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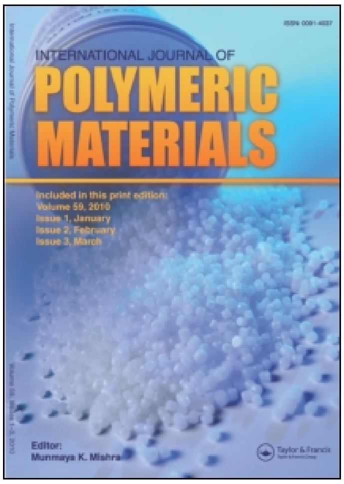

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Lee, D. H. T. and Lyman, D. J.(1993) 'Multicomponent Diffusion Through Cuprophane and a Copolyether-Urethane Membrane', International Journal of Polymeric Materials, 21: 3, 199 — 206

To link to this Article: DOI: 10.1080/00914039308012047

URL: http://dx.doi.org/10.1080/00914039308012047

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Intern. J. Polymeric Mater., 1993, Vol. 21, pp. 199–206
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Multicomponent Diffusion Through Cuprophane and a Copolyether-Urethane Membrane

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(Received December 7, 1992)

The permeability of urea, sucrose, *L*-alanine and their mixtures through a cellulose (Cuprophane) membrane and a copolyether-urethane membrane based on polyoxyethylene glycol were measured. It was found that solute diffusion through the copolymer membrane was affected by the presence of a second solute. This effect appears to be related to the water-structure breaking (with urea) or water-structure making (with sucrose) nature of the co-solute with the water/polyoxyethylene phase of the copolymer membrane. This effect was not seen for the cellulose membrane.

KEY WORDS Copolyether-urethane, cuprophane, membrane, multi-component diffusion, permeability.

INTRODUCTION

The newer block copolyurethane membranes based on polyoxyethylene glycol allow separation of solutes on the basis of both size and chemical structure.[1–3] This appears to be due to the diffusion being through the water swollen areas of lower chain density, i.e., the hydrated polyoxyethylene blocks, in which solute-membrane interaction may be large. Earlier work has shown that the viscosity of water/polyoxyethylene glycol solutions can be altered by this solute interaction.[1,2] For example, solutes of the water-structure breaking type (such as urea) reduced the viscosity while solutes of the water-structure making type (such as sucrose) increased the viscosity. Since these viscosity changes should influence solute diffusion, it was of interest to see the effect of urea and sucrose on multi-component diffusion through these copolyurethane membranes. For comparison, similar studies were done using a cellulosic, pore-type membrane (Cuprophane) where the permeation rate of solutes appears to be solely dependent on solute dimensions and their free diffusion coefficients.[3–6]

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EXPERIMENTAL

Materials

The cellulose membrane (Cuprophane PT-150, J. T. Bemberg & Co.), was soaked in distilled water for at least two days with frequent changes of water before being used in the dialysis studies.

The block copolyether-urethane membrane polymer was synthesized from methylene bis(4-phenylisocyanate) (Multrathane, Mobay Chemical), polyoxyethylene glycol (mol. wt. 1450, Union Carbide Corp.) and 1,10-decanediol (Sigma Chemical) using a modified solution polymerization technique described in detail earlier.[7] The molar ratio of polyoxyethylene glycol to 1,10-decanediol was 0.30/0.70. Membranes were prepared by solvent casting of a 16% solution of the dried copolymer in *N,N*-dimethylformamide onto glass plates, then dried in a forced draft oven at 70°C for 45 minutes. The membranes were then soaked in distilled water to remove them from the glass plates and to remove any residual solvent.

Measurement of Permeability

A modified Leonard-Bluemle Dialysis cell,[2] which has been well characterized with regards to the hydrodynamic boundary-layer resistance adjacent to the membrane[8,9] was used to study the true membrane permeability of selected solutes through the Cuprophane and the copolyurethane membrane (at 30°C and 200 rpm). The wet membrane thicknesses were measured using a light wave micrometer (Van Keuren Co.). The concentration of the dialyzing solute in the dialysis bath was determined by isotopic tracer techniques, using radioactively labeled ^{14}C-urea, ^{14}C-sucrose, and ^{14}C-*L*-alanine (New England Nuclear). The sampling aliquots were mixed with 15 ml scintillant (Aquasol-2, New England Nuclear) and counted in a Beckman LS-7500 liquid scintillation counter.

The initial concentration of the urea, sucrose and *L*-alanine was 0.25 wt.% in each experimental run and the molar concentration ratio for the mixtures was varied from zero to two. A 0.2 μ Curie sample of the ^{14}C labeled solute was added to each prepared solution just before the dialysis experiment. To verify that the activity of tagged solute could be accurately used for the concentration of the bulk solution, the permeability data for a single solute through a membrane by the tracer technique was compared to the data obtained using a differential refractometer; similar results for both techniques confirmed that the tracer technique used in this study is appropriate.

Data Analysis

The total diffusional resistance R_o across the membrane in the dialysis cell is comprised of membrane resistance R_m and hydrodynamic boundary-layer resistances $2R_f$. That is,

$$R_o = R_m + 2R_f \tag{1}$$

and in terms of mass-transfer coefficients

$$1/U = 1/P_{m'} + 2/K_{p'} \qquad (2)$$

where U is the overall mass transfer coefficient; $P_{m'}$ is the membrane permeability; and K_p is the hydrodynamic boundary-layer mass-transfer coefficient. K_p can be calculated from the following equation[9,10]:

$$(K_p d)/D = 0.105[\mu/(eD)]^{0.32}(d^2\Omega e/\mu)^{0.68} \qquad (3)$$

In this equation, d = impeller diameter, 7.18 cm; Ω = angular velocity, ($200 \times 2\pi/60$) rad/s; μ = viscosity of water at 30°C, 0.7975×10^{-2} g/s-cm; e = density of water at 30°C, 0.995646 g/cm^3; and D = diffusion coefficient of solute in water at 30°C (1.55×10^{-5} cm^2/s for urea, 0.70×10^{-5} cm^2/s for sucrose and 1.033×10^{-5} cm^2/s for *L*-alanine). Substituting these values into the above equation, the K_p values can be obtained for the standard experiments in this work: K_p for urea is 3.088×10^{-1} cm/min; for sucrose, 1.798×10^{-1} cm/min; and for *L*-alanine, 2.338×10^{-1} cm/min.

Based on the mass balance for a specific solute, it can be shown for the dialysis cell that

$$-\ln[(1 + V_1/V_2)C_{1t}/C_{1o} - V_1/V_2] = US(1/V_1 + 1/V_2)t \qquad (4)$$

where C_{1t}/C_{1o} is the concentration ratio of specific solute at time t versus at time zero in the V_1 compartment. V_1 and V_2 are the corresponding solution volumes in each compartment and S is the membrane area for diffusion. For the dialysis cell used in this work, V_1 = 232 cm^3, V_2 = 231 cm^3 and S = 43.65 cm^2. The concentration ratio of C_{1t}/C_{1o} of a specific solute can be determined from the activity count of the tagged solute. Thus the overall permeability U can be determined.

The membrane permeability $P_{m'}$ can then be calculated from the K_p and U values. The true membrane permeability, which normalizes the effect of membrane thickness, is $P_{m'}/L$.

RESULTS AND DISCUSSION

The permeabilities for the various solute systems (urea and *L*-alanine in the presence of varying amounts of sucrose, and sucrose and *L*-alanine in the presence of varying amounts of urea) through the Cuprophane membrane are shown in Figures 1(A), 2(A) and 3. The data plotted in Figures 1(A) and 2(A) indicate that the permeability of either urea or sucrose through the Cuprophane membrane is essentially not affected by the presence of the other solute. Previous studies[11,12] have shown that the coupling between urea and sucrose is negligible as compared to the main diffusion term. Also, the water structure in the Cuprophane membrane is primary unbound water[13,14] and thus the water structure-breaking nature of urea should have little effect on the sucrose diffusion. There does appear to be a slight

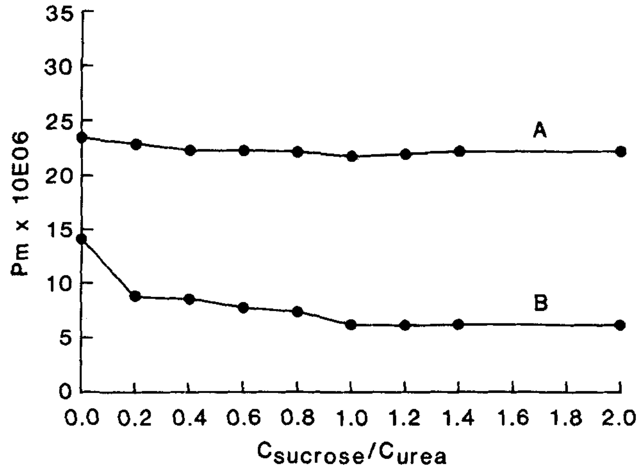

FIGURE 1 Membrane permeability (P_m) for urea in the presence of increasing amounts of sucrose through a Cuprophane membrane (A) and a copolyurethane membrane (B).

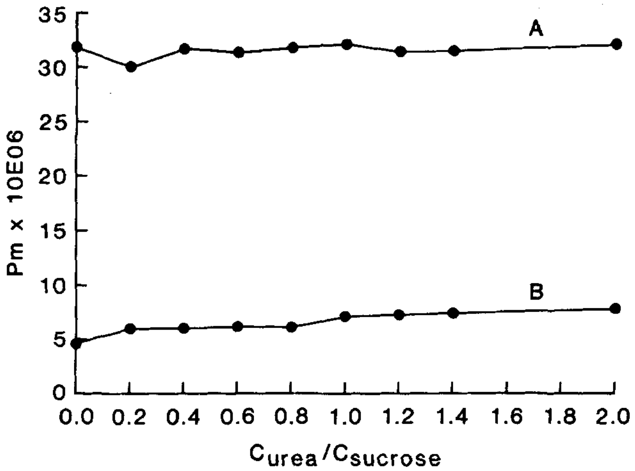

FIGURE 2 Membrane permeability for sucrose in the presence of increasing amounts of urea through a Cuprophane membrane (A) and a copolyurethane membrane (B).

initial decrease in the urea permeability as sucrose is added, possibly indicating a slight increase in bound water in the Cuprophane membrane.[1-15] However, due to the small interaction between solute and membrane[16,17] the water structure-making nature of sucrose is not strong enough to build up more bound water in the Cuprophane membrane with increasing concentration of sucrose.

Similarly, the permeability of *L*-alanine was not affected by the presence of either urea or sucrose (Figure 3). This suggests that the coupling between *L*-alanine and urea or sucrose is not significant. This also suggests that little or no water structuring differences occurred in the mixed-solute diffusions. Similar results were also obtained when *L*-alanine permeability was measured in the presence of both urea and sucrose.

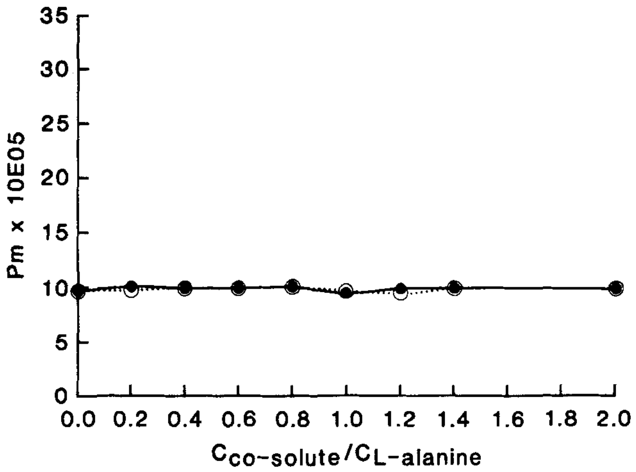

FIGURE 3 Permeability of *L*-alanine through Cuprophane in the presence of increasing amounts of urea (○) and sucrose (●).

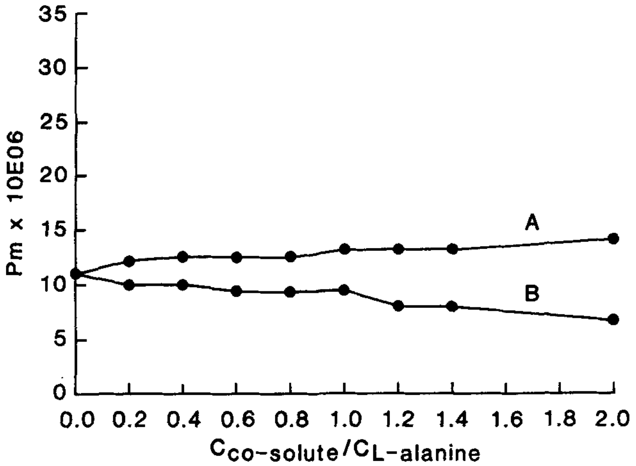

FIGURE 4 Permeability of *L*-alanine through the copolyurethane membrane in the presence of increasing amounts of urea (A) and sucrose (B).

In contrast, the permeabilities for the same solute systems through the block copolyether-urethane membrane (shown in Figures 1(B), 2(B), 4 and 5) do show an effect from the presence of the second solute. For example, the permeability of urea decreases as sucrose is added to the dialyzing solution (see Figure 1(B)). This effect continues until the concentration of added sucrose to urea reaches a molar ratio of 1. Further additions of sucrose has no effect on the permeability of urea. Since the coupling between urea and sucrose is negligible,[11,12] the data suggests that the water structure-making effect of sucrose increases the amount of structured water and thus increases the viscosity of the water-polyoxyethylene phase of the membrane. This increased viscosity would slow the transport of urea through

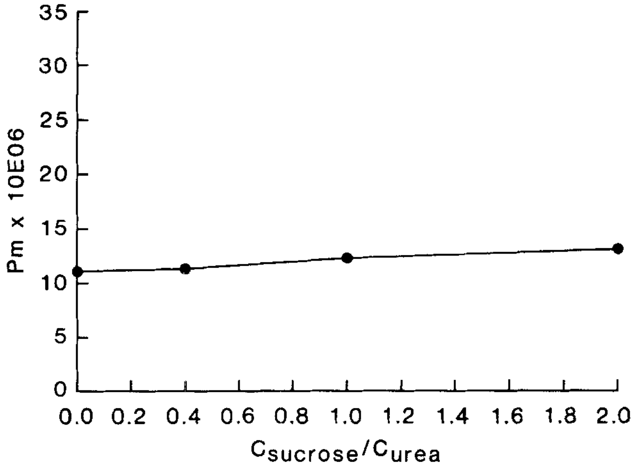

FIGURE 5 Permeability of *L*-alanine through the copolyurethane membrane in the presence of varying concentration ratios of urea to sucrose.

the copolyurethane membrane. Earlier studies have indicated that solute-membrane interaction may be large in this type of copolyether-urethane membrane[2,3]; thus, the water structure-making nature of sucrose could significantly increase the bound water (or freeze the water structure) and thereby decrease the permeation rate of other solutes.[15,18]

In the reverse system (shown in Figure 2(B)), the permeability of sucrose increases as urea is added to the dialyzing solution. Again the permeability of sucrose reaches a plateau value when its molar ratio with urea is 1. Thus, the data suggests that the water structure-breaking nature of urea may significantly decrease the amount of bound water (or defreeze the water structure) in the membrane[17,18] and thereby reduce the viscosity in the water-polyoxyethylene phase of the membrane. Again, the large solute-membrane interaction in the copolyurethane membrane[2,3] would be expected to favor the water structure-breaking nature of urea.

These effects of the water structure-breaking nature of urea and the water structure-making nature of sucrose are well demonstrated by their effects on the permeability of *L*-alanine through the copolyurethane membrane. The presence of urea in the dialyzing solution leads to an increase of transport of the *L*-alanine (Figure 4(A)), while the presence of sucrose leads to a decrease in the transport of the *L*-alanine (Figure 4(B)). However, the permeabilities do not plateau when the molar ratio of the co-solute approaches 1.

It is also interesting to see the relative effectiveness of urea and sucrose when they are in the same solution. The permeability of *L*-alanine in the presence of a steadily increasing molar concentration of sucrose relative to the molar concentration of urea is shown in Figure 5. The increase in *L*-alanine permeability roughly parallels that shown when just urea is added, indicating that the water structure-breaking effect of urea is more pronounced in the water-polyoxyethylene phase of the block copolyurethane membrane than is the water structure-making effect of sucrose.

CONCLUSIONS

The Cuprophane membrane is of the microporous type. There are relatively large and fixed pores within this cellulosic membrane, and water in these pores may be more similar to bulk water. Since the interaction between solutes and membrane are considered to be very small in cellulosic membranes, the permeability of solutes appears to be primarily dependent on solute size (shape) and solute diffusivity in bulk water. Thus, in multicomponent diffusion, if the coupling between the solutes is small, one would expect that the permeability of one solute will not be significantly affected by the presence of another solute. This was observed.

In contrast, the block copolyether-urethane membranes are considered to be nonporous types of membranes, with diffusion occurring through the water-swollen polyoxyethylene phases. In these types of membranes, the solute-membrane interactions appear to be large, and the permeation rates of solutes appear to depend on both the chemical structure of the solute as well as its physical size. In addition, the water structure in the polyoxyethylene phases is considered to be composed of bound water, interfacial water and bulk-like water (unbound water) and appears to be more ordered (less free) than that in the cellulosic membrane. Thus, when more than one solute is present (and if the coupling between solutes is small), it would be expected that the permeability of one solute would be influenced by the interaction between the second solute and the water swollen membrane. With the copolyether-urethane membrane, it was shown that the permeability of one solute was affected by the presence of the second solute. The water structure-breaking nature of urea appears to break the inter-molecular and intra-molecular hydrogen bonding of water to the hydrophilic polyoxyethylene segments, thereby decreasing the viscosity in the transport channel. This would favor an increased rate of solute transport through the membrane. Similarly, the water structure-making nature of sucrose appears to increase the bound water in the membrane. This would tend to increase the viscosity in the transport channel and thus impede the permeation of the second solute. Thus, for adequate permeability characterization of these new block copolyurethane membranes based on polyoxyethylene glycol, one must determine both their individual and mixed solute diffusion characteristics.

Acknowledgment

This work was supported in part by the National Institute for General Medical Sciences, Grant GM 24487-06.

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