

Thermally responsive novel anion exchange membranes for electro dialysis

Toshikatsu Sata, Shin-ichiro Emori and Koji Matsusaki

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai 2557, Ube City, Yamaguchi Prefecture, 755, Japan

Anion exchange membranes containing *N*-isopropylacrylamide as a component showed a decrease in osmotic flux through the membrane, and an increase and decrease respectively in the transport numbers of NO_3^- and SO_4^{2-} relative to Cl^- with increasing temperature.

The concentration of NO_3^- in groundwater has been greatly increasing because of excessive use of artificial fertilizers. The EC proposed that the concentration of NO_3^- in drinking water should be below 25 ppm, however, it exceeds this in many places in Europe and also in Japan. A high NO_3^- concentration in drinking water can endanger human health because this can lead to the formation of nitrosamines and nitriles which cause cell poisoning. Many methods to remove NO_3^- from groundwater have been proposed and tried: reverse osmosis, electro dialysis, ion exchange, *etc.* It is important to preserve the properties of natural water, and electro dialysis is the most suitable method for this purpose. Although it is desirable to perform electro dialysis at high temperature to save energy, using a NO_3^- permselective anion exchange membrane, osmotic flux of water through the ion exchange membranes increases with increasing temperature, and the amount of water processed therefore decreases.

Poly(*N*-isopropylacrylamide) is a well known heat-sensitive polymer.¹ It is soluble in water at room temperature but undergoes a phase separation at temperatures higher than its lower critical solution temperature (LCST, *ca.* 32 °C). At higher temperatures, the intrinsic affinity of *N*-isopropylacrylamide polymer chains for themselves is enhanced due to thermal dissociation of hydrating water molecules from the polymer chains. Hydrophobic interactions between isopropyl groups drastically increase and the polymers condense with each other, precipitating rapidly in the solution. Cross-linked copolymers containing *N*-isopropylacrylamide as a monomer have been also extensively studied as hydrogels used in solute separation,² immobilization of enzymes,³ drug release regulating systems,⁴ *etc.* Cross-linked copolymer gels containing ionic monomers such as acrylic acid, 2-methyl-2-acrylamidopropane sulfonic acid, *etc.*, were also reported to show similar swelling and deswelling properties with change in temperature. If ion exchange membranes contain *N*-isopropylacrylamide as a component, it is expected that the membranes will show a thermal response.

Two types of cross-linked anion exchange membranes containing *N*-isopropylacrylamide were prepared: (i) 1 part (part by mass) of acrylonitrile–butadiene rubber was dissolved in a mixture of 5 parts of *N*-isopropylacrylamide (supplied by Kojin Co., Ltd.), 10 parts of glycidyl methacrylate, 5 parts of ethylene glycol dimethacrylate and 0.24 parts of benzoyl peroxide (M-1 membrane), (ii) 1 part of acrylonitrile–butadiene rubber was dissolved in a mixture of 5 parts of *N*-isopropylacrylamide, 10 parts of dimethylaminoethyl methacrylate, 5 parts of ethylene glycol dimethacrylate and 0.24 parts of benzoyl peroxide (M-2 membrane). The two obtained pasty mixtures were coated on a woven fabric made of poly(vinyl chloride), and polymerized at 85 °C for 24 h under an N_2 atmosphere after covering with a polyester film on both sides. After polymerization, the copolymer membrane from the M-1

composition was immersed in a 1 M aqueous NMe_3 (75 mass%) and acetone (25 mass%) mixed solution for 48 h at room temperature to introduce quaternary ammonium groups on the glycidyl groups. The M-2 copolymer membrane was immersed in a methyl iodide (60 mass%)–hexane (40 mass%) mixed solution for 24 h to quaternize the tertiary amino groups. A commercial anion exchange membrane, NEOSEPTA AM-1 (Tokuyama Corp.; benzyltrimethylammonium groups; cross-linkage, 10%) was used as a standard anion exchange membrane. Before use, the membranes were equilibrated with 1.0 M HCl and 0.5 M NH_3 alternately several times, and then equilibrated with solutions to be used in the measurements.

Reduced osmotic flux through anion exchange membranes was measured between pure water and 4.0 M NaCl at different temperatures with stirring according to the reported⁵ methods. Transport numbers, calculated from a membrane potential, and electrical resistance of the membrane were measured at different temperatures. Water content and ion exchange capacity of the membranes were determined by conventional methods.⁵ Electro dialysis was carried out in a four-compartment cell with Ag–AgCl electrodes (solution in each compartment, 100 cm³; effective membrane area, 2 × 5 cm).⁶ The two middle compartments were separated from the anolyte and catholyte, which consisted of NaCl solution of the same Na^+ concentration as that of the solution to be measured, by a cation exchange membrane (NEOSEPTA CM-2, Tokuyama Corp.; transport number of Na^+ was > 0.99 in the electro dialysis of 0.50 M NaCl solution at a current density of 20 mA cm⁻²). The anion exchange membrane to be studied was placed at the center of the cell, and a 1 : 1 mixed salt solution, either 0.02 M NaNO_3 –0.02 M NaCl ($[\text{Na}^+] = 0.04$ M) or 0.25 M Na_2SO_4 –0.25 M NaCl ($[\text{Na}^+] = 0.50$ M) was electro dialyzed at a current density of 1 or 10 mA cm⁻² for 60 min under vigorous agitation (stirring at 1500 ± 100 rpm). Studied temperatures for electro dialysis were 25.0, 30.0, 32.0, 35.0 and 40.0 °C. All measurements were performed after the membranes, solutions and the cell had been equilibrated at the respective temperature (immersed in a thermostat for > 24 h). After electro dialysis, the change in the concentrations of the anions in the middle compartments was determined by the Mohr method, and chelate back titration or ion chromatography (Hitachi Ion Chromatography L-6000). Then the transport number of anions A relative to chloride ions was calculated by following equation: $P_{\text{Cl}}^{\text{A}} = (t_{\text{A}}/t_{\text{Cl}})/(C_{\text{A}}/C_{\text{Cl}})$, where t_{A} and t_{Cl} are the transport numbers of anions A and Cl^- in the membrane, and C_{A} and C_{Cl} are the average concentrations of anions A and Cl^- ions in the desalting side solution during electro dialysis, respectively. P_{Cl}^{A} represents the permeated equivalent of anions A through the membrane when 1 equiv. of Cl^- is permeated through. The current efficiency was calculated from the amount of transported anions and electricity measured by coulometry.

Table 1 shows the characteristics of the prepared anion exchange membranes and the commercial membrane. The electrical resistances of the M-1 and M-2 membranes was high and their water content was low compared with those of the commercial membrane because of their low ion exchange capacity. Although transport numbers of the M-1 and M-2 membranes were lower than that of the commercial membrane

Table 1 Characteristics of anion exchange membranes

	NEOSEPTA		
	AM-1	M-1	M-2
Electric resistance ^a	1.1	17.8	12.7
Transport number ^b	0.94	0.84	0.90
Ion exchange capacity ^c	2.25	1.18	0.92
Water content ^d	0.27	0.12	0.07
Thickness/mm	0.13	0.12	0.10
Reinforcing	PVC	PVC	PVC

^a $\Omega \text{ cm}^2$; measured with 1000 Hz ac at 25.0 °C after equilibration with 0.5 M NaCl. ^b Calculated from a membrane potential generated from 0.50 M NaCl | Membrane | 2.50 M NaCl at 25.0 °C. ^c Mequiv. per g (Cl^-) dry membrane at 25.0 °C. ^d g (H_2O) per g (Cl^-) dry membrane, measured at 25.0 °C after equilibration with pure water.

at 25.0 °C, they increased with increasing temperature and reached 0.89 (M-1) and 0.94 (M-2) at 35.0 °C (the transport number of the commercial membrane slightly decreased with increasing temperature: 0.94 at 25 °C, 0.93 at 35 °C). The electrical resistances of both M-1 and M-2 membranes were constant between 32 and 35 °C, while that of the commercial membrane decreased monotonously with increasing temperature.

Fig. 1 shows the change in the reduced osmotic flux through M-1 and commercial membrane. In general, the reduced osmotic flux of water through ion exchange membranes increases with increasing temperature as found for the commercial membrane. However, the M-1 membrane showed completely different behavior: the reduced osmotic flux decreased from 25 °C with increasing temperature and attained a constant value from 32 °C. This is thought to be due to the decrease in hydrophilicity of membrane originated from the aggregation of isopropyl groups in the membranes. In fact, water contents of both M-1 and M-2 membranes decreased with increasing temperature and attained a constant value from 32 °C (water content of the commercial membrane increased: 27% at 25.0 °C; 31% at 40 °C).

Fig. 2 shows the transport number of NO_3^- relative to Cl^- . Although $P_{\text{Cl}^-}^{\text{NO}_3^-}$ of the commercial membrane did not change with temperature, it should be noted that NO_3^- selectively permeate through the anion exchange membranes containing *N*-isopropylacrylamide with increasing temperature. It was reported that hydrophilicity of anion exchange membranes greatly affects the permselectivity between two anions: with decreasing hydrophilicity of the membranes, less hydrated anions such as NO_3^- and Br^- selectively permeate through the

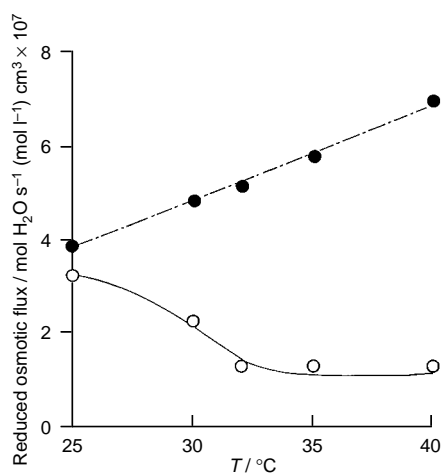


Fig. 1 Change in reduced osmotic flux with temperature. (●) Commercial anion exchange membrane (NEOSEPTA AM-1); (○) M-1 membrane. Measurements in 4.0 M NaCl | Membrane | pure water; effective membrane area = 10 cm².

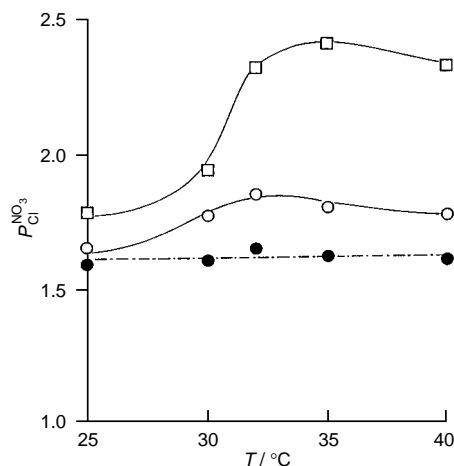


Fig. 2 Change in transport number of NO_3^- relative to Cl^- with temperature. (●) Commercial anion exchange membrane (NEOSEPTA AM-1); (○) M-1 membrane; (□) M-2 membrane. A 0.02 M NaNO_3 -0.02 M NaCl mixed solution was electro dialyzed at different temperatures (current density = 1 mA cm⁻²).

membrane, and the permeation of strongly hydrated anions, F^- and SO_4^{2-} , decreases.⁶ Because the aggregation of isopropyl groups in the M-1 and M-2 membranes makes the membranes hydrophobic with increasing temperature, the permeation of NO_3^- is thought to be enhanced. Though the ratio of mobilities between NO_3^- and Cl^- in the membrane phase did not change in all membranes with temperature, the ion exchange equilibrium constant between NO_3^- and Cl^- of the M-1 membrane increased with increasing temperature: $K_{\text{Cl}^-}^{\text{NO}_3^-} = 1.5$ at 25 °C and 2.2 at 35 °C ($K_{\text{Cl}^-}^{\text{NO}_3^-}$ of the commercial membrane was 1.95 and independent of temperature.) It is apparent that the decrease in hydrophilicity of the M-1 and M-2 membranes with increasing temperature caused selective uptake of the less hydrated anions NO_3^- (Gibbs hydration energies of NO_3^- and Cl^- are 270 and 317 kJ mol⁻¹, respectively).⁷ The decrease in the hydrophilicity of the membranes also decreased permeation of SO_4^{2-} remarkably since SO_4^{2-} is strongly hydrated.⁷ This is a desirable property for anion exchange membranes because precipitation of CaSO_4 in electro dialyzers and in membranes is a serious problem in electro dialysis. $P_{\text{Cl}^-}^{\text{SO}_4^{2-}}$ of the commercial membrane increased slightly with increasing temperature. Finally, the current efficiencies of the M-1 (96%) and M-2 membranes (93%) were slightly lower than that of the commercial membrane (99%). Anion exchange membranes containing *N*-isopropylacrylamide are suitable in electro dialysis to remove NO_3^- from groundwater with low energy without precipitation of CaSO_4 .

Notes and References

† E-mail: HAG07574@niftyserve.or.jp

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