



Counterion condensation and rapid transport of polyelectrolytes through aqueous polymer solutions

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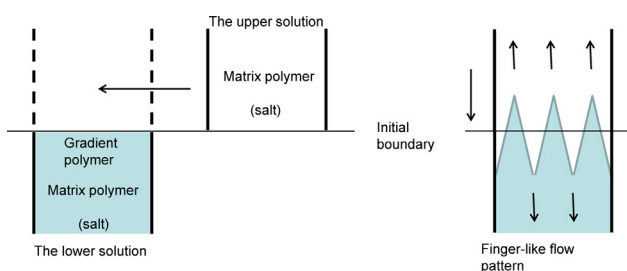
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HIGHLIGHTS

- ▶ A rapid transport of polyacrylates through aqueous dextran solutions is reported.
- ▶ The transport rate increased with the charge density.
- ▶ The counterion condensation manifests itself in the nonlinear transport process.
- ▶ The transport rate decreased with increasing salt concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

A rapid transport of polyacrylates through aqueous dextran solutions was reported. The transported amount Q linearly increased with time t instead of $t^{1/2}$. The rapid transport is associated with the formation of finger-like flows, a kind of dissipative structure. The transport rate V increased with the linear charge density of polyacrylic acid but became constant independent of the charge density if the latter exceeds a critical value. The counterion condensation was strongly suggested from this peculiar dependence on the charge density. The transport rate decreased with increasing NaCl concentration. At 0.5 M NaCl, the transport was no longer rapid but took place as a diffusion process. As another matrix–gradient system, transport of polyvinylpyrrolidone (PVP) through aqueous sodium polyacrylate solutions was also examined and rapid transport of PVP was found.

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1. Introduction

When an aqueous solution of dextran is placed above another aqueous solution consisting of dextran of the same concentration and polyvinylpyrrolidone (PVP), the diffusion of PVP from the lower solution to the upper solution is expected to occur. The situation is schematically shown in Fig. 1A where the matrix polymer is dextran and the gradient polymer is PVP. However, a rapid transport of PVP has been observed by Preston et al.

[1,2] when both dextran and PVP concentrations exceeded respective critical values. This rapid transport was found to be due to the occurrence of a finger-like structured flow as schematically shown in Fig. 1B and it was characterized by the linear dependence of the transported amount on time t rather than on $t^{1/2}$ (diffusion process). The system is called matrix–gradient system where PVP moves through the dextran solution matrix as a result of a given concentration gradient. We have reported that the PVP transport in dextran–PVP system is enhanced in the presence of a simple salt (the same concentration in both upper and lower solutions). The extent of enhancement depends on the kind of ions and is correlated with the density of solutions [3–5]. The molecular mechanism of the phenomenon is not yet fully elucidated.

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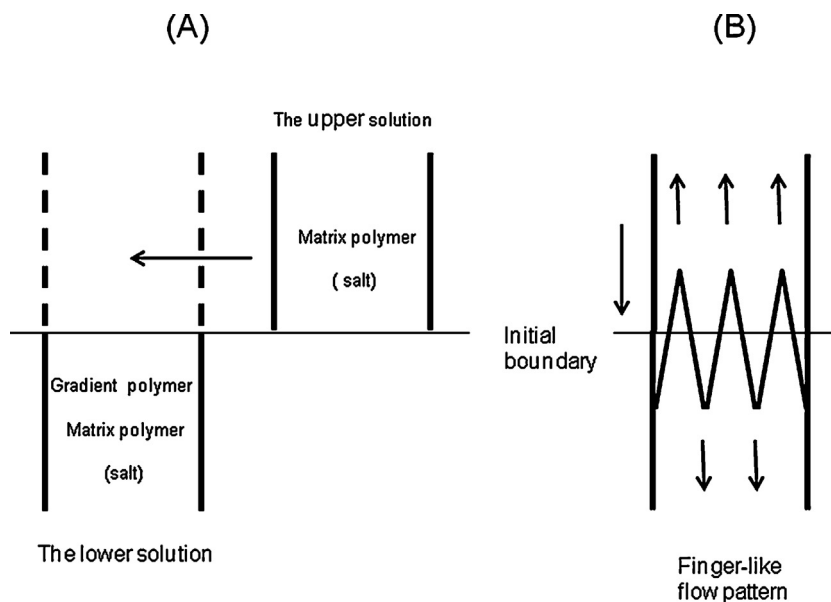


Fig. 1. A schematic representation of the measurements with Sundelöf cells. (A) At time 0, two compartments are brought into the contact position to stratify the two solutions. (B) After a duration of time, finger-like flow pattern appeared in case that the conditions for the dissipative structure are satisfied.

As to the effects of electric charge, a few reports on the transport of biological polyelectrolytes are found, such as chondroitin sulfate through proteoglycan matrix [6] or hyaluronic acid matrix [7] and sodium hyaluronate through dextran matrix [8]. We have examined the transport of a polyelectrolyte, polyacrylate, through a dextran matrix focusing on the effects of counterion species. The transport rates were in the following order [5]: $(\text{Pr})_4\text{N}^+ > (\text{Me})_4\text{N}^+ > \text{Li}^+ > (\text{Bu})_4\text{N}^+ > \text{Na}^+ > \text{NH}_4^+ > \text{Cs}^+$. The order was linearly correlated with the partial specific volume except for $(\text{Bu})_4\text{N}^+$, to which the effect of the viscosity was suggested [5]. The effects of the charge density of polyacrylate and the salt concentration will be presented in the present report. Also, some results on transport of PVP through aqueous NaPAA solutions, a new matrix (NaPAA)–gradient (PVP) system, will be reported. A preliminary experiment using an ionic micelle as a gradient component will be also reported.

2. Materials and methods

Dextran (Nacalai Tesque Inc.) was used as received. Polyacrylic acid was recovered from sodium polyacrylate (Toa Gosei Chemicals Co.) by repeated precipitation-dissolution by HCl and NaOH. Number-average molecular weights M_n of dextran and PAA were 3.5×10^4 and 5.9×10^4 , respectively, as determined by osmotic pressure measurements (Knauer membrane osmometer) using cellulose membranes (Y1245, Knauer) of pore size $0.005 \mu\text{m}$. Weight-average molecular weights M_w of NaPAA was 2.1×10^5 as determined by light scattering (Malvern PCS100SM). Polyvinylpyrrolidone ($M_n = 3.2 \times 10^5$) was the same sample as used in a previous study [5]. PAA was labeled with 9-chloromethylantracene (Tokyo Kasei Kogyo Co. Ltd.) in dimethylformamide containing tetramethyl ammonium hydroxide. The extent of label was about one dye molecule per 1000 residues. The transport of PAA was measured at $23 \pm 1^\circ\text{C}$ with Sundelöf cells. A Sundelöf cell consisted of two identical compartments. Each compartment was a cylinder of ca 1 cm long and ca. 0.2 cm^2 cross section area A . At time 0 ($t=0$), the upper and the lower solutions were stratified as shown in Fig. 1A. After a time interval t elapsed, the two compartments were separated and brought back to the original position and the amount of PAA in the upper

compartment Q was determined by the absorption at 257 nm. Details of the measurement are given in the previous reports [3,4]. To control pH values of the solutions proper buffer systems were used. Finger-like flow patterns were observed using a microscope after an upper solution was slowly added by a pipette onto a lower solution in a glass cell (depth 1 mm, 1 cm wide). A sharp initial boundary was obtained almost always in this way.

3. Results

3.1. Effects of the charge density of PAA on the transport rate

The transported amounts Q of PAA from the lower compartment to the upper compartment were measured as functions of time t at different pH values. Identical pH values for both the upper and the lower compartments during the measurement were expected to be maintained by using proper buffer solutions: acetate buffers (pH 4.2–5.5), phosphate buffers (pH 5.9–6.9) and trisHCl (pH 8.0–9.0). Buffer concentrations were 30–50 mM. The PAA concentration present in the lower compartment C_0 was $3 \text{ kg (Na salt basis) m}^{-3}$ (ca 30 mM). Dextran concentration was 80 kg m^{-3} . In all cases examined, Q increased linearly with time t indicating a non-diffusive transport. The transport rates V were evaluated according to Eq. (1). Also, the apparent diffusion constants D_{app} were evaluated according to Eq. (2).

$$\frac{Q}{AC_0} = Vt \quad (1)$$

$$\left[\frac{Q}{AC_0} \right]^2 = \left(\frac{D_{app}}{\pi} \right) t \quad (2)$$

The results are summarized in Table 1 and the transport rates V are plotted against the degree of ionization α in Fig. 2. Four solutions (open symbols in Fig. 2) were prepared by adjusting the degrees of neutralization. For other solutions, the degrees of ionization α were approximately evaluated from the measured pH values with the aid of a reported titration data in 20 mM and 50 mM NaCl [9].

The apparent diffusion constants D_w of NaPAA in the absence of dextran evaluated according to Eq. (2) were $0.2\text{--}0.3 \pm 0.05 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at both $\alpha = 0.25$ and 0.64 . These values are smaller than D_{app} values shown in Table 1, providing

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