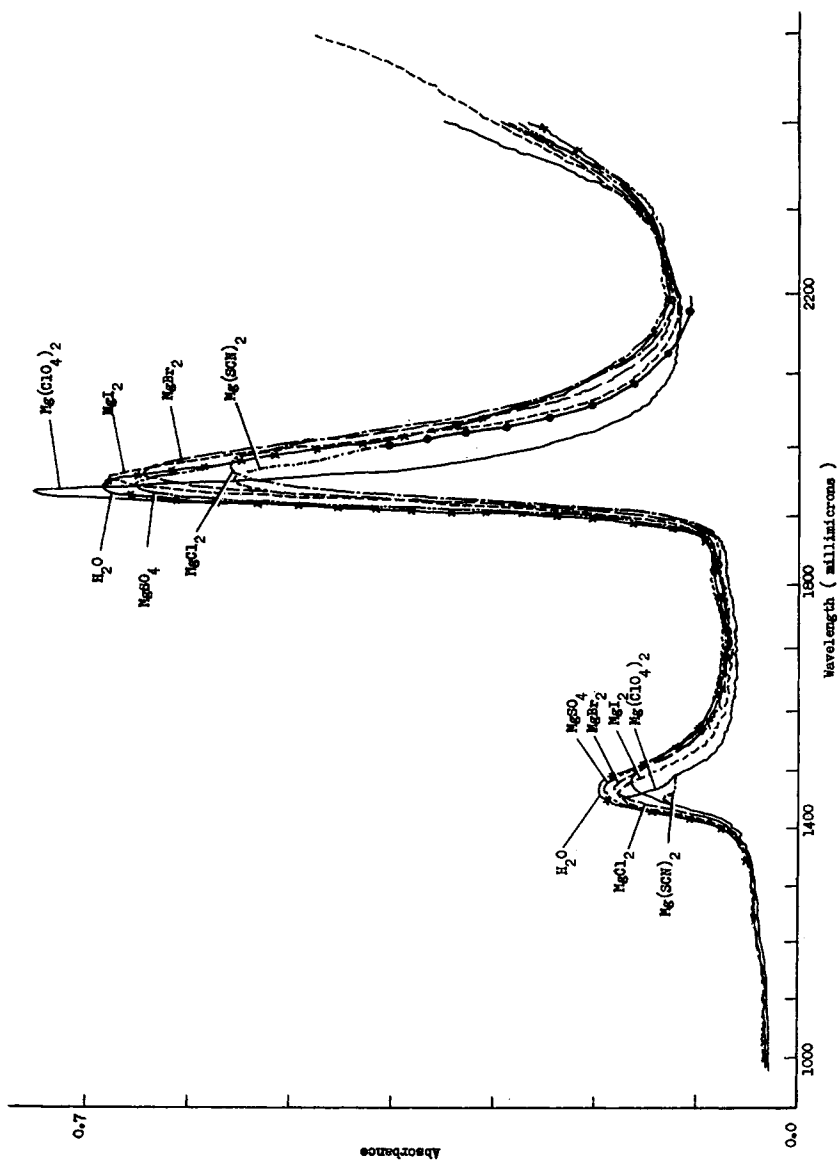


Fig. 3. Near infrared absorption spectra of aqueous solutions of magnesium salts.

clouds constituting the covalent bonds between the oxygen and hydrogen atoms of water center more closely about the oxygen atom. The driving force for this electron displacement is the ion-dipole interaction between the metal cation and the oxygen atom of water. The result of this interaction is to weaken the bond between the oxygen and hydrogens of water, thereby accounting for the red shift which is observed. The increase in absorption which is noticed for that portion of the spectrum which is adjacent to the adsorption maxima of the beryllium chloride solution is attributable to the presence of hydronium ions which result from hydrolysis. Apparently a sufficiently high cationic charge density will result in what may be viewed as a partial metathesis between the salt cation and a water hydrogen. The extinction coefficients of the OH band at 1.94μ decrease proportionately with the increase in charge density of the cations. This is indicative of a polymerization of the water molecules, presumably of those which are hydrating the cation. Alignment in the electric field of the cation probably results in packing of water molecules in a manner analogous to the effect of increased pressure,²⁰ and the assumption by water of a more polymeric nature. This is also indicated by the viscosity increases which have been attributed to hydration of the cation.

The near infrared absorption spectra of a series of potassium and magnesium salts have been utilized to determine the effects of various anions upon the structure of water (Figs. 2 and 3). Striking changes in the OH bands of water at 1.46 and 1.94μ have been observed which are believed, as in the case of the cations, to be functions of ionic charge density. With the noteworthy exception of the fluoride ion, all the anions appear to cause a breakdown in the polymeric structure of water. A saturated solution of KF undergoes a shift in the third OH band of water from 1.46 to 1.50μ . This shift in conjunction with the extensive broadening of the 1.95μ OH band clearly illustrates the hydration capacity of the fluoride ion. This was also quite evident from viscosity results. The breakdown in the structure of water which the other anions produce becomes more intense, the larger the anionic radius, reaching a maximum in the case of the perchlorate and thiocyanate ions which cause a substantial blue shift of both the 1.46 and 1.94μ bands of water. Additional changes which are observed for the spectra of aqueous solution of these ions include both a narrowing of the 1.94μ OH band and an increase in its extinction coefficient as well as the emergence of a doublet in the 1.46μ band. All of these shifts and increases in resolution provide strong evidence for a depolymerization reaction involving the breaking of hydrogen bonds between water molecules. It is difficult to conceive of any positive effect which a large anion might exert which would actively assist in breaking down hydrogen bonds between water molecules. It may be that once dissolution of the salt has occurred, for which the electrophilic attraction of the cationic portion of the salt for the oxygen atoms of water may be credited, large anions remain in solution because their tendency to undergo hydration, although weak, is of sufficient strength to prohibit their penetration through the hydration shells of the

cations. Thus, the fact that larger anions remain in solution is no indication that they themselves are strongly hydrated. Since, however, anions occupy space, they will cause an increased separation between those water molecules which are not hydrated to cations. This may result in a dilution of the water and help to explain the decreased hydrogen bonding between water molecules which is mirrored in the spectral and viscometric changes.

E. The Nature of the Salt-Polymer Interactions

1. Swelling of Secondary Cellulose Acetate

Since membrane salts which were added to the casting solutions neither became integral parts of the membrane structure, nor effected any chemical changes in the polymer substrate, but did themselves hydrate (as evidenced by the spectrophotometric and viscosity experiments) it was hypothesized that the sole function of such species was to swell the cellulosic gel. Accordingly, quantitative studies were inaugurated to determine the amount of water which was incorporated within the membrane (Tables V and VI). The dimensions of a number of membranes were also measured and found to increase as a function of the concentration of magnesium perchlorate in the casting solution (Table VII).

A brief discussion of the nature of swelling follows. Generally speaking, the term swelling usually refers to the phenomenon wherein the inclusion of liquid within a gel structure in addition to that which was present prior to the onset of the phenomenon occurs. Thus swelling results in an increase in the total volume of the polymer-liquid system and has as its (sometimes attainable) limit complete solution of the polymer, i.e., the disappearance of the two-phase system. In order for swelling to occur, the polymer-liquid interaction forces must exceed that of polymer-polymer cohesive energy; in other words, juncture points (crosslinking sites) must be ruptured in the polymer system. In the case at hand, secondary cellulose acetate has been shown to swell, and even dissolve, in aqueous solutions of certain inorganic salts such as magnesium perchlorate.²¹ Since water *per se* cannot significantly swell cellulose acetate, it may be assumed that

TABLE V
Membrane Water Content versus Swelling Agent Concentration

Swelling agent	Weight fraction water in membrane at various swelling agent concentrations ^a			
	0.0	9.0 moles × 10 ⁴	17.9 moles × 10 ⁴	26.9 moles × 10 ⁴
None	0.57	—	—	—
NaNO ₃	0.57	0.58	0.59	—
Mg(ClO ₄) ₂	0.57	0.64	0.67	0.70
ZnCl ₂	0.57	0.66	0.71	0.73
BF ₃ etherate	0.57	0.60	0.62	0.63

^a Formulation: acetone, 66.7 g.; cellulose acetate, 22.2 g.; water, 10.0 g.

TABLE VI
Swelling and Conductivity Relationships of Magnesium Salts

Anion	Ionic crystal radii, A.	Swelling ability, % water in membrane ^a	Limiting equivalent conductance, mhos/cm. ²	Solubility in acetone-water at 0°C., g./l. ^b
Cl ⁻	1.81	°	3.4	8.15
Br ⁻	1.95	60.82	15.0	40.3
I ⁻	2.16	61.60	16.0	63.3
ClO ₄ ⁻	2.92	64.20	18.0	76.9

^a Ratio of Mg⁺² to cellulose acetate hydroxyl groups maintained constant at 0.176.

^b Composition of acetone-water, 6.67:1.

^c MgCl₂ too insoluble to permit preparation of casting solution.

TABLE VII
Effect of Membrane Salt Concentration upon the Dimensions of Cellulose Acetate Gels

Weight of Mg(ClO ₄) ₂ in casting solution, g. ^a	Gel thickness, mm.		Gel diameter, mm.		Swelling ratio, wet volume/dry volume
	Wet	Dry	Wet	Dry	
0.0	0.0635	0.0406	76	66	1.8
1.1	0.0761	0.0508	76	57	2.0
3.8	0.0889	0.0559	76	53	2.2 _s
6.5	0.1109	0.0610	76	50	2.7 _t

^a Other casting solution components: cellulose acetate 22.2 g.; acetone 66.7 g.; water 10.0 g.

the hydrated salt ions are capable of association (complex formation) with certain sites on the polymer with the eventual result that polar crosslinking sites are ruptured and additional water is incorporated into the gel network. The formation of complexes is postulated because the mere presence of highly hydrated ions in an aqueous solution contiguous to a set polymer gel would not swell the network unless the ions would be absorbed together with their waters of hydration within the gel structure. In the absence of an ion-dipole interaction between polymer and hydrated cations, no driving force for the inclusion of additional water is present, and swelling will not occur. This will be the case not only for conventional swelling, wherein additional water is present as a result of the rupture of crosslinks, but also for the case in which these salts are incorporated in a casting solution prior to the formation of a gel structure. In the latter instance, "swelling" is attributable to the prevention of the formation of certain crosslink sites, which would otherwise have formed in the absence of the hydrated ions of which the membrane salt (swelling agent) is comprised. It is apparent, therefore, that when salt-polymer interactions are sufficiently strong to effect swelling of a gel whose structure has already been set, the inclusion of such salts in a casting solution containing polymer and water will result in

similar salt-polymer interactions and the formation of a more open, more highly swollen network than would have occurred in the absence of such salts. The studies which clarified the behavior of the individual components with respect to the nature of polymer-salt interaction in aqueous solution of the most widely used membrane salt, magnesium perchlorate, clearly showed that hydration of the magnesium ion predominates over that of the anion. It was shown that the perchlorate anion not only does not hydrate, but even depolymerizes water aggregates. The fluoride ion, on the other hand, is hydrated to some extent. However, although the fluoride ion possesses the lowest radius among the anions, the magnitude of its charge density is insufficient to permit the additional spheres of solvation necessary to encompass electrophilic groups on the cellulosic substrate and swelling does not occur. Finally, since the perchlorate anion is well known for its inability to form complexes, it was postulated that any complex formation between salt ions and the polymer substrate would involve the cationic portion of the salt and certain nucleophilic groups along the polymer chains.

The formation of ion-dipole interaction complexes in solution between salt cations and both hydroxyl and acetate groups is then likely. In order to test this hypothesis, the water contents of membranes as a function of the concentration of swelling agent in their casting solutions were determined, and spectrophotometric evidence for the formation of complexes between salt ions and cellulose acetate was sought. The choice of salts for this study was made for various reasons.

Magnesium perchlorate was selected because of the extent of work which had been done on this compound as a membrane salt; boron trifluoride etherate, because, as a strong Lewis acid, it typified the behavior which was postulated for the electrophilic cations; zinc chloride, because it is one of the most important swelling agents for cellulosic materials, and also because it would further demonstrate that the cation, rather than the anion, is significant with respect to the swelling mechanism. The water contents of the membranes as functions of the concentration of swelling agent in the casting solution are presented in Table V. As many as 80 waters of hydration are aggregated about each Mg^{+2} from $Mg(ClO_4)_2$ (Fig. 4). This was calculated on the basis that the entire difference in water content between those membranes prepared from casting solutions containing salt and those from casting solutions which were saltless, was attributable to water of hydration about the magnesium ions. Such high values for the number of waters of hydration, although uncommon, have been reported for undisturbed systems; e.g., the value of 86.3 for the Mg^{+2} ion which Samoilov has calculated from self-diffusion measurements.²² On a molar basis, zinc chloride is somewhat more effective, and BF_3 etherate is a somewhat less effective swelling agent than magnesium perchlorate. Sodium nitrate (although soluble in the casting solution) does not greatly increase the water content and may not, therefore, be classified as a membrane salt (Table V). By the same token, the presence of a highly hydrated anion such as F^-

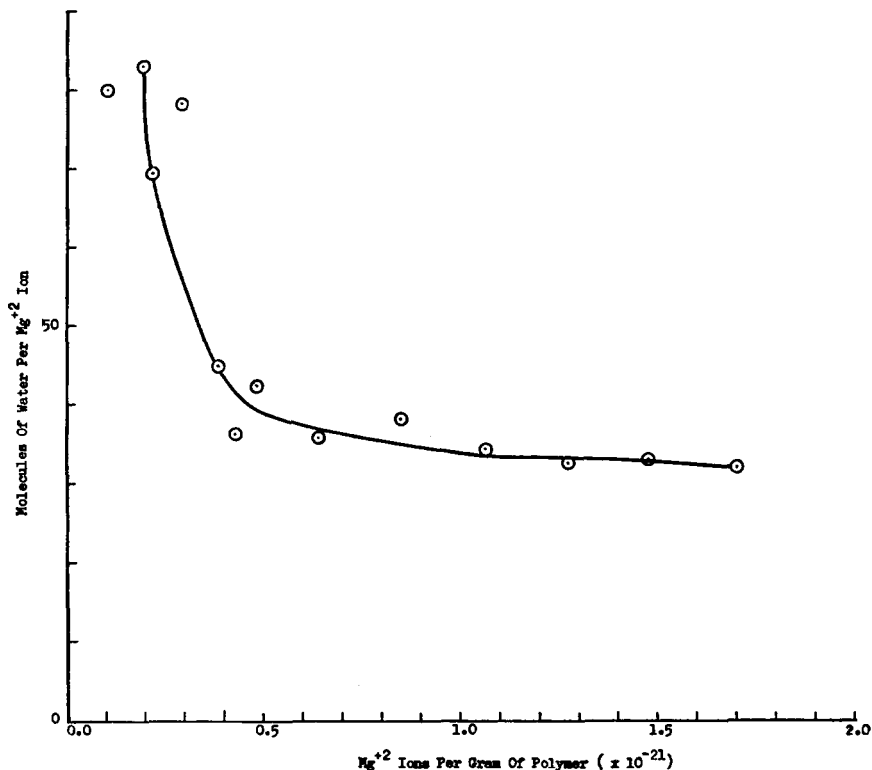


Fig. 4. Hydratability of Mg^{+2} ion in casting solutions of secondary cellulose acetate.

(from KF) is not sufficient to effect swelling of the polymer substrate. Neither, as has been shown for the case of MgF_2 , is it possible to effect swelling by virtue of the copresence of cations and anions of high charge-density, since strong ion-ion interactions result in the insolubility of such a salt. It should also be remarked that whereas effective swelling agents such as $Mg(ClO_4)_2$ are highly soluble in both ethyl acetate and methanol and give off large exotherms upon going into solution, ineffective salts, i.e., those possessing cations with a low charge density, are comparatively insoluble in these solvents.

Strong evidence for the formation of complexes between ethyl formate and magnesium perchlorate has been obtained (Table VIII). The red shift of the $C=O$ band from 5.85 to 5.92μ which results when $Mg(ClO_4)_2$ is dissolved in ethyl formate is indicative of an ion-dipole association between the Mg^{+2} ion and the carbonyl function of the ester group. A identical red shift was observed after a thin film of cellulose diacetate had been treated with an aqueous 10% $Mg(ClO_4)_2$ solution (Fig. 5). Sodium nitrate and other salts which are ineffective as swelling agents do not cause spectral shifts in the carbonyl band.

The absorption spectra of saturated methanolic solutions of inorganic salts have proven useful in the determination of alcohol-ion interactions

TABLE VIII
Ion-Polymer Interactions

Polymer type	Nucleophilic group(s)	Model compound(s)	Ion-dipole interaction complex(es)	Spectral changes in solvent saturated with $Mg(ClO_4)_2$
Cellulose acetate	$-OH, -OCOCH_3$	$CH_3OH, HCOOC_2H_5$	$CH_3-O \cdots M^+ \begin{array}{c} \curvearrowright \\ \text{H} \end{array} \begin{array}{c} \text{H} \\ \text{C}=\text{O} \cdots M^+ \\ \text{OC}_2\text{H}_5 \end{array}$	Red shift + broadening of OH bands; red shift of CO band from 5.85 to 5.92 μ
Cellulose	$-OH$	CH_3OH	$CH_3-O \cdots M^+ \begin{array}{c} \text{H} \\ \\ \text{H} \end{array}$	Red shift + broadening of OH bands
Starch	$-OH$	CH_3OH	$CH_3-O \cdots M^+ \begin{array}{c} \text{H} \\ \\ \text{H} \end{array}$	Red shift + broadening of OH bands
Polyacrylonitrile	$-C \equiv N$	CH_3CN	$CH_3-C \equiv N \cdots M^+$	Change in relative absorption of both halves of the primary $C \equiv N$ stretch doublet
Polypeptides	$-C(=O)-NH-$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{O} \\ \\ \text{H}-\text{C}-\text{N} \\ \\ \text{OH}_2 \end{array}$	$\begin{array}{c} \text{O} \cdots M^+ \\ \\ \text{H} \rightarrow \text{C}-\text{N}(\text{CH}_3)_2 \end{array}$	Modification of first CH overtone

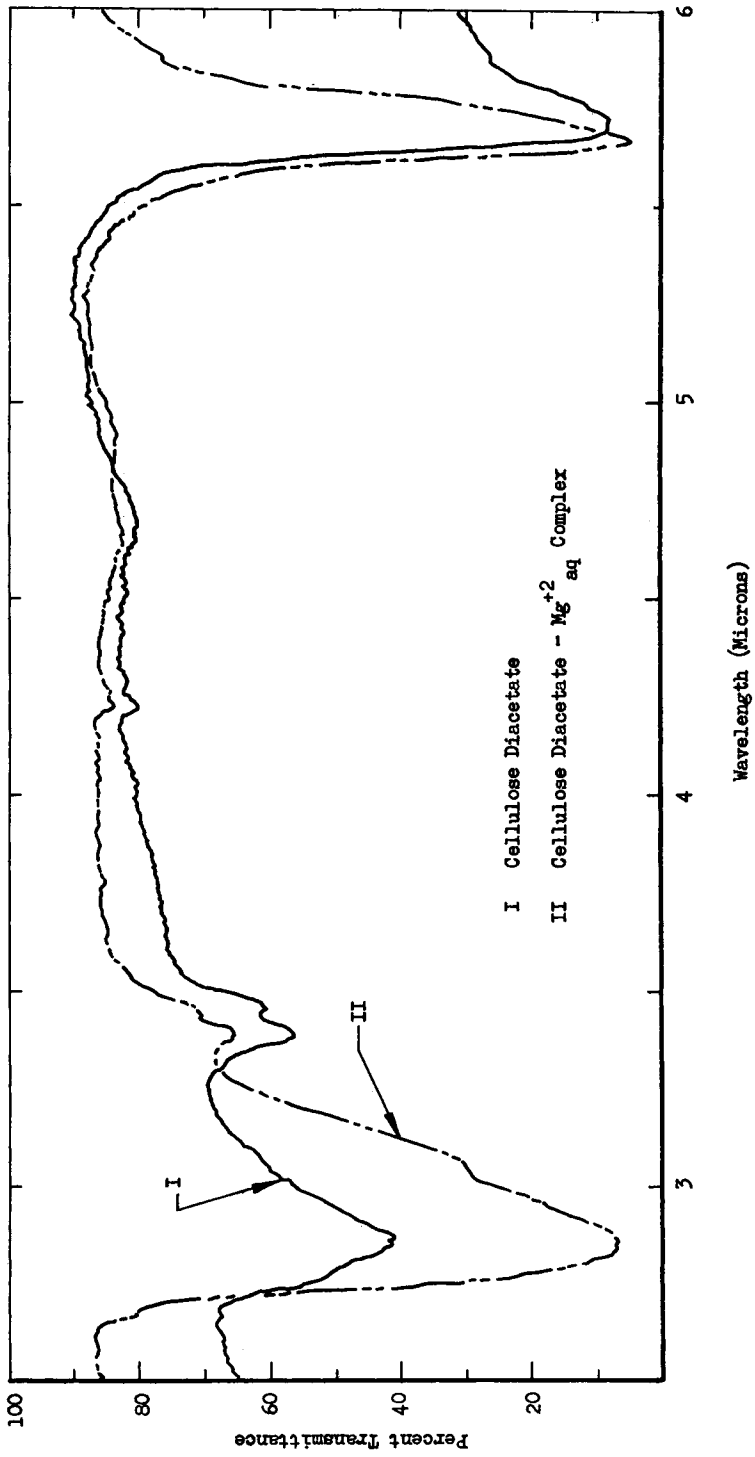


Fig. 5. Infrared spectra of cellulose diacetate: (I) cellulose diacetate; (II) cellulose diacetate- Mg^{+2} complex.

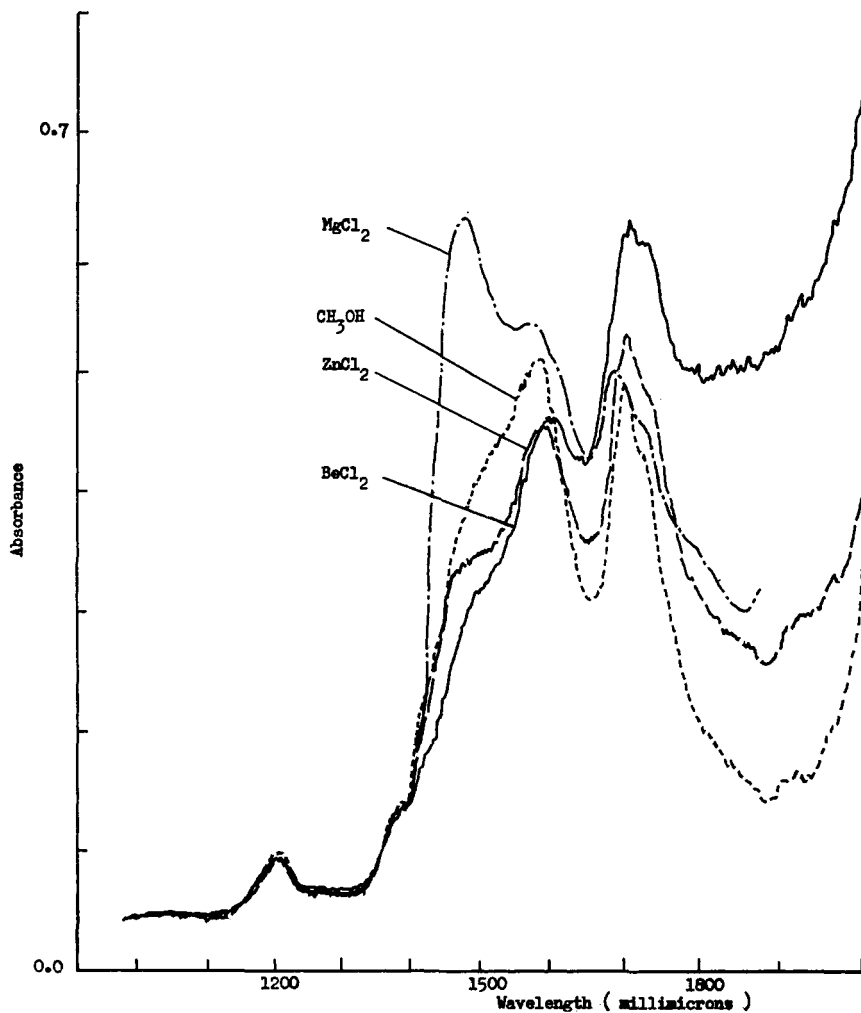


Fig. 6. Near infrared absorption spectra of methanolic solutions of metallic chlorides.

(Figs. 6-8). The first overtone of the O—H stretching band in the near infrared occurs in the case of methanol in the neighborhood of $1580\text{ m}\mu$ and has been ascribed to hydrogen-bonded O—H stretching. The shoulder which appears at $1515\text{ m}\mu$ has been attributed to nonhydrogen-bonded O—H stretching and is so suppressed as to indicate that the pure alcohols are involved in a high degree of intermolecular hydrogen bonding. The effects of the various anionic species upon the structure of alcohols have been ascertained for two series in which the cation remained constant. The spectra of both the potassium and magnesium series show a decrease in the intensity of the hydrogen-bonded O—H stretching band and the emergence of a doublet (where only a shoulder had existed in the pure solvent) for the case of the nonhydrogen-bonded O—H stretching absorp-

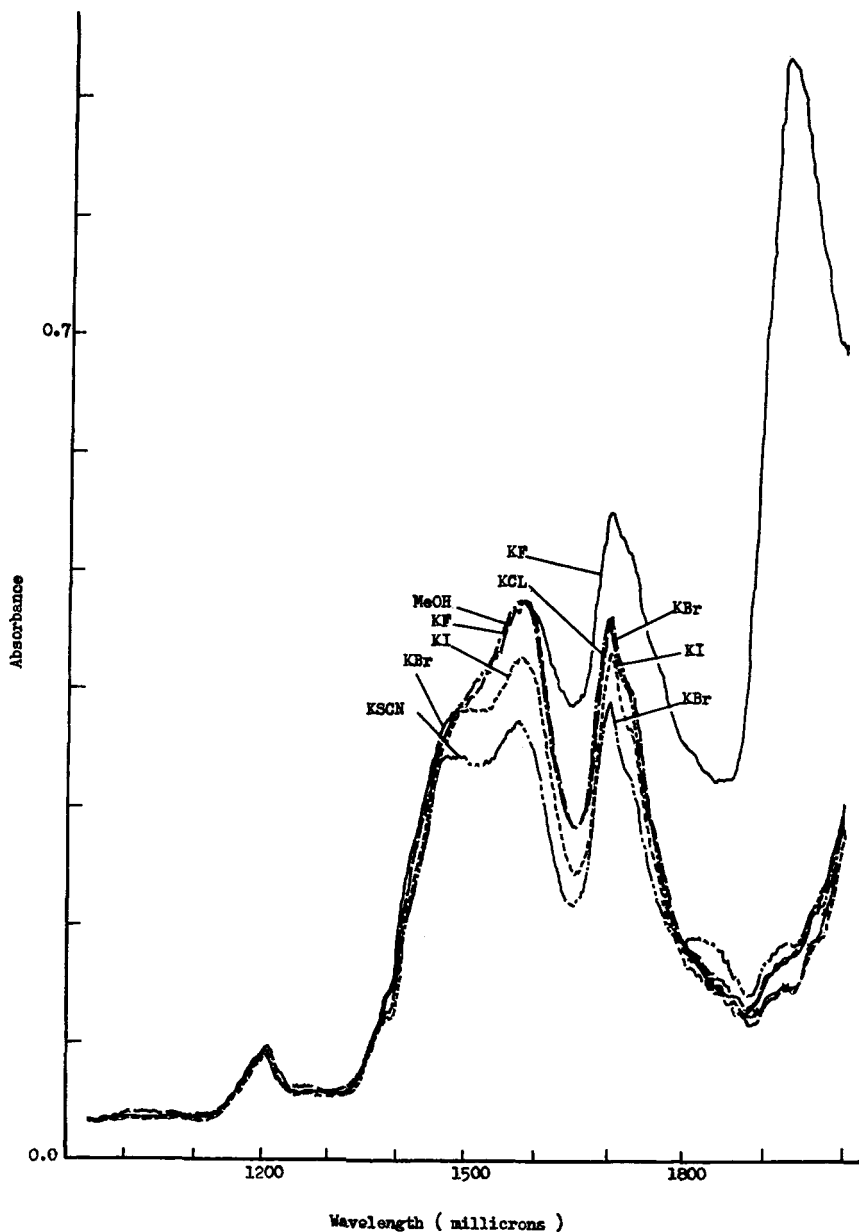


Fig. 7. Near infrared absorption spectra of methanolic solutions of potassium salts.

tion (Figs. 6 and 7). Furthermore, the appearance and extent of the blue shift which accompanied the emergence of the doublet corresponding to nonhydrogen-bonded O—H stretching appears to be inversely related to the charge density of the anionic species involved ($\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$). The fluoride ion on the other hand, causes a depression of the

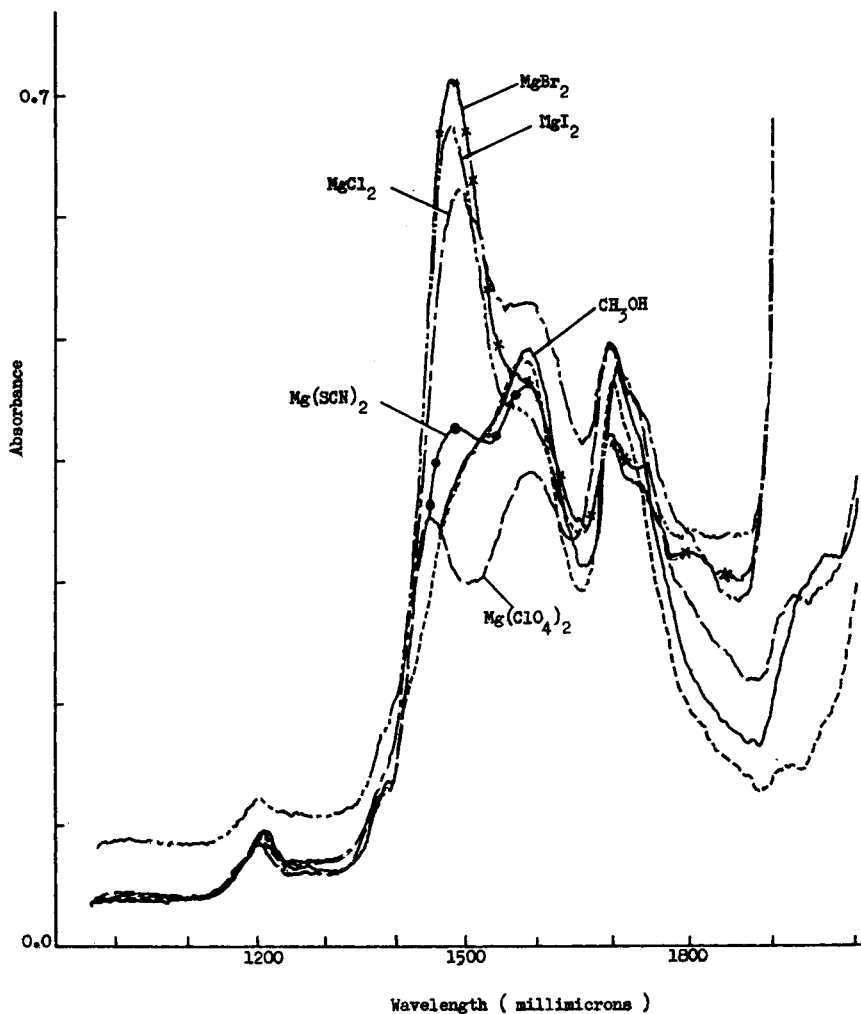


Fig. 8. Near infrared absorption spectra of methanolic solutions of magnesium salts.

nonhydrogen-bonded O—H shoulder and some broadening of the hydrogen-bonded O—H band, both of which effects attest to its hydratability. As expected, anionic depolymerization was more pronounced for the case of the magnesium than for the potassium series, which is indicative of the greater charge density of the magnesium ion and hence the greater solubility of its salts. Solvation of the magnesium ion by the alcohols is evidenced by a broadening of the 1580 $m\mu$ band, but the red shift due to cationic solvation is masked by anionic depolymerization of the alcohol. However, the more pronounced effects which accompany solvation of the Zn^{+2} and Be^{+2} ions, viz., the broadening and red shift of the 1580 $m\mu$ band of the alcohol, constitute evidence for the solvation of these species, i.e., for the

formation of complexes between membrane salt cations and alcoholic hydroxyl groups (Figure 6).

It has, therefore, been demonstrated that membrane salts are swelling agents. Moreover, the capacity of a given salt for swelling cellulose acetate has been related to the electrophilicity of the cationic portion of the salt which in turn effects the capacity of this species for both hydration and complex formation with the nucleophilic hydroxyl and acetate groups of cellulose acetate.

One further aspect of the role of the anion may be clarified. It has been observed that some magnesium salts, e.g., the chloride, do not have the capacity to increase the flux of water through membranes of cellulose acetate.¹³ It is felt that differences in swelling capacity between a series of salts in which the cation is held constant and the anion varied are attributable to interaction between the two species. Ion-ion interactions might lead to association, which, in turn, would result in a decrease of the effective charge density of the cation. In an extreme case, such as MgF_2 , association could be so strong as to result in insolubility of the salt. Studies of the ion association for a series of magnesium halides in ethanol have been made and very definitely support the concept that the association of the Cl^- ion with the Mg^{+2} ion is greater than are similar associations involving the Br^- and I^- ions.²³ In the solvent system which is employed for the casting solutions from which semipermeable membranes of cellulose acetate are cast, acetone predominates over water. The dielectric constant of the acetone-water medium is substantially lower than that of pure water, and the possibility of ion associations is consequently greatly enhanced. Since, however, it is not always possible to predict the results in a mixed solvent from those in either pure solvent because of the possibility of a changing solvent structure and dielectric constant in the zone of solvent surrounding the ions,^{17b} it was decided to investigate the phenomenon of ion association in the acetone-water system. The results of the swelling and conductivity experiments clearly indicate that for any given cation, the charge density of the anion with which it is associated, is the most important factor in determining the extent to which ion association occurs (Table VI). Therefore, the relative swelling capacities of a given salt series, in which the cation is held constant and the anion varied, depends upon anionic size (the larger the anion, the more effective the cation).

It should be apparent, moreover, that cation-anion association is not limited to ion pairs and that the formation of even larger ion aggregates would serve to further decrease cationic hydratability and hence salt swelling capacity.

2. Swelling of Other Polymers

Although the immediate goal of the present study has been to explain the factors which result in the efficacy of various ion combinations as swelling agents for secondary cellulose acetate and hence account for their positions on the Hofmeister ion series, it is, nevertheless, apparent that the general

swelling mechanism will also be applicable to other polymeric systems. A literature search has indicated both that there is much current interest in the ability of aqueous solutions of inorganic salts to dissolve polyacrylonitrile,⁹ amylose,⁸ cellulose,⁷ and polypeptides¹⁰ and that the mechanism whereby such solution occurs is not well understood. It is, therefore, postulated that the swelling or dissolution of polymers containing polar atoms or groups of atoms occurs by a common mechanism involving the formation of complexes between the hydrated cationic portion of the salt and certain nucleophilic groups on the polymer substrates.

Some preliminary evidence for the broad applicability of the postulated swelling mechanisms has been obtained for several cases involving magnesium perchlorate and a number of nonaqueous solvents which have served as model compounds for various polar polymers (Table VIII). Model compounds of high dielectric constant were chosen to favor interaction in the solution and solvent-salt systems. Infrared and near infrared absorption spectroscopy was the technique employed to demonstrate complex formation although it was also qualitatively apparent that salt dissolution was almost invariably accompanied by a large exotherm. Somewhat oversimplified interpretations of the observed spectral changes are interpreted on the basis of ion-dipole interactions (Table VIII). The absorption of magnesium perchlorate was determined from the absorption spectra of this salt in nitromethane, a solvent whose structure is apparently relatively unaffected by the presence of Mg^{+2} ions. Although these studies are necessarily of a preliminary nature, they strongly indicate the existence of unifying principles with respect to lyotropic swelling of polymers containing polar groups and suggest methods whereby hitherto unstudied polymer swelling agents may be systematically investigated.

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Résumé

Le rôle de certains sels inorganiques accroissant l'écoulement de l'eau à travers des parois semi-perméables d'acétate de cellulose est attribué à la propriété des ions constituants de ces sels de faire gonfler la membrane cellulosique. Le mécanisme a été examiné par lequel des ions placés au sommet de la série lyotropique de Hofmeister gonflent et dissolvent le diacétate de cellulose. Le gonflement se produit par formation de complexes métastables impliquant la fraction cationique hautement hydratée du sel et également les groupes hydroxyles et acétyles de l'acétate de cellulose. Les anions effectifs possèdent de larges rayons ioniques et provoquent une rupture de la constitution de l'eau, ce dernier fait accroissant de l'hydratation des cations. En conséquence, des anions possédant une plus grande densité de charge électrique tendent à se combiner avec les cations et à diminuer la tendance électrophile de ces derniers et par conséquent à diminuer leurs tendances à l'hydratation. La densité de charge ionique est le facteur d'importance principale simultanément et relativement à l'aptitude à l'hydratation des cations et à la tendance en direction de la dépolymérisation de l'eau tout autant que l'association de ions des anions. Le mécanisme impliqué dans le gonflement du diacétate de cellulose est rapporté aux phénomènes de gonflement se produisant également avec beaucoup d'autres polymères contenant des groupes polaires.

Zusammenfassung

Die Fähigkeit gewisser anorganischer Salze die Geschwindigkeit des Wassertransportes zu erhöhen liegt darin, dass die Bestandteile der Salze eine Quellung des Cellulosesubstrats verursachen können. Der Mechanismus wobei die hoch auf der Hofmeister Reihe stehenden Ionen Celluloseacetat quellen und auflösen vermögen wird untersucht. Die Quellung findet durch die Bildung labiler Komplexen zwischen den hydratierten kationischen Bruchteil des Salzes und den Hydroxyl- und Acetatgruppen des Celluloseacetats statt. Wirkvolle Anionen besitzen grosse ionische Durchmesser und verursachen einen Zusammenbruch der Wasserstruktur, was zu zunehmender Hydratation des Kations führt. Nicht wirkende Anionen besitzen eine höhere Ladungsdichte und die Tendenz mit Kationen Paare zu bilden, was zur Minderung deren Elektronenanziehungskraft und Hydratation führt. Die ionische Ladungsdichte ist der höchst-wichtigste Faktor in Bezug auf die Hydratation des Kations und die anionische Tendenzen die Wasserstruktur zu zerstören und sich mit Kationen zu paaren. Der Mechanismus der Quellung von Celluloseacetat ist mit Quellungsphänomena anderer Polymertypen verwandt.

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