

Uphill and Selective Transport of Uranyl Ions through 2,3-Epithiopropyl Methacrylate-2-Acrylamide-2-Methyl Propane Sulfonic Acid Copolymer Membranes

TAKAMASA NONAKA, HIROFUMI OGAWA, MASATERU MORIKAWA, and HIROAKI EGAWA

Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860, Japan

SYNOPSIS

Cation exchange membranes were prepared with 2,3-epithiopropyl methacrylate (ETMA)-2-acrylamide-2-methylpropane sulfonic acid (AMPS) copolymers. Transport of uranyl ion against its concentration gradient through the membranes was investigated by using a system containing carbonate solution (left side) and uranyl ion (and other metal ion) solution (right side). ETMA-AMPS copolymer membranes transported UO_2^{2+} against its concentration gradient. Na_2CO_3 solution was most effective as receiving solution for the uphill transport of UO_2^{2+} . The transport was greatly affected by the composition of the copolymer membranes. Highly selective transport of UO_2^{2+} from the solution containing UO_2^{2+} and other metal ions was observed by using Na_2CO_3 solution in the left side. The main driving force for this transport of UO_2^{2+} is the high complex-formation ability of UO_2^{2+} with CO_3^{2-} .

In the previous article,¹ we reported that alkali and alkaline earth metal ions could be transported against their concentration gradient through membranes made of 2,3-epithiopropyl methacrylate (ETMA)-2-acrylamide-2-methylpropane sulfonic acid (AMPS) copolymers. We have also reported that uranium in seawater could be selectively adsorbed with macroreticular resins containing amidoxime groups and then uranium adsorbed on the resins was concentrated in the eluate.² The development of membranes which can transport uranyl ion against its concentration gradient is expected to recover uranyl ions in the eluate. So far transport of uranyl ion against its concentration gradient through polymer membranes has not been reported.

In this article, the uphill and selective transport of uranyl ions through ETMA-AMPS copolymer membranes were investigated.

EXPERIMENTAL

Synthesis of ETMA-AMPS Copolymers

ETMA was prepared by the method reported earlier.³ AMPS was provided by Nitto Riken Kogyo

Co. Ltd. and it was used without further purification. ETMA-AMPS copolymers with various AMPS contents were prepared by solution polymerization in *N,N*-dimethylformamide (DMF) using azobisisobutyronitrile as an initiator at 50°C for 16 h. The mole ratio composition of ETMA-AMPS copolymers was calculated from the nitrogen content of the dried polymers as determined by elemental analysis.

Membrane Preparation

ETMA-AMPS copolymers became insoluble in any organic solvent if precipitated in organic solvent and dried once. Consequently, the membranes were made by pouring 4 cm³ of 5% ETMA-AMPS copolymer DMF solution into a flat laboratory dish (4.8 cm diameter) immediately after polymerization, and the solvent was allowed to evaporate at 50°C for the desired time. The membranes prepared were removed from the dish in water. The thickness of dried membranes was about 60 μm.

Apparatus and Measurement

Transport experiments were carried out at 30°C with magnetic stirring, using a diaphragm glass cell (22

cm³) consisting of two detachable parts. The membrane was set in the middle of the two parts of the cell, which was clamped and sealed tightly with silicon rubber packing. The effective membrane area in the cell was 3.14 cm². The concentration of metal ions in both left (L) and right (R) cells was determined by inductively coupled argon plasma atomic emission spectrophotometry with a Nippon Jarrel-Ash ICAP-575. We call the solutions in the R side and L side feed solution and receiving solution, respectively. The pH of the solution was measured with a pH meter (Model HM-20, TOA Electronics Ltd.). The electronic potential difference between the R side and L side of the membrane in a diaphragm cell was measured by a electrometer HE-104 (Hokuto Denko Ltd.) with two reference electrodes HS-907 (TOA Electronics Ltd.).

The transport fraction and initial transport rate were defined as

$$\text{transport fraction (\%)} = \frac{C_{\max} - C_{L_0}}{C_{R_0}} \quad (1)$$

where C_{\max} = maximum concentration of metal ion on the L side, C_{L_0} = initial concentration of metal ion on the L side, C_{R_0} = initial concentration of metal ion on the R side, and

$$\text{transport rate (mmol h}^{-1} \text{ cm}^{-2}\text{)} = \frac{m_t - m_0}{ts} \quad (2)$$

where m_t = the amount (mmol) of metal ion in the L side after t hours at the initial stage m_0 = initial amount of metal ion in the L side, t = transport time (h), and s = effective membrane area (cm²).

Measurement of the Cation Exchange Capacity of the Membranes

The dried copolymer membrane (0.25 g) was placed in a 100 cm³ glass-stoppered Erlenmeyer flask. Then 50 cm³ of 0.1 mol dm⁻³ NaOH-1 mol dm⁻³ NaCl solution was poured into the flask. The mixture was shaken at 30°C for 48 h. The cation exchange capacity was determined by titrating the concentration of NaOH in the supernatant with a 0.1 mol dm⁻³ HCl solution.

Measurement of the Water Content and Swelling Ratio of the Membrane

The water content of the membrane was calculated by the use of the following equation:

$$\begin{aligned} &\text{water content (\%)} \\ &= \frac{\text{wt wet membrane (g)} - \text{wt dry membrane (g)}}{\text{wt dry membrane (g)}} \\ &\quad \times 100 \quad (3) \end{aligned}$$

The wet membrane was prepared by immersing dry membrane into deionized water for 24 h at room temperature, drying the surface of the membrane by wiping with filter paper, centrifuging at 3000 rpm for 10 minutes. The membrane was then weighed. With the same sample preparation the swelling ratio of the membrane was calculated as follows:

$$\text{swelling ratio} = v'/v \quad (4)$$

where v and v' are the volume of dry and wet membrane, respectively. The volumes of dry and wet membranes were calculated from the length of two sides and thickness of rectangular membranes in dry and wet state measured with a ruler or micrometer.

Measurement of Adsorption Capacity of the Membranes for UO₂²⁺

The dried copolymer membrane (0.25 g) was placed in a 100-cm³ glass-stoppered Erlenmeyer flask. Then 50 cm³ of 0.01 mol dm⁻³ (UO₂(NO₃)₂) solution (pH 3.17) was poured into the flask. The mixture was shaken at 30°C for 72 h. The adsorption capacity was calculated by determining the concentration of UO₂²⁺ in the supernatant by colorimetry with salicylic acid.

RESULTS AND DISCUSSION

Synthesis of ETMA-AMPS Copolymers with Various AMPS Contents

The ETMA-AMPS copolymer membranes with various AMPS contents used in this research are listed in Table I. The numbers in the abbreviations for the membranes such as E8A2 and E7A3 in Table I represent the weight ratio of ETMA and AMPS in the feed before copolymerization, for example, E8A2 has a weight ratio 8 ETMA to 2 AMPS. The cation exchange capacity, water content, and swelling ratio increased with increasing content of AMPS in the copolymer membranes.

Uphill Transport of UO₂²⁺

The transport of UO₂²⁺ through the ETMA-AMPS copolymer membrane (E6.5A3.5) was carried out by the use of a system containing mineral acids (H₂SO₄ and HCl) with different concentrations (L

Table I Characterization of (ETMA-AMPS) Copolymer Membranes with Various AMPS Contents

Abbreviation of Copolymer	Feed				ETMA/AMPS in Copolymer (mol ratio)	Cation Exchange Capacity (meq/g)	Water ^a Content (%)	Swelling ^b Ratio
	ETMA (g)	AMPS (g)	ETMA/AMPS (mol ratio)	DMF (cm ³)				
E8 A2	1.6	0.4	84/16	20	85/15	1.1	10	1.0
E7.5A2.5	1.5	0.5	80/20	20	79/21	1.7	11	1.2
E7 A3	1.4	0.6	75/25	20	74/26	1.9	17	1.2
E6.5A3.5	1.3	0.7	71/29	20	66/34	2.3	20	1.4
E6 A4	1.2	0.8	66/34	20	58/42	2.6	27	1.6
E5.5A4.5	1.1	0.9	62/38	20	52/48	3.0	38	1.9

$$^a \frac{[\text{Wt. of wet membrane (g)}] - [\text{Wt. of dry membrane (g)}]}{\text{Wt. of wet membrane (g)}} \times 100$$

$$^b \frac{[\text{Vol. of wet membrane (cm}^3\text{)}]}{[\text{Vol. of dry membrane (cm}^3\text{)}]}$$

side) and 0.01 M $\text{UO}_2(\text{NO}_3)_2$ (R side). The results are shown in Figure 1. In Figure 1, a transport fraction of more than 50% means that UO_2^{2+} was transported against its concentration gradient. Figure 1 shows that UO_2^{2+} could be transported against its concentration gradient by this system, that the transport fraction increased with increasing H^+ concentration up to 0.5 equivalents dm^{-3} and decreased when 1 equivalent dm^{-3} acid was used, and the transport fraction of UO_2^{2+} using H_2SO_4 is higher than that by using HCl. The maximum transport fractions using 0.5 equivalents dm^{-3} H_2SO_4 and HCl were 95 and 90%, respectively.

In the previous article,¹ we reported that alkali and alkaline earth metal ions such as Li^+ and Ca^{2+}

were transported against their concentration gradient through the ETMA-AMPS copolymer membranes using the system having an aqueous HCl solution (L side) and LiCl (or CaCl_2) solution (R side). We have also proposed a tentative mechanism of transport in which metal ions were incorporated into the membrane by an ion exchange reaction on the R side of the membrane, metal ions in the metal sulfonate were released by an ion exchange reaction with H^+ which in turn migrated from the L side by a proton jump mechanism,⁴ and the metal ions released were transported to the acidic (L) side by the electric potential gradient through the membrane. We have concluded that the main driving force for the transport is the electric potential difference. Therefore, it is considered that UO_2^{2+} on the R side in Figure 1 was transported by the same mechanism as in the case of alkali or alkaline earth ions when acid was used in the L side.

It is well known that UO_2^{2+} can form stable anion carbonate complexes with CO_3^{2-} such as $\text{UO}_2(\text{CO}_3)_2^{2-}$ or $\text{UO}_2(\text{CO}_3)_3^{4-}$ and that $\text{UO}_2(\text{CO}_3)_3^{4-}$ predominates over $\text{UO}_2(\text{CO}_3)_2^{2-}$ exist in alkaline solution above pH 7.4.⁵ Therefore, a Na_2CO_3 solution was used as the receiving solution in the L side instead of mineral acids. The transport of UO_2^{2+} through the E6A4 membrane was carried out by using the system containing different concentrations of a Na_2CO_3 solution (L side) and 0.01 mol dm^{-3} $\text{UO}_2(\text{NO}_3)_2$ (R side) (Fig. 2). The transport rate and transport fraction increased with increasing Na_2CO_3 concentration up to 0.015 mol dm^{-3} and they decreased when 0.02 mol dm^{-3} Na_2CO_3 was used. It was thus found that UO_2^{2+} was transported against its concentration gradient using lower concentrations of Na_2CO_3 than of mineral acids. Almost 100% of the UO_2^{2+} was transported from the R side to the

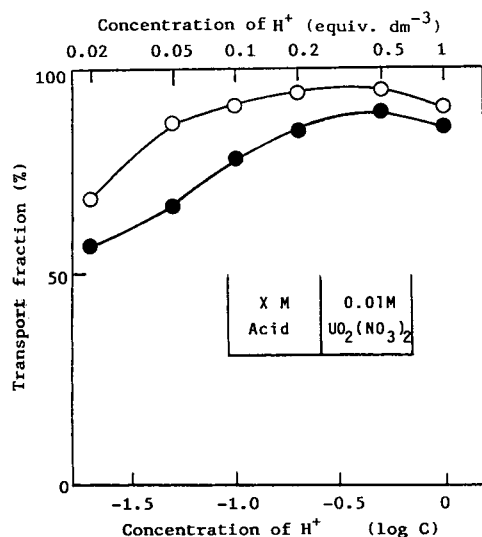


Figure 1 Transport of UO_2^{2+} through the ETMA-AMPS copolymer membrane. Membrane: E6.5A3.5. Acid: (○) H_2SO_4 ; (●) HCl.

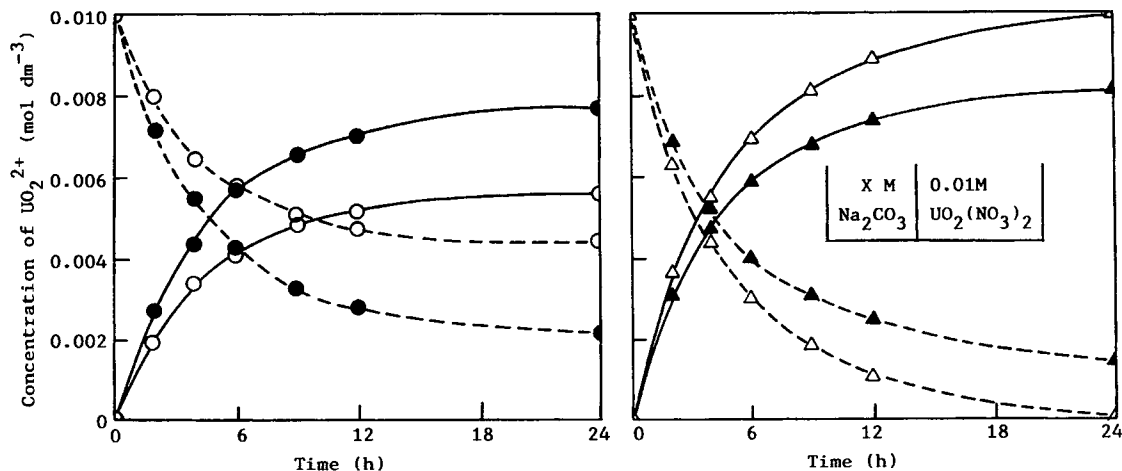


Figure 2 Changes in concentration of UO_2^{2+} on the two sides of the membrane. Membrane: E6A4; (—) L side; (---) R side. Na_2CO_3 concentration (mol dm^{-3}): (○) 0.0075; (●) 0.010; (△) 0.015; (▲) 0.020.

transported from the R side to the L side after 24 h when $0.015 \text{ mol } dm^{-3} Na_2CO_3$ was used.

The transport of UO_2^{2+} was investigated by using other carbonates such as ammonium carbonate or sodium bicarbonate instead of sodium carbonate in the L side. In addition to these, the disodium salt of ethylenediaminetetraacetic acid ($EDTA \cdot 2Na$) and NaOH were also used for comparison with these carbonates. The results are shown in Figure 3. All the carbonates and $EDTA \cdot 2Na$ transported UO_2^{2+} against its concentration gradient, whereas NaOH did not transport UO_2^{2+} at all. In all cases except NaOH, the transport fraction increased with increasing concentration of carbonates in the receiving solutions but decreased when the carbonate solution

was above a certain concentration. The order of transport fraction by carbonates is as follows: $Na_2CO_3 > (NH_4)_2CO_3 > NaHCO_3$. The concentrations of $(NH_4)_2CO_3$, Na_2CO_3 , $EDTA \cdot 2Na$, and $NaHCO_3$ at which the maximum transport fraction was observed are 0.01, 0.015, 0.05, and $0.05 \text{ mol } dm^{-3}$ when the concentration of $UO_2(NO_3)_2$ on the R side was $0.01 \text{ mol } dm^{-3}$, respectively. From these results, it was found that Na_2CO_3 solution is the most effective for the uphill transport of UO_2^{2+} .

The transport of UO_2^{2+} through the ETMA-AMPS copolymer membranes with various compositions was studied using the system containing $0.015 \text{ mol } dm^{-3} Na_2CO_3$ (L side) and $0.01 \text{ mol } dm^{-3} UO_2(NO_3)_2$ (R side) (Figure 4). The ETMA-AMPS

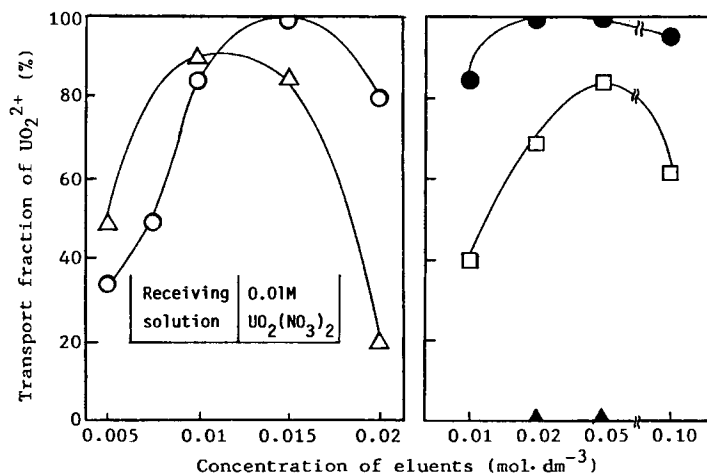


Figure 3 Effect of receiving solution on transport fraction of UO_2^{2+} . Membrane: E6A4. Receiving solution: (○) Na_2CO_3 ; (△) $(NH_4)_2CO_3$; (●) EDTA; (□) $NaHCO_3$; (▲) NaOH.

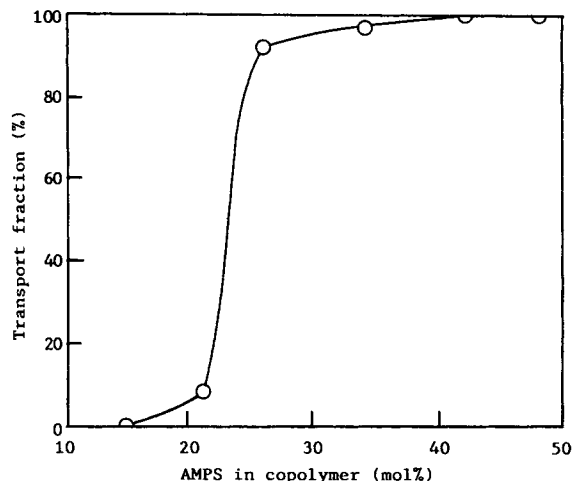


Figure 4 Effect of AMPS in copolymer on transport fraction of UO_2^{2+} .

copolymer membranes having 34–48 mol % AMPS moiety exhibited a transport fraction of 97–100%. The ETMA–AMPS copolymer membranes having less than 21 mol % AMPS moiety exhibited a very low transport fraction. It was thus found that the transport of UO_2^{2+} was greatly affected by the composition of the membranes.

We have previously reported that the transport fraction of Li^+ through the ETMA–AMPS copolymer membranes decreased when using membranes with an AMPS moiety of over 42 mol %. We concluded that this phenomenon was brought about by the reverse diffusion of transported Li^+ side caused by the concentration gradient owing to the high swelling of the membrane. However, in this study, the transport fraction of UO_2^{2+} did not decrease, even when the membranes with an AMPS moiety of 42–48 mol % were used. This is attributed to the fact

that no reverse diffusion of UO_2^{2+} occurred, because UO_2^{2+} formed stable anion complexes with CO_3^{2-} , such as $\text{UO}_2(\text{CO}_3)_3^{4-}$ or $\text{UO}_2(\text{CO}_3)_2^{2-}$, on the L side.

Transport Mechanism of UO_2^{2+}

In order to study the transport mechanism of UO_2^{2+} by using carbonates, the changes in concentration of UO_2^{2+} and Na^+ , the pH on both sides, and the electric potential difference with time were measured in the system having $0.015 \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3$ (L side) and $0.01 \text{ mol dm}^{-3} \text{ UO}_2(\text{NO}_3)_2$ (R side) (Figure 5). The electric potential difference in Figure 5(B) is expressed in electric potential of the R side when the electric potential of L side was taken as zero. That is, the negative values indicate that the electric potential in the R side is lower than that in the L side. As shown in Figure 5, UO_2^{2+} was transported from the R side to the L side against its concentration gradient, while Na^+ was transported from the L side to the R side against its concentration gradient. After 24 h, the concentration of Na^+ transported was almost twice that of UO_2^{2+} and was in the opposite direction. This means that approximate equivalents of positive cations migrated in opposite directions in this system. The electric potential difference was almost zero at the early stage; it decreased markedly with time and quickly became negative. This means that the electric potential on the L side became higher than that on the R side. The pH on both sides became almost the same (pH 7) after 24 h. From these results, we propose a tentative mechanism for the transport of UO_2^{2+} through the membrane in the system in which one side contains Na_2CO_3 solution (L side) and the other side $\text{UO}_2(\text{NO}_3)_2$ solution (R side), as is shown in Figure 6. On the R side of the membrane, UO_2^{2+} is incor-

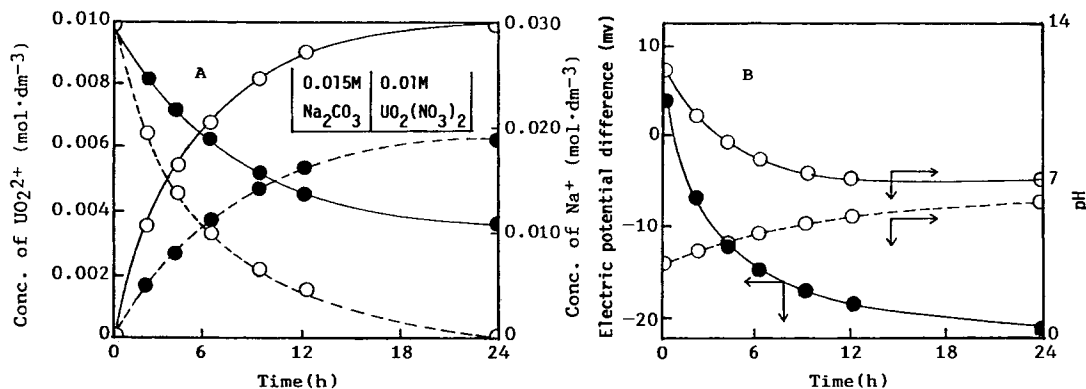


Figure 5 Changes in concentration of UO_2^{2+} and Na^+ (A), electric potential difference, and pH on the two sides of the membrane (B). Membrane: E6A4, (—) L side; (---) R side, and metal ion in (A): (○) UO_2^{2+} ; (●) Na^+ .

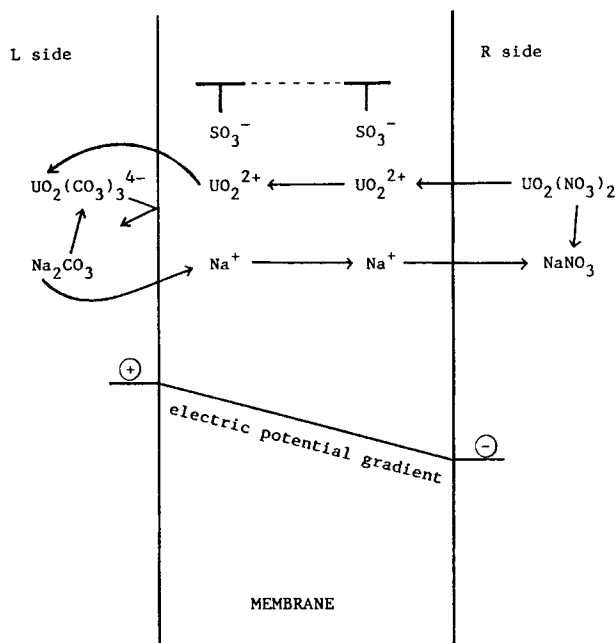
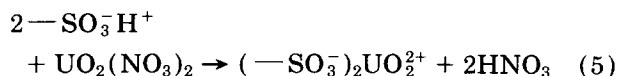
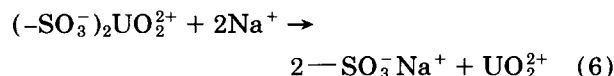


Figure 6 Tentative mechanism of transport of uranyl ions through cationic polymer membrane containing sulfonic acid groups.

ported into the membrane by the ion exchange reaction



On the other hand, Na^+ could migrate from the L side to the R side by following the concentration gradient. When migrating Na^+ reached the region where the uranyl sulfonate was formed, UO_2^{2+} was released by the ion exchange reaction



It is considered that when the UO_2^{2+} was released it was transported to the L side by diffusion along its concentration gradient in the membrane. Complexation of UO_2^{2+} with CO_3^{2-} on the L side of the membrane, was followed by release into the receiving solution as an anion carbonate complex. An anion complex such as $\text{UO}_2(\text{CO}_3)_3^{4-}$ cannot penetrate into the membrane due to the negative charge on the membrane (Donnan exclusion effect). Na^+ migrated to the R side and resulted in the formation of NaNO_3 . As a result, uranyl ions were transported from the R side to the L side and Na^+ travelled in the opposite direction to UO_2^{2+} . From these results, we consider that the main driving force for the transport of uranyl ions is the complexation of uranyl ions with CO_3^{2-} .

Selective Transport of UO_2^{2+} in the presence of Na^+ or Cu^{2+}

The selective transport of UO_2^{2+} and Na^+ was investigated using the system containing various receiving solutions (L side) and a solution containing 0.01 (or 0.03) mol dm^{-3} NaNO_3 and 0.01 mol dm^{-3} $\text{UO}_2(\text{NO}_3)_2$ (R side). The receiving solutions were 0.25 mol dm^{-3} H_2SO_4 , 0.01 mol dm^{-3} $(\text{NH}_4)_2\text{CO}_3$, and 0.015 mol dm^{-3} Na_2CO_3 (Figure 7). In the case of 0.25 mol dm^{-3} H_2SO_4 , both UO_2^{2+} and Na^+ were transported from the R side to the L side against their concentration gradient, and UO_2^{2+} was transported faster than Na^+ . The concentration of UO_2^{2+} and Na^+ on the L side began to decrease after 12 h. This is attributed to the reverse diffusion of metal ions from the L side to the R side due to the concentration gradient. In the case of 0.01 mol dm^{-3} $(\text{NH}_4)_2\text{CO}_3$, UO_2^{2+} was transported from the R side to the L side against its concentration gradient, whereas Na^+ was slightly diffused from the R side

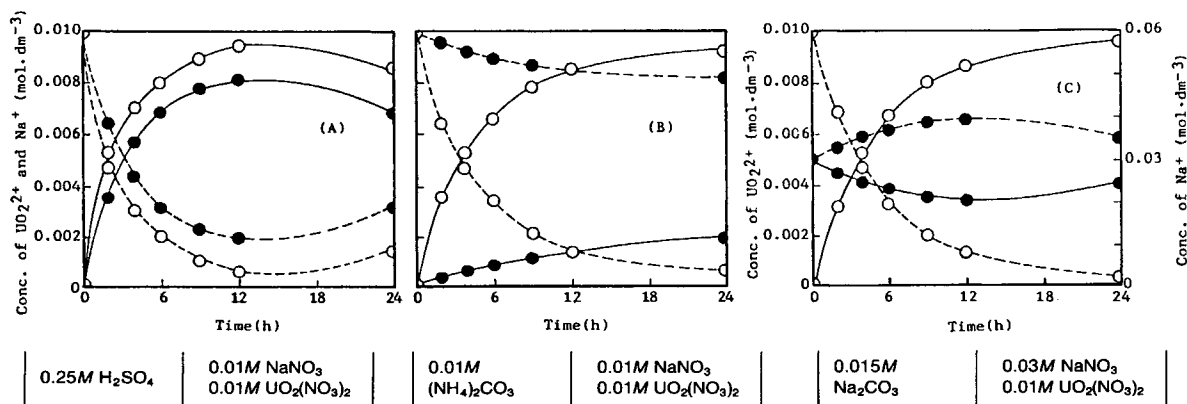


Figure 7 Changes in concentration of UO_2^{2+} and Na^+ through the membrane. Membrane: E6A4, (—)L side; (---)R side, (○): UO_2^{2+} , (●): Na^+ .

to the L side by its concentration gradient. In the case of 0.015 M Na_2CO_3 , the concentration of Na^+ on both sides at first remained the same. As UO_2^{2+} was transported from the R side to the L side against its concentration gradient, Na^+ was transported in the opposite direction to UO_2^{2+} , from the L side to the R side. It was thus found that highly selective transport of UO_2^{2+} could be carried out by using carbonates on the L side.

Figure 8 shows the electric potential difference between the R side and the L side of each system shown in Figure 7. In the case of 0.25 mol dm^{-3} H_2SO_4 , the electric potential on the R side at first is higher than that on the L side but it decreased rapidly with time. However, it is still positive even after 24 h. In this case, it is considered that UO_2^{2+} and Na^+ on the R side were transported against their concentration gradient by the electric potential gradient, as reported previously.¹

In using carbonate solution on the L side, UO_2^{2+} was transported from the R side to the L side, although the electric potential on the L side is higher than that on the R side. These results also suggest that the main driving force for the transport is not the difference in potential but, as mentioned before, the large tendency of UO_2^{2+} to form complexes with CO_3^{2-} . However, the exact transport mechanism of ions in a binary system is considered to be more complicated, because Nakagaki et al. have reported theoretically and experimentally that an uphill

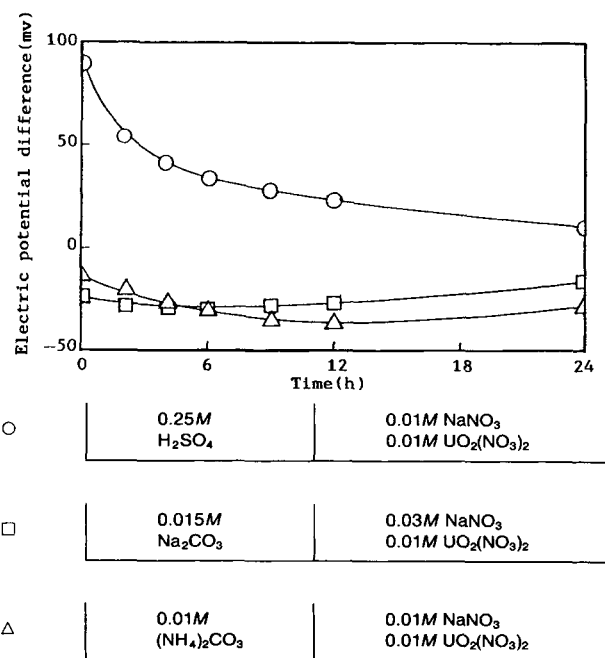


Figure 8 Changes in electric potential difference on the two sides of the membrane. Membrane: E6A4.

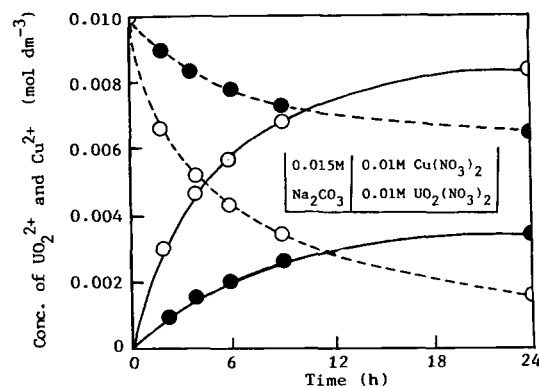


Figure 9 Changes in concentration of UO_2^{2+} and Cu^{2+} through the membrane. Membrane: E6A4; (—) L side; (---) R side; (○) UO_2^{2+} ; (●) Cu^{2+} .

transport of ions occurred in a system containing different concentrations of HCl and CaCl_2 in both cells, even when a porous plate was used instead of an ion exchange membrane.⁶

The selective transport of uranyl ion and Cu^{2+} was also investigated using the system containing 0.015 mol dm^{-3} Na_2CO_3 (L side), and 0.01 mol dm^{-3} $\text{Cu}(\text{NO}_3)_2$ and 0.01 mol dm^{-3} $\text{UO}_2(\text{NO}_3)_2$ (R side) (Figure 9). The ion UO_2^{2+} was transported more rapidly than Cu^{2+} , and only UO_2^{2+} was transported against its concentration gradient. The selective transport of $\text{UO}_2^{2+}/\text{Ca}^{2+}$ and of $\text{UO}_2^{2+}/\text{Zn}^{2+}$ was also carried out. Almost the same selective transport as that in the system of $\text{UO}_2^{2+}/\text{Cu}^{2+}$ was observed in the early stage in both systems. However, in both cases, precipitates were formed after 9 h in the L side.

Transport of UO_2^{2+} with Other Membranes

Transport of UO_2^{2+} was studied using the system containing 0.015 mol dm^{-3} Na_2CO_3 (L side) and 0.01 mol dm^{-3} $\text{UO}_2(\text{NO}_3)_2$ (R side) through an ETMA-AMPS copolymer membrane and ETMA-methacryloxyloxyethyl phosphoric acid (MP) copolymer membrane containing phosphoric acid groups.⁷ We reported previously that ETMA-MP copolymer membranes could transport alkali and alkaline earth metal ions against their concentration gradient.⁷ The ETMA-AMPS (E6.5A3.5) membrane and ETMA-MP (E7P3) membrane had cation exchange capacities of 2.6 and 2.3 meq g^{-1} , respectively. As shown in Figure 10, only the ETMA-AMPS copolymer membrane transported UO_2^{2+} against its concentration gradient. For comparison, the transport of UO_2^{2+} through the commercial cation exchange membrane, Selemion DLE (Asahi Glass Co. Ltd.) prepared for electro dialysis, was also studied using

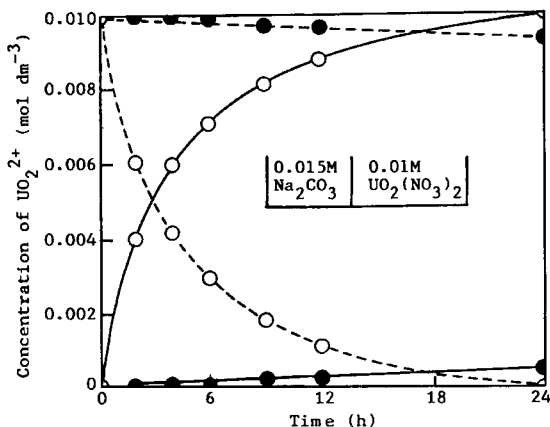


Figure 10 Changes in concentration of UO_2^{2+} on the two sides of the membrane. Membrane: (○) E6.5A3.5; (●) E7P3; (—) L side; (---) R side.

the same system. It is said that Selenion DLE was made of styrene-divinylbenzene copolymer and has sulfonic groups. It had a cation exchange capacity of 4.3 meq g^{-1} and a swelling ratio of 2.7. Uphill transport of UO_2^{2+} was not observed (the result is not shown in Fig. 10).

To clarify the phenomena, the adsorption capacity of these membranes for UO_2^{2+} was measured. The ETMA-AMPS copolymer membrane had an adsorption capacity for UO_2^{2+} of 0.48 mmol g^{-1} resin, whereas the ETMA-MP copolymer membrane had a very low adsorption capacity (0.03 mmol g^{-1} resin). These results suggest that the transport of UO_2^{2+} occurred after UO_2^{2+} was adsorbed on the membranes in the R side.

CONCLUSION

From these results, it was found that

1. ETMA-AMPS copolymer membranes transported UO_2^{2+} against its concentration gra-

2. Carbonate solutions were effective as receiving solutions for uphill transport of UO_2^{2+} . Transport rate and transport fraction were affected by the kinds of carbonates and their concentration. Among the carbonates, Na_2CO_3 was most effective for the transport of UO_2^{2+} .
3. Transport fraction was greatly affected by the composition of the ETMA-AMPS copolymer membranes.
4. The main driving force for this transport of UO_2^{2+} is high tendency for complex formation of UO_2^{2+} with CO_3^{2-} .
5. Highly selective transport of UO_2^{2+} from the solution containing UO_2^{2+} and other metal ions was observed by using Na_2CO_3 solution as receiving solution.

REFERENCES

1. T. Nonaka and H. Egawa, *J. Appl. Polym. Sci.*, **41**, 2869 (1990).
2. H. Egawa, T. Nonaka, and M. Nakayama, *J. Macromol. Sci., Chem.*, **A25**, 1407 (1988).
3. H. Egawa and T. Nonaka, *Kobunshi Ronbunshu*, **35**, 21 (1978).
4. T. Uragami, R. Nakamura, and Sugihara, *Polymer*, **24**, 559 (1983).
5. H. J. Schenk, L. Astheimer, E. G. Witte, and K. Schwochau, *Sep. Sci. Technol.*, **17**, 1293 (1982).
6. M. Nakagaki and S. Kitagawa, *Bull. Chem. Soc. Jpn.*, **49**, 1748 (1976).
7. T. Nonaka and H. Egawa, *J. Appl. Polym. Sci.*, **40**, 769 (1990).

Received March 4, 1991

Accepted July 24, 1991