doi:10.1246/cl.2010.970

Control of Ag^+ Permeation by Na^+ Concentration on the Basis of Volume Change in Poly(acrylic acid) Gel

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A molecular gate for Ag^+ ion, consisting of poly(acrylic acid) (PAA) gel-coated Au mesh, was developed based on a volume change of the gel in response to the Na^+ concentration. The permeation of Ag^+ through the gate was reduced when the Na^+ concentration was lower than 1×10^{-3} M where the gel swells, whereas it increased when the concentration was higher than 1×10^{-2} M where the gel contracts.

Molecular valves that are capable of self-regulating flow control upon external stimuli have recently attracted a great deal of attention for uses in nano- and microfluidic systems. The automatic operation of the polymer gel valves is achieved by change in the volume responding to various stimuli such as temperature,[1,2] pH,[3–5] and solvent composition.[2] Similarly, molecular gates have been developed consisting of polymer gels, which are able to control permeation of substances.[6] However, to the best of the authors' knowledge, there have been no reports on gates in which the permeation of the substance is controlled by the same type of a substance (stimuli). In this letter, we report on a molecular gate consisting of PAA gel, which regulates a cation (Ag^+ ion) permeation via another cation (Na^+ ion). PAA gel is known to exhibit universal volume change upon changes in concentrations of alkali and alkali earth metal cations[7] and transition and rare earth metal ions.[8–10] The gate in this study operates on the basis of changes in affinity of Ag^+ ion to the carboxylate of the gel resulting from changes in the gel volume, which is controlled by Na^+ concentration.

The structure and preparation of a molecular gate were similar to that of a molecular valve reported previously.[11] In brief, PAA gels were synthesized on a Au mesh ($10 \times 10\,mm^2$, 100 mesh, Nilaco Co.) by radical polymerization of acrylic acid (700 mM) and *N*,*N*′-methylenebis(acrylamide) (7 mM) with ammonium peroxodisulfate (3.5 mM) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (8 μM) as an initiator and an accelerator, respectively. The gel-modified Au meshes were set in between homemade holders (polycarbonate, 5.0 mm i.d.) via O-rings (4.8 mm i.d.). The experimental setup for a permeability monitoring is illustrated in Figure 1. A set of the holders was held horizontally and L-shaped glass tubes (120 mm length, 4 mm i.d. at the holder end, and 20 mm i.d. at the other end) were attached to the both sides. The tubes were then filled with 5.0 mL of various electrolyte solutions. A Ag-ISE (DKK-TOA Co.) and a lab-made double junction Ag/AgCl reference electrode (Ag/AgCl|KCl||KNO_3||sample soln.) were set in both sides. The emf's of the Ag-ISEs were monitored with ion meters (IOL-50, DKK-TOA Co.). All measurements were performed in a dark box at room temperature (25 ± 2 °C).

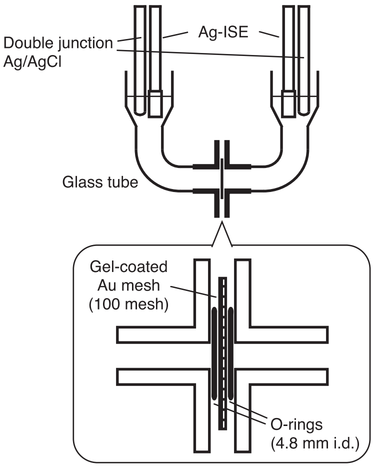

Figure 1. Experimental setup of the molecular gate.

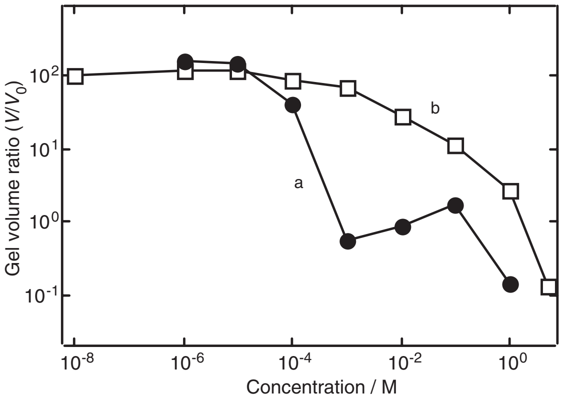

Figure 2. Dependencies of volume ratio of a poly(acrylic acid) gel on concentrations of (a) $AgNO_3$ and (b) $NaNO_3$[11] aqueous solutions. The volume of the gel as synthesized (cylindrical shape, $\phi 3 \times 5$ mm) was used as standard (V_0).

The volumes of the cylindrical PAA gels (3 mm diameter × 5 mm length as synthesized) were measured in various concentrations of $AgNO_3$ solutions after they reached equilibrium (at least 10 days) and are shown in Figure 2 with those in $NaNO_3$ solutions.[11] The volume change was evident at 10^{-5}–10^{-3} M for Ag^+ and $>10^{-5}$ M for Na^+, indicating that if the concentrations of Ag^+ and Na^+ are less than 10^{-5} M, the gel remains swollen. In addition, the dependence of the gel volume on the concentration of $NaNO_3$ solution containing 1×10^{-5} M $AgNO_3$ appeared to be virtually the same as that in the absence of Ag^+ (Figure 2). This indicates that by keeping the Ag^+ concentration less than 1×10^{-5} M the volume of the gel can be controlled by the Na^+ concentration.

Based on the above, a permeation of 1×10^{-5} M Ag^+ through the PAA gel gate was evaluated by changing Na^+

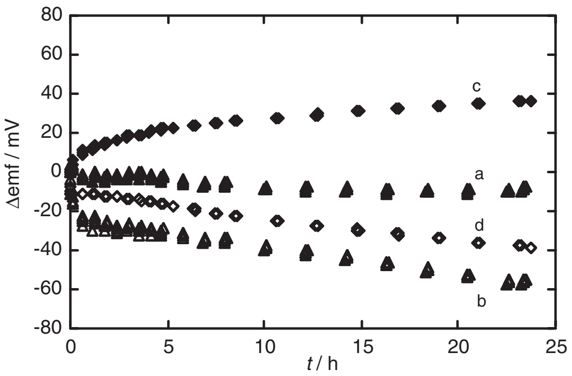

Figure 3. Time courses of Δemf after injection of Ag^+ (final concentration: 1×10^{-5} M) into a 1×10^{-6} M $NaNO_3$ solutions at (a) Na^+ side and (b) $Na^+ + Ag^+$ side and into a 1 M $NaNO_3$ at (c) Na^+ side and (d) $Na^+ + Ag^+$ side.

concentration over a range from 1×10^{-6} to 1 M. Figure 3 shows typical changes in the Δemf ($= E - E_{ini}$, where E_{ini} is the potential when Ag^+ was injected) of the Ag-ISEs in the chamber (tube) to which Ag^+ was added ($Na^+ + Ag^+$ side) and that in the other side (Na^+ side) at $NaNO_3$ concentration of 1×10^{-6} and 1 M as representatives. Here, the potentials were monitored intermittently (0.5, 1, or 2 h interval and each measurement was for 5 min), and in the mean time the reference electrodes in both sides were taken out from the solution to prevent leakage of inner electrolyte in the electrodes which gives rise to contraction of the gel film. As can be seen in Figure 3, the Δemf for the Na^+ side in a 1×10^{-6} M Na^+ solution appeared to remain virtually constant within an error, whereas that in a 1 M Na^+ increased by ca. 20 mV and reached a steady state. These results suggest that in a 1 M Na^+ solution Ag^+ ions permeated through the film and that it was not the case in the 1×10^{-6} M solution. Unfortunately, it was difficult to calculate absolute Ag^+ concentrations due to relatively large errors of at most 67 mV, which corresponds to tenfold concentration, observed even with the same electrode in a 1×10^{-5} M Ag^+ solution. However, the stability of the potential before the injection of Ag^+ was less than ±1 mV/30 min, the changes in the potential should be ascribed to changes in the Ag^+ concentration. In addition, the permeation of Ag^+ ion was further supported by AAS measurements.[12]

The Δemf's for the $Na^+ + Ag^+$ side at all Na^+ concentrations examined were found to monotonically decrease, indicating a decrease in Ag^+ concentration even at 1×10^{-6} M Na^+ where the gel expands and unlikely allows ions to permeate. This could be rationalized by taking into account the absorption of Ag^+ into the gel. In fact, a gel the same size as that on the mesh immersed in a 1×10^{-5} M $AgNO_3$ (3.3×10^{-7} mol) solution containing 1×10^{-6} M $NaNO_3$ for 24 h was found to incorporate 2.2×10^{-8} mol Ag^+ by AAS. The amount of Ag^+ ion in the solution decreased to 1.6×10^{-7} mol. On the other hand, in the case of 1 M $NaNO_3$, the gel contained only 7.8×10^{-9} mol Ag^+, and the Ag^+ concentration in the solution remained constant (1×10^{-5} M) before and after the immersion.

The difference in the potential (Δemf_{24h}) between right after (E_{ini}) and 24 h after (E_{24h}) the Ag^+ injection was plotted against Na^+ concentration (Figure 4). Here the ΔE was defined as $E_{24h} - E_{ini}$. At the concentration above 1×10^{-3} M Δemf_{24h} for the Na^+ side was found to be larger, indicating the permeation of Ag^+. The larger Δemf_{24h} values at the $Na^+ + Ag^+$ side at lower Na^+ concentrations would be manifestation of absorption of Ag^+ ion into the gel as mentioned above. Based on the above, the mechanism of the permeation is proposed as follows. At a lower Na^+ concentration where the gel swells and thus carboxylate groups of the gel are accessible, Ag^+ ions are trapped. On the other hand, at a higher concentration where the gel shrinks, they are hardly trapped and/or are excluded by competition with Na^+ ions, resulting in permeation. It should be noted that no solution passed the gate indicating that the current gate is different from the molecular valve we previously developed,[11] which regulates solution flow.

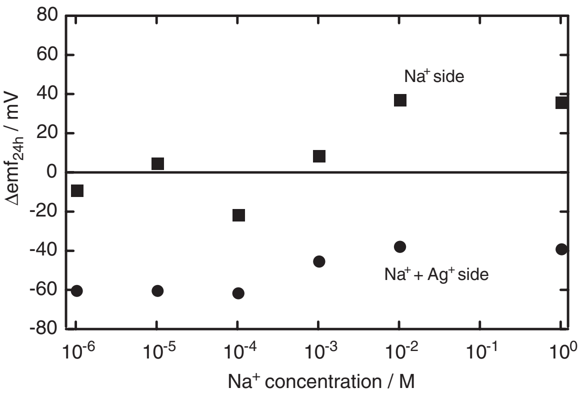

Figure 4. Dependencies of Δemf_{24h} at Na^+ side and $Na^+ + Ag^+$ side on Na^+ concentration.

At this stage, although it is difficult to eliminate the errors in the potential measurements due to a relatively low concentration of the target ion, the present work demonstrated the possibility of automatic permeation control of cation by coexistence of a different cation. This system could be used as an automatic ion gate for reactors. Studies toward more precise control and a reversible operation will be performed and will be reported elsewhere.

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.