Temperature Effect on the Permeation through Poly(2-Hydroxyethyl Methacrylate) Membrane

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Synopsis

The temperature dependence of permeability through highly syndiotactic poly(2-hydroxyethyl methacrylate) [P(HEMA)] membrane is reported for highly polar organic solutes such as ureas, methyl substituted ureas and amides, and for NaCl and Na_2SO_4. The membranes used were equilibrated in distilled water at each temperature before measurements. From the linear correlationship between the excess heat capacities, ϕC_p^0(excess) in aqueous solution at infinite dilution and the permeability parameter $PM^{1/3}$, it is found that the water structure perturbing capability of the polar organic solutes is a controlling factor in the permeation mechanism at relatively low temperature, where P(HEMA) membrane has higher water content and more structured water. In addition, it is found that the poor separation for urea of cellulose acetate membrane in the reverse osmosis practice is due to the higher water structure-breaking capability of urea.

INTRODUCTION

It has been reported[1,2] that the aqueous swelling behavior of P(HEMA) gel at various temperatures shows a swelling minimum at about 50–60°C. Warren and Prins[2] suggested that the negative value of partial molar heat of dilution, $\Delta H_{1,dil}$, below the minimum swelling temperature might be ascribed to the formation of additional water structure with more hydrogen bonding caused by the encounter with the hydrophobic backbone of P(HEMA). Recently, Gregonis et al.,[3] also, observed a swelling minimum for tactic HEMA polymers.

Although the transport properties of some P(HEMA) membranes have been examined before,[4–6] a systematic study on the temperature dependence of the transport of various solutes through P(HEMA) membrane has not been undertaken. From the temperature dependence of aqueous swelling of P(HEMA) gel it is expected that the permeation mechanism of a solute is different at varying degrees of water content in P(HEMA) membrane at various temperatures.

The concept of water structure-breaking and -making effect of solutes has been used as a powerful indirect tool for interpreting solute–water interactions in aqueous solution,[7–9] but this was seldom used in a kinetic phenomenon such as diffusion. In this study, the permeability data obtained are interpreted in terms of the water structure shift effect.

The selected solutes are the highly polar organic substances which include ureas, methyl substituted ureas, and amides. NaCl and Na_2SO_4 are, also, chosen for the model solutes to investigate the mechanistic difference of permeation between organic and inorganic ones without specific interactions. Uncrosslinked highly syndiotactic P(HEMA) membrane is selected as the target material because of its more hydrophobic nature[6] than isotactic P(HEMA) and unperturbed structure.

EXPERIMENTAL

The detailed description for the preparative method of P(HEMA) membranes with different tactic precursors and the measurement of permeability and partition coefficient was reported in the previous paper.[6] All the measurements were made using the membranes equilibrated in distilled water at each temperature for 3 days. The permeability data P are reproducible within 3–5% and the partition coefficient K_{D_2} within 6–10%.

1,3-Dimethylurea, propionamide, and methylurea were recrystallized by a conventional method. Tetramethylurea was vacuum distilled before use. All the other solutes were of reagent grade purity and used as received from E. Merck.

RESULTS AND DISCUSSION

For the uncrosslinked highly syndiotactic P(HEMA) membrane, the permeability data P of ureas, methyl substituted ureas, and amides are plotted against the experimental temperatures in Figure 1. It is noticeable that thiourea has the steepest temperature dependence among the solutes in this study.

The data of inorganic solutes such as NaCl and Na_2SO_4 are shown in Figure 2. It is interesting to note the minimum permeability of these solutes for uncrosslinked P(HEMA) membrane, while 2.5 mol % hexamethylene diisocyanate (HMDIC) crosslinked membrane does not show the minimum within experimental error. It was reported[2,4,5] that the hydrogel from atactic P(HEMA) has a certain amount of supramolecular ordering of hydrophobic and hydrogen-bonded portions. This means that there might exist water pockets[2,5] of clustered water, considering the total water content within the gel. From the equilibrium
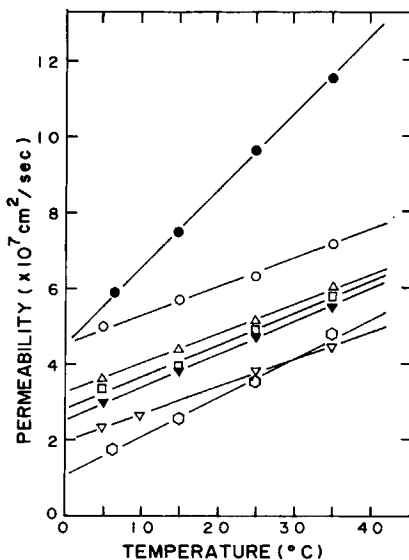

Fig. 1. The permeability of organic solutes through uncrosslinked syndiotactic P(HEMA) membrane as a function of temperature: (●) thiourea; (○) urea; (△) acetamide; (□) methylurea; (▼) propionamide; (▽) 1,3-dimethylurea; (○) tetramethylurea.
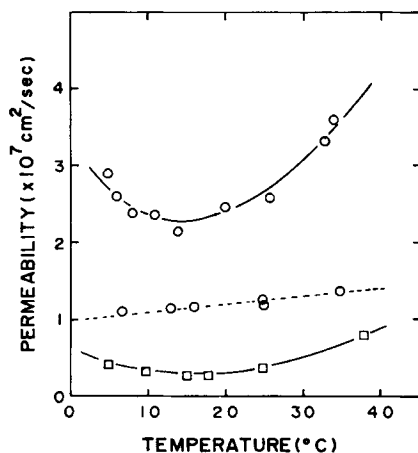
Fig. 2. The permeability of electrolytes as a function of temperature: (O) NaCl; (□) Na$_2$SO$_4$; (—) uncrosslinked syndiotactic P(HEMA); (- - -) 2.5 mol % HMDIC crosslinked syndiotactic P(HEMA).

stress–strain data, Warren and Prins[2] deduced that an increase in apparent molecular weight between crosslinks up to the minimum point of aqueous swelling indicates the gradual elimination of hydrophobically induced order. That is, with increasing temperatures, the size of water pockets might decrease. This fact results in the lowering of the local dielectric constant of the regions available for the transport of the charged ions. The charged ions prefer to remain in a high dielectric constant medium, such as normal water, rather than in a lower dielectric region of polymer surrounded with bound water.[10–12] Therefore, one might infer that the minimum permeability phenomenon occurs through the reconcilation of temperature increase and water content decrease. On the contrary, the minimum permeability is not exhibited by organic solutes because of their possible accessibility to the polymer region through some interactions such as dipole–dipole, H-bonding, etc. This indicates that for organic solutes, the temperature increase overrides the water content decrease of membranes.

When the molecular size weighted permeability[13] $PM^{1/3}$ (by the cube root of the molecular weight as a first approximation) was plotted against the partition coefficient, the plot gave the scattered points. This indicates that at 25°C, the solutes permeate under both the influences of their solubilities and kinetic factors.

Bonner et al.[14] reported the apparent molal heat capacities for eight ureas and substituted ureas, and calculated excess apparent molal heat capacities ϕC_p^0(excess) and group contributions to the excess heat capacities in aqueous solutions. The values of ϕC_p^0(excess) at infinite dilution in aqueous solution are given along with the limiting values[15] of the diffusion coefficient D of the solutes in aqueous solution at 25°C in Table I. The Stokes–Einstein relation for a large spherical particle of radius r diffusing in a continuous medium of bulk viscosity η is

$$D = kT/6\pi\eta r \tag{1}$$

where k is the Boltzmann constant and T the absolute temperature. The plot of the molecular size weighted diffusion coefficient $DM^{1/3}$ in aqueous solution

Solutes	Abbr.	Molecular weight	Dipole moment (Debye)	ϕC_p^0(excess) in aqueous solution (cal·deg^{-1}·mol^{-1})	Diffusion coeff in aqueous solution at 25°C ($\times 10^5$ cm^2/s)
Thiourea	TU	76.12	4.89	−17.4	1.331
Urea	U	60.06	4.56	−5.8	1.382
Methylurea	MU	74.08	—	10.7	1.168
1,3-Dimethylurea	DMU	88.11	4.80	25.6	0.998
Tetramethylurea	TMU	116.16	3.47	50.1	—
Acetamide	A	59.07	3.70	9.2	1.252
Propionamide	PA	73.10	3.47	19.2	1.093

vs. ϕC_p^0(excess) shows a very good linear correlation. Since ϕC_p^0 is a measure of the water structure-perturbing capability of solutes, that is, the decrease in the quanity ϕC_p^0(excess) enhances the water structure breaking effect,[7,14] it is thought from the linear correlation that the diffusion mechanism of these very highly polar organic solutes, as is seen from the dipole moment data in Table I, can be interpreted in terms of water structure-breaking and -making concept.

$DM^{1/3}$ is a characteristic parameter; since the effect of the solute is primarily restricted to the first solvation layer,[16] the translational and rotational mobility of water molecules in the immediate proximity of the solute is different for every
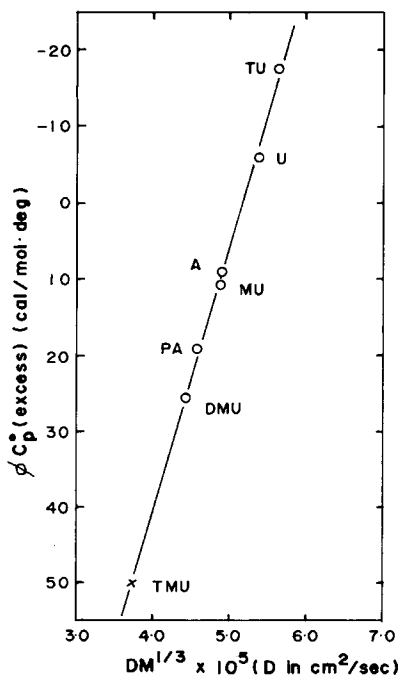

Fig. 3. The correlation between the excess molal heat capacity, ϕC_p^0 and the diffusivity parameter $DM^{1/3}$, in aqueous solution.
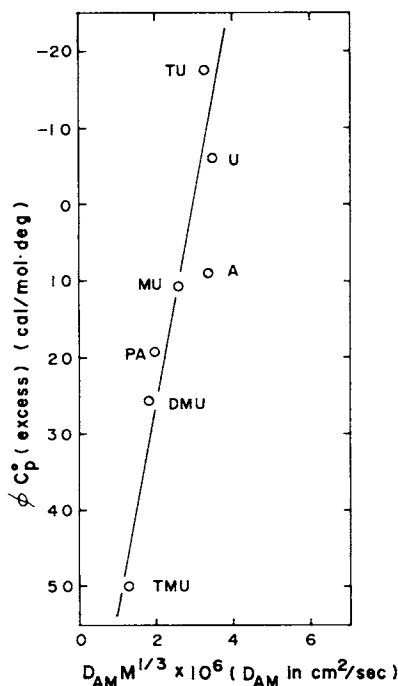
Fig. 4. The correlation between the excess molal heat capacity ϕC_p^0 and the diffusivity parameter $D_{AM}M^{1/3}$ at 25°C within syndiotactic P(HEMA) membrane.

functional group, that is, the constant, $DM^{1/3}$ is a characteristic value for the solute, which implies the microviscosity near the solute molecule. The ϕC_p^0(excess) values of methylurea and propionamide were calculated from group contributions to the excess heat capacities, where in the case of propionamide the contribution of methylene group was assumed approximately to be 10.0 cal·deg^{-1}·mol^{-1}. As can be seen in Figure 3, among the solutes in this study thiourea has the highest $DM^{1/3}$ value expected from ϕC_p^0(excess) values, and the gradual increase of the number of methyl groups in the alkyl-substituted ureas induces the decrease of the constant $DM^{1/3}$, which is reasonable because of the water structure enhancing effect of alkyl groups.[7,14,16]

For the less polar solutes of alcohols, the linear correlation between ϕC_p^0(excess) and $DM^{1/3}$ is not obtained. This may be due to the nonlinear increment in ϕC_p^0(excess) per methylene group[7,17,18] and the higher cavity and structure terms in the interaction enthalpy per CH_2 than the dispersion and dipole-induced dipole terms.[19,20] Therefore, the linear correlation for ureas and amides might partly consist in their very high dipole moments.

The apparent diffusion coefficient D_{AM} of a permeant, which is a criterion for its mobility within membrane phase, is obtained from the equation $D_{AM} = P/K_{D_2}$. From the K_{D_2} data[21] for the organic solutes, the calculated apparent diffusivity parameters $D_{AM}M^{1/3}$ at 25°C for uncrosslinked highly syndiotactic P(HEMA) membrane are shown in Figure 4. The relatively good linear correlation suggests that the mobility of solutes within membrane is governed by the water structure-perturbing capability, and that the membrane has some structurally ordered regions of polymers and clustered water.[2,4-6]
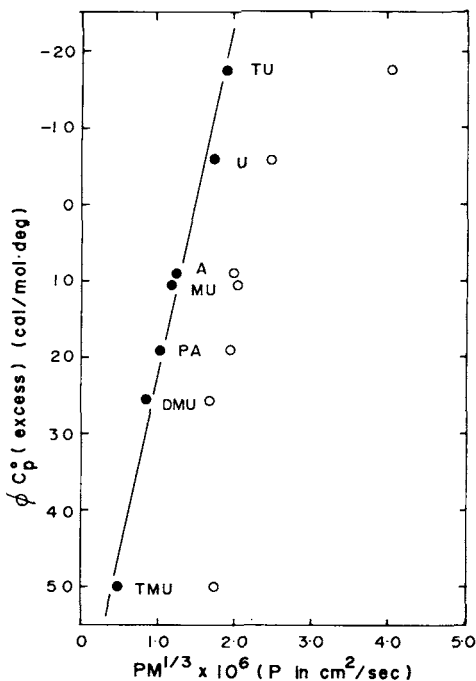
Fig. 5. The correlation between the excess molal heat capacity, ϕC_p^0 and the permeability parameter $PM^{1/3}$; (●) the data extrapolated to 0°C; (○) the data at 25°C.

In Figure 5, we show the temperature dependence of the permeability parameters $PM^{1/3}$ against ϕC_p^0(excess). The extrapolated values to 0°C have a good linear correlation, but with increasing the temperature the correlation becomes poorer by degrees. That is, the permeation at near 0°C is mainly controlled by the water structure-breaking capability of solutes. At this lower temperature P(HEMA) membrane retains more water content[1-3] and more structured water.[2,7] As the temperature increases, the contribution of solubility—the interaction with polymer matrix—to permeability becomes greater and greater. Thiourea has the highest affinity to the membrane,[21] and it is the most powerful structure breaker in this study, which one may see from its steepest temperature dependence on the permeability.

It is known[22] that cellulose acetate membrane exhibits poor urea separation in the reverse osmosis process. However, a clear cut elucidation for the poor separation has not as yet been given. Sourirajan and his group[23] have discussed the logarithmic value of the reverse-osmosis transport parameter $D_{AM}/K \cdot \delta$ in terms of Taft's number $\Sigma\sigma^*$ for the transport of organic solutes such as alcohols, phenols, aldehydes, ketones, ethers, and esters, where K is the partition coefficient and δ the effective membrane thickness. Recently, Kiso et al.[24] obtained the reverse-osmosis performance data for amides and ureas in the cellulose acetate membrane. The plot of ln $(D_{AM}/K \cdot \delta)$ from Kiso et al.'s data vs. ϕC_p^0(excess), also, gives a linear correlation as in Figure 6. The reason for the poor urea separation of cellulose acetate membrane is now clarified from Figure 6. Here, all the values of ϕC_p^0(excess) other than in Table I were calculated from group contributions to the excess heat capacities.
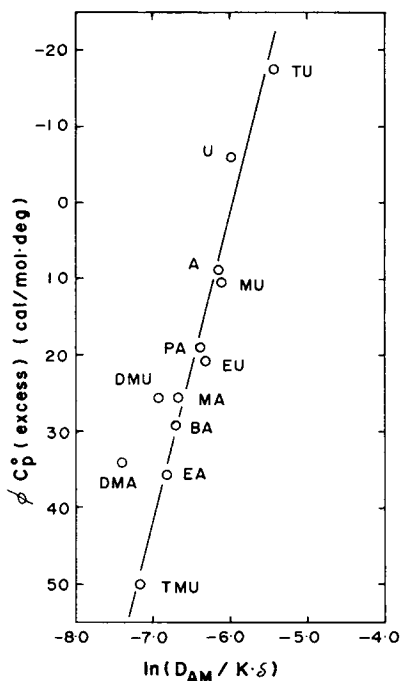
Fig. 6. The correlation between the excess molal heat capacity ϕC_p^0 and the transport parameter $\ln(D_{AM}/K\cdot\delta)$ at 20°C for cellulose acetate membrane in the reverse osmosis performance; BA, butyramide; MA, N-methylacetamide; DMA, N,N-dimethylacetamide; EA, N-ethylacetamide; EU, ethylurea.

CONCLUSION

P(HEMA) gel has an exothermic and endothermic aqueous swelling behavior on temperature variations. When the membranes equilibrated at each experimental temperature are used, the permeation phenomena can be summarized as follows:

1. The ureas and amides of very high dipole moment have positive temperature dependence on the permeability, while the inorganic solutes such as NaCl and Na_2SO_4 show the minimum permeability; this may be due to the inaccessibility of the ionic species without specific interaction to polymer regions.

2. The mobility of the organic solutes within membrane phase is mainly governed by the water structure-perturbing capability of the solutes. Its contribution to permeability is increased with decreasing temperatures.

3. In the reverse osmosis performance of cellulose acetate membrane, the poor urea separation is ascribed to the higher water structure-breaking power of urea.

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