Transport Properties of Eastman Cellulose Acetate Membranes: Influence of Diffusant Size and Shape on Permeability

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Synopsis

Eastman cellulose acetate membranes (acetyl content = 40%) have been studied by means of dialysis rate experiments with uncharged permeants of selected sizes and shapes. The experimental results show that the high flux membranes exert no molecular size or shape selectivity on the transport of permeants whose molecular weights are less than 1152. The membranes used in desalination, however, are selective as to molecular size and shape. Desalination membranes, therefore, may be useful in separations where differences in size and shape are present.

INTRODUCTION

Numerous reports in the scientific literature describe the behavior of specially treated cellulose acetate membranes in reverse osmosis. These membranes, which have an active or dense surface that preferentially rejects dissolved sodium chloride, have proved to be particularly useful in the desalination of water. The nature of the salt-rejecting surface has been the subject of considerable discussion by those who have studied the Loeb-Sourirajan-type membranes, and there are two depictions of what this surface is like. One is that the surface is composed of a polymer gel into which a permeant must first dissolve and then diffuse until it reaches the porous or coarse substrate that comprises most of the membrane. This view has been held by Lonsdale, Merten, and Riley,[1] by Kesting, Barsh, and Vincent,[2] and by Banks and Sharples.[3] An alternative picture of the active surface has been espoused by Meares[4] and by Kopecek and Sourirajan,[5] who believe that the surface is microporous. Indeed, Meares has speculated that the pore size is on the order of 6–9 Å.

Whatever the nature of the active surface, it is certain that this surface can effect some remarkable separations. In addition to being able to reject substantially a charged solute, desalination membranes can distinguish between permeants according to their size and shape. It is the effect of permeant size and shape on transport rate through the membrane that is the subject of the present research. The data to be presented are from dialysis rate measurements with permeants that are nonionized in water solu-

tion. By using dialysis rate measurements with no externally applied pressure, membrane compaction was avoided. The use of uncharged permeants permitted primarily the examination of molecular size and shape as variables influencing transport rates.

EXPERIMENTAL

The Eastman membranes that were examined in this study are identical with those that are commercially available from Eastman Chemical Products. The four varieties of Eastman membrane chosen for study here were HF-35, HT-00, RO-89, and RO-97. Although other types are available, these four were believed to represent most or all of the range of behavior displayed by these cellulose acetate membranes. For instance, HF-35 and HT-00 are high-flux membranes with slight, if any, salt-rejecting capability. The two that carry the prefix RO are salt rejecting, and the two-digit number identifies approximately the percentage rejection under reverse osmosis conditions. (Eastman Chemical Products Inc. specifies that the test conditions in reverse osmosis are 600 psi, 78°F, 5000 ppm (0.5%) NaCl solution.)

The acetyl content in all of the Eastman membranes is 40%. All membranes are manufactured according to the general procedure of Manjikian, Loeb, and McCutchan.[6] Their procedure involves casting of the polymer in an acetone and formamide solution, briefly exposing the cast film to air, and then gelling it by immersion in cold water. The salt rejection property is imparted by tempering the film in hot water at various temperatures. For types RO-89 and RO-97, the tempering water temperatures are 80.5 and 81.5°C, respectively.

TABLE I
Permeability Data for Eastman Membranes

			Membrane			
Permeant	Mole weight	$D_{H_2O} \times 10^7$	HF-35	HT-00	RO-89	RO-97
				$D'K \times 10^7$ (cm²sec⁻¹)		
Methanol	32.0	159	34.6	...	29.6	29.8
Ethanol	46.1	124	28.5	23.8	20.3	21.6
n-Butanol	74.1	95.2	...	...	21.0	22.1
Isobutanol	74.1	93.3	...	...	...	18.2
sec-Butanol	74.1	92.2	...	...	...	16.0
$tert$-Butanol	74.1	87.9	...	...	14.3	7.65
1,5-Pentanediol	104.2	...	...	...	13.5	8.55
2,2-Dimethyl-1,3-propanediol	104.2	...	...	...	9.88	1.75
Pentaerythritol	136.2	76.1	16.7	...	...	1.71
Glucose	180.2	67.3	14.6	12.7	2.63	0.3₉
Mannitol	182.2	68.2	...	...	5.07	...
Raffinose	594.5	43.4	8.55	...	...	...
Cycloheptaamylose	1152.	32.2	7.07	6.31	...	0.0
NaCl	58.4	148.3	...	41.2	15.6	1.81

The permeants that were used are listed in Table I.   With the exceptions of the Schardinger dextrin (cycloheptaamylose) and sodium chloride, these were obtained in the highest purity available from Eastman Chemical Products and used as received.   It is to be noted that all of the permeants (sodium chloride excepted) are water-soluble nonelectrolytes and that these should not differ greatly from one another in their chemical interactions with a wet cellulose acetate membrane.   Thus, it was assumed that permeant size and shape were the most important parameters controlling permeation.   Cycloheptaamylose is especially useful in the characterization of membranes because of its nearly spherical shape.[7]   The cycloheptaamylose used here was obtained from the Pierce Chemical Company.
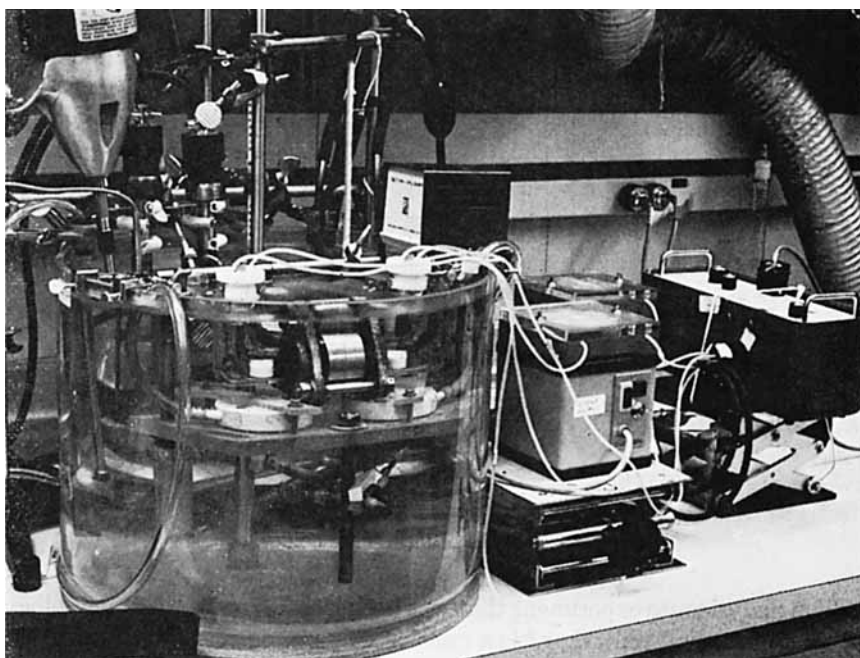

Fig. 1. Overall view of experimental apparatus showing dialysis cell in thermostat, peristaltic pumps, and (far right) part of optical unit of flowing differential refractometer.

The dialysis cell is shown in Figure 1.   It is based on two Pyrex conical pipe elbows, which form the compartments of the cell.   The membrane is held in the two-piece metal case, the details of which are shown in Figure 2.   The use of the case permits one to mount a membrane reproducibly and without damage to it.   With thick membranes, for example, the two sections of the case can be held apart to the necessary degree by using shim washers.   After the membrane is mounted in the case, the cell assembly is completed by inserting silicone rubber or Teflon washers in the ends of the case and then bolting the Pyrex elbows to the case with the yokes visible in Figure 1.

Also visible in Figure 1 are the magnetic "roto-stirrers" that were used to keep the fluid in each compartment well stirred. It cannot be stated that all stagnant layer effects at the solution–membrane interfaces, such as those discussed by Smith and co-workers,[8] were eliminated. However, an attempt was made to discern and measure the extent of such effects with the HF-35 high-flux membrane. The results of this attempt indicated that the total stagnant layer thickness amounted to less than 20% of the membrane thickness. Presumably this is the greatest degree to which the results from these experiments are in doubt, because the HF-35 membrane was the most permeable of those examined.
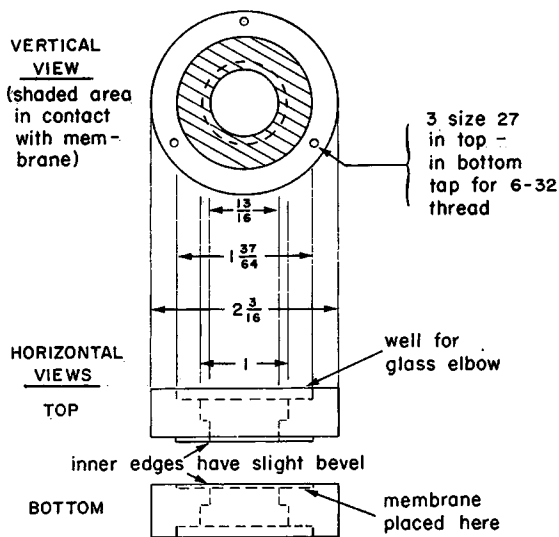

Fig. 2. Details of membrane holder.

The dialysis rate experiment that was performed here, in the terminology of Garrett and Chemburkar,[9] is a quasi-steady-state experiment. That is, permeant is added to one compartment of the cell at the beginning of an experiment and the rate of approach to dialysis equilibrium is monitored. From this rate and the equation

$$J = \frac{V}{A}\frac{dc_2}{dt} = \frac{D'K}{l}\,[c_1(t) - c_2(t)], \tag{1}$$

the product $D'K$, the permeability coefficient, can be computed. Here, J represents flux, V is the volume of one compartment of the dialysis cell, A and l are the area and the thickness, respectively, of the wet membrane, $c_1(t)$ and $c_2(t)$ are the permeant concentrations at time t in the retentate and diffusate compartments, respectively, D' is the diffusion coefficient of the permeant in the membrane, and K is the partition coefficient of the permeant between the membrane and solution phase. For the purposes

of experimental precision and operational ease, eq. (1) can be integrated and rearranged to yield

$$\log[c_1(t) - c_2(t)] = \log[c_1(0) - c_2(0)] - \frac{2D'KAt}{2.303lV}. \tag{2}$$

Thus, by plotting the logarithm of the concentration change across the membrane versus time, one can obtain $D'K$ from the slope of the plot. Garrett and Chemburkar[9] performed dialysis rate experiments similar to this and also steady-state experiments in which the concentration gradient across the membrane was nearly constant in time. Although the steady-state experiment was preferred by these workers, they found that permeability data from the two kinds of experiments were in agreement.

The concentration change across the membrane was monitored continuously by the use of a flowing differential refractometer. The arrangement for doing this is shown in Figure 1. Fluid from one compartment of the dialysis cell was pumped by an LKB 10202 Perpex pump to one cell in the refractometer and thence back to the dialysis cell. A similar arrangement was used to circulate fluid from the second dialysis cell compartment through the other cell in the refractometer. The refractometer was a Laboratory Data Control Model 1103 Refractomonitor. The optical unit of this instrument is visible in the far right of Figure 1. The signal from the refractometer was continuously recorded.

All experiments were performed in a thermostat at 25.0°C. In a typical experiment, V, the fluid volume in one compartment, was 60.0 ml, and c_2-(0), the initial concentration of permeant in the diffusate compartment, was zero. To begin an experiment, permeant was added to the retentate compartment so that $c_1(0)$, the initial concentration in this compartment, was less than or equal to 1×10^{-2} g/ml. Frequently $c_1(0)$ equalled 1×10^{-3} g/ml. The retentate compartment was adjacent to the dense surface of the membrane in the experiments with RO-89 and RO-97.

The experimental precision was such that the permeability coefficient data were reproducible to within $\pm 10\%$. The value of $D'K$ for ethanol was checked at the end of a long series of experiments with a membrane in order to determine if the membrane had changed during the experiments. Such checks revealed no appreciable changes in membrane properties.

The data to be presented were obtained using a specimen from each of the four types of membrane that were examined. These data were confirmed by examining the permeability properties of other specimens of Eastman membranes. Although there are minor variations in the specimen-to-specimen behavior, the data reported here are representative of the effects that one observes. In particular, the transport rates of various permeants through different specimens of the most interesting of these membranes, type RO-97, were checked exhaustively and found to be reproducible.

The volume fraction of polymer in a wet membrane, v_2, was determined by taking the dimensions and weight of the wet membrane, drying the membrane to constant weight at 60°C under vacuum, and using the weight difference to find the volume of water in the wet membrane. The volume fraction data obtained in this way were not precise and, because of this, no correlation between v_2 and salt rejection capability was observed. For v_2, therefore, an average and approximate value of one third is reported here, and this applies to all of the Eastman membranes.

RESULTS AND DISCUSSION

The results are presented in Table I, which, in addition to the permeability data, includes diffusion coefficients of the permeants in water when these could be obtained from handbook or other tabulations.[10, 11]

In Table II, dialysis rate data for sodium chloride through HT-00, RO-

TABLE II
Sodium Chloride Rejection

Membrane	Quoted	$(D'K/D_{H_2O})$
HT-00	0–20%	0.27_8
RO-89	86–92%	0.10_5
RO-97	96–98%	0.01–0.02

89, and RO-97 are compared with the quoted sodium chloride rejections in reverse osmosis. From this tabulation, it is evident that there is a general correspondence between the reverse osmosis salt rejection percentages and the $D'K$ data from dialysis rate measurements.

Some of the data in Table I are plotted in Figure 3. Here, the uppermost plot is of the logarithms of the diffusion coefficients of selected permeants (methanol, ethanol, n-butanol, pentaerythritol, glucose, raffinose, and cycloheptaamylose) in water versus the logarithms of their molecular weights. These water diffusivity data are shown in order to indicate the effect of molecular weight on D_{H_2O} and to have a reference with which the membrane data can be compared.

The middle plot in Figure 3 is a logarithmic plot of the permeability coefficients of ethanol, glucose, and cycloheptaamylose in HT-00 versus molecular weight. A comparison of these data with the water diffusivity data shows that the membrane permeability data lie on a plot that is below and very nearly parallel to the water diffusivity data. (If the data for HF-35 had been plotted here, the same commentary would apply.) It is noteworthy that for HT-00 the ratio of $D'K$ to D_{H_2O} for every uncharged permeant is well represented by the average value of this ratio for all three permeants, 0.19_2.

On the basis of the data in Table I and Figure 3, one can conclude that, aside from the effects of molecular size and shape that are observed in water, HF-35 and HT-00 are not molecular size selective in the molecular
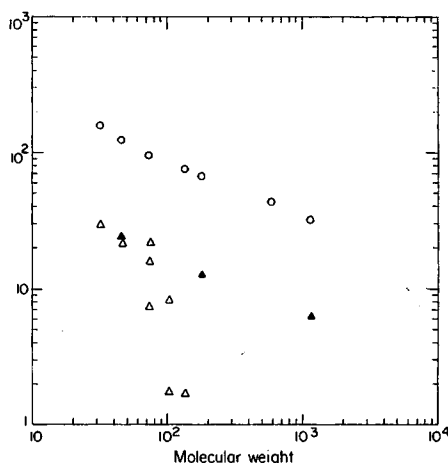
Fig. 3. Detailed representation of log permeability coefficient versus log molecular weight of several permeants (see text) for Eastman membranes: (O) $\log D_{H_2O} \times 10^7$; (▲) $\log D'K \times 10^7$ for HT-00; (△) $\log D'K \times 10^7$ for RO-97.

weight range that was examined ($M_w \leq 1152$). In addition to this, two other tentative conclusions are possible: (a) The parameter that controls differences in permeability in HF-35 and HT-00 is D_{H_2O}, i.e., D'/D_{H_2O} is probably constant or nearly so for each membrane. Thus, the membrane structure is probably an open one, and the diffusants traverse the membrane by moving through a tortuous aqueous channel which is larger than the diffusant itself. (b) The assumption mentioned in the experimental section, viz., that there are no large differences in the chemical interactions between the uncharged permeants and the wet cellulose acetate membrane, is valid. If K had varied significantly with permeant, then, in all likelihood, the close dependency of $D'K$ in the high-flux membranes on D_{H_2O} would not have been observed.

In contrast to the permeability-versus-molecular weight plot for HT-00 (or HF-35), the corresponding plots for the desalination membranes exhibit severe drops in permeability with increasing molecular weight. An example of this behavior can be seen in the lowest plot in Figure 3, which presents the data for RO-97. A more complete comparison between the different membranes is presented in Figure 4, which shows schematically the approximate dependence of permeability in the Eastman membranes on molecular weight. From Figure 4, it is clear that the RO-89 and RO-97 membranes imparted profound molecular size effects to the movement of the permeants and that these effects became pronounced at a lower permeant molecular weight in the more salt-rejecting RO-97.

A close examination of the data in Table I for RO-89 and RO-97 reveals that, besides the molecular weight or size effects, there were also what appear to be molecular shape effects in these membranes. In the case of RO-97 and the butanol isomers, the permeability coefficient increased as

the permeant molecule became less branched. This tendency for the more linear isomer to permeate the membrane more rapidly is also evident from the data for 1,5-pentanediol and 2,2-dimethyl-1,3-propanediol in RO-97, the former having the higher permeability coefficient. There appears to be some shape selectivity in RO-89 with the isomers of molecular weights 74.1 and 104.2, but these effects were not so pronounced as they were in RO-97.

With regard to the apparent shape selectivity in the desalination membranes, three things should be mentioned. First, these effects have been observed in elastomers[12] and with diffusants in water.[13] Second, the differences in permeability for the butanol isomers in RO-97 resemble the differences in butanol isomer rejections in reverse osmosis that were reported by
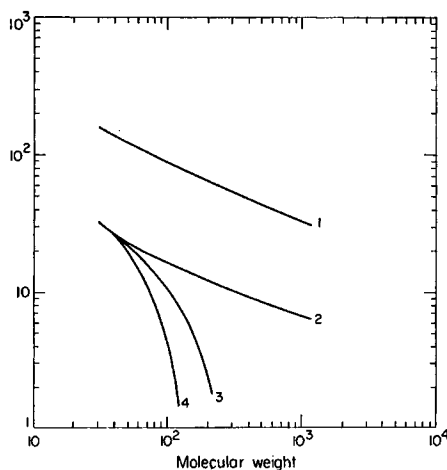

Fig. 4. Schematic representation of log permeability coefficient versus log molecular weight of several permeants (see text) for Eastman membranes: (1) $D_{H_2O} \times 10^7$; (2) $D'K \times 10^7$ for HT-00; (3) $D'K \times 10^7$ for RO-89; (4) $D'K \times 10^7$ for RO-97.

Sourirajan.[14] Third, the differences in the shape selectivities of the cellulose acetate desalination membranes at different molecular weights imply that these membranes might be tailor made for separations where shape differences are present.

As indicated previously, it is probable that differences in the transport rates of permeants through the high-flux HF-35 and HT-00 membranes are governed by differences in the water diffusivities of the permeants. With regard to the desalination membranes, however, a conclusion of this type is not warranted on the basis of the data presented here. The severe drops in permeability with increasing permeant molecular weight that were observed with the RO-89 and RO-97 membranes could have been caused by sharp decreases in either D' or K or both of these. Thus, it would be instructive to have data concerning the dependence of only D' (or K) on molecular weight so that one could determine how much the transport rate is controlled by restricted diffusion and how much it is controlled by exclu-

sion from the membrane phase.   The obtainment of the data required for
making this distinction is, unfortunately, made difficult by the inhomo-
geneity of the desalination membranes.

One can, using the data reported here, speculate about the nature of the
salt-rejecting surface in a desalination membrane.   For instance, one
might propose that the microporosity viewpoint has been enhanced by
these data and use the following argument in favor of this picture: The
structure of the HT-00 membrane, which is the precursor of the RO-89 and
RO-97 membranes, is a coarse, or open one, as is evidenced by the lack of
any molecular size effects up to a molecular weight of 1152.   The treat-
ment that imparts the salt-rejecting surface to HT-00 to transform it to a
desalination membrane preferentially shrinks the larger openings in one
surface of the membrane.   Thus, in forming RO-97 from HT-00, one does
not reduce the number of openings per unit area of surface, but simply
shrinks the larger openings.   (A similar explanation was used by Loeb and
Sourirajan in describing their early work with membranes from cellulose
acetate.[15])   This would explain the convergence of the $D'K$ data for HT-
00, RO-89, and RO-97 as the permeant molecular weights become lower
(cf. Fig. 4).   Furthermore, the observance of increased molecular size
selectivity with increased salt-rejection capability is consistent with the
microporosity picture because profound molecular size selectivities have
been predicted for membranes with narrow pore size distributions (see
Stein,[13] pp. 112–113).

In the author's opinion, the preceding arguments in favor of the micro-
porous structure, although certainly appealing, are not conclusive.   The gel
viewpoint and these dialysis data also could be considered as consistent
with one another.   One could conjecture that the formation of the dense
surface is accompanied by the subdivision of the large openings in the mem-
brane face into smaller ones.   Such subdivision might occur by spacing
more closely polymer chains over the surface of the membrane, i.e., by the
melting of crystallites to form a gel.

What is needed in order to understand better the structure of the active
surface is further experimentation along two avenues.   First, the molecular
size selectivities of known polymer gels should be determined.   From this
sort of investigation, one could obtain an estimation of how dense a gel is
necessary for the achievement of the molecular size selectivities that are
evident in the desalination membranes.   (Current work in this laboratory
with gels based on poly(vinyl alcohol) indicates that, at a v_2 value of 0.51,
the molecular size selectivity is not as great as in the desalination mem-
branes.)   Second, the activation energies of transport of the various per-
meants through a desalination membrane, a dense gel-type membrane, and
a membrane with small pores should be determined and compared.   Should
the activation energies of transport through the desalination membrane
closely approximate those for either the gel-type membrane or the porous
membrane, then a clear indication of which structure is present would be
available.

In summary, the results of this research have shown that the salt-rejecting surfaces of desalination membranes based on cellulose acetate are highly selective as to the molecular size and shape of uncharged permeants.   This selectivity is greater the more salt rejecting the membrane.   It is possible, therefore, that cellulose acetate desalination membranes can also be used to achieve separations according to molecular size and shape.

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