Permeability Studies with Cellulose Acetate Membranes

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Summary
    The diffusive permeability of cellulose diacetate membranes
was measured using NaCl as solute and distribution coefficients
were calculated. Water and salt permeability coefficients derived
from dialysis-osmosis experiments were also given. The results
obtained were discussed with the aid of scanning electron micro-
graphs and chlorine distribution maps.

Introduction
    Ever since the discovery of the skinned membranes (LOEB and
SOURIRAJAN 1962), there has been a great deal of effort in order
to understand the mechanism of permeation of solute molecules
through cellulose diacetate membranes (LONSDALE et al. 1965,
YASUDA et al. 1968, LONSDALE et al. 1971, COLTON et al. 1971,
FROMMER et al. 1973, KIMURA 1973, HEYDE and ANDERSON 1975, PUSCH
1977, TANNY 1977, KAMIZAWA 1978, BENDER et al. 1978). However,
these studies usually refer to dense homogeneous membranes. The
objective of this work was to determine the diffusive permeabi-
lity to sodium chloride of Loeb-type cellulose acetate membranes
exhibiting large morphological differences. Indeed, it was shown
(LEMOYNE et al. 1980) that, as the evaporation time involved in
the membrane-making procedure increases, there is a progressive
replacement of a 3-layer membrane by, first, a 2-layer membrane,
then, an unilayer membrane. In this paper a comparison was made
between the distribution coefficients and the solute permeability
coefficients determined from the exchange fluxes previously mea-
sured in dialysis-osmosis tests under well defined conditions
(HALARY et al. 1979 a). In addition, membranes were also charac-
terized in terms of thickness, total water content and water per-
meability coefficient. Some chlorine distribution maps, which
provide a quantitative estimate of the salt uptake from the NaCl
solution, are also reported and discussed in relation to the
different structures of the layers.

Experimental
    Membrane preparation : The casting solutions were prepared
from a common source of Eastman Kodak E - 398 - 3 and analytical
reagent grade acetone. The casting solutions, consisting of
22.2 g cellulose diacetate, 66.7 g acetone, 10 g water and
1.11 g of an anhydrous inorganic salt [KSCN or $Mg(ClO_4)_2$]

were cast at 2°C in a ca. 0.15 mm thick film. The cast films were allowed to evaporate at 2°C for a predetermined period (2 to 480 secs) and then immersed into an ice-water bath (LEMOYNE et al. 1980). In this paper, membranes are designated according to their preparation procedure. The letters stand for the nature of the additive in casting solution [MG = $Mg(ClO_4)_2$, K = KSCN] and the additional number represents the duration of the evaporation phase.

Measurements of sodium chloride permeability : samples of known dimensions (30.2 cm^2 area) were punched in the membrane. Their wet thickness was measured to - 0.5 mμ with a sensitive micrometer. At least three repeat measurements were made at different points and the results averaged. In these determinations, the standard deviation about the mean was generally less than 5 %. Each sample was then equilibrated with NaCl solution at 2°C. Although preliminary experiments have indicated that ion sorption depends on the salt concentration, in order to establish correlations with previous transport coefficient measurement (HALARY et al. 1979 a) experiments were performed at 0.1 M. The equilibration time varied, depending on the diffusivity of NaCl in the membrane but was long compared with the characteristic diffusive time. The sample was then removed from the solution, quickly rinsed with distilled water and blotted dry of surface water. After blotting the sample was immediately transferred into a small vial containing 2 ml of concentrated nitric acid (R.P. NORMAPUR for toxicology, sodium-free) and heated at 80°C. After nitric acid evaporation, the residual material was dissolved in a known amount of bidistilled water. Thus obtained solution was analyzed for sodium by atomic absorption technique with a UNICAM Instrument (Model SP 90 A) equipped with an air-acetylene burner. The calibration was determined by a standardization curve in the concentration range of interest. To take into account possible effects of glucosic fragments, standardization solutions were prepared from normal membranes which had been only nitric-acid treated after preparation. The data were reproducible to within 10 %. The values reported are the average of six measurements performed at various points on each membrane.

Scanning electron microscopy : For the scanning electron micrographs of membrane cross-sections, samples were prepared by fracturating the membranes at liquid nitrogen temperature, lyophilizing and coating with gold.

The chlorine distribution maps were obtained at 20 kv on a scanning electron microscope (Cameca 07) equipped with a X-ray energy analyzer (energy dispersive analysis of X-Rays). Results thus obtained were checked by point analyses performed at three different points chosen in the upper part, in the middle and in the lower part of the membrane cross-section, respectively. The point size was 5 μm diameter and the counting time was 20 seconds. The integral of all the counts (relative to the chlorine-K_α emission) falling within the selected window is characteristic of the chlorine concentration.

Results and Discussion

Table I summarizes the results in terms of k, the distribution coefficient, defined as :

$$k = \frac{\text{grams NaCl/cc membrane}}{\text{grams NaCl/cc solution}}$$

The thickness e, the volume fraction of water ϕ_W, the water permeability coefficient P_W and the salt permeability coefficient P_S are also reported in Table I.

Table I
Permeability of cellulose acetate membranes

Expt. No	Membrane	e_μ	ϕ_W	$10^4\ P_W$ cm/s·atm	$10^4\ P_S$ cm/s	k
1	K 2	60	0.732	0.02	0.07	0.26
2	K 30	54	0.705	0,05	0.11	0.19
3	K 60	48	0.681	0.23	0.57	0.13
4	K 90	45	0.682	0.46	0.61	0.09
5	K 120	44	0.686	1.31	2,66	0.11
6	K 150	42	0.639	0.61	2.05	0.06
7	K 240	35	0,461	0.49	1,13	0.04
8	K 480	33	0,435	0.31	0,79	0.02
9	MG 2	74	0,716	0.91	1.45	0.18
10	MG 30	66	0,673	1.30	1.76	0.08
11	MG 60	61	0.638	2.00	2,57	0.07
12	MG 90	58	0.616	2.70	3,36	0.07
13	MG 120	57	0,611	2.34	2,60	0.05
14	MG 150	55	0,604	0,70	1,33	0.04
15	MG 240	36	0,492	0,74	1,20	0.03
16	MG 480	32	0.408	0,37	0,67	0.01

The volume fraction of water ϕ_W was calculated from the relation:

$$\phi_W = \frac{H\rho_{CA}}{H\rho_{CA} + (1-H)\rho_W}$$

where the density of water, ρ_W, and cellulose diacetate, ρ_{CA}, were taken to be 1.0 and 1.33 g/cc (BARKER and THOMAS 1964), respectively, and the total water content H was taken to be the values reported in a previous publication (LEMOYNE et al. 1980).

The coefficient of water permeability P_W and the coefficient of salt permeability P_S were calculated from the ratios :

$$P_W = \frac{J_W}{\Delta P} \quad \text{and} \quad P_S = \frac{J_S}{\Delta C}$$

where the volume flux J_W and the solute flux J_S had been previously obtained from dialysis-osmosis experiments. In performing these calculations, the appropriate values of 0.2 atm and 0.01 M have been adopted for the hydrostatic pressure difference, ΔP, across the membrane and the difference, ΔC, of the salt concentrations of the solutions on the two sides of the membrane,

respectively. The apparatus and the experimental procedures have
been earlier described (HALARY et al. 1979a).

For both K and MG systems, the distribution coefficient, k,
decreases with increasing evaporation time. It is immediately appa-
rent from Table I that the evolution of the membrane hydration ver-
sus evaporation time is similar. Correlations between the distri-
bution coefficient, k, and the membrane hydration have been pre-
viously reported (YASUDA et al. 1968, KIMURA 1973). Indeed, in so
far as no salt is expected to dissolve in the cellulose diacetate
matrix, all the salt may be considered as solvated by the water in
the membrane. In order to show the dependence of k on the membrane
hydration, k is plotted as a function of the reciprocal volume
fraction water $1/\phi_w$ in Fig. 1. As can be seen from Fig. 1, the
experimental data lie on two straight lines which intersect at
$1/\phi_w \simeq 1.48$, that is to say at $\phi_w \simeq 0.67$. As $1/\phi_w$ increases, the
values of k first strongly decrease from an extrapolated value of
about 1 up to 0.08. Then, there is only a very weak dependence of
k on the membrane hydration. Independent electron microscopy inves-
tigations (LEMOYNE et al. 1980) show that the highest values of
k correspond to membranes containing voids and large pores, which
are highly swollen and opaque. An increase in the evaporation
period involved in the membrane-making procedure eliminates the
formation of voids and cavities and causes a rapid reduction of
the pore size until membranes contain no large pores and, as a
consequence, become transparent. The evaporation time required
to obtain membranes which appear uniform at a magnification of,
say, 9000 is about 110-120 seconds for the K system and 30 seconds
for the MG system. Since the change in slope in Figure 1 is
correlated with these morphological changes it seems to indicate
that, in membranes with large pores, the NaCl solution is essen-
tially in clusters large enough to solvate ions and the extent
of the polymer-salt interactions is limited. On the contrary,
the NaCl solution sorbed in uniform membranes may be assumed to
interact with the polymer. Independent investigations (HALARY
1979 b) are supporting this conclusion.

Representative data of volume fractions of water, distribu-
tion coefficients and permeabilities are shown in Figure 2 where
the results obtained from highly porous and uniform membranes
are compared for the K system. It is obvious from Figure 2 that,
at evaporation times longer than 120 seconds, k and P_s as well
as ϕ_w and P_w simultaneously decrease in agreement with results
previously obtained for transport coefficients of dense homoge-
neous membranes (HALARY et al. 1979 a).

On the contrary, at short evaporation times, P_s and P_w
increase although k and ϕ_w decrease. Such a behavior can be under-
stood by a deeper inspection of the membrane morphology. Indeed,
membranes which were prepared from casting solutions containing
KSCN and immersed in the leaching bath within a few seconds from
their casting can be considered as 3-layer membranes (LEMOYNE et
al. 1980). Electron micrographs of cross-sections of such membra-
nes (Fig. 3 a) reveal an upper thin uniform layer, a sub-layer,
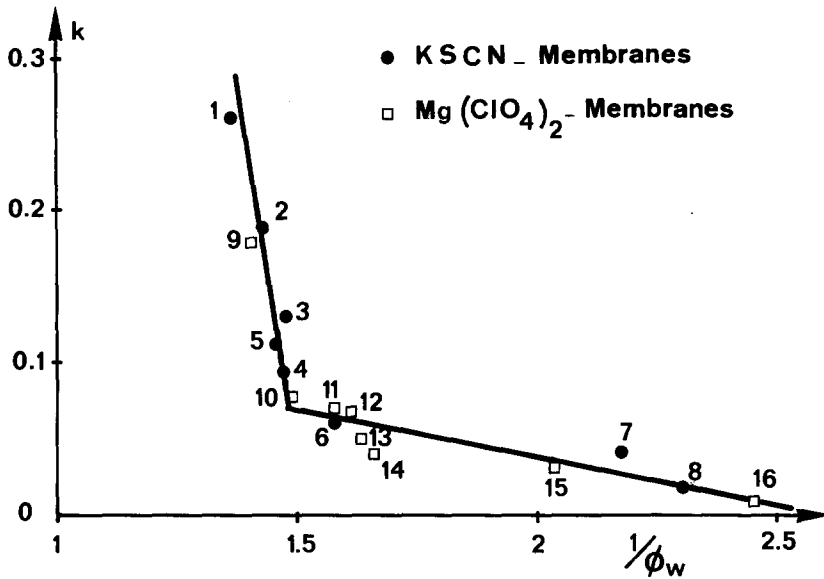which is an open network of pores, and a lower layer which contains

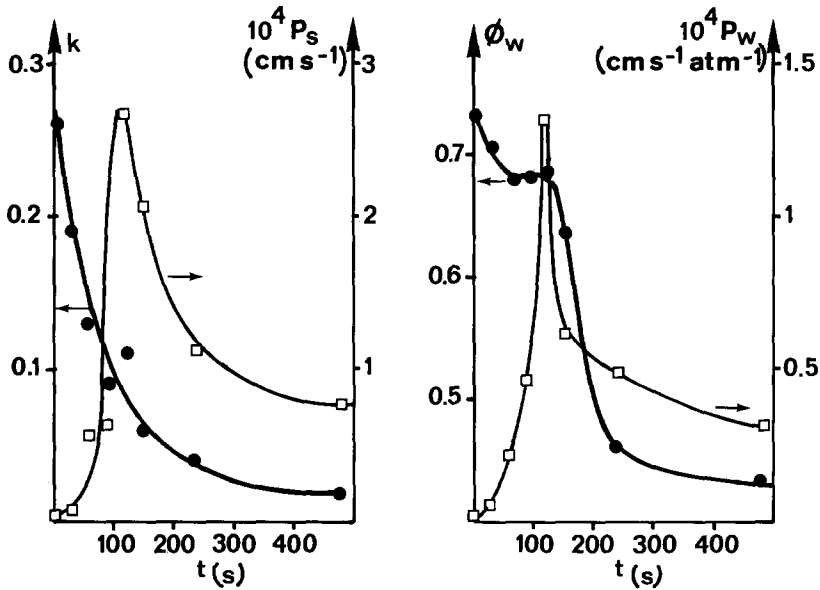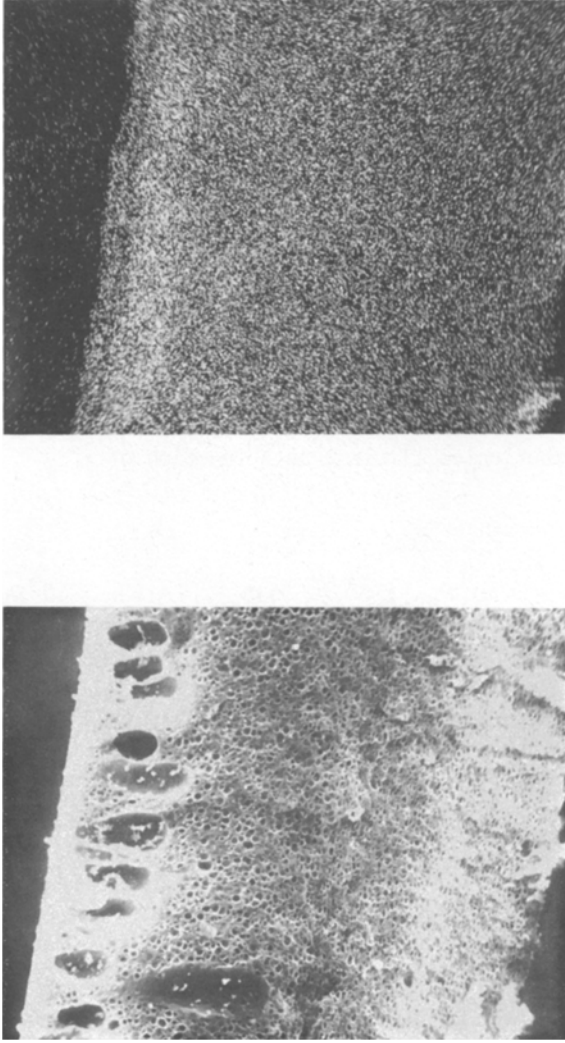Fig. 1 - Distribution coefficient as a function of $1/\phi_W$

Fig. 2 - Relations between k, P_S, ϕ_W or P_W and the evaporation time t

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(a)

(b)

Fig. 3   Scanning electron micrograph (a) and chlorine distribution map (b) of cross-section of a 2 sec evaporation time KSCN membrane

large closed pores and is impermeable owing to the great thickness and density of the interpore walls (LEMOYNE et al. 1980, HALARY et al. 1979 a). For these membranes, the high values obtained for k and ϕ_W can be explained by considering the large volume of voids and the highly porous sub-layer while the low values of P_S and P_W have to be ascribed to the structure of the lower layer. The chlorine distribution maps (Fig. 3 b) effectively reveal that the NaCl solution is essentially sorbed by the upper layer and the sub-layer. The NaCl concentration in the lower layer is much smaller. As the evaporation time increases from 2 to 120 seconds, the structure of the lower layer changes and some interpore connections appear so that P_S and P_W increase. However, as membranes are formed from more and more concentrated solutions, voids disappear and the pore size in the upper layer and the sub-layer decreases, which results in a decrease of ϕ_W and k.

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