Anion Exchange Membranes for Nitrate Ion Removal from Groundwater by Electrodialysis

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Anion exchange membranes having high selectivity for nitrate ions in electrodialysis are obtained by introducing hydrophobic anion exchange groups into the membranes.

The concentration of nitrate ions NO_3^- in groundwater has been increasing because of excessive use of artificial fertilizers. The EC suggests that the NO_3^- concentration in drinking water should be below 25 ppm, but it exceeds this in many parts of Europe. A high NO_3^- concentration in drinking water can endanger human health since this can lead to the formation of nitrosamines and nitriles which cause cell poisoning. Many methods for the removal of NO_3^- from groundwater have therefore been proposed and tried, *e.g.* ion exchange, reverse osmosis,[1] electrodialysis,[2] anaerobic biological digestion and electrolysis using electrodes modified by enzymes.[3] It is important to preserve the properties of natural water, and electrodialysis is the most suitable method for this purpose if an NO_3^- permselective anion exchange membrane can be developed. Several such anion exchange membranes have been reported: those having tertiary amino groups in the membrane[4] and monovalent anion permselective membranes which have been used to produce edible salt from sea water.[5] Though introducing tertiary amino groups into the anion exchange membrane enhances permeation of NO_3^- through the membrane, the electrical resistance of the membrane increases and the transport number of the anions decreases with increasing content of tertiary amino groups in the membrane.[4] Commercial anion exchange membranes with an outer layer comprising both weakly and strongly basic anion exchange groups have high NO_3^- permselectivities compared with conventional membranes.[5] When an anionic layer was formed on the conventional anion exchange membranes, permeation of NO_3^- was enhanced.[6] However, higher permselectivity for NO_3^- is required to preserve the properties of natural water and to save energy.

Anions migrate in the aqueous solution and travel through the anion exchange membrane along with water of hydration. The Gibbs hydration energies $-\Delta G_h^0$ of Cl^-, SO_4^{2-} and NO_3^- are 317, 1000 and 270 kJ mol^{-1}, respectively.[7] Since NO_3^- ions are relatively hydrophobic compared with Cl^- ions, it is thought that if hydrophobic anion exchange groups are introduced into the anion exchange membrane, NO_3^- can permeate selectively through the membrane by reason of hydrophobic affinity. In this work, anion exchange membranes bearing groups with different hydrophobicities were prepared and the permselectivity of NO_3^- relative to Cl^- through the membranes was examined.

The anion exchange membranes were prepared by reactions of a membranous copolymer of chloromethylstyrene and divinylbenzene with trimethylamine, triethylamine, tri-*n*-propylamine, tri-*n*-butylamine and tri-*n*-pentylamine. The membranous copolymer was prepared according to the paste method:[8] 82% *m/m* chloromethylstyrene, 10% *m/m* divinylbenzene (*ortho/para* mixture), 5% *m/m* acrylonitrile–butadiene rubber and 3% *m/m* benzoyl peroxide were mixed. The pasty material obtained was coated on woven PVC fabric and polymerized at 80 °C for 16 h under an N_2 atmosphere after being covered on both sides with a polyester film. Separate pieces of this copolymer membrane were immersed in a 1.0 mol dm^{-3} amine solution for a suitable period (aq. trimethylamine, 24 h, 30 °C; triethylamine methanol solution, 48 h, 50 °C; tri-*n*-propylamine methanol solution, 48 h, 50 °C; tri-*n*-butylamine methanol solution, 72 h, 50 °C; tri-*n*-pentylamine ethanol solution, 96 h, 50 °C). Reactions were continued until the ion exchange capacity attained a constant value. After

reaction, the membrane was washed with MeOH or EtOH, washed with a 1.0 mol dm^{-3} HCl solution and pure water, and then stored in a 0.5 mol dm^{-3} NaCl solution. Before use the membranes were equilibrated with a mixed solution to be electrodialysed.

Electrodialysis was carried out in a device with four compartments with Ag/AgCl electrodes (amounts of solution in each compartment, 100 cm^3; effective membrane area, 2 × 5 cm).[6] The two inner compartments were separated from the anolyte and catholyte, which consisted of NaCl at the same Na^+ concentration as that of the solution to be measured, by cation exchange membranes (NEOSEPTA CM-2, Tokuyama Corp.; Na^+ transport number > 0.99 in the electrodialysis of 0.5 mol dm^{-3} NaCl solution at a current density of 20 mA cm^{-2}; 2.8 Ω cm^2 electrical resistance equilibrated with 0.500 mol dm^{-3} NaCl solution, 1000 Hz ac, at 25.0 °C). Each anion exchange membrane to be evaluated was placed at the centre of the cell, and a 0.04 mol dm^{-3}, 1:1 mixed salt solution, either $NaNO_3$–NaCl or Na_2SO_4–NaCl ([Na^+] = 0.04 mol dm^{-3}), was electrodialysed at a current density of 1 mA cm^{-2} for 60 min at 25.0 °C under vigorous agitation (stirring at 1500 ± 100 rpm). After electrodialysis, the changes in the concentrations of the anions in the middle compartments were determined by the Mohr method, and chelate back-titration or ion chromatography (Hitachi Ion Chromatography L-6000). Then the relative transport number was calculated using $P_{Cl}^A = (t_A/t_{Cl})/(c_A/c_{Cl})$, where t_A and t_{Cl} are the transport numbers of anions and Cl^- ions, respectively, in the membrane, and c_A and c_{Cl} are the average concentrations of anions and Cl^- ions in the solution on the desalting side. The current efficiency was calculated from the amount of transported anions and electricity measured by coulometry (Nikko Digital Coulometer NDCM-4, Nikko Keisoku Ltd). The voltage drop across by the membrane during electrodialysis was measured with Ag/AgCl probe electrodes, which were placed close (*ca.* 2 mm) to the membrane surfaces and recorded by an X-t recorder (Toa Electronics Co., EPR-2T).

Table 1 shows the characteristics of the anion exchange membranes with different anion exchange groups. With increasing chain length of the alkyl groups, the electrical resistance increased and the ion exchange capacity and water content of

Table 1 Characteristics of anion exchange membranes with different anion exchange groups

Anion exchange group[a]	Electrical resistance[b]/ Ω cm^2	Ion exchange capacity[c]	Water content[d]	Thickness/ mm
Trimethylbenzyl	1.1	2.20	0.28	0.136
Triethylbenzyl	2.5	1.62	0.23	0.130
Tri-*n*-propylbenzyl	7.9	1.14	0.13	0.137
Tri-*n*-butylbenzyl	12.2	1.11	0.08	0.138
Tri-*n*-pentylbenzyl	143	0.70	0.07	0.110

[a] All transport numbers > 0.98, measured by electrodialysis with 0.50 mol dm^{-3} NaCl solution at 20 mA cm^{-2}. [b] Measured with 1000 Hz ac at 25.0 °C after equilibration with 0.500 mol dm^{-3} NaCl. [c] mequiv. per g(Cl^-) of dry membrane. [d] g(H_2O) per g(Cl^-) of dry membrane.

the membranes decreased. These effects are attributed to both steric hindrance in the reaction of bulky amines with chloromethyl groups of the copolymer membranes and the increase in hydrophobicity. It is thought that if amines of higher molecular mass were used in the reaction, anion exchange groups would be introduced near the surface rather than uniformly throughout the membrane, and an experiment was devised to confirm this idea. After the membrane with various amines had been equilibrated with an aqueous 1.0 mol dm^{-3} HBr solution, washed with pure water and dried, distribution of Br$^-$ across the cross-section of the membrane was measured by EPMA (electron probe micro analysis; JXA-8621M, JOEL). Though the amount of Br$^-$ in the membrane decreased with increasing molecular mass of the amines, distribution of Br$^-$ appeared to be homogeneous for all of the membranes. Hence the uniform distribution of ion-exchange sites must be attributed to the long reaction times and the swelling solvent. It is also noteworthy that the transport number of Cl$^-$ ions was very high in spite of the decrease in ion exchange capacity.

Fig. 1 shows the transport number of NO$_3^-$ relative to Cl$^-$ in the membranes with different ion exchange groups. In general, although NO$_3^-$ ions permeate selectively through conventional anion exchange membranes as compared with Cl$^-$ ions, $P_{Cl}^{NO_3}$ increased remarkably with increasing chain length of the alkyl groups, so that $P_{Cl}^{NO_3}$ of the anion exchange membrane with tri-n-pentylbenzyl ammonium groups was 16.5. However, the current efficiency of all the membranes was greater than 99%. The voltage drop across the membrane increased with increasing chain length of the alkyl groups, and the electrical resistance calculated from the voltage drop agreed with the value in Table 1 as measured by ac. Table 2 gives the ion exchange equilibrium constants between NO$_3^-$ and Cl$^-$ of the membranes with different ion exchange groups when the membranes were
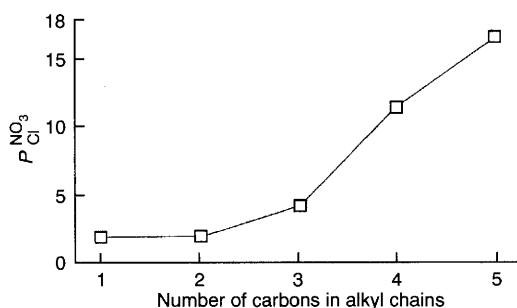

Fig. 1 Effect of anion exchange groups on relative transport number between NO$_3^-$ and Cl$^-$ ($P_{Cl}^{NO_3}$). Electrodialysis was carried out using a 1 : 1 mixed salt solution of 0.02 mol dm^{-3} NaNO$_3$ and 0.02 mol dm^{-3} NaCl (c_{Na} 0.04 mol dm^{-3}) at 1.0 mA cm^{-2} for 60 min.

Table 2 Ion exchange equilibrium constant between NO$_3^-$ and Cl$^-$ in anion exchange membranes with different anion exchange groups[a]

Ion exchange groups	$K_{Cl}^{NO_3}$
trimethylbenzyl	3.64
triethylbenzyl	7.39
tri-n-propylbenzyl	7.75
tri-n-butylbenzyl	8.20

[a] After the anion exchange membranes had been equilibrated with a 1 : 1 mixed solution of 0.02 mol dm^{-3} NaNO$_3$ and 0.02 mol dm^{-3} NaCl [Na$^+$] = 0.04 mol dm^{-3}, anions in the membranes were eluted with 0.2 mol dm^{-3} NaNO$_3$ and Cl$^-$ in the eluent were determined by the Mohr method. The amount of NO$_3^-$ ions was calculated by subtracting the amount of Cl$^-$ from the ion exchange capacity of the membranes.

equilibrated with the same mixed salt solution as that used in electrodialysis. Selective absorption of NO$_3^-$ increases with increasing chain length of the alkyl groups, i.e. with increasing hydrophobicity of the anion exchange groups. However, according to Table 1, the ion exchange capacity of the membranes decreases with increasing alkyl chain length. In order to confirm whether the increase in $P_{Cl}^{NO_3}$ is owing to the decrease in the ion exchange capacity or the increase in hydrophobicity of the anion exchange groups, anion exchange membranes with different ion exchange capacities were prepared from copolymer membranes having different amounts of chloromethyl groups and tri-n-butylamine. When the ion exchange capacity was 0.82 mequiv. g^{-1} dry membrane, $P_{Cl}^{NO_3}$ was 12.4, compared with 11.3 in the membrane of capacity 1.11 mequiv. g^{-1} dry membrane. Although $P_{Cl}^{NO_3}$ increased slightly with decreasing ion exchange capacity of the membrane, it is apparent that the hydrophobic effect is the predominant factor in the increase in $P_{Cl}^{NO_3}$.

Sulfate ions, which are common anions in groundwater, are relatively hydrophilic. The relative transport number of SO$_4^{2-}$ to Cl$^-$ was measured by the method described. In general, since SO$_4^{2-}$ ions are bulky and divalent, $P_{Cl}^{SO_4}$ is below unity in most of the commercial anion exchange membranes.[9] $P_{Cl}^{SO_4}$ of the anion exchange membranes in this work was also below 0.25 and decreased markedly with increasing alkyl chain length. This is owing to increasing hydrophobicity and clogging of the membrane pores by the long chain. Consequently, a kind of monovalent anion permselective membrane was obtained.

Table 1 shows the increase in electrical resistance of the membranes with increasing alkyl chain length. The high resistance of the membrane restricts practical application. However, since the anion exchange membranes with higher hydrophobicity selectively absorb NO$_3^-$ as shown in Table 2, it is suggested that an anion exchange membrane with high NO$_3^-$ permselectivity and low electrical resistance can be obtained by forming a thin layer with hydrophobic anion exchange groups on the desalting side of the membrane, e.g. the membrane with trimethylbenzylammonium groups. The salt concentration 0.04 mol dm^{-3} in this work was high compared with that of actual groundwater, but this was necessary for evaluating properties. However, $P_{Cl}^{NO_3}$ and $P_{Cl}^{SO_4}$ had almost the same values as those measured at 0.01 mol dm^{-3}.

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