Interaction of Some Solutes with Certain Cationic Polymers and Its Effect on Film Permeability

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Synopsis

Permeabilities of cast films of certain cationic acrylate methacrylate copolymers have been determined using a double (donor and acceptor) compartment cell. Permeation rates of urea (nonionic permeant) and sodium chloride (ionic permeant) were determined as functions of the polymer cation content. A decrease in film permeability accompanied the decrease in polymer cation content generally; the change was more marked with sodium chloride compared with urea. The films were also generally more permeable to urea; the difference increased at lower polymer cation content to about 400-fold. While urea promoted film swelling, sodium chloride decreased it. Electron micrographs of the film section displayed compact skin zones which must be swelled to allow solute permeation. Asymmetry characterized the flux, the film lower surface (in contact with the mold during casting) being more permeable than its upper surface. This effect was more pronounced when sodium chloride was used as permeant.

INTRODUCTION

Solutes permeate microporous polymer films by diffusion through aqueous filled channels. Such flux is restricted by the viscous drag of the molecules along pore walls as given by the expression[1]

$$D_p/D_f = \left(1 - r_s/r_p\right)^4 \tag{1}$$

D_p is the porous diffusivity, D_f free aqueous diffusivity, r_s solute molecular radius, and r_p the pore radius. This theory predicts equal permeability for different solutes having similar molecular size. However, differences may arise when the test solutes interact with the polymer. For instance, urea is known to weaken hydrogen bonds in polymer structure to cause film swelling[2]; also ionic solutes may interact with electrostatic charges on the polymer to cause attraction or repulsion of the ion leading to a lower permeability.

Another aspect which has not been considered is the adsorption of ionic solutes by polar groups in the polymer to prevent film hydration and swelling and thus reduce permeability. The effects of these factors were considered in this study.

MATERIALS AND METHODS

Two acrylate methacrylate copolymers designated A and B (Eudragit RL 100 and Eudragit RS 100, respectively) were obtained from Rhom Pharma Darmstadt. A and B differ only in their content of quarternary ammonium

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TABLE I
Cation Content and Film Permeabilities of the Polymers used

Polymer	Mole cation/ mole polymer chain	Permeation rates (mg h^{-1}) of:		Permeability ratio U/S
		urea (U)	sodium chloride (S)	
A	66	480	12.4	39
A.8[a]	59	157	1.2	131
A.6	53	53	0.3	171
A.4	46	35	0.1	438
A.2	40	30	0	$\propto$
B	33	1	0	$\propto$

[a] The decimal number denotes the fraction of A in the mixed polymers, A and B.

(cationic) groups in a ratio 2 : 1 (A : B). The presence of the cationic groups confers a hydrophilic swelling property. A and B were mixed in various proportions to obtain polymers of intermediate cation contents (see Table I). Total nitrogen in the polymer was determined by a micro-Kjeldahl method,[3] 1 mol nitrogen was taken as equivalent to 1 mol cation. Acetone (analar grade, BDH) was used as solvent in film casting and glycerol triacetate (reagent grade, BDH) as plasticizer. Urea and sodium chloride (both analar grade, BDH) were selected as test permeants because of their similarity in molecular weight and size.

Film Casting and Evaluation

Films (thickness 19.8 ± 0.3 μm) were cast on PTFE molds from acetone solution containing the polymer 2.5% w/v and the plasticizer 0.5% w/v, allowing 24 h for every evaporation of the solvent.

Resulting films were equilibrated (3 h, 30°C) in water or aqueous solutions of the permeants to determine the fluid uptake (index of film swelling), which was expressed as the volume fraction of fluid in the film at the equilibrium point.

Permeation was conducted at 30 ± 0.5°C using the double (donor and acceptor) compartment cell previously described by Abdel-Aziz et al.[4] At time zero, the donor compartment contained 10% w/v permeant solution (aq.) and in the acceptor compartment, water, which were stirred 300 rev min^{-1} with magnetic stirrers.

Film surface area exposed to permeant solution was 23 cm^2 and in different experiments, the film lower surface (in contact with the mold during casting) or its upper surface (in contact with air) was upstream. Samples were taken from the acceptor fluid at hourly intervals and analyzed, urea by a spectrophotometric method[5] and sodium chloride by a flame photometry (EEL flame photometer Mark II). Permeation rates were calculated from the slopes of plots of amount of permeant transferred vs. time. Each experiment was carried out in five replicates and the mean result was calculated; individual results were reproduced to ±6.5% of the mean.

Film specimens (surface or cross section) were vacuum-coated with carbon using the Balzer evaporator BA3 followed by a thin gold coat (gold shadow).

The specimens were examined with a scanning electron microscope (Phillips SEM 500) at various magnifications up to 10,000, which was the limit for clear resolution. Mean pore size $\overline{X}$ was calculated using the formula:

$$\overline{X} = \sum FX / \sum F \qquad (2)$$

where F is the frequency of each size X. For each film, three representative micrographs were used for pore size determination.

RESULTS AND DISCUSSION

Measurable pores were not observed on the film surfaces even at a magnification of 10,000; perhaps the pore sizes were below the limit of resolution of the microscope. The micrographs of the film cross section (Fig. 1) revealed a spongy porous core bounded by compact surface zones (skins) each about 4 μm thick.
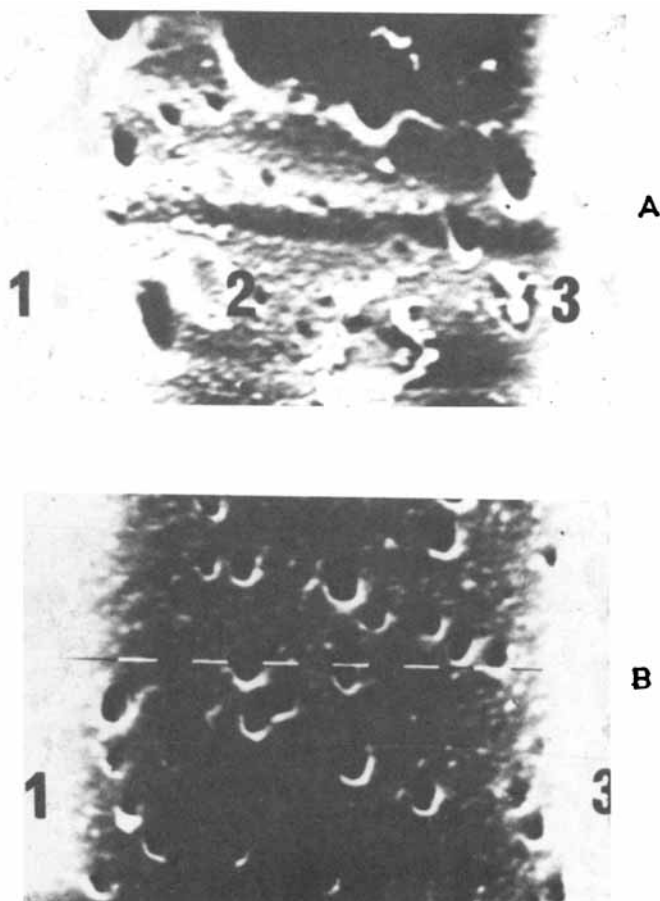

Fig. 1. Electrograph ($\times$10,000) of cross-sections of films of polymers A and B showing: (1) the lower surface skin; (2) porous film core; and (3) the upper surface skin. Bar 5 μm. Note the glossy appearance of gold coat on the compact skin layers and the periphery of the pores.

TABLE II
Film Swellability in the Permeant Solution

| Permeant conc (%) (w/v) | Film Swellability (i.e., vol fraction of fluid in films)[a] | | | |
| | Polymer A | | Polymer B | |
	U	S	U	S
0	0.38	0.38	0.33	0.33
1	0.39	0.21	0.30	0.10
2.5	0.41	0.21	0.32	0.09
5	0.43	0.15	0.29	0.09
7.5	0.44	0.13	0.30	0.08
10	0.44	0.12	0.30	0.10

[a] U = urea (aq) and S = sodium chloride (aq).

Mean pore sizes in the film core were 2.5 ± 0.7 μm (polymer A) and 0.6 ± 0.1 μm (polymer B). A with the higher cation content was therefore more porous than B. It has been suggested that the mutual repulsiveness of the cationic groups opposes polymer chain cohesion during film formation[6] to produce a more porous structure.

Film swellability depended on type and concentration of permeant (Table II); thus urea caused slight swelling of films of polymer A but was ineffective in promoting similar swelling in polymer B, perhaps because of stronger polymer chain cohesiveness in B. Sodium chloride, on the other hand, decreased film swelling generally and, in B, the effect was maximal at a low permeant concentration 1%. The latter effect (i.e., decreased swellability) has been associated with a high osmolarity of the salt solution[7]; but since initially there was no water in the polymer phase, a model of competitive occupation of the hydrophilic (cationic) sites by adsorption of the anionic moiety (Cl^-) of the ionic solute instead of water molecules may be more consistent with the observation. On this basis, it can be said that the fewer number of cationic sites in polymer B were therefore more readily saturated by low concentrations of sodium chloride, and this was reflected in the film swellability data for B in Table II.

Films of polymer A were considerably more permeable to urea than sodium chloride (Fig. 2); this finding relates to the swelling behavior of the films in the permeant solutions. It is considered that pores in the skin zones of the film (Fig. 1) would only reach permeable sizes after swelling; hence the film swellability determined its permeability. The films also displayed asymmetric permeability, the film lower surface being more permeable than its upper surface (Fig. 2); the phenomenon has been associated with a corresponding porous asymmetry on the film surfaces.[4] In the present study, the degree of asymmetry (permeability ratio : lower/upper) depended on permeant type, urea (1.7) and sodium chloride (8.7); this difference relates to insufficient swelling of the upper surface pores to readily permeable sizes (while in contact with sodium chloride solution), reflecting a situation where r_s approximates to r_p [see eq. (1)]. A decrease in polymer cation content caused decreases in film permeability generally (Table I); this finding has been associated with a corresponding decrease in film pore size and swellability.[6] The decrease was
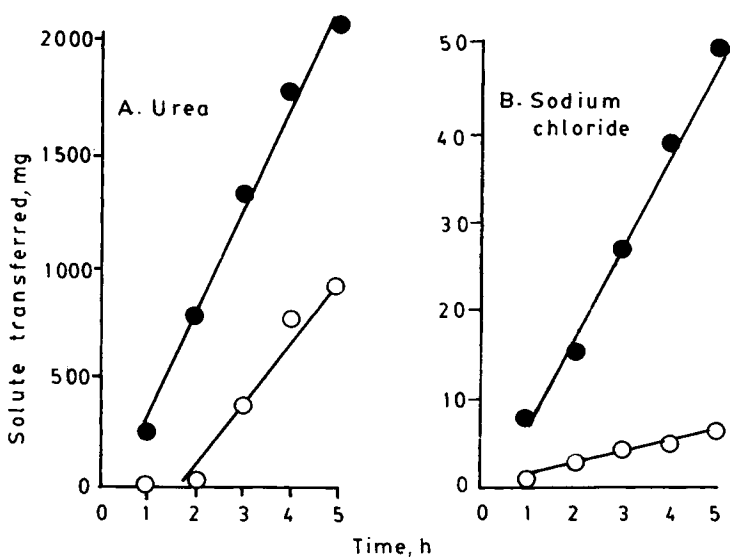
Fig. 2. Amount of solute permeating the films of polymer A when lower (●) or upper (○) surface was upstream in permeation experiments.

more marked with sodium chloride as reflected by the increase in permeability ratio, urea/sodium (Table I); the polymers such as B with fewer hydrophilic centers were more readily saturated with the ionic solute to prevent film swelling. Interaction of charged groups on the film pore walls with ionic solutes to cause their attraction and/or repulsion has been proposed as a solute mechanism for lower permeability of ionic solutes in polymer films.[1] On this basis, the urea/sodium chloride permeability ratio was expected to decrease at low polymer cation content where the effects of the electrostatic interaction would be minimal; on the contrary, the ratio increased (Table I), suggesting that the contribution of this factor to the observed permeabilities was insignificant.

It is suggested that urea promoted film swelling by disrupting hydrogen bonds in the polymer structure[2] while sodium chloride reduced the swelling by competitively blocking water sorption to hydrophilic (cationic) sites in the polymer. Therefore, in spite of the similarity in molecular size of the two permeants, their permeabilities differed markedly. The implication of this finding is that ionic solutes may be used to control film permeability to neutral solutes or vice-versa. Furthermore, the salt rejection potential of the films studied may be enhanced by placing the film upper surface upstream during sea water desalination processes.

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