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Molecular valve consisting of poly(acrylic acid) gel

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ABSTRACT

A molecular valve, consisting of poly(acrylic acid) gel-coated Au mesh, was developed based on volume change of the gel in response to cation concentration. The valve closed when concentration of cations such as H^+, Na^+, K^+, Ca^{2+}, Cu^{2+}, or Al^{3+} was low, whereas opened upon increase in its concentration. The valve re-closed when water was flowed. The concentration where the valve opens was found to increase in the order of Al^{3+}, Ca^{2+}, and Na^+ (2×10^{-4}, 5×10^{-4}, and 6×10^{-3} M, respectively). The response to Cu^{2+} ion showed similar behaviour, but the opening concentration was ca. 2×10^{-4} M, which is lower than that of Ca^{2+} ion. The valve appeared to close over the pH range from 3 to 12, whereas to open below and above it. The fastest response time to open the valve (less than 1 min) was obtained for a solution of pH 1–2. The valve showed repeatability at least 25 cycles upon successive loading of a solution of pH 2 and water. Effects of anions and pressure were also studied.

1. Introduction

Recently the molecular valves have received a great deal of attention due to the demand on miniaturized sizes required in flow control in nano- and micro-fluidic systems. Conventional electromagnetic valves require external power for operation and should consist of sensing, signal transmission, and actuation parts. On the other hand, molecular valves consisting of polymer gels are capable of self-regulating flow control on the basis of volume change responding to various stimuli such as temperature [1,2], pH [3–5], and solvent composition [2]. In other words, they do not require external power and operate automatically upon changes in surrounding environment. In addition, they could be in molecular size in theory.

In the case of the temperature responsive valves, poly(*N*-isopropylacrylamide) or its copolymer gel has most widely been used as it expands at temperature below lower critical solution temperature (LCST, 32 °C) whereas contracts above it. For pH responsive gates, poly(acrylic acid) gel or its copolymer has commonly been employed, since it swells and shrinks at lower pH and higher pH, respectively. This volume change is attributed to changes in osmotic pressure and electrostatic interaction between charges on the polymer chain and counter ions [6,7]. Poly(acrylic acid) gel is also known to exhibit volume change upon changes in alkali and alkali earth metal cation concentration [7]. In this case the concentration of univalent ions giving rise to volume phase transition is 4000 times higher than that of divalent ions. These volume changes are mainly ascribed to changes in osmotic pressure and electrostatic interaction. Further, the volume of poly(acrylic acid) gel is also known to be affected by concentration of transition and rare earth metal ions which coordinatively, in addition to electrostatically, interact with carboxylate groups in a poly(acrylic acid) [8–10]. Thus, poly(acrylic acid) gel shows universal volume phase transition upon changes in cation concentration.

As mentioned above, there have been several reports on pH responsive molecular valve consisting of polymer gel. However, to the best of our knowledge, there have been only a few reports on cation responsive molecular valve consisting of polymer [11]. In that work, poly(acrylic) acid (not a gel) was utilized and only fixed concentration of Na^+ and Ca^{2+} as cations was studied. Further, reversibility and repeatability of the valve remained unknown. In the present paper, on the basis of the above-mentioned universal volume change of poly(acrylic acid) gel, we developed a reversible molecular valve, consisting of a Au mesh covered with the gel, which closes at lower cation concentration as the gel expands to block the mesh, whereas opens at higher concentration as the gel contracts to make spaces in the mesh. The valve responds to a variety of cations including H^+, Na^+, K^+, Ca^{2+}, Cu^{2+}, and Al^{3+} and bears repeated use to some extent. A potential application of the molecular valve in the present work could be an automatic concentration controller keeping the cation concentration less than a certain value. This controller could detect changes in the cation concentration in its own and stay opened to drain the solution as long as the concentration is higher than some value which depends on kinds of the cation. When the solution is diluted, the controller spontaneously closes and keeps the solution.

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2. Experimental

2.1. Materials and apparatus

Acrylic acid (reagent grade, Wako Pure Chemical Industries, Ltd.) was distilled prior to use. Calcium nitrate was dried over P_2O_5 under vacuum. All other reagents were of at least reagent grade quality and were used without further purification unless otherwise noted. Aqueous solutions are prepared with distilled-deionized water.

2.2. Preparation of poly(acrylic acid) gel-modified Au mesh

Poly(acrylic acid) gels were prepared 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. An Au mesh (10 mm × 10 mm, 100 mesh, Nilaco Co.), which was cleaned with a piranha solution prior to use, was immersed in a solution containing above-mentioned reagents. The mesh was immediately taken out and heated at 60 °C in an ambient environment to complete gelation. This process was repeated twice to make the film thicker. The average of thickness of the resulting film after immersion in water for 15.5 h was 3.5 ± 0.5 mm (n = 7, average of 5 points on each sample).

2.3. Procedures

The above-mentioned poly(acrylic acid) gel-modified Au meshes were set in between home-made holders (polycarbonate, 5.0 mm i.d.) via O-rings (fluoro rubber, 4.8 mm i.d.) (Fig. 1A). The holders were then set horizontally and filled with water and left for at least 15.5 h to remove unreacted reagents and to allow the gel to reach equilibrium volume. A picture of the gel-coated Au mesh at the swollen state is shown in Fig. 1B. For permeability monitoring, the holders were set vertically and a glass tube (120 mm length × 4.8 mm i.d.) was attached to the upper holder. To check leakage of the gel film, the fluid level of 2 ml water was monitored for 2 h. After this test, the water was replaced with 2 ml of various electrolyte solution and a volume of the solution passed the film (valve) was measured for 2 h unless otherwise noted. All measurements were performed at room temperature (25 ± 2 °C).

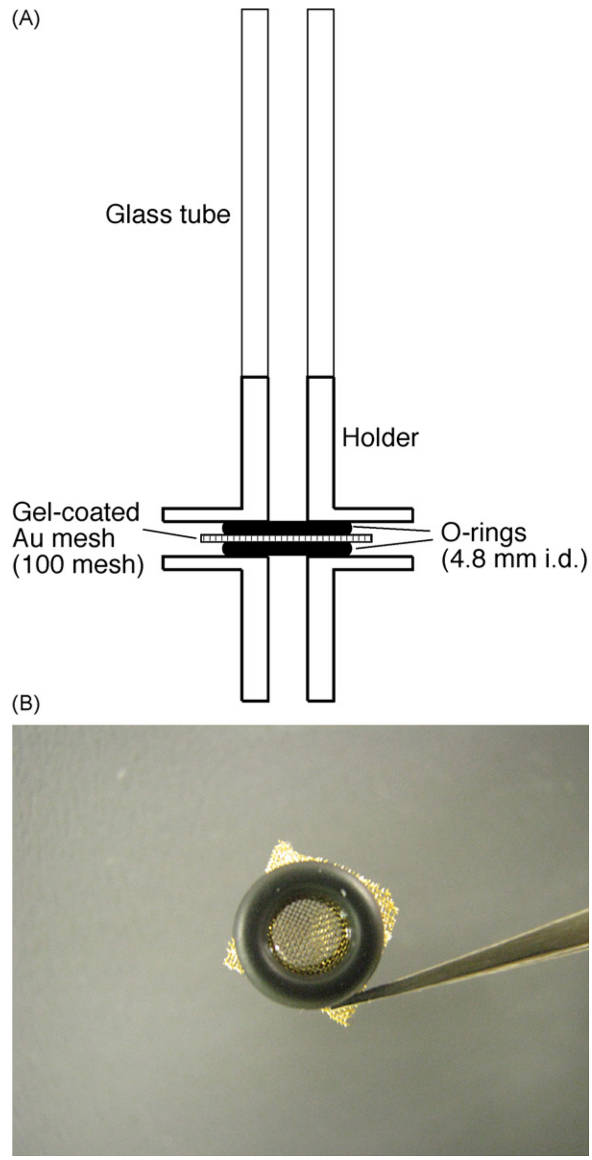

Fig. 1. (A) Schematic illustration of a poly(acrylic acid) gel molecular valve. (B) A picture of the gel-coated Au mesh at the swollen state.

3. Results and discussion

3.1. Response to cations

Fig. 2 shows dependencies of volume passed the poly(acrylic acid) gel-coated Au mesh on concentration of $NaNO_3$, $Ca(NO_3)_2$, and $Al(NO_3)_3$ aqueous solutions. At lower concentration the valve remained closed, whereas at higher concentration all solutions (2 ml) were passed. The concentration where the valve opens appears to increase in the order of Al^{3+}, Ca^{2+}, and Na^+ (2×10^{-4}, 5×10^{-4}, and 6×10^{-3} M, respectively). KNO_3 was also found to give the same valve opening concentration as Na^+ ion. Thus, hereafter Na^+ ion will be discussed as representative of K^+ ion. A cylindrical poly(acrylic acid) gel (3 mm diameter × 5 mm length as synthesized) contracts at lower electrolyte concentration whereas expands at higher concentration (Fig. 3). Here, the volumes of the cylindrical gels were measured from changes in volume of water in a cylinder upon immersion of the gel which reached at equilibrium (at least 10 days). As can be seen in Fig. 3, the volume change was evident at 10^{-6} to 10^{-4} M for Al^{3+}, 10^{-5} to 10^{-2} for Ca^{2+}, and 10^{-5} < M for Na^+. Since the concentrations where the gel valves open are in the range of those where the volume change takes place, the actuation of the valve could be attributed to shrinking of the gel. The difference in the concentration at which the valve opens is

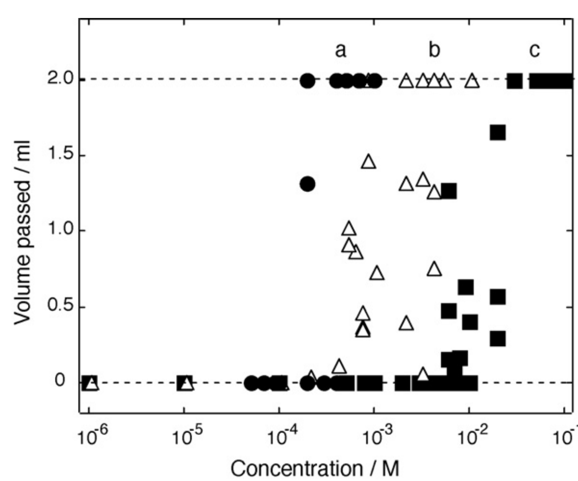

Fig. 2. Dependencies of solution volume passed the valve on concentration of (a) $Al(NO_3)_3$, (b) $Ca(NO_3)_2$, and (c) $NaNO_3$ aqueous solutions. Loaded volumes of the solutions were 2.0 ml.