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MECHANISM OF WATER TRANSPORT THROUGH

REVERSE OSMOTIC MEMBRANES

2-2

A Thesis

Presented to the Department of Chemistry Brigham Young University

In Partial Fulfillment

of the Requirements for the Degree

Master of Arts

by Cheryl Kay Murphy August 1969 This thesis, by Cheryl Kay Murphy, is accepted in its present form by the Department of Chemistry of Brigham Young University as satisfying the thesis requirement for the degree of Master of Arts.

(Completion Date)

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iii

TABLE OF CONTENTS

ACKNOWLE	DGEMI	EN	rs	0	0	0	•	0	٥	0		0		0	0	٥	o	0	•	0	٥	0	0	0	0	0	0		iii
LIST OF	TLLU	STI	RAI	CIC	ONS	5	0	•	÷	•	•	6	٠	Ð	•	•	٠	*	۰	•	٠	0	0	Ð	9	0	0	0	v
INTRODUC	TION	0		٩	٥	0	0	0		0	c	e			0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
LITERATU	IRE RI	EVI	IEV	V	٥		•	0	ø	0		0	0	o		0	0	ø	0	0	٥	0	٥	ø	o	0	0	0	3
EXPERIME	NTAL	D	0		0	٥		•	0	0			0	8	•	٥	٥			•	9	0	0	0	0	0	0	0	10
RESULTS	AND I	DIS	SCI	JSS	SIC	N		e	0	0	Ð		•	0	•	•	•		٥	0	0	0	٥	9	0	0		0	13
CONCLUSI	ON .	0	9		0	0 •	0	•		0	•	0		•	0	0	0	0	0		•	0		0	0	0	0	0	25
REFERENC	ES 。	D	Đ	e		0		0	a	ø	•	0	•	0		•		0	0	Ø	8	•	o	a	0	0	٩	0	28

LIST OF ILLUSTRATIONS

Figure		Page										
1.	Diagram showing different direction of fluid flow in osmotic systems	2										
2.	Membrane Cross Section	7										
3.	Diagram of a portion of a cellulose triacetate polymer showing the <i>A</i> -linkage and the three acetyl groups per anhydroglucose unit											
4.	Model of M-D Glucose Pentaacetate	12										
5.	Schematic drawing of water moving down a cellulose triacetate polymer by the simultaneously bonded hydrogens	14										
6.	Graph showing the chemical shift of water with ~ -D Glucose Pentaacetate in Chloroform	16										
7.	Graph showing chemical shift of water with 0.1752 M <pre>Q-D GPA in CHCl3 at various temperature</pre>	17										
8.	Graph showing that increased water concentration also increases bonded water molecules around tetrahydropyran .	18										
9.	Graph showing the identical and non-interacting hydrogen bonding sites for water in THP	19										
10.	Graph showing at least 18 water molecules on the CTA polymer by NMR	21										
11.	Graph showing the calibration curves of Q-D GPA and phenol in CCl4 by osmometry	23										
12.	Graph showing the number of hydrogen bonding sites for phenol on <-D GPA in CCl4 by osmometry	24										
13.	Graph showing the enhanced affinity for phenol to bind <-D GPA after first site is bound	26										

MECHANISM OF WATER TRANSPORT THROUGH REVERSE OSMOTIC MEMBRANES

Introduction

The abundance of pure water is elementary to the progress of man. The oceans provide the world with its most abundant supply of water, but the 35,00 ppm salt content of sea water prevents its use for many of man's needs. Other sources of water supply are the lakes, rivers, and streams that man has so thoroughly polluted with detergents, bacteria, and industrial waste that they must be purified to make the water potable. With seventy-three per cent of the earth's surface covered by water, there is more than enough water to supply the needs of man forever if it can be reclaimed for repeated use on an economical basis.

Water in its various states of pollution has been given three general classifications. Brackish water is water in which the salt content is higher than can be tolerated for drinking. The desirable limit is 500 ppm in salt content while 1000 ppm is a permitted limit. It is recommended or required that this water be put through a desalination process before it is used in domestic and municipal utilities.

Salt water generally refers to water containing more than 10,000 ppm of dissolved solids. The chemical composition of brackish and salt water varies widely with regard to the nature and quantity of each dissolved salt from one source to another. The chemical composition of sea water is very uniform. The total quantity of dissolved salt is generally understood to mean water that contains 35 g of dissolved salt per liter. The total quantity of dissolved salts varies from place to place, but the nature of the dissolved salts and the relative percentage of each one are practically constant.

A biological method of water purification is osmosis through a cellulosic membrane. If a semipermeable membrane separates two solutions of different concentrations, the diffusion of the fluid tends to equalize the concentration on both sides of the membrane. This diffusion is defined as osmosis. If the two solutions and membrane are confined, then the flow of the fluid into the more concentrated solution causes an increase in the pressure on the side containing the more concentrated solution. The pressure required to just stop the flow of the fluid through the membrane is called osmotic pressure.

If a pressure greater than the osmotic pressure is applied to the concentrated solution, a reverse flow of the fluid through the membrane is obtained. This process is appropriately called reverse osmosis and results in the purified fluid permeating to one side of the membrane.





The fact that no phase change is necessary in the reverse osmosis process gives it a distinct advantage over many other processes. Generally the removal of the pure water from the saline solution is by transport in a phase different from that of the solvent. In solvent extraction like reverse osmosis there is no change in the liquid phase of the solvent and therefore energy costs may be held at a considerably lower level.

In the desalting program of the Office of Saline Water Research, under the authorization of the United States Department of Interior, the development of the reverse osmosis process is receiving priority. This process has not only attracted very broad industrial interest in the desalination program but also appears to hold potential in other areas. It offers a process for not only desalting mildly brackish waters, and eventually sea water, but it is also being extended to work on special problems, such as irrigation return flows, acid mine waters, and the recovery of potable water from treated sewage. Reverse osmosis is being applied in the recovery of valuable process chemicals, concentration of fruit juices and beverages, dewatering crude oil, and producing special waters for industrial use.

Literature Review

Since reverse osmosis is an economical process for water desalination, the problem becomes that of finding a suitable semipermeable membrane which meets the following three requirements: (1) It must adequately desalinize a given feed water. (2) At reasonable pressures, it must have an adequate desalinized water flux (flow rate per unit area of membrane). (3) It must possess the above two characteristics for a reasonable length of time. If the mechanism of

3

water transport were to be determined, then the information could be used in the designing of semipermeable membrances for specific problems.

There are two pure mechanisms or hybrids thereof into which all theories regarding material transport through semipermeable membranes may be grouped. These are either Poiseville (viscous) flow through pores, or solution flow by virtue of physical-chemical interaction. The Poiseville flow theory is based on the assumption that pores exist prior to the introduction of the permeant species, and the permeant passes through the membrane with little or no chemical affinity between the permeant species and the membrane. Whether the permeant species are transported or retained depends on their respective sizes relative to the membrane's pores.

In solution transport the permeating substance has an affinity for certain functional groups of the membrane. This results in the formation of complexes between the species and the membrane. The partial molal volume of the permeant species will generally exceed zero in such a complex and the host membrane will swell to accomodate the complex. The permeant species will then be further transferred by a series of displacement reactions until it reaches capillary spaces. At this juncture the mechanism of transport will be by Poiseville flow due to its lower energy requirement.

If Poiseville (viscous) theory of flow through pores were the mechanism of transport, it would mean that the membrane must discriminate between two substances on the basis of size. This is readily imagined when the distinction is between water and colloidal particles or dissolved substances of very high molecular weight. In this situation the membrane would function as a sieve, retaining the larger particles, while the smaller water molecules would pass through to the other side of the membrane.

It is rather difficult to believe, as pointed out by Breton (1957), that any sieve could make a sharp distinction between water molecules in various states of aggregation and small ions in various states of hydration. Data by Reid and Breton (1959), Reid and Kuppers (1959), Keiiin (1965), and others show that cellulosic membranes apparently discriminate between permeant ions and molecules by their chemistry rather than their size. This supports the solution-diffusion mechanism and this is the general theory applied to explain the movement of solvent through the semipermeable membrane.

From salt rejection data the desalination capacity of a membrane may be expressed in several ways. The statement of the desalinizedwater salt content, which can be compared with the U.S. Public Health Service standard of 500 ppm or less, must be accompanied by a statement of the feed-brine concentration in order to give adequate information.

Another expression indicating desalination capacity is the per cent salt rejected. This is defined as 100 times the difference between the feed- and product-water concentration divided by the feed-water concentration. The use of per cent salt rejection tends to obscure important changes in membrane performance. For example, in order to produce fresh water with only a 500 ppm salt content from seawater requires a 98.6% salt rejection. However, desalinized water having 1500 ppm of salt would be unacceptable but if produced from seawater the salt rejection would be 94.5%.

The salt-reduction factor is defined as the feed-water concentration divided by the product-water concentration. This is a more sensitive term, the salt-reduction factor, as it is the reciprocal of the relative permeability (Keilin, 1965). Either of these terms reflects slight changes in membrane fabrication or other variables affecting desalination.

In 1957 Reid and Breton reported that cellulose acetate was a membrane which would permit water to pass through but rejected salt and certain other impurities. Asymmetric cellulose acetate was used to establish a criteria for the desalination and water flux of semipermeable membranes. Asymmetric cellulose (2.5) acetate membranes consist essentially of a thin dense layer of cellulose (2.5) acetate (39.8% acetyl content), which is the salt rejecting layer, on top of a relatively thick porous layer of cellulose (2.5) acetate.

The number 2.5 refers to the degree of substitution of a cellulose derivative and is defined as the average number of molecules of substituent introduced for each anhydroglucose unit. The percentage 39.8 refers to the degree of substitution expressed as the per cent of substituent groups or element. Taking W as the formula weight of the substituent group and W_1 as the net increase in formula weight of cellulose resulting from the introduction of one substituent group in one anhydroglucose unit (162 parts of cellulose), the percentage Y_W of substituent is determined by the equation:

$$Y_{W} = \frac{100 \text{ SW}}{162 + \text{SW}_{1}}$$

The degree of substitution, S, is determined by the equation:

$$S = \frac{162 \text{ Y}_W}{100 - \text{Y}_W \text{W1}}$$

The asymmetric (meaning a thin active layer on top of a thick porous layer) membrane has given in dynamic flow through equipment, at sufficiently high feedwater circulation rates (to minimize concentration polarization), salt rejection as high as 99.5% with fluxes in the range of 20 to 30 gfd (gallon per square foot per day), at pressures of 600-800 psi, for salt concentration up to 5000 ppm.



Fig. 2.--Membrane Cross Section

A great deal of research has been done on modifications and refinements in membrane technology which have resulted in membranes tailored to fit a variety of applications. Water flux and salt rejection can be varied over a wide range by selective control of manufacturing conditions.

Since the morphology of the membrare determines its water flux and salt rejections, experiments were made with specific group substitution on cellulose. These results were reported in the 1966 Saline Water Conversion Report published by the Department of Interior. (1) Cellulose triacetate (44.8% acetyl) gave favorable results when evaluated as ultrathin membranes. They gave a salt rejection of over 99% at 1500 psi for a 3.5% NaCl solution. (2) Addition of substituents forming a pendant alkyl group larger than one carbon atom always decreased the water flux. Even small amounts of larger pendant alkyl or aryl groups on cellulose tend to block the transport of water molecules. (3) The most active substituents for promoting water transport are those containing several oxygen, nitrogen, or sulfur atoms grouped closely together.

P.S. Francis (1966) reported that the addition of a very-shortchain substance such as sucrose octaacetate to a cellulose triacetate membrane reduced the water flux appreciably. This indicates that the water movement is along the polymer chains rather than across them. If water is preferentially transported along the cellulose molecule, the presence of very-short-chain fragments of practically identical structure should decrease the flow rate.

If water were passed from chain to chain rather than down the chain, there would be the same number of jumps no matter how long or short the polymer chain. However, since shorter chains caused a reduction in water flux, the rate determining step must be the jumping from the end of one chain to another. The presence of shorter chains would require the water to make more jumps.

Work at Aerojet-General (Saline Water Conversion Report, 1966) supports the evidence that the rate-determining step takes place inside the membrane as diffusion rather than at the surface as absorption. The studies showed that the activation energy of water transport through the membrane was independent of pressure, feed solution type, or concentration.

In 1959 Reid and Breton postulated that the mechanism of water transport through cellulose acetate was by hydrogen bonding to the carbonyl oxygens. Water molecules on the active side of the membrane would be aligned by hydrogen bonds. The water would then migrate to the other side of the membrane by being transferred from one hydrogen bonding site to another with pressure being the driving force. Reid and Breton further postulated that ions and molecules which could combine with the membrane by hydrogen bonding would be transported across the membrance by being transferred from one hydrogen bonding site to another.

A strongly electronegative element having one or more unshared pairs of electrons is able to form an electrostatic attraction with the positive nucleus of a hydrogen atom which has been activated by the covalent bonding of a strongly electronegative element. The electrostatic attraction is called a hydrogen bond.

The strongest hydrogen bonds are formed when: (a) the hydrogen atom is covalently bonded to strong electronegative elements, such as fluorine, oxygen, or nitrogen in that order; (b) the electronegative element with the unshared pair electrons has a highly exposed and highly concentrated electron shell. These are the electronegative elements nitrogen, oxygen, and fluorine.

The carboxylic oxygens in the acetyl groups on a cellulosic membrane have an exposed and concentrated electron shell. The hydrogens in water activated by the electronegative oxygen are attracted to the acetylated cellulose which could provide sites for the formation of hydrogen bonds for the transportion of water through the membrane as postulated by Reid and Breton.

This mechanism is supported by Lonsdale, Merten, and Tagami (1967) in their work with phenol which showed a higher permeability than sodium chloride in the membrane. The permeability coefficient for phenol is reported as $4 \times 10^{-8} \text{ cm}^2/\text{sec}$ with sodium chloride as $3 \times 10^{-11} \text{ cm}^2/\text{sec}$.

Blunk (1964) reported a lower percentage rejection than NaCl for hydrogen peroxide, ammonium hydroxide, <u>n</u>-butanol, phenol, nitric acid, hydro-fluoric acid, and others, all of which were capable of hydrogen bonding.

Experimental

Ultrathin layers of cellulose triacetate (CTA) membranes are reported (Cohen and Riggleman, 1969) to have very high water flux rates combined with very high salt rejections. CTA also has the important advantage of having a much greater resistance to biological degradation due to its composite membrane than cellulose acetate. CTA has three acetyl groups per anhydroglucose unit of cellulose and the carbonyl oxygens are postulated as providing a site for hydrogen bonding.



Fig. 3.--Diagram of a portion of a cellulose triacetate polymer showing the *B*-linkage and the three acetyl groups per anhydroglucose unit.

For the above reasons CTA was chosen as the research polymer. Water and phenol were used in order to determine the plausibility of the acetyl oxygens as hydrogen bonding sites in the postulated water transport mechanism.

10

Model

A Fisher Scientific Space-filling Model of CTA was constructed to visually determine if water or phenol could be passed down the chain by the oxygens in the acetyl groups.

Nuclear Magnetic Resonance

According to the theory of nuclear magnetic resonance (NMR) the hydrogen bonding between water and the acetyl oxygens should be detectable by the change in the chemical shift of water protons. This change in the chemical shift is due to the environmental change of the hydrogen in water. A Varian A-60A NMR Spectrometer with a temperature probe and tetramethylsilane (TMS) as the internal reference were used.

Reagent grade chloroform (CHCl₃) was chosen as a solvent because it would dissolve the acetylated saccharides and would form a hydrogen bond with the oxygen in water leaving the hydrogens free to form hydrogen bonds with the acetyl oxygens.

The trace amounts of ethanol were removed from the CHCl₃ by washing three or four times with half the volume of water and drying it over anhydrous calcium chloride.

In order to prepare a 0.1855 M (nearly saturated) solution of water in CHCl₃, it was necessary to sonicate the solution at 75 Watts for 3 minutes. The water aggregates were broken apart and the NMR showed a monomeric peak at 1.59 x 10^6 6 while aggregated water has a peak at 4.61 x 10^6 6 with respect to TMS.

Solutions of various concentrations were prepared by dissolving the acetylated saccharide, \neg -D Glucose Pentaacetate (\neg -D GPA) (Eastman Organic Chemicals), into a 0.1855 M solution of water in CHCl₃.



Fig. 4 .-- Model of -D Glucose Pentaacetate

Tetrahydropyran (THP) ('Baker Grade' J.T. Baker Chemical) is a six membered ring including an oxygen. By determining the affinity of the water molecule for THP, the information could be considered in the interpretation of water binding to the CTA polymer.

A specific amount of THP was dissolved into various concentrations of a sonicated water-CHCl₃ mixture.

Methyl Sulfoxide (DMSO) and <u>p</u>-Dioxane are the only two solvents known that will dissolve both CTA and water. However, in the NMR spectrum of a solution of CTA-water-dioxane, the water peak is obscured by dioxane peaks. For this reason DMSO (Eastman Organic Chemicals) was used in the titration data of CTA (Eastman Organic Chemicals) and water.

Osmometer

A Mecholab Osmometer Model 301 with a 39°C, non-aqueous thermistor was used to determine the number of bonding sites on the acetylated saccharide.

Calibration curves were determined from solutions of phenol ('Baker Analyzed' Reagent) and α -D GPA dissolved in reagent grade carbon tetrachloride (CCl₄). The number of bonding sites was determined by mixing various concentrations of the phenol solution to a constant concentration of \prec -D GPA solution. The data were then plotted as \checkmark versus the logarithm of the phenol concentration.

Figures for $\overline{}$, defined as the moles of combined phenol divided by the total moles of \triangleleft -D GPA, were calculated from the equations:

$$C_{a} = \frac{m_{g} C_{g}^{o} + m_{\phi} C_{\phi}^{o} - R_{obs}}{m_{\phi}}$$
$$\vec{\nabla} = \frac{C_{a}}{C_{\phi}^{o}}$$

The molar concentration of the combined phenol and \heartsuit -D GPA is C_a ; m_g and m_g are the calibration curve slopes of \blacklozenge -D GPA and phenol, respectively; C_g^{\circlearrowright} and C_g^{\circlearrowright} are the initial molar concentrations of \image -D GPA and phenol, respectively; R_{obs} is the amount of resistance necessary to null the osmometer at the particular phenol concentration.

Results and Discussion

Model

From the space-filling model it was determined that with the flexibility of the polymer chain, the acetyl groups were free to rotate 360° about the oxygen-ring carbon bond with very little steric hindrance. Since the acetyl groups are exposed and not covered by the polymer chain, the oxygens are possible hydrogen bonding sites.

It is possible to align the acetyl groups on the polymer so an incoming water molecule will see a double row of hydrogen bonding sites. Both hydrogens of water could therefore by simultaneously hydrogen bonded, each one to a different acetyl group. By flexing the chain in a wave motion the water may move down the chain without being in a nonhydrogen bonding area.

Fig. 5.--Schematic drawing of water moving down a cellulose triacetate polymer by the simultaneously bonded hydrogens.

Another method of transport could be a "passing down" of the water molecules by the acetyl groups. This is visualized by the relative freedom of the acetyl groups about the carboxlic oxygen. In either method the hydrogens should always find themselves in a hydrogen bonding area and should generally be found in a hydrogen bond.

The "passing down" method could be the same mechanism by which phenol is transported through the membrane. The bulkiness of phenol probably obscures some of the possible water bonding sites which causes the decreased water flux when phenol is present in solution.

Nuclear Magnetic Resonance

Pimental (1960) states that hydrogen bonds are all negative meaning that chemical shifts are at a lower field than originally observed in the spectrum. At a single concentration this means very little but if plotted as chemical shift versus concentration, curves are obtained which can be correlated with hydrogen bonding properties of the substances. Besides concentration, temperature will also cause a change in the chemical shift. The lower the temperature the more hydrogen bonding and the chemical shift moves downfield the same as an increase in the concentration.

The chemical shifts of monomeric water observed at the various concentrations of $\not\leftarrow$ D GPA in the CHCl₃ solution were plotted against the concentration of $\not\leftarrow$ -D GPA. The results are plotted in Figure 6.

If the movement of the chemical shift to a lower field can be intrepreted as being caused by the hydrogen bonding of water to the \sim -D GPA, then a possible conclusion would be that the acetoxy oxygens on an acetylated saccharide could be sites for hydrogen bonding. Then H₂O could be moved down the polymer by transferring to different hydrogen bonding sites as postulated. The water would not be attracted to the methyl groups and the only other site would be the ring oxygen.

The 0.1752 solution of $\not\leftarrow$ D GPA was run at various temperatures by using the temperature probe. From Figure 7 it is noted that the chemical shift moves to the lower field as the temperature is lowered indicating a possible increase in hydrogen bonding as Pimentel stated.

To determine the number of water molecules bonded to the THP, the data of the chemical shifts were calculated and plotted as versus the logarithm of the water concentration. Figure 8 shows that as the water concentration increased so did the number of water molecules bonded.

Since no plateaus were observed the data were replotted as $V \approx$ versus V_{c} , Figure 9. According to Tanford $\stackrel{}{\sim}$ versus $\stackrel{}{\sim}$ should result in a linear plot if the combining sites are identical and do not interact with each other. According to the graph, the bonding sites for water in THP are identical and non-interacting.

The intercept will be K when, 1/2:0. From this it is concluded

15







Fig. 7.--The chemical shift of water (0.1855 M) with 0.1752 M \prec -D GPA in CHCl₃ at various temperatures.



Fig. 8.--Graph showing that increased water concentration also increases bonded water molecules around tetrahydropyran.



that the ring oxygen has no affinity for the water because there is no plateau and n goes to infinity. The chemical shift of the bonded water is probably due more to diamagnetic shielding as water does not dimerize in CHCl₃.

In doing work with the polymer CTA and water, it was found that the peak for water bonded to the CTA could not be detected and it was concluded that it was broadened until it spread over the entire spectrum. However, any free water could resonate to show a sharp peak.

By using the NMR integrator the amount of water bonded to the polymer could be determined from the integral of the free water subtracted from the total amount of water in solution. Figure 10 is the plot of these data and shows that there are at least 18 water molecules on the CTA polymer. The maximum could not be calculated as accuracy was lost with the instrument at higher concentration.

The high numbers of water were attributed to the fact that in DMSO, CTA forms a gel with trapped water molecules in its confines. These water molecules are bonded, tightly enough to appear as bound water (at least they are held for 10^{-3} second as a sharp peak is not detected) ir the spectrum.

Going to more dilute concentrations of CTA and water, the data loses precision and accuracy due to the limits of the NMR. It does appear that there are 1 to 4 water per ring of polymer when the water concentration is 1.9444 M and the CTA concentration is 0.0087169 M anhydroglucose units per liter.

Osmometer

To correlate the NMR data with the number of bonding sites on \neg -D GPA for water, the osmometer was used. With a 39°C, non-aqueous





thermistor the vapor pressure of the water-chloroform mixture exceeded chloroform's vapor pressure and resulted in a calibration curve with a small negative slope. Due to water cooling faster than chloroform, the instrument is insensitive for the readings to be adequately reproduced.

By using solutions of phenol and \checkmark -D GPA in CCl₄, calibration curves were plotted by the difference in resistance (ΔR) versus the molar concentrations. These are plotted on Figure 11.

From Figure 12 which is of k versus log Cø there appear to be two hydrogen bonding sites per d-D GPA molecule for phenol.

The ΔR for solutions at higher and lower concentrations in phenol could not be determined by this method because of instrumental limitations.

After knowing the number of bonding sites the nature of these sites were sought. According to Tanford, if a constant equilibrium value (\underline{k}) was obtained at each point, then the bonding sites were identical and completely independent. However, if the \underline{k} varied then the sites interacted (still assuming identical sites) either increasing the affinity for bonding or interfering with it.

The effect of the interaction of one site to another is described by defining a completely arbitrary function $\mathscr{I}(\overline{\varphi})$, such that, for $\overline{\varphi} > 0$ $k = k_{int} e^{-\mathscr{I}(\overline{\varphi})}$ where k_{int} is defined as an intrinsic association constant which will be limiting the value of <u>k</u> when $\overline{\varphi} = 0$.

If then the $\log \frac{1}{n-\tau} - \log C$ (which is equal to the <u>k</u> and therefore also to $\log k_{int} - 0.434 \sqrt[6]{r}$) is plotted against \overline{r} , a positive slope will depict an affinity for binding after the first site is bonded while a negative slope shows interferance in binding.







Fig. 12.--The number of hydrogen bonding sites for phenol on $d_{-}D$ GPA in CCl₄ by osmometry.

24

It was concluded from Figure 13 that once a phenol is bonded to an - D GPA molecule there is an enhancement in the binding for the next site.

To be sure these were measurements of the equilibrium of binding, two solutions of the same concentrations were prepared by two different methods. Tanford (1966) concluded that if the same datum was obtained from each solution, the system is in equilibrium.

One solution was prepared by mixing the phenol and \checkmark -D GPA solutions and then diluting with CCl₄. The other was prepared by diluting the phenol and \checkmark -D GPA solutions first and then mixing them together. The AR for the first as 24.00 Ohms while the Δ R for the second was 24.70 Ohms. Though this is a difference of -0.70 or 2.9% error it was concluded that the error could be attributed to dilution errors. The second solution had four dilution measurements and a mixing of the two solutions while the first solution involved no mixing and only three dilution measurements.

Conclusion

It was proposed that water was transported through Cellulose Triacetate membranes by water binding to hydrogen bonding sites and then being passed down the polymer.

The NMR data for *Q*-D Glucose Pentaacetate shows that water is capable of hydrogen bonding to the acetyl groups. The ring oxygen was eliminated as a hydrogen bonding site by work with Tetrahydropyran. The NMR data show that Tetrahydropyran has no specific hydrogen bonding site for water. Also from NMR data, Cellulose Triacetate shows an affinity for water. The titration data indicate that Cellulose Triacetate is able to bind at least 18 water molecules, as a gel.

Osmometric data were used to find that -D Glucose Pentaacetate



Fig. 13.--Graph showing the enhanced affinity for phenol to bind d-D Glucose Pentaacetate after the first site is bound.

has two identical and interacting hydrogen bonding sites for Phenol. It is speculated that in the polymer Phenol is bound to the acetoxy oxygens stronger than water thus blocking the sites for water. Thus when Phenol is present is the system the water flux is decreased according to the Phenol concentration.

Conclusive proof that this is the only mechanism of water transport is not possible from these data. However, all data reported in this thesis are in accord with the proposed mechanism of water transport. The water molecules are bound to the acetoxy oxygens of Cellulose Triacetate and then transferred down the polymer from one site to another.

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ABSTRACT

Cellulose acetate membranes show a higher permeability to water than to salt and are being used for desalination of salt water by reverse osmosis. Use of highly acetylated cellulose membranes give a higher salt rejection but also decrease flow rate of the water. The addition of very-short-chain substances or alkyl groups larger than one carbon atom to the cellulose membrane also decreases water flux.

A proposed mechanism of thansport through the membrane is that the water molecule is passed along the chain by hydrogen bonding with the acetyl groups. The NMR shows a change in the chemical shift of water with an increasing concentration of an acetylated saccharide or with decreasing temperature which indicates hydrogen bonding. The ring oxygen of Tetrahydropyran is a poor hydrogen bonding site according to NMR data. Also from NMR data, Cellulose Triacetate ties up at least 18 water molecules. The osmometer data indicates that *q*-D Glucose Pentaacetate has two hydrogen bonding sites per molecule with Phenol.