Semipermeable Membranes of Cellulose Acetate for Desalination in the Process of Reverse Osmosis. II. Parameters Affecting Membrane Gel Structure*

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Synopsis

A quantitative study has been made of the effects on the membrane gel structure of parameters whose significance with respect to desalination performance had previously been empirically established. The composition of the polymer solutions, the fabrication temperatures, and the pressure employed during desalination are shown to be related, in that they all influence the swelling behavior of the gel structure. The relationship which has been found between the water content and the rate of water transport across semipermeable membranes of cellulose acetate is explained on the basis of a solution transport mechanism.

ˎINTRODUCTION

Semipermeable membranes of cellulose acetate have been developed which are highly effective in the removal of dissolved salts from water by reverse osmosis. In this study the effects of the membrane fabrication variables on its operation were examined. As a result of this study a model for the structure of the membrane was developed which explains the effects of each step in the fabrication and is consistent with the observed transport phenomena.

Although comparatively little attention has been given to problems involving the structure of semipermeable membranes of cellulose acetate, a copious amount of work in the related fields of cellulose chemistry and ultrafiltration has been reported. Manegold[1] and Elford[2] have investigated the structure of collodion membranes, and Maier and Scheuermann[3] have treated the sequence of events in the casting solution immediately preceding gelation.

Baker, Fuller, and Pape[4] have studied the structure of cellulose acetate and concluded that ordered amorphous regions are present. With respect to the disposition of water in the gel structure, it has long been believed that water in cellulosic materials concentrates in the amorphous regions[5a] and in

the case of cellulose esters is almost exclusively associated with hydroxyl rather than ester groups.[6]   In one of the few attempts which have been made to establish the microcrystalline structure of semipermeable membranes of cellulose acetate, Reid[7] was unable to obtain meaningful x-ray diffraction patterns.

An improved desalination membrane prepared from a casting solution containing inorganic salts has been developed by Loeb[8] and workers in our laboratories.[9]   The fabrication process involves casting at a low temperature, desolvating in ice water, subjecting the gelled membranes to heat treatment, and pressurizing to effect desalination.   The inorganic additive or membrane salt has been shown to function as a swelling agent,[10] but no explanation of the relationship between swelling phenomena and other fabrication parameters and gel structure has yet appeared.

From the unidirectional behavior of the cellulose acetate membranes in desalination performance, it was deduced[9] that the top and bottom sides of the membranes differed from one another.   This difference, which was subsequently interpreted in terms of an "active" top layer is consistent with earlier work which called attention to differences between surface and bulk membrane properties.

EXPERIMENTAL PROCEDURES

Fabrication and Testing

Semipermeable membranes of secondary cellulose acetate have been fabricated and tested according to procedures which have been described elsewhere.[9]   A solution containing cellulose acetate, acetone, water, and a swelling agent (e.g., $ZnCl_2$) is cast onto a glass plate at 0°C.   The solution is partially evaporated, set by immersion in ice water and then heated in water.   Pressurization and subsequent desalination by reverse osmosis is carried out in a vessel of the type indicated in Figure 1.   The effects upon membrane structure and performance of variations in the composition of the casting solution, drying time, gelation bath temperature, thermal treatment, and pressurization are discussed in this paper.   The unheated membranes have been characterized in terms of their physical appearance, thickness and gravimetric swelling ratios (wet weight/dry weight) and the heated membranes in terms of their water transport and salt retention characteristics.

Considerations of Structure

The x-ray diffraction spectra of the dried membranes were obtained with a Norelco 12045 diffractometer by imbedding the base of the somple in a holder located at the center of a 114-mm. Debye-Scherrer powder camera. Kodak No-Screen medical x-ray film was exposed for 4 hr., after which an equatorial tracing was made with an optical densitometer.
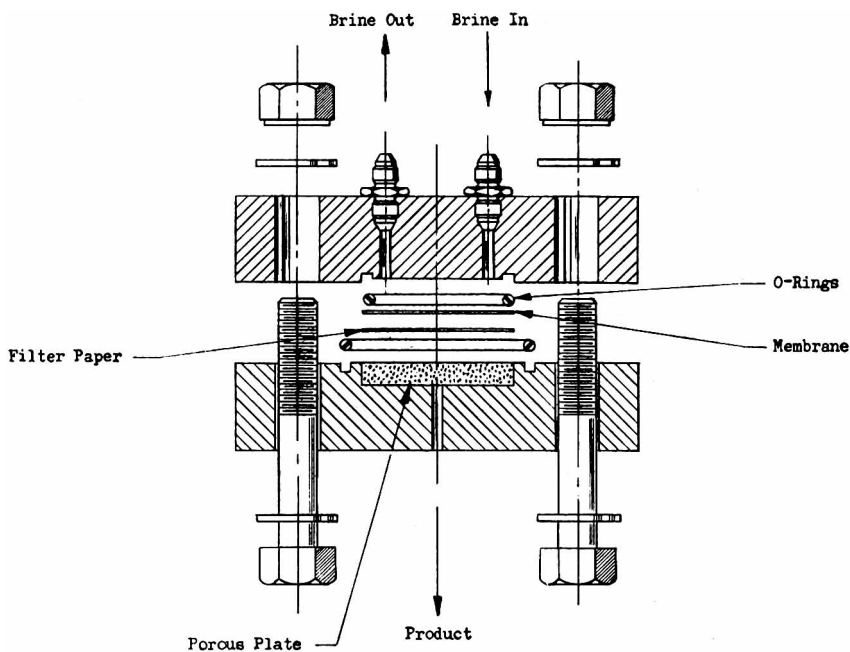
Fig. 1. Desalination cell.

Cellulose membranes, prepared by hydrolysis of membranes of cellulose acetate, were dyed with a 2% solution of Victoria Blue B in a 1:9 water–dioxane solution and a 2% solution of Calcomine Brilliant Yellow. Cellulose acetate membranes were dyed with aqueous solutions containing 1.2% Diphenyl Fast Red 58L Supra I and also with solutions containing 2.8% Chlorantine Fast Green BLL.

EXPERIMENTAL RESULTS AND DISCUSSION

Primary Membrane Gel Structure

The Gelation Process—Description of Model

The formation of desalination membranes is a gelation process, involving the coagulation of a cellulose acetate solution into a comparatively rigid mass incorporating a large amount of water. The finished membranes may be categorized according to the various gel types by means of their optical properties and are discussed herein in terms of the microgel-ultragel nomenclature of Elford.[2]

In Elford's terminology, a microgel structure is that produced upon the coagulation of polymer aggregates into chains yielding an open-pore, sponge-like structure. The microgel is opaque, and its elements are discernible under a microscope. The ultragel structure is submicroscopic and transparent (or opalescent in the transition region between microgel and ul-

tragel).   It occurs in films cast under conditions where the freedom of inter-
action between aggregates is limited by electrostatic repulsion such that de-
solvation proceeds more uniformly.   The nature of the polymer aggregates
in the casting solution was left an open question by Elford, but has recently
been suggested by Maier.[3]   The use of concepts of Elford and Maier, to-
gether, with suitable modifications derived from new experimental data,
leads to a description of the gelation process which occurs in the preparation
of semipermeable membranes from cellulose acetate.

It is a reasonable assumption that the size and uniformity of the cells of
which a desalination membrane is composed are functions of the size and
uniformity of the pregelation polymer aggregates in the solution and are in-
fluenced by such factors as casting solution composition, gelation tempera-
ture and uniformity of desolvation.   In dilute solutions of secondary cellu-
lose acetate, the polymer molecules are random coils, enclosed in an enve-
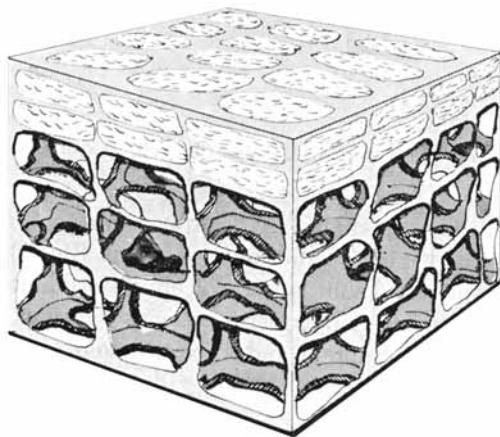lope of solvent which acts as a barrier to contact between macromolecules.

Fig. 2. Membrane gel structure.

As the concentration of polymer is increased, polymer molecules come into
contact and aggregation occurs.[11]   It is believed that the ensuing steps in
membrane formation can be divided into five phases: (1) coacervation, (2)
polymer desolvation (solvent removal), (3) syneresis, and (4) capillary de-
pletion.

Coacervation refers to the coalescence of sol particles whose solvent enve-
lopes can diffuse into one another.[12]   Coacervating groups of sol particles
tend to assume a spherical droplet configuration as a solution becomes more
concentrated.   Spherical polymer aggregates of secondary cellulose acetate
in acetone–water are believed to be about 400 A. in diameter.[13]   Although
still a matter of some dispute, it is probably true that most of the solvent
which is associated with the coacervate droplets is merely physically encap-
sulated in the interior of the spherical polymer aggregates, but a small

amount is more strongly held to the individual polymer molecules by Van der Waal forces.[14]

Polymer desolvation may occur gradually by solvent evaporation or more suddenly by immersion of the polymer solution into a gelation medium such as water in the case of cellulose acetate in acetone.   After desolvation has progressed to a certain degree, coacervate droplets come into contact, deform into polyhedra, and finally bond together through intermingling of polymer molecules from neighboring polyhedra.   When a film is cast and immediately immersed into a polymer nonsolvent, solvent is rapidly removed from the surface of the droplets (causing contraction of the exterior surfaces) and less rapidly from the interior of the droplets (causing the aggregation of polymer from the droplet interiors at the surfaces).   Depletion of the polymer from the interior of the droplet appears to be a more likely explanation for the existence of hollow interiors (filled with non-solvent) than an initial formation of hollow coacervates.   Because of the rapid desolvation which occurs at the droplet surface, stresses are introduced which cause the walls to rupture.   The resultant membrane may be termed the primary gel structure and is composed of an open-cell foam or pore system filled with nonsolvent (Fig. 2).

Casting Solution Composition Studies

The effects of variations in the concentrations of water, polymer, and solvent on membrane gel properties and desalination performance have been determined for both salt-free and salt-containing casting solutions and a number of speculations as to the nature of the various gel structures have been made on the basis of the coagulating droplet model described in the previous section.

In order to ensure a correct interpretation of the effects of the casting solution composition and other fabrication parameters on gel structure, membrane thicknesses and swelling ratios were determined for "primary gel structure," i.e., by using membranes which had not been subjected to syneresis and capillary depletion as a result of heating and pressurization treatments.   Membrane transport phenomena, on the other hand, have been investigated by utilizing secondary gel structures in order to compare the ultimate salt retention capacities which are obtained by depletion of capillary water from the active layer.

Effects of Water and Salt in the Casting Solution.   The results of the present study show that increasing the concentration of water in the casting solution results in corresponding increases in both the thickness and gravimetric swelling ratios of the resultant membranes (Table I).   It is also apparent that the rate of water transport is negligible in the case of membranes which have been cast from salt-free solutions.   The role of the salt is to increase the water content (swell) of the membrane as discussed in the first paper in this series.[10]   Membranes prepared with salt are changed in appearance from a brittle and opaque microgel structure to a more uniform and transparent ultragel type.   Experimental evidence[10] supports the be-

TABLE I
Casting Solution Water Concentration Effects

Water concentration, g./formulation[a]	Swelling agent concentration, g. $ZnCl_2$/formulation[a]	Description of membrane	Wet thickness of unheated membrane, mm. $\times 10^2$	Gravimetric swelling ratio of unheated membrane, wet wt./dry wt.	Rate of water transport, ml./cm.^{2} day[b]		Salt retention, %
					Deionized water feed	0.6M NaCl feed	
0	0	Brittle, opaque (microgel)	5.8	1.47	<1	—	—
5	0	Brittle, opaque (microgel)	6.4	1.77	<1	—	—
10	0	Brittle, opaque (microgel)	7.1	1.99	<1	—	—
15	0	Brittle, opaque (microgel)	8.0	2.35	<1	—	—
0	5	Clear (ultragel)	8.7	2.53	24	16	90.3
5	5	Opalescent (ultragel)	9.0	2.79	34	22.8	97.2
10	5	Opalescent (ultragel)	9.2	2.85	72	48	98.5
15	5	Opaque (ultragel–microgel)	9.6	2.92	136	82	96.2

[a] Formulation: cellulose acetate, 22.2 g.; acetone, 66.7 g. (doctor blade gap 0.25 mm.).
[b] Rate of water transport and salt retention at 102 atm. pressure for heated membranes (86°C. for 5 min.).

lief that the cations of the membrane salt participate in formation of complexes with the nucleophilic hydroxyl and acetate groups of cellulose acetate.   Therefore, the spherical polymer aggregates possess positive charges resulting in mutual repulsion in a solvent medium of low dielectric constant such as acetone–water.   Thus desolvation of the acetone from between the charged droplets will proceed more uniformly, and contact between polymer aggregates will be delayed for a greater length of time than in the absence of salt.   A consequence of the uniform rate of desolvation is greater regularity in the size of the individual polymer droplets at the time contact is made between them.   In the absence of salt, the polymer droplets may coalesce at various stages of desolvation, resulting in the eventual gelation of aggregates of a large variety of sizes.

The effects of the simultaneous presence of both water and salt in the casting solution are extremely complex even to the point of being additive in some aspects and opposing in others.   An apparently additive effect is the increase in water content and the rate of water transport across the membrane with increasing concentrations of both salt and water (Table I). The salt will, of course, tenaciously hold that water originally present in the casting solution in addition to osmotically attracting water into the casting solution before its structure has been fixed.   Thus, a more highly swollen membrane will result.   In the presence of a large amount of swelling agent, a substantial amount of water will diffuse into the membrane during the gelation process even when no water is present in the casting solution.

While salt tends to produce an ultragel structure, water in the casting solution has the opposite effect.   This effect may result from two mechanisms. First, acetone containing large concentrations of water becomes a poorer solvent, and polymer–polymer interaction, and hence the capacity for aggregation, increases.[5b]   The solvent capacity of the aggregates is also reduced, and the formation of the larger and more irregular polymer aggregates characteristics of a microgel is favored.   Water-induced polymer aggregation is evident in the increase of gravimetric swelling ratios, membrane dimensions, and water-transport rates with increasing water in the casting solution.   From this it may be deduced that water causes the coacervate spheres to make contact at an earlier stage of compaction, and the cells resulting from gelation have a greater capacity for capillary water and hence a lesser resistance to flow than those which are produced from an anhydrous solution (Table I).   The second effect of the presence of water in the casting solution is to increase the dielectric constant of the solvent system.   A higher dielectric constant in the solvent system acts to diminish charge repulsion effects of absorbed salt cations thereby favoring irregular aggregation and microgel formation.

In the complete absence of water in the casting solution desolvation will be further advanced before droplet formation, coalescence, and gelation occur.   As a result, much of the potential capillary space in the center of the droplets will have disappeared, and the resultant membrane will be quite dense and impermeable.   It is apparent that a proper balance between the

TABLE II
Casting Solution Solvent and Polymer Concentration Effects

Acetone concentration, g./formulation[a]	Swelling agent concentration, g. ZnCl₂/ formulation[a]	Description of membrane	Wet thickness of unheated membrane, mm. × 10²	Gravimetric swelling ratio of unheated membrane, wet wt./dry wt.	Rate of water transport, ml./cm.²·day[b]		Salt retention, %
					Deionized water feed	0.6M NaCl feed	
50.0	0	Brittle, opaque (microgel)	10.2	1.61	<1	—	—
66.7	0	Brittle, opaque (microgel)	7.9	1.99	<1	—	—
80.0	0	Opaque, opalescent (microgel–ultragel)	7.4	2.06	<1	—	—
50.0	5	Clear (ultragel)	12.7	2.55	840	768	0
66.7	5	Opalescent (ultragel)	10.2	2.85	72	48	98.5
80.0	5	Opalescent, opaque (ultragel–microgel)	9.1	3.40	88	64	98.6

[a] Formulation: cellulose acetate, 22.2 g.; water, 10.0 g. (doctor blade gap 0.25 mm.).
[b] Rate of water transport and salt retention at 102 atm. pressure for heated membranes (86°C. for 5 min.).

membrane salt and water contents of the casting solution is essential to the control of the gelation process and the production of more uniform ultragel structures.

Solvent-to-Polymer Ratio. Polymer molecules will be more highly aggregated in more concentrated solutions and a higher degree of intermingling will occur between polymer molecules of adjacent coacervate droplets. Consequently, the walls of the open-cell foam structure will be thicker, with the result that a lesser amount of water will be incorporated in the gel network. Membranes which were cast from 50.0 g. acetone solutions both with and without membrane salt contained grainy particles that indicated the occurrence of some gelation prior to immersion in the gelation bath. The membrane prepared with salt had a very high rate of water transport but no capacity for desalination (Table II). The decrease in desalination capacity and great increase in the rate of water transport are both indicative of the absence of, or at least a greatly modified, surface layer. Perhaps the cells of those membranes cast from extremely viscous solutions are too large to permit the capillary closure which normally occurs at the surface during the heating and pressurization treatments. The result is that material transport through such membranes occurs primarily by viscous flow. Those solutions which contained 80.0 g. of acetone produced membranes of excellent material transport and desalination properties.

Conditions Affecting the Primary Gel Structure

Having investigated the effects of concentration on the structure and properties of the membrane, attention was turned to the effects of drying time and gelation-bath temperatures on the membrane. The results again have been interpreted in terms of the model proposed for the gelation process.

Drying Time. Extending the drying time after casting and before aqueous gelation causes a diminution in membrane thickness, gravimetric swelling ratio, and water transport rate (Table III). These effects are attributed to the increased droplet compaction which occurs during extensive desolvation and the resultant decrease in the volume of the unit cells and the amount of capillary water contained therein. The reason for the sudden decrease in salt retention capacity which occurs at a drying time of approximately 10 min. is the same as that for the similar decrease which occurs in the case of membranes which are cast from concentrated solutions (see previous section). After the point of incipient gel formation has been passed, aggregation and compaction have progressed to such an extent that the walls of the cells have thickened enough to limit syneresis and capillary depletion during heating and pressurization. For this reason some capillaries will remain in the active layer, and salt retention will decrease. At the same time the rate of transport decreases owing to a substantial decrease in the amount of capillary water contained in the substructure.

Gelation-Bath Temperature. Increasing the gelation bath temperature produces very clear changes in the structure and osmotic behavior of semi-

TABLE III
Drying Time Effects[a]

Drying time, min.[b]	Description of membrane	Wet thickness of unheated membrane, mm. × 10²	Gravimetric swelling ratio of unheated membrane, wet wt./dry wt.	Rate of water transport, ml./cm.²-day[c]		Salt retention, %[c]
				Deionized water feed	0.6M NaCl feed	
1	Opaque-opalescent (microgel blending into ultragel)	13.9	2.88	116	72	98.0
3	Opalescent (ultragel)	12.2	2.98	84	50	98.6
5	Opalescent (ultragel)	10.2	2.65	86	54	98.8
10	Opalescent-clear (ultragel)	8.5	2.41	80	50	96.3
20	Clear (ultragel)	5.8	1.75	72	50	75.1
30	Clear (ultragel)	5.3	1.60	50	36	71.5

[a] Casting solution composition: cellulose acetate, 22.2 g.; acetone, 66.7 g.; water, 10.0 g.; ZnCl₂, 5.0 g. (doctor blade gap 0.25 mm.).
[b] Drying time = interval between casting at −11°C. and immersion into gelation bath (0°C.).
[c] Rate of water transport and salt retention at 102 atm. pressure for heated membranes (86°C. for 5 min.).

TABLE IV
Gelation-Bath Temperature Effects[a]

Gelation-bath temperature, °C.	Membrane appearance	Intrinsic viscosity [η] of cellulose acetate in acetone–water (66.7:100)[b]	Wet thickness of unheated membrane, mm. $\times 10^2$	Gravimetric swelling ratio of unheated membrane, wet wt./dry wt.	Rate of water transport, ml./cm.^{2} day[c]		Salt retention, %[c]
					Deionized water feed	0.6M NaCl feed	
0	Opalescent	0.985	9.2	2.85	84	50	98.6
10	Opaque	0.940	14.0	3.80	83	50	97.1
25	Opaque	0.905	22.8	5.80	90	58	90.1
40	Opaque	0.745	31.0	6.98	118	74	81.1

[a] Casting solution composition: cellulose acetate, 22.2 g.; acetone, 66.7 g.; water, 10.0 g.; ZnCl$_2$, 5.0 g. (doctor blade gap 0.25 mm.).
[b] Measured at the corresponding gelation bath temperature.
[c] Rate of water transport and salt retention at 102 atm. pressure for heated membranes (86°C. for 5 min.).

permeable membranes of cellulose acetate.   The ultragel structure which
results from the immersion of casting solution into water at 0°C. rapidly
gives way to a microgel type at higher gelation bath temperatures (Table
IV).   Membrane dimensions, gravimetric swelling ratios, and material
transport rates all increase with increasing gelation-bath temperatures.
These effects are explicable on the basis of gelation occurring at an early
phase in the coacervation process.   The rapid depletion of the solvent sur-
rounding the polymer droplets ensures contact between adjacent droplets
before much compaction has occurred.   It may be assumed that once con-
tact between coacervate droplets has occurred, particularly in a medium
which favors interdiffusion of polymer molecules into adjacent droplets,
further compaction will no longer be an unhindered process.   This is be-
lieved to be the reason for the dramatic increases in thickness of membranes
which are immersed in gelation baths at high temperatures.

Inhomogeneity of Gel Structure—The Active Layer

It became apparent, at an early stage in the development of semi-perme-
able membranes of cellulose acetate, that differences exist between the top
or "active" and bottom surfaces of the film.   The top or active surface
refers to the surface first exposed to water when the glass plate with the film
of casting solution is immersed in the ice-water bath.   In particular it was
noted that: (1) desalination is only effected when the "active" surface is in
contact with the saline solution;[9] (2) osomotic removal of water from the
gel structure occurs only when the active surface is brought into contact
with alcohols, saline solutions, etc.;[9] and (3) electron microscopy indicates a
grainy substructure and a clear top layer.[15]   The existence of a similar layer
in the case of nitrocellulose membrane has been discussed by Elford.[2]
Since the active layer is all-important with respect to desalination, knowl-
edge of the origin, extent, and nature of this structure becomes one of the
prerequisites to the understanding of the mechanism(s) of salt retention and
water permeation.

Origin of the Active Layer.   Differences between the nature of the top
or active and substructure layers of the membrane are readily explicable in
terms of the charged droplet model which has been proposed.   In a dilute
polymer solution, the spherical droplets are completely covered by solvent
molecules.   As desolvation proceeds, contact between droplets occurs and
excess solvent disappears.   Because of surface tension effects, the droplets
tend to lose their spherical shapes at the air–solution interface and assume
flattened configurations.   As a consequence, the surface droplets may be
somewhat larger in diameter and of lesser depth than droplets located in the
interior of the casting solution.   When the casting solution is immersed in
the ice-water bath, extremely rapid desolvation occurs.   The droplet walls
contract rapidly and rupture, releasing encapsulated acetone.   Because of
the lesser depth of the droplets at the casting solution surface and the lack of
restraining influences of other droplets above, contact between top and bot-
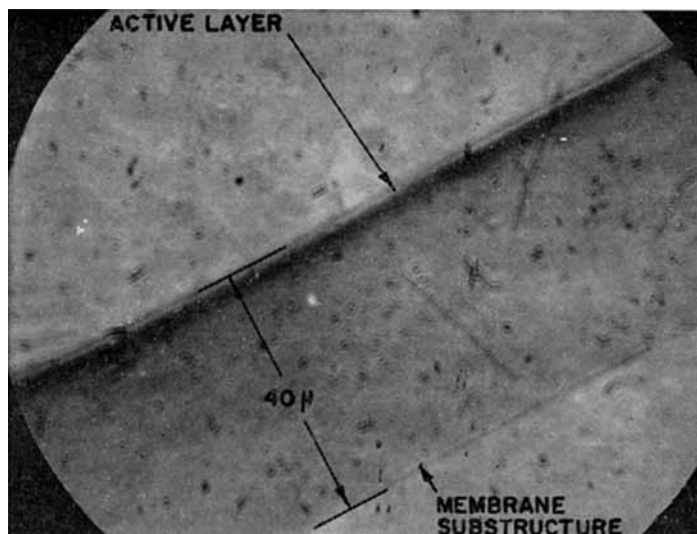tom surfaces of the flattened droplets is favored.   Thus the surface droplets

Fig. 3. Cross-section of a dyed and leached hydrolyzed desalination membrane.

tend to exist as compacted masses of polymer molecules rather than the open-cell foam structure which predominates in the substructure. These differences between surface and substructure layers are illustrated in Figure 2. In terms of events taking place on the microcrystalline level it is possible that the extremely rapid desolvation of flattened polymers droplets which occurs at the surface of the casting solution will result in the simultaneous formation of many crystalline nucleation sites such that no given crystallite can achieve great size. A similar hypothesis has been made in the case of viscose rayon.[16] The large number of small crystallites will severely restrict the motion of the amorphous regions which are spaced between the crystallites. The net result of rapid desolvation of flattened surface droplets may be the formation of a highly crystalline structure in which the capacity for displacement between any two polymer chains will be small. The crystallinity of the active layers will be further discussed below.

Depth of the Active Layer. Before any attempt can be made to determine quantitatively the depth of the active surface, the criteria which distinguish between active and substructure layers must be delineated. The active layer, as referred to in this and other papers of this series, is that portion of the membrane which is capable of effecting desalination of a $0.6M$ saline feed solution at 102 atm. Two techniques have been employed to establish the depth of the active layer: differential dyeing of active and substructure layers and stepwise hydrolysis of the active layer with subsequent salt permeation studies.

Much work has been done in the field of cellulose chemistry on the presence of "skin and core" effects in viscose rayon fibers.[16,17] When a polymeric material (be it fiber or film) is immersed in a solution of dye, the dye will penetrate the more open regions of the polymer structure first. Given suffi-

TABLE V
Surface Hydrolysis of Cellulose Acetate Membranes[a]

Duration of hydrolysis, min.	Rate of water transport water flux, ml./cm.²-day		Salt retention, %[b]	Acetyl content, %
	Fresh water feed	0.6M NaCl feed		
0	96	50.0	98.9	39.3
1.0	—	58.0	99.0	39.2
2.5	—	77.2	98.3	38.3
5.0	—	86.0	86.9, 50	37.1, 34.7
10.0	176	160.0	0.0	—

[a] Hydrolysis by aqueous 0.4M NaOH.
[b] Test conducted with 0.6M NaCl at 102 atm.

cient time the denser regions may also be permeated by these molecules. If, after both regions have been dyed, the polymer is immersed in a solvent for the dyestuff, the dye molecules will be preferentially leached from the more porous portion of the polymer, and if the leaching process is carefully controlled, will remain in the denser regions. It was assumed, a priori, that the active surface would constitute the denser region and hence would hold the dye more tenaciously. Since it had not been established that the skin-core effects found in viscous rayon fibers were analogous to the active-substructure layers in the cellulose acetate desalination membrane, a dye system was selected (Victoria Blue B and Calcomine Brilliant Yellow) which had proven successful with viscose rayon. The dyes were applied to a cellulose film which had been fabricated by hydrolysis of a cellulose acetate desalination membrane.[18,19] After dyeing and differential extraction the dense layer appeared as a green band 4 μ thick or about 10% of the total thickness of the dried membrane (Fig. 3). This dye system requires a dioxane–water solvent which is also a solvent for cellulose acetate. Consequently, dyeing of the cellulose acetate membranes was carried out with a water solution of Diphenyl Fast Red 5BL Supra I and Chlorantine Fast Green BLL. Dyeing and leaching of the cellulose acetate membranes also showed a 4 μ top layer, indicating that the depth of the top layer was identical for both cellulose acetate and the derived cellulose membranes.

It then remained to be demonstrated that the top layer found in the cellulose acetate membranes by dyeing corresponds to the layer effective in desalination. This demonstration was accomplished by stepwise hydrolysis of the acetate groups from the top surface to produce a salt-permeable cellulose layer. It was expected that the salt retention would drop precipitously when the active layer had been completely hydrolyzed. The thickness of the active layer could then be calculated from the difference in acetyl content of the whole membrane before and after hydrolysis of the active layer. Hydrolysis of the top surface of the membrane with 0.4M sodium hydroxide produced the expected results (Table V). Between 2.5 and 5.0 min. of

TABLE VI

Swelling Relationships of Partially Hydrolyzed Cellulose Acetate Membranes[a]

Hydrolysis time, min.	Hydroxyls/ glucose unit	Thickness, mm. $\times 10^2$		Diameter, cm.		Volume, mm.^{3}		Volume wet/volume dry
		Wet	Dry	Wet	Dry	Wet	Dry	
(Starting material) 0	0.64	8.1	6.6	7.7	5.52	9.86	5.73	1.72
10	2.58	8.1	6.1	7.4	4.95	9.48	4.75	1.99
20	2.87	7.6	5.1	7.3	4.85	8.74	3.88	2.25

treatment, the salt retention began to drop, and became zero after 10 min. From the two experiments with 5 min. treatment, two different active layer thicknesses were calculated.   The difference in acetyl content for the samples which had been hydrolyzed for 5 min. is apparently related to the fact that 5 min. was close to the time required for penetration of the active surface.   Once this surface was penetrated, the caustic solution rapidly permeated the substructure and caused a rapid change in acetyl content within a short time, thus reducing the accuracy of the thickness calculation.   At any rate, evidence from both dyeing and hydrolysis studies indicates that the thickness of the layer which is active in desalination is between 5 and 12% of the total membrane thickness.

Secondary Gel Structure

Parameters Affecting the Formation of a Secondary Gel Structure

Subjection of the primary gel structure to thermal and pressurization treatments causes the formation of a more compact and less permeable gel which may be referred to as the secondary gel structure.   The effects of these treatments are discussed in the following sections.
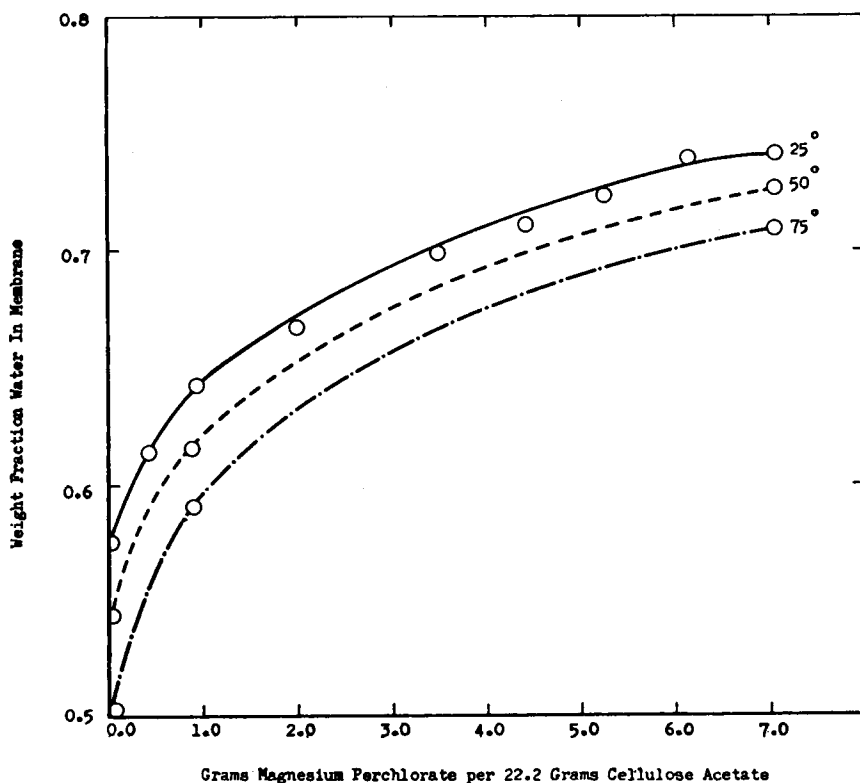

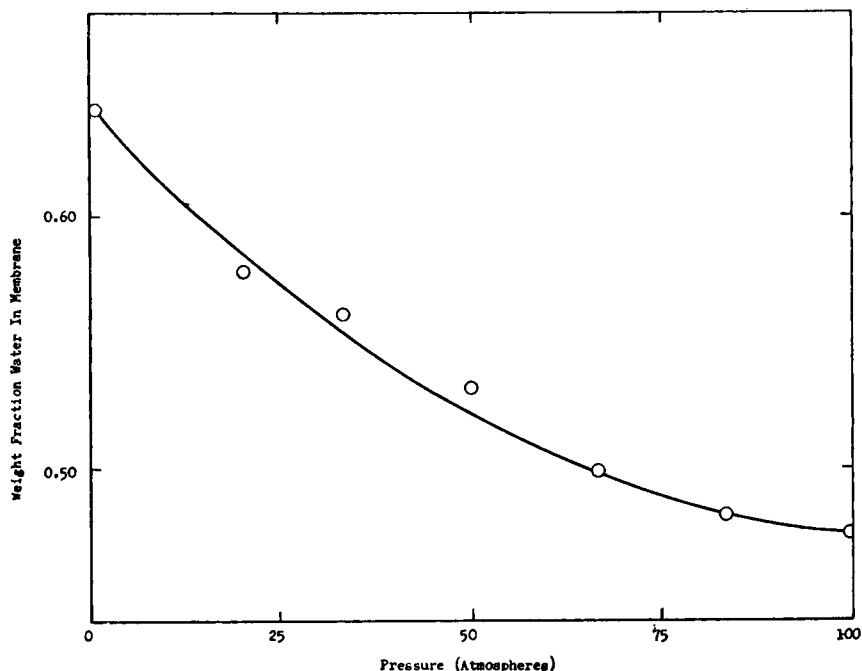Fig. 4. Membrane water content as a function of temperature.

Fig. 5. Membrane water content as a function of pressure.

Thermal Treatment. Films of cellulose acetate in the primary gel stage exhibit high water transport rates but low salt retentions. Heating of these films in water results in shrinkage accompanied by loss of water (Fig. 4). This syneresis probably results from the formation of greater numbers of or stronger ligand bonds between polar sites (hydroxyl and acetate groups) on the polymer chains. Heating introduces the energy required to bring these sites into bonding distance. After conversion to the secondary gel structure, the membranes exhibit reduced water transport rates and high salt retentions.

The water in the gel structure exists in two different forms; that which bonds directly to specific groups in the polymer structure (bound) and; that which fills interstices within the structure without any specific solvent-polymer interaction (capillary). The concept of bound water will be treated more fully in the third paper of this series. It was assumed, *a priori*, that the water which is expelled from the gel structure is primarily of the capillary type, i.e., unassociated water which still retains its capacity for dissolving salt ions. In support of this concept was the fact that heat treatment improved the capacity of the membrane for salt retention.[9]

Pressurization. The membrane is subjected to 102 atm. pressure in the desalination process, during which time additional water is eliminated from the gel structure (Fig. 5). Most of the water which is removed from the membrane is believed to be of the capillary type since capillary water is not

only less tightly held than is bound water but also constitutes the bulk of the water present in the porous substructure of the membrane.

Crystallinity of Secondary Gel Structure of Cellulose Acetate

The x-ray diffraction spectra of the cellulose acetate membrane matched those which have been obtained by other workers[20] for cellulose triacetate II.   The equatorial tracing is quite diffuse, and only the important cellulose acetate interferences (101, 10$\bar{1}$, and 002 planes) are evident (Fig. 6).   All of the samples have poor local order as a result of heterogeneity in the molecular segments along the chain molecules, but the spectra of fine fibers and thin films are more highly resolved and hence indicative of a somewhat more ordered structure.   It is the consensus of the workers in the field that cellulose diacetate can crystallize in the same arrangement as cellulose triacetate, the unit cells of which are well established.[16,17]
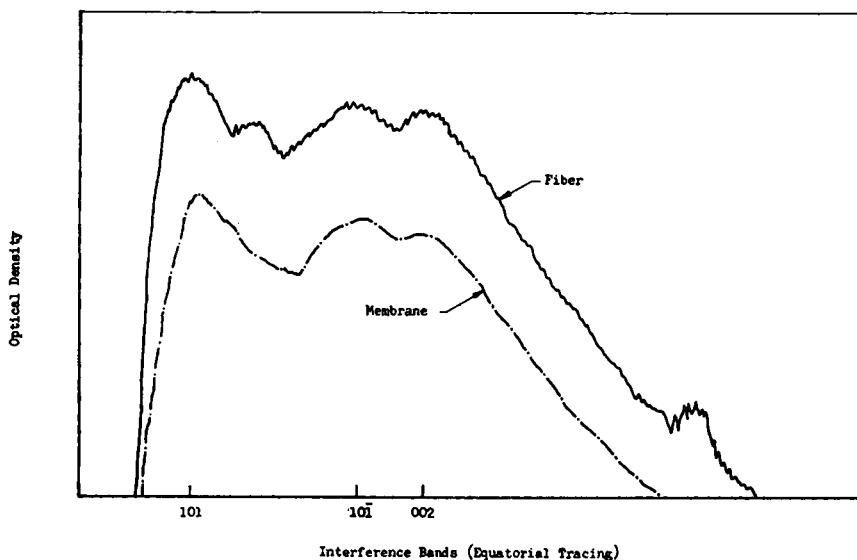

Fig. 6. X-ray diffraction spectrum of the desalination membrane.

The degree of crystallinity in the gel substructure appears to be quite low as evidenced by the diffuse bands of the x-ray diffraction spectra.   However, crystallites are believed to be present in significant numbers in the active layer.   If this layer were completely amorphous, it appears likely that pores would exist which are large enough for the passage of solvated salt. Therefore, it was postulated that the active layer consisted of a large number of small crystallites which held the interchain distances (even in amorphous regions) within narrow limits.

A method of establishing the crystalline content in cellulosic materials by the technique of deuteration has been described in which the extent of deuteration is determined by infrared spectroscopy.[21]   Infrared spectra have

been made of undeuterated, deuterated, and rehydrogenated thin (presumably composed entirely of active layer) films of cellulose acetate (Fig. 7). Four specimens of the thin membranes exhibited an average crystallinity of 64%. In order to compare the results of this test with literature values for crystallinity of cellulose, a thin cellulose acetate membrane was hydrolyzed in 0.4M ethanolic NaOH and subsequently deuterated and rehydrogenated.
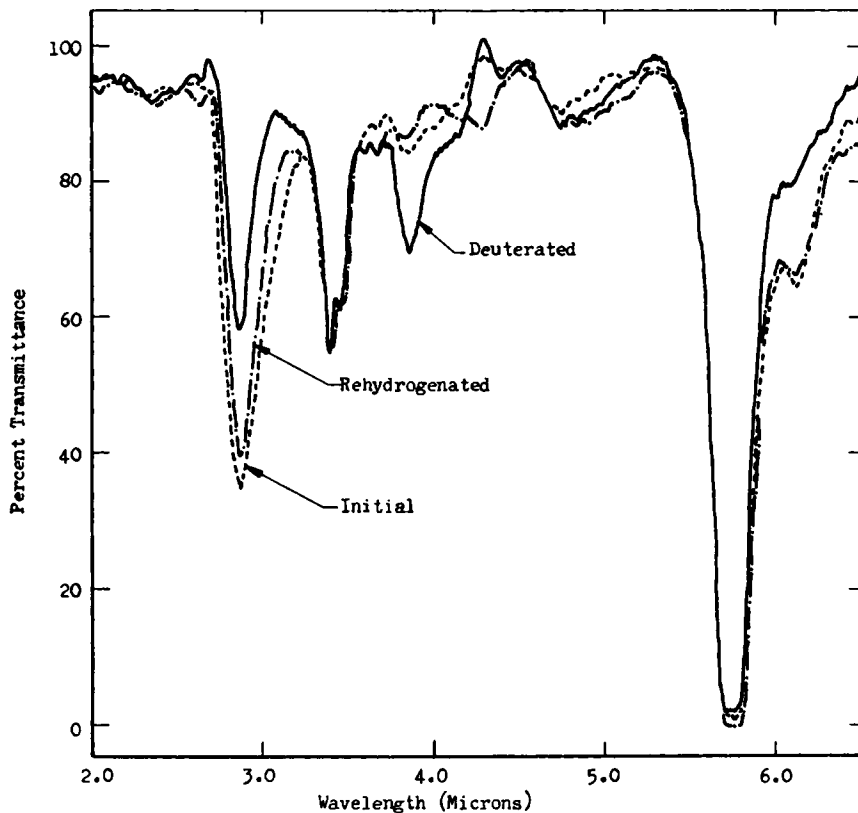

Fig. 7. Infrared spectrum of deuterated secondary cellulose acetate.

This yielded a result of 61.5% crystallinity and appeared to confirm the previous results with the acetate. Accordingly it is felt that the limited accessibility to D_2O exhibited by thin films of cellulose acetate indicates a high degree of crystallinity consistent with the *a priori* assumptions which have been made.

Mechanism of Water Transport

The preceding sections have described the effects of various fabrication parameters and handling processes on both primary and secondary gel structures. This section in turn describes the relationship which has been established between the rate of water transport and the degree to which a
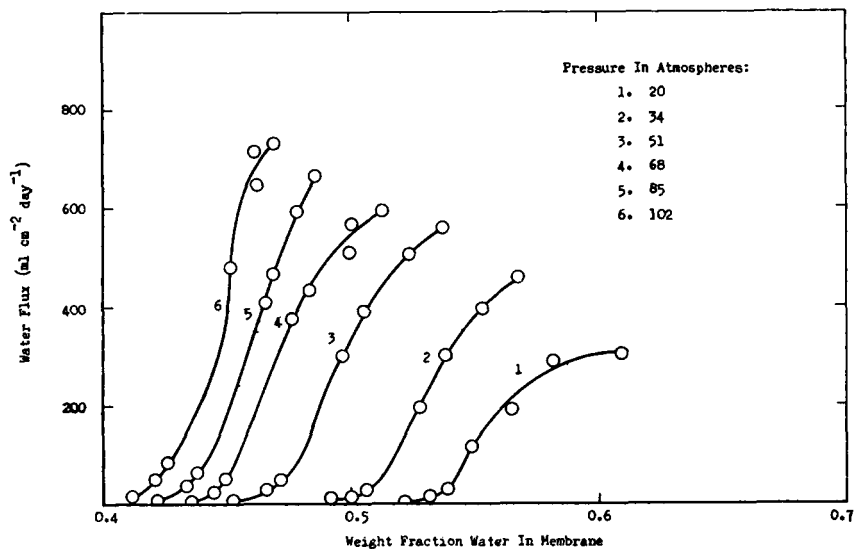
Fig. 8. Water flux as a function of membrane water content and pressure.

membrane is swollen.   Increases in product flux with membrane water content have previously been observed for ultrafiltration membranes.[22]

The flux of water through a desalination membrane was found to increase with its water content (Fig. 8).   The fluxes of water through the membranes were obtained (within 10 min.) after the desired pressures had been attained.   The reasons for having measured initial rather than equilibrium flux values are; first, the membrane water contents were determined under these same circumstances and; second, it was desirable to obtain values before realignment and compaction of the gel structure by the applied pressure had complicated initial relationships.

The most important facts to emerge from the study are: (1) the higher the pressure, the lower the membrane water content (Fig. 5) and (2) along a given isobar there exists a certain water content above which a dramatic increase in water flux occurs (Fig. 8).   These facts may be interpreted as follows.   Pressure causes compaction of the primary gel structure and exclusion of much of the water.   As a result of the gel compaction, intermolecular distances are decreased, additional crosslinks are formed, and desalination improves.   The abrupt change in slope along the flux versus water content isobar may be interpreted on the basis of a change in the mechanism of water transport from a solution type, involving interaction of water with the membrane to form bound water, to a Poiseuille type, involving viscous flow of capillary water through pores.

Since those membranes which are capable of desalination are all in the region of high resistance to flow, it may be concluded that water is transported across the membrane by a solution rather than by a viscous flow mechanism. Quantitative treatments of the concepts of ion exclusive by bound water and

water permeation by solution in the membrane will be developed in the third paper of this series.

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Résumé

On a effectué une étude quantitative de l'influence de certains paramètres sur la structure de la membrane gel; leur importance pour l'efficacité de la desalinisation avait antérieurement été établie empiriquement. On montre que la composition des solutions de polymère, les températures de fabrication et la pression employée pendant la désalinisation influencent le gonflement du gel. Sur la base d'un mécanisme de transport, on explique la relation qui a été trouvé entre la teneur en eau et la vitesse du transport d'eau à travers les membranes semiperméables d'acétate de cellulose.

Zusammenfassung

Eine quantitative Untersuchung des Einflusses gewisser Faktoren, deren Bedeutung für das Verhalten von Membranen bei der Entsalzung schon früher empirisch festgestellt worden war, wurde durchgeführt. Die Zusammensetzung der Polymerlösungen, die Fabrikationstemperaturen und der Druck während der Entsalzung stehen insofern in Beziehung zueinander, als sie alle das Quellungsverhalten der Gelstruktur beeinflussen. Die Beziehung zwischen dem Wassergehalt von halbdurchlässigen Celluloseacetatmembranen und der Geschwindigkeit des Wassertransports durch dieselben wird auf der Grundlage eines Lösungstransportmechanismus erklärt.