Polymer Bulletin 2, 89-96 (1980)

Polymer Bulletin

Analysis of Transport Phenomena in Cellulose Diacetate Membranes

III. General Relationships Between Hydration and Dialysis Coefficients of Unilayer Membranes

J. L. Halary, C. Noël and L. Monnerie

Laboratoire de Physicochimie Structurale et Macromoléculaire, Ecole Supérieure
de Physique et Chimie Industrielles de la Ville de Paris, 10, rue Vauquelin,
75231 Paris Cédex 05, France

SUMMARY

Osmosis-dialysis transport properties and hydration characteristics were determined for various Manjikian type membranes. Some analogies were established between the behaviour of these membranes and the membranes of Loeb type. Particular attention was paid to show the generality of the correlations between the specific transport coefficients and the state of water (free or bound) in unilayer membranes.

INTRODUCTION

As shown by different authors (KEDEM 1958, SCHLÖGL 1964), the transport behaviour of a membrane in osmosis-dialysis conditions may be determined by three transport coefficients ℓ_p, $\ell_{p\pi}$ and ℓ_π. These phenomenological coefficients are defined using linear relations between fluxes and conjugated forces, according to the equations of nonequilibrium thermodynamics :

$$J_V = \ell_p \Delta P + \ell_{p\pi} \Delta\pi \qquad (1)$$

$$J_D = \ell_{p\pi} \Delta P + \ell_\pi \Delta\pi \qquad (2)$$

where J_V, J_D, ΔP and $\Delta\pi$ are the volume flux, the exchange flux, the pressure difference and the osmotic pressure difference, respectively.

In a previous paper (HALARY 1979 a), transport coefficients ℓ_p, $\ell_{p\pi}$ and ℓ_π were determined for various Loeb type cellulose acetate membranes which exhibit strong morphological differences from one to another. Indeed, it was shown (LEMOYNE 1980, HALARY 1979 a) that morphology of such membranes can be depicted mainly using three different types of structure, namely A, B and C, the relative extent of which depends on the duration of the evaporation period involved in the membrane-making procedure. These A, B and C structures can be understood by considering the precipitation pathway of the casting solution during the membrane formation. The type C, evidenced for the shortest evaporation times, is a porous structure. It is formed by immersing not very concentrated casting solutions in a water bath. By increasing the evaporation time, the polymer concentration in

0170-0839/80/0002/0089/$01.60

the casting solution is increased and the system can undergo a sol-gel transition. The processes taking place during immersion of a gel in water are different from those occurring during immersion of a sol and a more-or-less uniform B type structure is obtained. Finally, the structure A is mainly formed by evaporation of solvent prior to contact with water. It can be understood by considering a shrinkage or syneresis of the primary gel. For such a structure, electron microscopy does not reveal any porosity, even at a magnification of 40 000.

Transport coefficient measurements led to the following conclusions : i/ the evolution of ℓ_p, $\ell_{p\pi}$ and ℓ_π values as a function of the evaporation time can be interpreted by the progressive replacement of a 2-layer (C - B) membrane by first, a 2-layer (B - A) membrane and then, by an unilayer membrane which exhibits only the A-type structure, and ii/ for unilayer A-type membranes, the values of L_p and L_π (defined as the product of the membrane thickness by ℓ_p and ℓ_π, respectively) are correlated with the amount of capillary water per gram of dry cellulose acetate (CA) whereas the $L_{p\pi}$ values are the only ones which depend on the amount of bound water per dry CA gram.

These findings are of particular interest in membrane science, because they permit description of both pressure effects (HALARY 1978) and heat-treatment effects (HALARY 1979 b) on permeability characteristics of reverse osmosis membranes, in terms of polymer-water and water-water interactions, and this, whatever the membrane morphology.

The objective of the present work is to comment on the generality of the relationship between dialysis coefficients, and membrane morphology and hydration. To this end, studies similar to those previously developed for Loeb type membranes were carried out on Manjikian type membranes which were prepared in the wet process from ternary dopes CA-acetone-formamide.

EXPERIMENTAL

Manjikian type membranes were cast at 20°C under a relative humidity of 30% from a solution of CA (Eastman 398-3) in acetone and formamide (25-45-30 parts by weight respectively). After a predetermined evaporation phase (2 to 480 sec) at 20°C, the film was immersed in a water bath at 20°C for about 1 hr, then kept in distilled water before study. By analogy to the nomenclature used for Loeb type membranes (i.e. symbols MG and K standing for the nature of the additive, $Mg(ClO_4)_2$ and KSCN respectively, with additional indication of the duration of the evaporation stage), the Manjikian type membranes will be designated by the symbol F (formamide) followed by the evaporation time (in sec).

Membrane hydration properties were determined as follows: the overall water content was measured by weighing membrane pieces, first in the wet state after a quick blotting of the surfaces, then in the dry state after a 24 hr drying at 75°C under 0.01 torr. Free water, corresponding roughly to the water molecules filling the pores of the membrane, was defined as nonfreezing water and its amount was measured by differential scanning calorimetry, according to the method developed by FROMMER(1972). The amount of bound water, which represents the water molecules H-bonded with the macromolecular chains, was taken as the difference between the overall and free water contents.

Determinations of transport coefficients ℓ_p, $\ell_{p\pi}$ and ℓ_π were carried out on 0.1 M NaCl aqueous solutions, using an apparatus and experimental conditions which were described in detail elsewhere (HALARY 1979 a). Salt and water fluxes were measured by applying the higher hydrostatic pressure to the side of the membrane corresponding to the air-casting solution interface.

RESULTSAND DISCUSSION

Transport coefficients ℓ_p, $\ell_{p\pi}$ and ℓ_π of the membranes under study are given in Table I, together with the corresponding values of the reflection coefficient σ, defined by STAVERMAN (1951) as the ratio $-\ell_{p\pi}/\ell_p$. The most noticeable effects of an increase in the evaporation time refer to the values of ℓ_p and σ. A maximum hydraulic permeability is observed for an evaporation period of about 20 sec, which coincides with polymer precipitation at the film surface as previously reported by OHYA(1971). In addition, a noticeable selectivity is observed only for the membranes which are prepared with an evaporation time as short as possible.

Membrane	$10^3\ \ell_p$ (cm.sec^{-1}.atm^{-1})	$-10^4\ \ell_{p\pi}$ (cm.sec^{-1}.atm^{-1})	$10^4\ \ell_\pi$ (cm.sec^{-1}.atm^{-1})	σ
F 2	0.23	0.47	0.24	0.20
F 20	0.79	0.32	0.37	0.04
F 45	0.65	0.24	0.40	0.04
F 60	0.40	0.20	0.37	0.05
F 90	0.37	0.14	0.39	0.04
F 120	0.29	0.15	0.29	0.05

Table I

Values of F Membrane Transport Coefficients ℓ_p, $\ell_{p\pi}$, ℓ_π and σ

Therefore, the interpretation based on a multilayer morphological model, which has been suggested to account for the evolution of the transport coefficients of the Loeb type membranes, seems also suitable in the case of Manjikian type membranes. As a consequence and in agreement with the electron microscopy studies of MOSSA(1976), the Manjikian type membranes prepared with an evaporation period equal to or longer than 60 seconds can be regarded as unilayer A-type membranes.

Table II gives the thicknesses and hydration characteristics (overall, free and bound water contents) of the Manjikian type membranes. Both sets of values of membrane thickness and overall water content show that F membranes are highly swollen membranes, even after a long evaporation stage. Furthermore, as previously reported for Loeb type membranes (LEMOYNE 1980), results show a decrease in swelling with increasing evaporation time. However, an inspection of the amounts of free and bound water per gram of dry CA shows that both quantities decrease monotonically with increasing evaporation time. Concerning free water, such a type of evolution is similar to that observed for Loeb type membranes. On the other hand, the monotonic decrease in bound water differenciates the Manjikian type membranes from the Loeb type ones, for which the bound water content sharply decreases as the A layer extends to the full thickness of the membrane (HALARY 1979 a, LEMOYNE 1980). The origin of such a difference is in fact difficult to establish, but it is obvious that the inversion phase process is more complex in the case of formamide membranes. Indeed, not only the solvent (acetone) but also the non-solvent (formamide) have to be replaced by water in the leaching bath.

Membrane	Thickness (μm)	Overall (wet membrane W %)	Free Water (gram per dry CA gram)	Bound Water (gram per dry CA gram)
F 2	103	69.8	1.29	1.02
F 10	94	68.0	1.20	0.93
F 20	92	67.7	1.21	0.89
F 30	90	65.9	1.09	0.84
F 45	85	63.9	1.05	0.72
F 60	80	62.4	0.88	0.78
F 90	73	60.3	0.84	0.68
F 120	70	56.5	0.72	0.58
F 480	64	50.3	0.49	0.52

Table II

Values of F Membrane Thicknesses and Hydration Characteristics

In the case of A-type membranes, we have calculated the specific transport coefficients L_p, $L_{p\pi}$ and L_π from experimental data given in Tables I and II, in order to examine their dependence on free and bound water amounts (Table III). Previous data relative to Loeb type membranes are also reported in Table III. A least-squares regression analysis shows that all these experimental data fit on exponential relations of the type $y = a\ e^{bx}$. The meanings of x and y and the related values of the coefficients a and b are given in Table IV.

Unilayer A-type Membrane [a]	Free Water (g per dry CA g)	$10^6 L_p$ ($cm^2.sec^{-1}.atm^{-1}$)	$10^6 L_\pi$ ($cm^2.sec^{-1}.atm^{-1}$)	Bound Water (g per dry CA g)	$- 10^7 L_{p\pi}$ ($cm^2.sec^{-1}.atm^{-1}$)
MG 240	0.38	0.27	0.17	0.35	0.29
MG 480	0.18	0.12	0.07	0.34	0.11
MG 1500	0.14	0.08	-	-	-
MG 2700	0.12	0.07	-	-	-
K 240	0.30	0.17	0.12	0.40	0.33
K 330	0.21	0.13	0.10	0.38	0.29
K 480	0.18	0.10	0.09	0.39	0.25
F 60	0.88	3.20	0.30	0.78	1.60
F 90	0.84	2.70	0.28	0.68	1.02
F 120	0.72	2.04	0.20	0.58	1.05

a. Data relative to MG and K membranes were reported by HALARY (1979 a)

Table III

Experimental data used to establish the correlations between L_p or L_π and free water and between $L_{p\pi}$ and bound water.

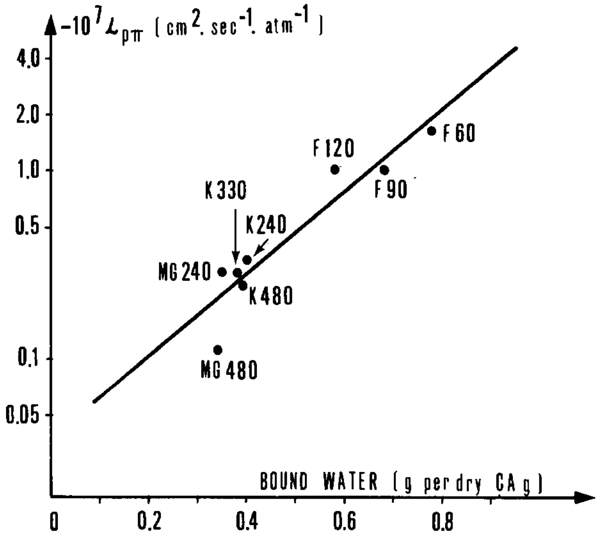

Fig.1-General relationship between $L_{p\pi}$(plotted in a logarithmic scale) and the bound water content of unilayer membranes

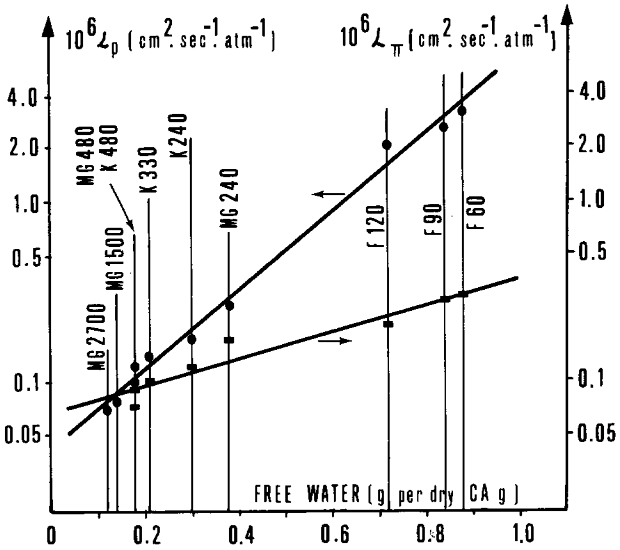

Fig.2-Plots of L_p (●) and L_π(▬) (in a logarithmic scale) versus the free water content of various unilayer membranes

y	x	a	b
$10^6\ L_p$ ($cm^2.sec^{-1}.atm^{-1}$)	Amount of free water (g per dry CA g)	0.0413	5.0641
$10^6\ L_\pi$ ($cm^2.sec^{-1}.atm^{-1}$)	Amount of free water (g per dry CA g)	0.0671	1.6990
$-\ 10^7\ L_{p\pi}$ ($cm^2.sec^{-1}.atm^{-1}$)	Amount of bound water (g per dry CA g)	0.0377	5.0203

Table IV

Meanings of x and y and values of a and b in the equation : $y = a\ e^{bx}$

This data processing leads to more refined relationships than the linear relations postulated previously (HALARY 1979 a). Indeed, as illustrated in figures 1 and 2, such correlations are available for both sets of unilayer Loeb type and Manjikian type membranes. In addition, this data processing gives a more satisfactory picture of the evolution of the ratio L_p/L_π as a function of the membrane water content. As shown in figure 2, L_π which is smaller than L_p in the case of highly hydrated membranes, can become larger for membranes containing less than 0.14 g of free water per dry CA gram, which agrees with some data reported by PUSCH(1975) for annealed CA membranes.

On the other hand, the finding of exponential relationships instead of linear ones does not affect in any way the validity of our molecular analysis of pressure effects on membrane reverse osmosis performance (HALARY 1978). Such an analysis indeed, is based on the existence of correlations between i/ L_p and free water and ii/ $L_{\pi p}$ and bound water but not on the analytical expression of these correlations.

References

FROMMER,M.A. and LANCET,D.: J. Appl. Polym.Sci. 16, 1295 (1972)
HALARY,J.L., NOEL,C. and MONNERIE,L.: Desalination 27, 197 (1978)
HALARY,J.L., NOEL,C. and MONNERIE,L.: J. Appl. Polym. Sci. 24, 985 (1979 a)
HALARY,J.L., NOEL,C. and MONNERIE,L.: Proceed. Intern. Congress on Desalination and Water Reuse, Nice, oct. 21-27, 1979, 3, 64 (1979 b)

KEDEM,O. and KATCHALSKY,A.:Biochem. Biophys. Acta 27, 229 (1958)
LEMOYNE,C., FRIEDRICH,C., HALARY,J.L., NOEL,C. and MONNERIE,L.: J. Appl. Polym. Sci. to be published (1980)
MOSSA,G.: J. Microscopy 107, 67(1976)
OHYA,H. and SOURIRAJAN,S.: J. Appl. Polym. Sci. 15, 705 (1971)
PUSCH,W.: Desalination 16, 65 (1975)
SCHLÖGL, R.: Stofftransport durch Membranen, Darmstadt: Steinkopff 1964
STAVERMAN,A.J.: Rec. Trav. Chim. Pays Bas 70, 344 (1951).

Received November 14, 1979