Permeability properties of polyelectrolyte complexes from carboxymethylcellulose and poly(2-vinyl-N-methylpyridinium iodide)

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Polyelectrolyte complexes between carboxymethylcellulose and poly(2-vinyl-N-methylpyridinium iodide) have been studied. The polycation of two different degrees of substitution was used to make complex precipitates that differ in the stoichiometry. The diffusive permeability of KCl and urea through the solution cast membranes of these complex precipitates has been studied. The polyelectrolyte complex membrane containing the polycation of higher degree of substitution has been found to possess good membrane properties.

Polyelectrolyte complexes formed by the ionic interaction between oppositely charged polyelectrolytes have been studied during the past three decades. They possess a wide range of physical and chemical properties and have useful applications. The high permeability of these ionic hydrogels to water and other microsolute which can be altered by controlling their charge content make these ionic hydrogels good candidates for membrane applications. The investigations on the membrane behaviour of polyelectrolyte complexes containing polysaccharides has attracted less attention. Some of them are reported to have selective transport and controllable permeability. In the present paper, polyelectrolyte complexes made from carboxymethylcellulose (CMC) and poly(2-vinyl-N-methylpyridinium iodide) (PC) have been studied. The effect of the degree of substitution (DS) of the polycation (PC) on the stoichiometry of the complex, preparation of the membranes and permeability of low molecular weight solutes namely KCl and urea through these membranes have been discussed.

Materials and Methods

Sodium carboxymethylcellulose (BDH) was used as such. The molecular weight ($M_w$) was determined to be $4.3 \times 10^5$. The degree of substitution was found to be 0.73 by the acid wash method. 2-Vinylpyridine (2VP) (Merck) was distilled twice under low pressure and was bulk polymerised at $60^\circ C$ using AIBN initiator to obtain poly(2-vinylpyridine) (P2VP). The high molecular weight fraction was separated by fractionation using benzene-hexane solvent pair. The molecular weight of this fraction was estimated to be $4.86 \times 10^5$ by viscometry. Poly(2-vinyl-N-methylpyridinium iodide) of low degree of substitution (PC-30) was prepared by refluxing the solution of P2VP (1 g, 9.52 mmol) in methanol (5%, 20 ml) with methyl iodide (2 ml, 31.9 mmol) at room temperature for 24 hr. The product was recovered by vacuum evaporation from excess of the reagent and was purified by precipitation from methanol in diethyl ether. The pale yellow solid obtained was dried at $50^\circ C$ under low pressure. The degree of quaternization was determined from Volhard's method of estimation of iodide using silver nitrate and was found to be 0.31. Poly(2-vinyl-N-methylpyridinium iodide) of high degree of substitution (PC-70) was prepared by heating the solution of P2VP (1 g, 9.52 mmol) in nitromethane (5%, 20 ml) with methyl iodide (3.6 ml, 57.6 mmol) at $50^\circ C$ for 72 hr. The product was separated by vacuum evaporation and was washed with ether. The deep yellow precipitate obtained was dried at $50^\circ C$ under low pressure. The degree of quaternization was 0.71.

Complex formation and measurements

The PEC precipitates (PEC-30 & PEC-70) were obtained by the direct addition of PC-30 and PC-70 solutions (0.01 mol dm$^{-3}$), respectively, to CMC (0.01 mol dm$^{-3}$) solution. The precipitates obtained were washed with distilled water to remove all the microions and were dissolved in formic acid. Membranes were cast from formic acid solution on glass plates and were analysed by IR spectroscopy (Hitachi 270-50). The characteristic IR bands were 1632 cm$^{-1}$, 1596 cm$^{-1}$ and 1065 cm$^{-1}$. The electron micrographs of gold coated PEC precipitates were recorded using the scanning electron microscope (JSM-840A).

For diffusion experiments, filter paper circles (Whatman No. 1) were coated with the formic acid solution of PEC-70 and PEC-30 and dried. They
are designated as coated PEC-70 and coated PEC-30.

Swelling measurements

The PEC-70 and PEC-30 membranes were equilibrated in distilled water and the equilibrium water content was calculated using Eq. (1), after blotting the surface with a filter paper.

\[ \text{H}_2\text{O content (\%) = \frac{(W_s - W_d)}{W_s} \times 100} \quad \ldots (1) \]

where \( W_s \) = weight of the swollen sample and \( W_d \) = weight of the dry sample. Similarly, the swelling capacity of the films in KCl (0.09 mol dm\(^{-3}\)) and urea (0.9 mol dm\(^{-3}\)) was also measured.

Diffusion experiments

A two-chambered horizontal diffusion cell made of glass was used. The membrane holder had an inner diameter of 2.1 cm. The coated filter papers were washed with water and the swollen membranes were fixed in between the two chambers using rubber gaskets. KCl (0.09 mol dm\(^{-3}\)) or urea (0.9 mol dm\(^{-3}\)) (34 ml each) was introduced in the left hand chamber and equal amount of distilled water was taken in the right hand chamber. The cell was placed in the thermostat at 30 ± 0.2°C. Efficient stirring was achieved by bubbling air through the solution. From each chamber, 0.1 ml of the solution was withdrawn and the change in concentration was measured at various time intervals. The concentration of KCl was determined by the estimation of K\(^+\) using atomic absorption spectroscopy (Perkin-Elmer-2380). Concentration of urea was measured spectrophotometrically by the p-dimethylaminobenzaldehyde method\(^{12}\) (Hitachi U3400 UV-spectrophotometer).

Equilibrium sorption

The partition coefficient, \( K \), which is defined\(^{13}\) as the ratio of the salt concentration in the membrane, \( C_{\text{mem}} \), to that in the outer solution, \( C_{\text{ex}} \), was determined for KCl (0.09 mol dm\(^{-3}\)) and urea (0.9 mol dm\(^{-3}\)) by desorption. The concentration of the solutes was determined as before and was expressed in ppm.

Results and Discussion

On addition of PC (0.01 mol dm\(^{-3}\)) solution to the polyion (PA) (0.01 mol dm\(^{-3}\)) solution, turbidity developed which increased in intensity with the progress of the titration. At a certain point, there was sudden coagulation of the precipitate which was taken as the end point of the titration. The ratio of PA to PC at the equivalence point was found to depend on the DS of the PA. We have determined the ratio of PA/PC in PEC-70 and PEC-30 to be 0.86 and 1.1 respectively. Since more than equivalent amount of PC solution is used up in making PEC-70, the precipitate and the membrane cast from it are expected to have excess positive charges in them. In a similar way, PEC-30 possesses excess negative charges on it.

The electron micrographs of the complex precipitates show that PEC-70 (Fig. 1a) is more compact in structure as compared to PEC-30 (Fig. 1b). This observation confirms the fact that in PEC-70, the neutralisation of charges takes place in a more orderly manner whereas in PEC-30, the random interchain neutralisation gives rise to a less compact structure. This difference in structure of the two PECs is expected to affect properties such as absorption of water, electrolytic behaviour and permeability.
Table 1—Swellability (S), partition coefficient (K) of PEC membranes & permeability coefficients (P & P_s) for the diffusion of KCl & urea through the PEC coated membranes

<table>
<thead>
<tr>
<th></th>
<th>S (%, w/w)</th>
<th>K</th>
<th>P \times 10^3 (g cm^{-1} h^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PEC-70</td>
<td>PEC-30</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90.2</td>
<td></td>
<td>94.5</td>
<td></td>
</tr>
<tr>
<td>KCl (0.09 mol dm^{-3})</td>
<td>82.7</td>
<td>83.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Urea (0.9 mol dm^{-3})</td>
<td>85.4</td>
<td>95</td>
<td>1.1</td>
</tr>
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</table>

*P, values are given in parenthesis.*

1. The permeability coefficients, P, (g cm^{-1} hr^{-1}) for the diffusion of KCl and urea has been calculated using the following equation derived from Fick's law of diffusion:

\[
\ln \left[ \frac{C_0}{(C_0 - 2C_t)} \right] = 2PA_t/xV 
\]

where C_0 is the concentration of the solute taken initially in the left hand chamber, C_t is the concentration of the permeant in the right hand chamber at time t, A is the area of the membrane exposed to diffusion, V is the volume of each cell and x is the amount of the polymer material deposited per unit area of the filter paper. A slight modification has been done in the original equation—instead of thickness of the membrane, the quantity x which is proportional to the thickness has been considered. This has been done due to the difficulty involved in measuring the thickness of the swollen films. The plot of \(\ln \left[ \frac{C_0}{(C_0 - 2C_t)} \right]\) as a function of time, t, is given in Fig. 2. The values of P calculated from the slopes of the straight lines are reported in Table 1. The permeability coefficient has also been calculated considering x as the weight of the deposited polymer when swollen with the permeant per unit area of the filter paper. It has been designated as P_s and reported in Table 1, in parentheses. The former value of the permeability coefficient, P, defined in this paper is characteristic of the chemical nature of the polymer material and is independent of the change in the thickness of the membrane on swelling whereas P_s includes the effect of the change in the free volume of the material on swelling.

The swelling capacity of PEC-30 for water and the two permeant solutes studied is more than that of PEC-70 due to the less compact structure. The ionic content per repeating unit of PC-70 is more than that in PC-30. Hence the total amount of CMC units present in PEC-70 is more than that in PEC-30. PC-30, due to its low degree of substitution contains more number of uncharged pyridine units. The excess charge content in PEC-30 might be even lesser than that expected from the stoichiometry as the excess COOH can protonate the free pyridine units. The partition coefficients reported in Table 1 can be explained on the basis of the amount of charge and the CMC content of the PEC precipitates. KCl, an ionic solute, is less absorbed on PEC-70 as compared to PEC-30 because of the higher charge content of PEC-70. The value of K for the nonionic solute, urea is higher in PEC-70 than in PEC-30. This might be due to the higher cellulose content of PEC-70, which has an affinity for urea due to the possibility of hydrogen bond formation.

![Fig. 2—Relation between ln \left[ \frac{C_0}{(C_0 - 2C_t)} \right] and measurement time for diffusion of (a) KCl, (b) urea. (■) Uncoated filter paper, (Δ) coated PEC-70, (○) coated PEC-30.](image-url)
The effect of the electrostatic interaction and the contribution from the free volume on swelling to the diffusion can be seen by comparing the $P$ and $P_s$ values reported in Table 1. The high $P_s$ value for urea in PEC-30 membrane shows that the permeability of a non-ionic solute is determined mainly by the free volume of the material available for diffusion which is high for PEC-30 due to its higher swelling capacity. The $P_s$ values for KCl in the two PEC membranes is comparable as the swelling nature is not the only factor affecting its permeability. The comparison of the $P$ values for the diffusion of KCl and urea shows that the chemical nature of the membrane contributes more towards the permeability in the case of the ionic solute due to the electrostatic interaction between the permeant and the membrane material. Diffusion of urea is little affected by the chemical nature of the membrane.

It can be concluded that the positively charged PEC-70 has better permeability for KCl and comparable permeability for urea, in spite of its compact structure. It has proved to be a better membrane material as it retains its structural stability.

Many of the polyelectrolytes made of synthetic polymers have shown good antithrombogenic character and suppress the coagulation of blood. PECs from CMC are also reported to have good blood compatible property. Hence, the presently studied materials involving CMC as one of the components might prove promising materials for biomedical applications such as dialysis membranes.

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References
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