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REMOVAL OF PERTECHNETATE ION $\left({}^{99m}TcO_4^-\right)$

FROM RADIOACTIVE WASTE USING
ANION-EXCHANGE PAPER MEMBRANE

In order to treat simply and safely the waste-containing radioactive technetium, a study of the removal of pertechnetate ion TcO_4^- (the main chemical form of technetium) from radioactive waste was carried out using an anion-exchange membrane in which trimethylhydroxylpropylammonium groups were homogeneously dispersed with high density. TcO_4^- flux through the paper membrane is larger than that through a polymer membrane; moreover, TcO_4^- in the paper membrane can exist in the membrane phase in spite of the presence of a large amount of Cl^-. The anion-exchange paper membrane possesses three outstanding characteristics: (1) higher fluxes of TcO_4^- and Cl^- than that of the polymer membrane, (2) almost the same occupation of TcO_4^- in available ion-exchange sites as in the polymer membrane, and (3) higher diffusional membrane permeability ratio $P_{TcO_4^-}^0 / P_{Cl^-}^0$ than that of the polymer membrane.

Keywords: *pertechnetate ion, radioactive waste, anion-exchange paper membrane, phenomenological equation, membrane permeability*

1. INTRODUCTION

Technetium is not found in nature. It occurs as one of the products of uranium fission and as the daughter nuclide of molybdenum-99. The ^{99m}Tc isomer of technetium is extensively used in nuclear medical diagnosis because its half-life is moderately short (approximately 6 hours), which reduces the internal exposure of the subjects, and because ^{99m}Tc can be conveniently produced by milking from ^{99}Mo as needed. The disposal of radioactive waste containing ^{99m}Tc is strictly regulated by environmental

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laws; nevertheless, ^{99m}Tc excreted by patients injected with nuclear medicines has been detected in sludge and in supernatant liquid from processing pool in the Kurume Central Sewage Treatment Plant in Japan [1]. When technetium is released to the environment, pertechnetate ion (TcO_4^-), the main chemical form of technetium, may be readily absorbed in the human body through agricultural products.

We have already developed the method for concentrating the waste containing radioactive iodine by means of an anion-exchange paper membrane. The process has a compact apparatus design with no large reservoir [2], and the used paper membrane can be safely incinerated. We have also shown that removal of radioactive iodine from waste using an anion-exchange paper membrane is not influenced by electroneutral substances such as glucose or urea [3]. It has been found that the introduction of trimethylhydroxypropylammonium group into the cellulose fibers improves radioactive iodine diffusion within the paper membrane and that the introduction of quaternary diethylaminoethyl groups improves the radioactive iodine solution/membrane distribution process [4]. In addition, the ratio of the electroconductive membrane permeability to radioactive iodine to that to radioactive chloride has been shown to be as high as 6.2 for an anion-exchange paper membrane containing trimethylhydroxypropylammonium groups [5].

In the present study, we systematically analyze the flux and the behaviour of membrane-phase pertechnate ions occurring in trace amounts in the conditions of large amounts of chloride ions (present in actual radioactive waste) using the anion-exchange paper membrane method. The results were compared with those for an anion-exchange polymer membrane. Membrane transport analyses were carried out using the linear phenomenological equations being based on nonequilibrium thermodynamics.

2. METHODS

Introduction of trimethylhydroxypropylammonium anion-exchange groups into cellulose fiber was carried out according to methods previously described [4], [5]. At first, the prepared cellulose fiber was refined to make their surfaces rough for better bonding. The paper membrane was then formed from a diluted fiber slurry, allowing the water to drain through a nylon net (100 mesh). The paper membrane was placed between unwoven clothes and pressed with a heated rolling pin to remove surplus water. Remaining free water was liberated by heating the membrane on a hot plate at 60 °C. The ion-exchange capacity of the prepared paper membrane was measured by standard methods. A univalent selective anion-exchange polymer membrane, NEOSEPTA® AM-1, donated by Astom Corporation, Japan, was used in the present study as a reference membrane. The table summarizes the thickness, the ion-exchange capacities, and the water contents in the paper membrane and the polymer membrane.

T a b l e

Basic properties of paper membrane and polymer membrane

Properties	Paper membrane	Polymer membrane
Thickness	0.19 mm	0.12 mm
Ion-exchange capacity	0.30 meq. g^{-1} dry memb.	1.6 meq. g^{-1} dry memb.
Water content *	161	0.36

* Water content is given by $(H_w – H_d)/H_d$, where H_w is the weight of the wet membrane and H_d is the weight of the completely dry membrane.

The measurements of the ion flux and ion concentration within membrane phase were carried out using the system shown in figure 1.

Phase I	**Membrane phase**	**Phase II**
TcO_4^- : 10–50 kBq Cl^- : 1×10^{-3} mol dm^{-3} (pH 5.5)	Anion exchange paper membrane or polymer membrane	Conductivity of water (pH 5.5)

Fig. 1. The system for measurements of ion flux and ion concentration in membrane phase

The prepared membrane was placed between the phase I and the phase II of aqueous solutions. The phase I of aqueous solution was composed of $^{99m}TcO_4^-$ and $^{36}Cl^-$. The radioactivity of the TcO_4^- ranged from 10 kBq/cm^3 (5.18×10^{-16} mol/cm^3) to 50 kBq/cm^3 (2.59×10^{-15} mol/cm^3). 1×10^{-3} mol dm^{-3} of Na^{36}Cl solution was prepared from conductivity water and extra-pure non-radioactive NaCl. The phase II of aqueous solution was conductivity water. pH values of both phases were adjusted to 5.5 with HCl and NaOH. All measurements were carried out at 25 ± 0.5 °C, with both solution phases stirred at 90 rpm in all cases. Each measurement point represents the mean value (without standard error) of five samples.

The $^{99m}TcO_4^-$ and $^{36}Cl^-$ fluxes were measured by monitoring the radioactivity in phase II using a γ-ray scintillation counter (Amersham Pharmacia Biotech; 1470 Wizard, NJ) and a liquid scintillation counter (Beckman; LS6500, CA), respectively. The above membrane samples, after having wiped off the adhering radioisotopes with filter paper, were also radioactively measured to determine the $^{99m}TcO_4^-$ and $^{36}Cl^-$ concentration within the membrane phase.

3. RESULTS AND DISCUSSION

TcO_4^- fluxes through both the paper and polymer membranes were increased with an increase in the concentration of the phase I (figure 2A-1), while Cl^- fluxes through both the paper and polymer membranes were not influenced by increasing TcO_4^- concentration of the phase I (figure 2A-2). The net fluxes of TcO_4^- and Cl^- through the paper membrane were almost by two orders of magnitude greater than those through the polymer membrane as shown in figures 2A-1 and 2A-2. The paper membrane can absorb about 450 times more water per dry weight than the polymer membrane as shown in the table. Moreover, the mean pore size of the paper membrane ranges approximately from 1 to 5 μm (as estimated from micrographical measurements), while that of the polymer membrane is less than 1 nm (as indicated by the manufacturer). Hydrated radii of the permeating ions, TcO_4^- and Cl^-, are almost equivalent of 3.5 Å and 3.0 Å, respectively [10], [11]. Therefore, TcO_4^- and Cl^- ions in the paper membrane can be transported more freely than those within the polymer membrane as shown in figures 2A-1 and 2A-2.
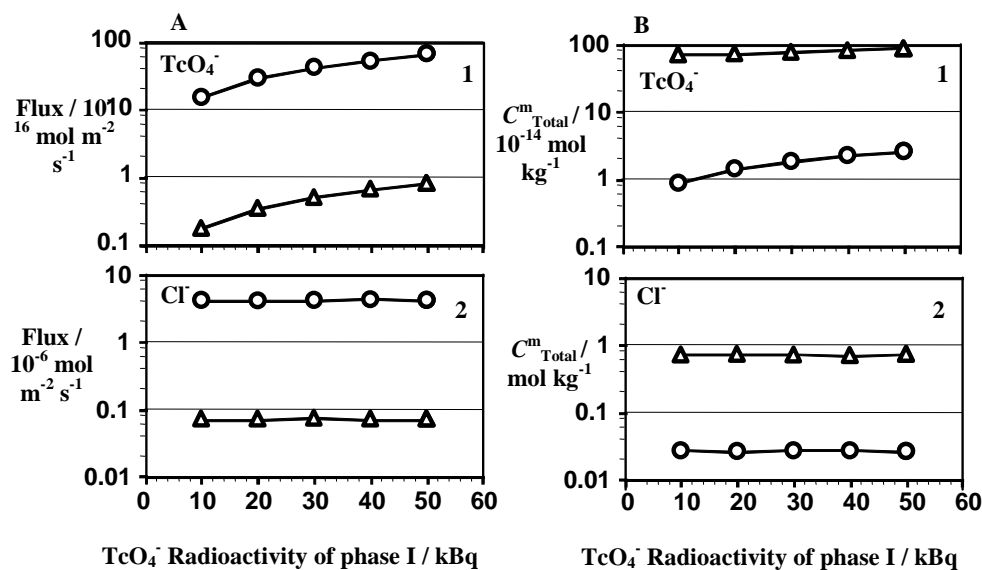

Fig. 2. Intercompartment ion flux (A) and its concentration (mol g^{-1}-dry membrane) in membrane phase (B) as a function of the TcO_4^- radioactivity of phase I. Upper frames (1) and lower frames (2) indicate flux and concentration of TcO_4^- and Cl^-, respectively. Circles and triangles denote paper membrane and polymer membrane, respectively

Figures 2B-1 and 2B-2 illustrate the TcO_4^- and Cl^- ion concentrations within the membrane phase as a function of the radioactivity of TcO_4^- in the phase I. The total amount of TcO_4^- per unit polymer membrane weight ($C_{TcO_4^-,total}^m$) was 33 to 79 times greater than that per unit weight of paper membrane (figure 2B-1). On the other hand, the total amount of Cl^- per unit weight of paper membrane ($C_{Cl^-,total}^m$) was constant and equal to 3.7% of the total amount of Cl^- per unit weight of polymer membrane (figure 2B-2). It was quite usual that a small quantity of TcO_4^- in the membrane phase increased, whereas large quantity of Cl^- in the membrane phase increased with an increasing amount of TcO_4^- in the phase I. Although the ratio of the external solution concentrations ($C_{TcO_4^-}^{external} / C_{Cl^-}^{external}$) ranged from 2×10^{-14} to 4×10^{-13}, the ratio of the ion concentrations in the membrane ($C_{TcO_4^-}^m / C_{Cl^-}^m$) ranged from 3.2×10^{-13} to 9.4×10^{-13} for the paper membrane and from 9.6×10^{-13} to 1.2×10^{-12} for the polymer membrane. TcO_4^- ions within the paper membrane and the polymer membrane were slightly concentrated.

A concept established on the basis of theoretical and experimental investigations of membrane transport phenomena is that ion transport through a charged membrane can be analyzed as a function of the solution/membrane distribution coefficient of permeating ions and of the migration speed of the ions in the membrane phase [8]. In the present system, the solution/membrane distribution of TcO_4^- in the polymer membrane takes priority over that in the paper membrane. On the other hand, the diffusion of TcO_4^- in the paper membrane takes priority over that in the polymer membrane.

It is convenient to make use of the membrane permeability analysis in order to evaluate synthetically the transport of TcO_4^- and Cl^- through a charged membrane. The matrix theory of the membrane permeability reported by KIMIZUKA et al. [9] has been shown to be useful for quantitative analysis of permselective ion transport across a charged membrane. In the paper-membrane transport process characterized by the ionic diffusion process (with no membrane current), thermodynamic analyses can be expressed by:

$$\begin{bmatrix} J_{Na^+} \\ J_{TcO_4^-} \\ J_{Cl^-} \end{bmatrix} = - \begin{bmatrix} P_{Na^+}^0 & 0 & 0 \\ 0 & P_{TcO_4^-}^0 & 0 \\ 0 & 0 & P_{Cl^-}^0 \end{bmatrix} \begin{bmatrix} -a_{Na^+}^I \exp(-FV_0/2RT) \\ -a_{TcO_4^-}^I \exp(FV_0/2RT) \\ -a_{Cl^-}^I \exp(FV_0/2RT) \end{bmatrix}, \quad (1)$$

where:
J is the ion flux,

P is the diffusional membrane permeability,

a is the ionic activity,

F is the Faraday constant,

V_0 is the membrane potential at zero membrane current,

R is the gas constant,

T is the absolute temperature,

the superscript I indicates the aqueous solution phase I and the subscripts Na^+, TcO_4^-, and Cl^- refer to co-ion Na^+ and counter-ions TcO_4^- and Cl^- [8].

The following equation is derived from equation (1):

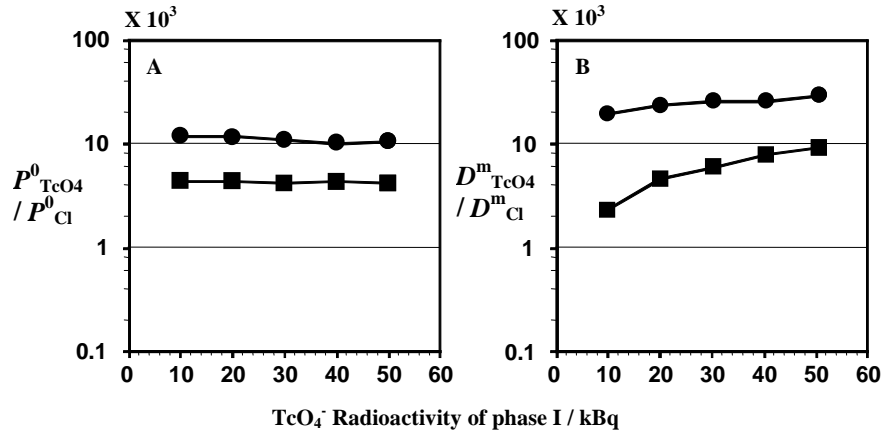$$\frac{P_{TcO_4^-}^0}{P_{Cl^-}^0} = \frac{\dfrac{J_{TcO_4^-}}{J_{Cl^-}}}{\dfrac{a_{TcO_4^-}^I}{a_{Cl^-}^I}} . \tag{2}$$

Fig. 3. Membrane permeability ratio $P_{TcO_4^-}^0 / P_{Cl^-}^0$ (A) and diffusion coefficient ratio $D_{TcO_4^-}^m / D_{Cl^-}^m$ (B) as a function of TcO_4^- radioactivity of phase I. Circles and squares indicate paper membrane and polymer membrane, respectively

On the other hand, the diffusional membrane permeability can be adequately approximated by the diffusion coefficient, i.e. D_α^m (α = TcO_4^- or Cl^-), and ion concentration within membrane phase (C_α^m (α = TcO_4^- or Cl^-)):

$$P_\alpha^0 \cong \left(\frac{D_\alpha^m}{\delta}\right)\left[\frac{C_\alpha^m}{(a_\alpha^I a_\alpha^{II})^{1/2}}\right], \tag{3}$$

where δ is the thickness of the membrane and the superscript m indicates the membrane phase.

The diffusional membrane permeability ratio of TcO_4^- to Cl^- ($P^0_{TcO_4^-} / P^0_{Cl^-}$) was derived from equation (2) and shown in figure 3A. $P^0_{TcO_4^-} / P^0_{Cl^-}$ ratios both in the paper membrane and in the polymer membrane were higher than unity and constant within the whole TcO_4^- radioactivity range of the phase I. Although the flux ratio of TcO_4^- to Cl^- ($J_{TcO_4^-} / J_{Cl^-}$) ranged from approximately 6.3×10^{-9} to 2.8×10^{-8} for the paper membrane and from 2.4×10^{-9} to 1.1×10^{-8} for the polymer membrane, the diffusional membrane permeability ratios of TcO_4^- to Cl^- ($P^0_{TcO_4^-} / P^0_{Cl^-}$) went in reverse: 1.1×10^4 and 4.2×10^3 in the paper membrane and in the polymer membrane, respectively. The diffusional membrane permeability based on the phenomenological equation is effective in expressing the ionic membrane transport without influencing the concentration of the external solution. Actually, it is possible to compare quantitatively the TcO_4^- transport with Cl^- transport through the membrane by deriving the diffusional membrane permeability as shown in figure 3A. The diffusion coefficient ratio of TcO_4^- to Cl^- ($D^m_{TcO_4^-} / D^m_{Cl^-}$) was estimated from equations (2) and (3) (figure 3B). The diffusion coefficient ratio ($D^m_{TcO_4^-} / D^m_{Cl^-}$) was almost the same as the diffusional membrane permeability ratio ($P^0_{TcO_4^-} / P^0_{Cl^-}$) as shown in figure 3. This is reflected by not large solution/membrane distribution of TcO_4^- to Cl^- in the present study.

4. CONCLUSIONS

The anion-exchange paper membrane possesses three outstanding characteristics: (1) higher fluxes of TcO_4^- and Cl^- than that of the polymer membrane, (2) almost the same occupation of TcO_4^- in available ion exchange sites as in the polymer membrane, and (3) higher diffusional membrane permeability ratio ($P^0_{TcO_4^-} / P^0_{Cl^-}$) than that of the polymer membrane. As a result, TcO_4^- transport through the paper membrane is higher than that through the polymer membrane. TcO_4^- flux in the paper membrane is higher than that in the polymer membrane, and TcO_4^- can exist in the membrane phase despite the presence of large amount of Cl^-.

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REFERENCES

[1] NAKAMURA A., OSAKI S., OSAKI T., HAYABUCHI N., *Output of radiopharmaceutical nuclides of known injected doses from a municipal sewage treatment system*, Health Physics, 2005, 88(2), pp. 163–168.

[2] INOUE H., KAGOSHIMA M., *Removal of ^{125}I from radioactive experimental waste with anion exchange paper membrane*, Applied Radiation and Isotopes, 2000, 52, pp. 1407–1412.

[3] INOUE H., *Transport of ^{125}I and ^{36}Cl across an anion exchange paper membrane*, Applied Radiation and Isotopes, 2002, 56, pp. 659–665.

[4] INOUE H., *Influence of glucose and urea on 125I transport across an anion exchange paper membrane*, Applied Radiation and Isotopes, 2001, 54, pp. 595–602.

[5] INOUE H., *Effects of co-ions on transport of iodine ions through a non-conventional anion exchange paper membrane*, Journal of Membrane Science, 2004, 228, pp. 209–215.

[6] INOUE H., KAGOSHIMA M., YAMASAKI M., HONDA Y., *Radioactive iodine waste treatment using electrodialysis with an anion exchange paper membrane*, Applied Radiation and Isotopes, 2004, 61, pp. 1189–1193.

[7] INOUE H., *Radioactive iodine and chloride transport across a paper membrane bearing trimethylhydroxypropylammonium anion exchange groups*, Journal of Membane Science, 2003, 222, pp. 53–57.

[8] KAIBARA K., INOUE H., ARITOMI T., *Multi-Ionic Potential and Membrane Permeability Matrix. III. Diffusion and Concentration of Ions within Membrane Phase as a Controlling Factor to Ion Permselectivity*, Bulletin of the Chemical Society of Japan, 1989, 62, pp. 2362–2368.

[9] KIMIZUKA H., NAGATA Y., KAIBARA K., *Nonequilibrium thermodynamics of the ion and solvent transports through ion-exchange membrane*, Bulletin of the Chemical Society of Japan, 1983, 56, pp. 2371–2379.

[10] MOYER B.A., BONNESEN P.V., *Physical Factors in Anion Separations*, [in:] *Supramolecular Chemistry of Anions*, Bianchi A., Bowman-James K., Garcia-Espana E.; Wiley-VCH, New York, 1997, pp. 1–44.

[11] KIELLAND J., *Individual activity coefficients of ions in aqueous solutions*, Journal of American Chemical Society, 1937, 59, pp. 1675–1678.