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# Enhanced Polymer Transport Due to the Presence of Salts in Multicomponent Convection

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Transport rate of poly(vinylpyrrolidone) in aqueous dextran matrix was enhanced by the addition of CsCl or NaCl but not by LiCl. This enhancement can be partly attributed to a decrease in hydrodynamic resistance.

When an aqueous solution of dextran is placed above another aqueous solution consisting of dextran of the same concentration and poly(vinylpyrrolidone)(PVP), diffusion of PVP is expected to occur. However, when both dextran and PVP concentrations exceed respective critical values, a rapid transport of PVP has been observed.[1] This rapid transport was ascribed to the occurrence of a finger-like structured flow[1,2] and was characterized by linear dependence on time $t$ rather than on $t^{1/2}$. The molecular mechanism of the phenomenon, which is an example of multicomponent convection, is not yet fully elucidated in spite of the extensive study carried out by an Australian group.[1-4]

Under similar experimental configuration as reported,[2,3] we have found that the transport of PVP is enhanced when CsCl or NaCl is present at the same concentration both in the upper and lower compartments of a Sundeloef cell[5]: each compartment is a cylinder of about 1 cm long with a cross section area $A$ of about 0.2 cm$^2$. Number average molecular weights

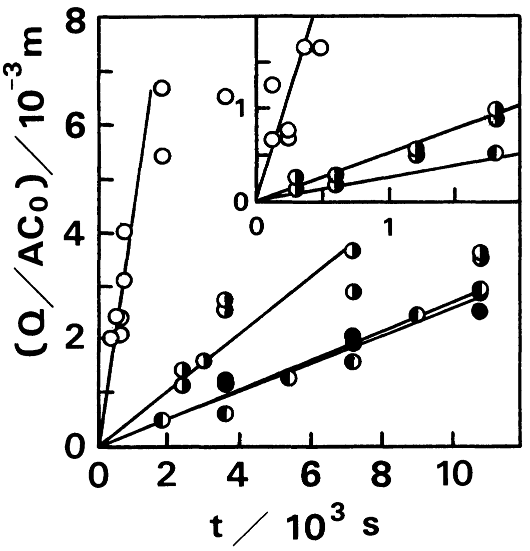


Fig.1. Transport rate in the presence of 2 M salt both in upper and lower compartments. (○) CsCl, (◑) NaCl, (◐) LiCl and (●) no added salt. Inset: enlarged plot for initial stage($t$< 2 X $10^3$s).

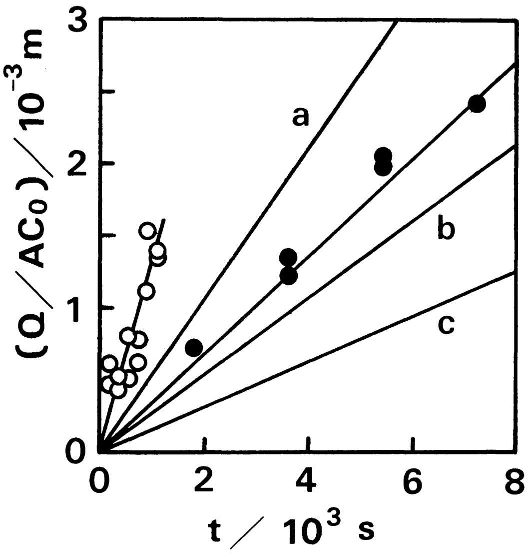


Fig.2. Transport rate in the presence of CsCl at different concentrations. (○) 0.614 M, (●) 0.2 M. Lines a,b and c represent the results with 2 M NaCl, no added salt and 2 M NaCl(upper)-2 M CsCl(lower).

(osmometry) of dextran and PVP labeled with remazol brilliant blue were (3.8 ± 0.1) x $10^4$ and (3.2 ±0.1) x $10^5$, respectively.

In Fig.1 amounts $Q$ of PVP transported per unit area to the upper compartment at 25℃ are indicated as functions of time $t$ in the presence of various salts at a concentration of 2 M (mol $dm^{-3}$). The initial PVP concentration in the lower compartment $C_0$ was 10 g/l (kg $m^{-3}$). Dextran concentration was 80 g/l. Enhancement of the transport is evident when CsCl or NaCl is present in both upper and lower compartments. Slopes of the lines in Fig.1 can be taken as a measure of transport rate ($v$): values of $v$($ms^{-1}$) are (4.5±0.6) x $10^{-6}$(CsCl), (5.2±0.4) x $10^{-7}$(NaCl) and (2.6±0.2) x $10^{-7}$(LiCl). The rate in the absence of salt is (2.7±0.3) x $10^{-7}$ $ms^{-1}$. The effect of KCl could not be examined because gelation occurred. Effect of CsCl concentration was examined as shown in Fig.2. The transport rates are (1.3±0.2) x $10^{-6}$ $ms^{-1}$ and (3.4±0.3) x $10^{-7}$ $ms^{-1}$, for 0.614 M and 0.2 M, respectively. It is noted

Table 1. Viscosities of PVP-MCl(2M)-$H_2O$ at 25 °C

| | $H_2O$ | LiCl | NaCl | KCl | CsCl |
|---|---|---|---|---|---|
| $\eta_{rel}$($C_{PVP}$ = 0) | 1 | 1.26 | 1.13 | 0.92 | 0.77 |
| $\eta_{rel}$($C_{PVP}$=0.1 g/dl) | 1 | 1.21 | 1.10 | 0.88 | 0.72 |
| [$\eta$](dl/g) | 1.39 | 0.86 | 1.05 | 0.58 | 0.46 |

Table 2. Viscosities of dextran(80g/l)-PVP-MCl(2M)-$H_2O$ at 25 °C

| | Dextran | LiCl | NaCl | CsCl |
|---|---|---|---|---|
| $\eta$ ($C_{PVP}$=0)(relative) | 1 | 1.32 | 1.22 | 0.82 |
| $\eta$ ($C_{PVP}$=0.8 g/l)(relative) | 1 | 1.33 | 1.22 | 0.81 |
| [$\eta$](dl/g) (PVP) | 0.53 | 0.58 | 0.51 | 0.44 |

that the rate $v$ is greater for 0.614 M CsCl than for 2 M NaCl, although these two salt solutions have the identical density. Consequently, the enhancement action of the salts cannot be simply related to their solution densities. In Fig.2 is also shown a result of the transport in the following configuration of the system: 2 M NaCl in the upper compartment and 2 M CsCl in the lower one. The rate of transport in this configuration is rather small, (1.6±0.2) x $10^{-7}$ $ms^{-1}$ determined based on 8 points up to 6 h (not shown), if compared with the rate in the absence of any salt.

The enhancement effect of salts revealed in Figs.1 and 2 could be related to several factors such as the effect on the polymer coil dimension, water structure, osmotic pressure and so on. To obtain information concerning the polymer coil dimension, viscosities of solutions were measured. Results on PVP-salt system and PVP-dextran-salt system are given in Tables 1 and 2, respectively. In the absence of dextran(Table 1), the intrinsic viscosity of PVP in the presence of salts decreases in the following order: NaCl > LiCl > KCl > CsCl. The intrinsic viscosities of PVP in the presence of dextran network are, on the other hand, rather insensitive to the kind of salts present(Table

2). These results suggest that random coil chains of PVP shrink considerably in dextran network even in the absence of salt and that addition of salts cannot reduce the coil dimension further to a significant degree. Thus, the effect of the salts on the coil dimension of PVP cannot be responsible for the enhanced transport. An important factor related to the enhanced transport is found on the first row of Table 1. The viscosity of CsCl solution(2 M) is much lower than that of pure water, which may be considered due to the structure-breaking effect. With the reduced viscosity, the velocity at the center of each finger is expected to increase and the transport of PVP is enhanced subsequently. However, this factor alone cannot explain the observed enhancement effect even qualitatively in the case of NaCl, since the viscosity of the salt solution is greater than that of water, whereas enhancement instead of suppression of the transport rate is observed. Further, in the case of CsCl, it is not clear at all whether a reduction of hydrodynamic resistance by about 23% could explain the enhancement (about 18 fold) of transport rate. Thickness of finger is certainly an important factor to determine the transport rate. In the case of CsCl, the 'finger' was so thick that it was visible even by naked eye though faintly.

References

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