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Transport of Iron and Cobalt Complex Ions through Liquid Membrane Mediated by Methyltrioctylammonium Ion with the Aid of Redox Reaction*

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Abstract

A new type of carrier-mediated metal transport through liquid membrane is presented. The system involves redox reactions rather than acid–base reactions which have often been utilized in metal transport systems. Iron ion was selectively transported and concentrated through the membrane via a chloride complex by use of a lipophilic quaternary ammonium ion, methyltrioctylammonium (MTOA, Q^+), as a carrier. The two aqueous solutions of different redox potentials were separated by a polymer-supported liquid membrane in which MTOA·chloride ($Q^+ \cdot Cl^-$) was dissolved as the carrier. Iron(III) ion in hydrochloric acid media formed a $FeCl_4^-$ type complex which was readily extracted to the organic membrane phase as an ion-pair complex $Q^+ \cdot FeCl_4^-$. On contact with a reducing agent on the other side of the membrane, iron(III) was reduced to iron(II) and liberated into aqueous solution; the chloride complexes of iron(II) are too hydrophilic to stay in the membrane phase. On the other hand, cobalt ion was transported via nitrilotriacetic acid (NTA) complex by MTOA carrier in a similar manner to the iron transport. The nature of the transport reactions was studied under various operational conditions (redox agents, carrier and ligand concentration, pH, coexisting metals, etc.). The extension of these transport reactions to a water-in-oil-in-water type emulsion system as well as to a photo-assisted transport system was studied.

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INTRODUCTION

Selective ion transport through liquid membrane is hoped to be a next generation separation method for industrial metal recovery (*1, 2*). Much research has been concerned with metal ion transport reactions which are driven by a pH gradient. Two aqueous solutions of different hydrogen ion concentrations were separated by an organic liquid membrane containing a carrier compound (*2*).

We have attempted to apply redox reactions and photoreactions to liquid membrane separation systems in place of conventional acid–base reactions. Redox reactions are used to regulate the extractability of metal ions on each side of the membrane, an ingenious system of metal transport may be previous works (*3*–*5*) a selective transport and concentration of copper ion through liquid membrane was achieved by using carriers such as Bathocuproine and tetrathioethers which could preferentially extract copper(I) species to organic solutions. Obviously, the use of redox reactions opens new possibilities for the separation and concentration of metal ions by the liquid membrane technique, which certainly deserves further exploration.

It is well known that a wide variety of anionic metal complexes are extracted to organic solutions by cationic liquid ion-exchangers, such as high molecular amines and quaternary ammonium salts, through the formation of an ion-pair association complex in the organic solutions ($Q^+ \cdot MX_n^-$; M^{n+}, metal ion; X^-, anionic ligand) (*6*). It is also known that the extractability of such metal complexes differs significantly from one valence state of the metal to another. Accordingly, by changing the valence state of the metal on each side of the membrane, an ingenious system of metal transport may be obtained.

In the present report the redox reaction-assisted transport of iron and cobalt ions which form extractable anionic complexes with chloride and NTA, respectively, is studied by using a lipophilic ammonium ion, methyltrioctylammonium, as a carrier.

EXPERIMENTAL

Material

MTOA · chloride is a commercial product (Capriquat) from Dojindo Lab. Ltd. (Kumamoto, Japan). The other chemicals were reagent grade and used as received.

Polymer-Supported Liquid Membrane

The apparatus used was the same as that described earlier (7). The cell consisted of two compartments, W_{red} and W_{ox} (each of 150 mL capacity), which were separated by a liquid membrane supported by a microporous polypropylene film (Duragard 2500, Polyplastics Ltd., Osaka, Japan). The effective membrane area was 28 cm^2. A diphenyl ether solution (~0.04 mL) containing a carrier was applied to the film.

In a typical run the W_{ox} compartment was initially filled with a hydrochloric acid solution (1 M, 1 M = 1 mol/dm^3, $pH < 1$) containing 5 mM iron(III) chloride, while the W_{red} compartment was filled with a hydrochloric acid solution (1 M, $pH < 1$) containing 5 mM iron(III) chloride and 15 mM ascorbic acid. The membrane phase (diphenyl ether) contained 0.5 M MTOA · chloride. The aqueous solutions were stirred magnetically at a fixed rate at 30°C, and the aliquots of the solutions were taken periodically and analyzed. The iron and other metal concentrations were determined by atomic absorption photometry using a Nippon Jarrel Ash AA-1 instrument.

Liquid Surfactant Membrane

The membrane system was made up of a water-in-oil-in-water (w/o/w) emulsion, i.e., oil-capsuled droplets of water (inner aqueous phase) were mechanically dispersed in bulk water (outer aqueous phase) with the aid of surfactants. The outer aqueous solution was named the W_{out} phase, while the inner aqueous solution was named the W_{in} phase.

Transport experiments were performed in a manner similar to that described in the previous paper (5). The W_{out} phase consisted of hydrochloric acid solution (1 M, $pH < 1$) containing 5 mM iron(III) chloride, while the W_{in} phase consisted of a hydrochloric acid solution (1 M, $pH < 1$) containing 30 mM ascorbic acid. The membrane phase (toluene) contained 2 wt% Span 80, a nonionic surfactant, and 5 mM MTOA · chloride. The toluene solution was emulsified with the W_{in} solution, and the resultant water-in-oil emulsion was then dispersed in the W_{out} solution under mechanical stirring (240 rpm, 25°C) to give the desired w/o/w emulsion; the volumes of each phase were approximately 200 mL (W_{out}), 33 mL (membrane), and 17 mL (W_{in}), respectively. At this stage the transport reaction starts. The change in the iron concentration in the W_{out} phase with an elapse of time was determined.

Solvent Extraction and Back-Extraction

A typical run was as follows. A buffered aqueous solution (40 m*M* Bicine–sodium hydroxide, pH 7.9, 10 mL; Bicine, *N*, *N*-bis(2-hydroxyethyl)glycine) containing 0.2 m*M* cobalt(II) nitrate, 1 m*M* NTA, 10 m*M* potassium chloride, and 0.1% hydrogen peroxide was shaken with a 1,2-dichloroethane solution (10 mL) containing 0.1 *M* MTOA·chloride at 25°C. After phase separation the cobalt concentration in the aqueous phase was measured. On the other hand, the organic solution separated (7 mL) was shaken with a buffered aqueous solution (40 m*M* Bicine–sodium hydroxide, pH 7.9, 10 mL) containing 15 m*M* ascorbic acid, 1 m*M* NTA, and 10 m*M* potassium chloride at 25°C, and the cobalt "back-extracted" into the aqueous solution was measured.

Photo-Assisted Transport

A sensitizer system (15 m*M* glucose–100 mg titanium oxide suspension in 150 mL solution) was used instead of ascorbic acid in the W_{red} phase in the polymer-supported liquid membrance system. The W_{red} compartment (Pyrex glass cell) was irradiated by a 500-W xenon lamp (Ushio Dinki Ltd., Tokyo, Japan) without filter.

RESULTS AND DISCUSSION

Transport of Iron Ion via Chloride Complex

Okazaki et al. studied the extraction of iron and zinc ions from hydrochloric acid media (< 3 *N*) by MTOA and found that the coexisting cobalt and nickel ions were scarcely extracted (*8*). The extraction behavior can be extended to selective metal transport through a liquid membrane. Figure 1 illustrates the transport reaction of iron ion. At the W_{ox}/membrane interface, the $\text{Fe}^{\text{III}}\text{Cl}_4^-$ complex generated in the W_{ox} phase (hydrochloric acid solution) is extracted to the membrane phase to form an ion-pair $Q^+ \cdot \text{FeCl}_4^-$. The ion-pair diffuses through the membrane, and at the other side of the membrane (W_{red}/membrane interface), iron(III) is reduced to iron(II) and liberated into the W_{red} phase (hydrochloric acid solution) on contact with a reducing agent; the chloride complexes of iron(II) are too hydrophilic to remain extracted in the membrane phase. Mechanistically, a process is also possible where FeCl_4^- is first released in the reducing aqueous phase and then reduced to the iron(II) species.

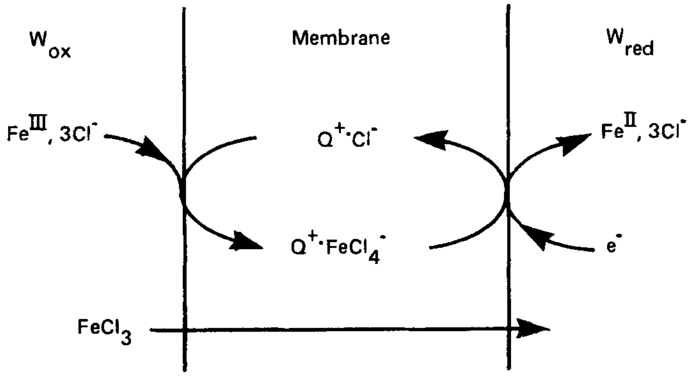

FIG. 1. Iron transport through liquid membrane mediated by quaternary ammonium ion, MTOA (Q^+), with the aid of redox reaction. W_{red}, reducing aqueous phase; W_{ox}, oxidizing aqueous phase; membrane, diphenyl ether solution on a porous polypropylene film.

The results obtained in the polymer-supported liquid membrane system are summarized in Table 1 and Fig. 2. Figure 2 shows the change in the concentration of iron ion in the W_{ox} phase and in the W_{red} phase against time. The iron concentration in the W_{ox} phase decreased as time elapsed, while that in the W_{red} phase increased to the same extent; this indicates that iron ion was transported from the W_{ox} to the W_{red} phase through the membrane against its concentration gradient (active transport).

As for a reducing agent, ascorbic acid was superior to molecular hydrogen (with a combined use of platinum asbestos catalyst) with respect to the initial rate of transport (Runs 1-1, 2). However, the rate dropped after about 3 h of reaction, and the yellow color of the iron(III)–chloride complexes in the W_{ox} phase disappeared in spite of the presence of a considerable amount of iron yet to be transported. This is explained by the fact that ascorbic acid in the W_{red} phase was partially soluble in the membrane phase and permeated through the membrane into the W_{ox} phase in the course of the transport reaction. The permeated ascorbic acid nullified the redox potential difference between the two aqueous phases. The reduction with molecular hydrogen was not accompanied with such undesirable side reaction. Once iron(II) species are formed in the reducing phase at the surface of the platinum asbestos catalyst, they can serve as an effective catalyst to reduce $FeCl_4^-$ at the W_{red}/membrane interface. This is reflected in a somewhat enhanced rate of iron transport at the middle portion of the transport reaction in Fig. 2 (filled circles).

When tin(II) chloride was used as a reducing agent in the batchwise extraction study, the stripping of iron from the organic solutions could be

TABLE 1
MTOA-Mediated Iron Transport

	Membrane	W_{ox}		W_{red}				
Run	[MTOA] (M)	[$FeCl_3$] (mM)	[HCl] (M)	[$FeCl_3$] (mM)	[Ascorbic acid] (mM)	[HCl] (M)	Initial rate of transport (mM/h)	Amount of iron transported[a] (%)
1-1	0.5	5	1	5	15	1	0.92	56
1-2	0.5	5	1	5	[b]	1	0.58	91
1-3	0.5	5	0.1	5	15	0.1	0.33	21
1-4	0.5	5	1	0	5	1	0.97	74
1-5	0.1	5	1	0	5	1	0.59	67
1-6	1	5	1	0	5	1	1.0	76
1-7	1	10	1	0	10	1	1.2	81
1-8	1	10	1.8	0	[c]	1.8	0.42	13

[a] Ratio of the amount of iron transported after 9 h reaction against that initially added in the W_{ox} phase.

[b] Molecular hydrogen (with a combined use of a 200-mg platinum asbestos catalyst) was used instead of ascorbic acid.

[c] 20 mM $SnCl_2$ was used.

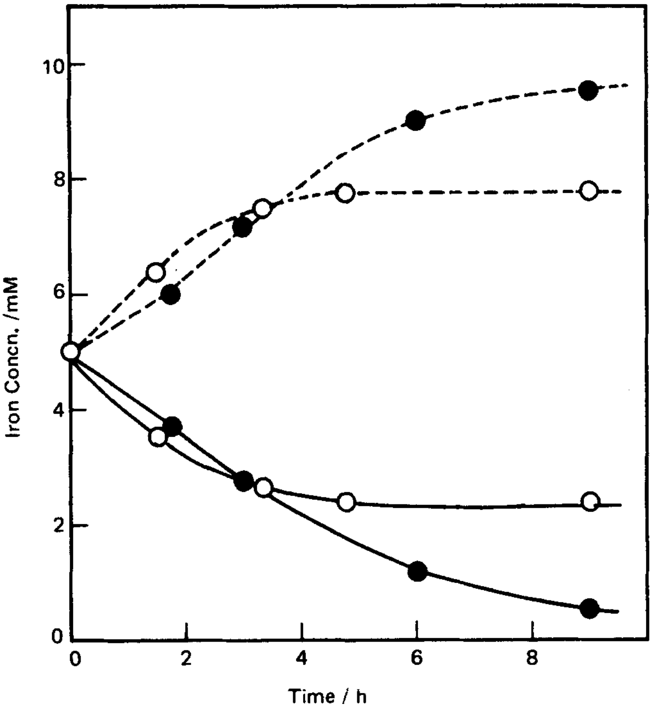

FIG. 2. MTOA-mediated iron transport. Change in the iron concentration in the W_{ox} phase (full line) and in the W_{red} phase (dotted line) against time under the conditions in Table 1: (○) Run 1-1; (●) Run 1-2.

effectively carried out in a similar manner to the use of ascorbic acid. However, the iron transport reaction occurred only to a small extent. It was found that the reducing agent itself was transported through the membrane into the W_{ox} phase by forming an ion-pair with MTOA ($2Q^+ \cdot SnCl_4^{2-}$, $Q^+ \cdot SnCl_3(H_2O)^-$, etc.) (Run 1-8).

From the values of the metal complex formation constant, it is possible to estimate the concentration of $FeCl_4^-$ generated in the aqueous solutions under various chloride concentrations. Under the initial conditions of Runs 1-1 and 3 in Table 1, the following approximate concentrations of $FeCl_4^-$ are obtained: 2 μM at $[Cl^-] = 1$ M, 0.006 μM at $[Cl^-] = 0.1$ M. The lowering in the chloride concentration in such a concentration range (from 1 to 0.1 M) resulted in only a limited decrease in the actual transport rate (to one-third of that of the control) (Runs 1-1, 3). Thus, the concentration of $FeCl_4^-$ in the W_{ox} aqueous solution cannot be as effective in increasing the initial rate of

TABLE 2
Competitive Transport of Other Metal Ions[a]

Run	Coexisting metal salt	Initial rate of transport (mM/h)		Amount of metal transported[b] (%)	
		Iron	Coexisting metal	Iron	Coexisting metal
2-1	None	0.97	—	74	—
2-2	$CoCl_2$	0.95	0	64	0
2-3	$NiCl_2$	0.97	0	60	0
2-4	$CuCl_2$	0.93	0.10	67	7

[a] The conditions were the same as in Run 1-4 in Table 1 except that 5 mM coexisting metal salt was further added in the W_{ox} phase.

[b] Ratio of the amount of metal transported after 9 h reaction against that initially added in the W_{ox} phase.

iron transport. On the other hand, a variation in the carrier concentration strongly affected the transport rate. However, in the higher concentration region (more than 0.5 M), the rate was almost saturated (Runs 1-4, 5, 6).

The results of competitive transport with other metal ions are summarized in Table 2. When cobalt, nickel, or copper ion initially coexisted with iron in the W_{ox} phase, the transport of iron was almost selective, and the rate of transport was scarcely affected by the coexisting metals.

Iron Transport through Liquid Surfactant Membrane

The transport reaction of iron ion could be extended to the liquid surfactant membrane system. By using the liquid surfactant membrane, a thin membrane with a large interface area for transport reactions is available, and hence larger fluxes than those in the supported liquid membrane are obtained.

Figure 3 shows the change in the iron concentration in the W_{out} phase against time under various initial conditions. When the system was complete, the iron concentration in the W_{out} phase decreased with an elapse of the time from 5 mM, the initial value, to 3 mM after 90 min, whereas in the absence of the reducing agent in the W_{in} phase, the iron concentration decreased only a little. After 90 min reaction, the w/o emulsion was separated from the W_{out} phase, dissolved in methanol containing acetylacetone, to get a homogeneous solution, and analyzed for iron. The amount of iron present in this solution was roughly equal to that decreased in the W_{out} phase. These results suggest that the transport of iron from the W_{out} to the W_{in} phase through the

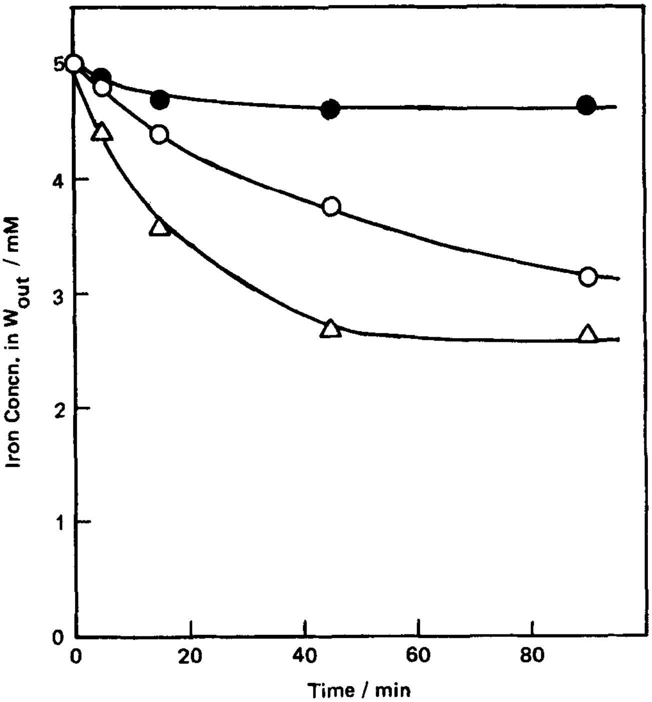

FIG. 3. MTOA-mediated iron transport through liquid surfactant membrane. Change in the iron concentration in the W_{out} phase against time under various initial conditions. (○) W_{out} contained 5 m*M* $FeCl_3$ and 0.5 *M* HCl, while W_{in} contained 30 m*M* ascorbic acid and 0.5 *M* HCl. 5 m*M* MTOA·chloride was present in the membrane. (●) Ascorbic acid was eliminated from the former conditions. (△) The carrier concentration was doubled (10 m*M*).

membrane did occur by the mechanism illustrated in Fig. 1. However, the transport was not as efficient as that of copper ion (by using a thioether carrier) mentioned in the previous paper (5). In the latter case the copper concentration in the W_{in} phase after 45 min reaction went up to 45-fold of that in the W_{out} phase, whereas in the present transport the concentration ratio of iron after 90 min reaction was 8-fold. This is ascribed to the leakage of the inner phase ascorbic acid to the W_{out} phase, which inhibits the iron transport. The addition of an oxidizing agent, cerium(IV) sulfate, in the W_{out} phase did not improve the transport reaction much.

The twofold increase in the carrier concentration led to a considerable enhancement in the initial rate of transport, but the concentration ratio after the reaction did not show much improvement as compared with the control (Fig. 3).

Extraction and Back-Extraction of Cobalt Ion

Irving et al. have examined the extraction of various metal complexes of such aminopolycarboxylic acids as EDTA and NTA by MTOA (*9*, *10*). The extractability of the complexes may be controlled on each side of the liquid membrane by changing the valence state of metal ions, and this will result in a cobalt transport similar to that of iron as illustrated in Fig. 1.

In the beginning, the extraction behavior of the cobalt–NTA complex by MTOA was studied in a water–1,2-dichloroethane system (Table 3). Cobalt ion in the aqueous phase containing NTA and an oxidizing agent, hydrogen peroxide, was readily extracted into organic phase (Run 3-1). Blank experiments (without NTA and without MTOA) confirmed that the cobalt–NTA–MTOA complex was the species extracted (Runs 3-2, 3). When a reducing agent, ascorbic acid or sodium dithionite, was used in the aqueous phase, the metal was not extracted at all (Runs 3-7, 8). These results indicate that the cobalt(III)–NTA complex is more extractable than the cobalt(II)–NTA species. Even in the absence of the oxidizing agent, the extraction of cobalt occurred to a considerable extent, suggesting that oxygen dissolved in the aqueous phase served as an oxidizing agent to some extent

TABLE 3
Extraction of Cobalt Ion[a]

Run	$[H_2O_2]$ (%)	[MTOA] (*M*)	% Extracted
3-1	0.1	0.1	100
3-2[b]	0.1	0.1	4
3-3	0.1	0	0
3-4	0	0.1	74
3-5	0.1	0.02	90
3-6	0.1	0.01	80
3-7[c]	0	0.01	0
3-8[d]	0	0.01	0

[a] Conditions: the aqueous phase (10 mL) contained 0.2 m*M* $Co(NO_3)_2$, 1 m*M* NTA, 10 m*M* KCl, H_2O_2, and 40 m*M* Bicine–NaOH buffer (pH 7.9), while the organic phase (1,2-dichloroethane, 10 mL) contained MTOA·chloride. Shaking time was 15 min.

[b] NTA was eliminated from the aqueous phase.

[c] 5 m*M* ascorbic acid was further added in the aqueous phase.

[d] 6 m*M* $Na_2S_2O_4$ was added in the aqueous phase.

TABLE 4
Back-Extraction of Cobalt[a]

Run	[Ascorbic acid] m(M)	Shaking time (min)	% Back-extracted
4-1	25	15	44
4-2	25	75	78
4-3	15	15	33
4-4	15	75	82
4-5	15	15	24
4-6	[b]	15	22

[a] Conditions: the organic phase (7 mL) contained ~0.14 mM cobalt ion extracted and 10 mM MTOA·chloride (refer to Table 3), while the aqueous phase (10 mL) contained ascorbic acid, 1 mM NTA, 10 mM KCl, and 40 mM Bicine–NaOH buffer (pH 7.9).

[b] 6 mM $Na_2S_2O_4$ was used instead of ascorbic acid.

(Run 3-4). The cobalt ion thus extracted to the organic phase was found to be stripped (back-extracted) to the aqueous phase under reducing conditions (Table 4).

Transport of Cobalt Ion via NTA Complex

These extraction and back-extraction behaviors were used to construct a cobalt transport system through a supported liquid membrane. The results are summarized in Table 5 and Fig. 4. Figure 4 shows the change in the cobalt concentration in the W_{ox} phase and in the W_{red} phase against time. The transport reaction was just as expected from the extraction behaviors; active transport of cobalt ion took place from the W_{ox} to the W_{red} phase through the membrane. Molecular hydrogen excelled ascorbic acid as a reducing agent in regard both to the initial rate of transport and to the final amount of cobalt transported (Runs 5-1, 2, 3).

The transport of cobalt was observed even in the absence of a reducing agent in the W_{red} phase (Table 5, Run 5-4). The transport reaction under the conditions in Run 5-5, i.e., both aqueous phases under oxidizing conditions, is solely due to the concentration gradient of the cobalt(III)–NTA complex in the two aqueous solutions, not involving any redox reactions. It is noted that the initial rate of transport in Run 5-4 was much higher than that in Run 5-5. In the case of Run 5-4, the cobalt(II) species in the W_{red} phase probably acted as a reducing agent which promoted the stripping step at the W_{red}/membrane interface.

TABLE 5
MTOA-Mediated Cobalt Transport[a]

Run	[MTOA] (*M*)	[Ascorbic acid] (m*M*)	Initial rate of transport (μ*M*/h)	Amount of cobalt transported[b] (%)
5-1	0.2	5	74	52
5-2	0.2	15	104	66
5-3	0.2	[c]	130	78
5-4	0.2	0	60	35
5-5[d]	0.2	0	38	27
5-6[e]	0.2	5	45	49
5-7	0.1	5	72	54
5-8[f]	0.1	5	74	57
5-9	0.5	5	88	49

[a] Conditions: W_{ox} contained 0.5 m*M* $Co(NO_3)_2$, 1 m*M* NTA, 10 m*M* KCl, 0.02% H_2O_2, and 20 m*M* Bicine–NaOH buffer (pH 7.9), while W_{red} contained 0.5 m*M* $Co(NO_3)_2$, 1 m*M* NTA, 10 m*M* KCl, ascorbic acid, and 20 m*M* Bicine–NaOH buffer (pH 7.9). MTOA·chloride was present in the membrane.

[b] Ratio of the amount of cobalt transported after 9 h reaction against that initially added in the W_{ox} phase.

[c] Molecular hydrogen (with a combined use of 180 mg platinum asbestos catalysis) was used instead of ascorbic acid.

[d] The addition of cobalt ion (0.5 m*M*) was limited to the W_{ox} phase, while 0.02% H_2O_2 was further added to both aqueous phases.

[e] 20 m*M* MES-NaOH buffer (pH 6.6, MES: 2(*N*-morpholino)ethanesulfonic acid) was used.

[f] The concentration of NTA added in both aqueous phases was 0.5 m*M*.

Under lower pH conditions, the transport rate decreased (Run 5-6). The effect of carrier concentration on the transport rate was rather small (Runs 5-1, 7, 9).

Redox potentials can be generated photochemically by the use of a sensitizing dye or a semiconductor suspension, and it is reported that the photoinduced redox reactions could be coupled with carrier-mediated transports (*4, 5, 11*). In the present cobalt transport, when a photosystem (titanium oxide–glucose) under illumination was applied in the W_{red} phase instead of the reducing agent, the transport rate of cobalt ion was accelerated as compared with the dark conditions (Fig. 5).

Other Metal Ions

Application of the MTOA-mediated transport to other metal ions such as manganese and copper ion was studied. Permanganate ion was easily

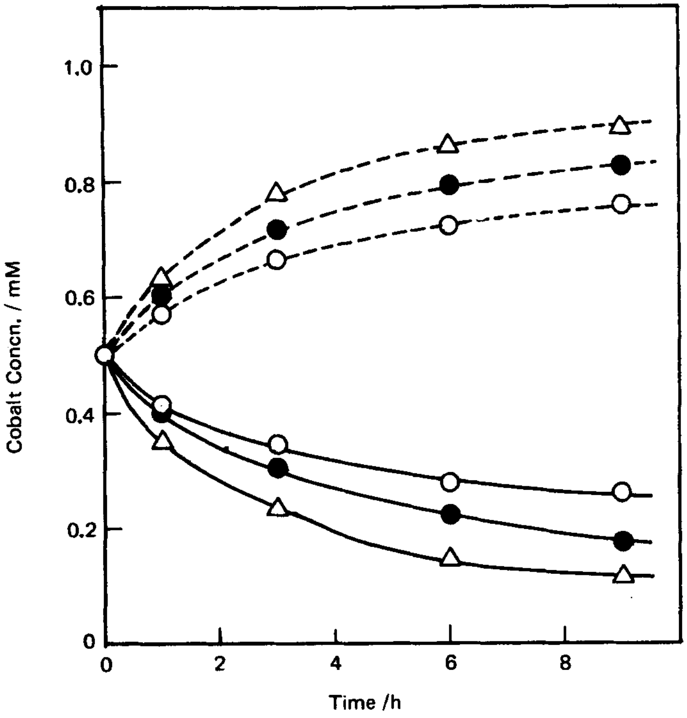

FIG. 4. MTOA-mediated cobalt transport. Change in the cobalt concentration in the W_{ox} phase (full line) and in the W_{red} phase (dotted line) against time under the conditions in Table 5: (○) Run 5-1; (●) Run 5-2; (△) Run 5-3.

extracted to the organic membrane phase by forming an ion-pair $Q^+ \cdot MnO_4^-$ with MTOA. The complex diffused to the other side of the membrane and decomposed, the metal becoming a lower valence state species with a reducing agent (ascorbic acid). However, it was found that after ~80% completion of the transport reaction, the back-transfer of manganese ion in the opposite direction through the membrane took place; the presence of such a process complicated the treatment of overall reactions. The back-transport may be due to the formation of some extractable complexes of reduced manganese ion with pyrophosphate which was specifically added to the reducing aqueous phase to prevent the precipitation of manganese(IV) oxide.

The transport of copper ion mediated by MTOA carrier was also studied. Copper(I) ion forms an anionic complex, $CuCl_2^-$, in hydrochloric acid media and is readily extracted by the carrier. However, we have not found favorable stripping conditions in the membrane transport system.

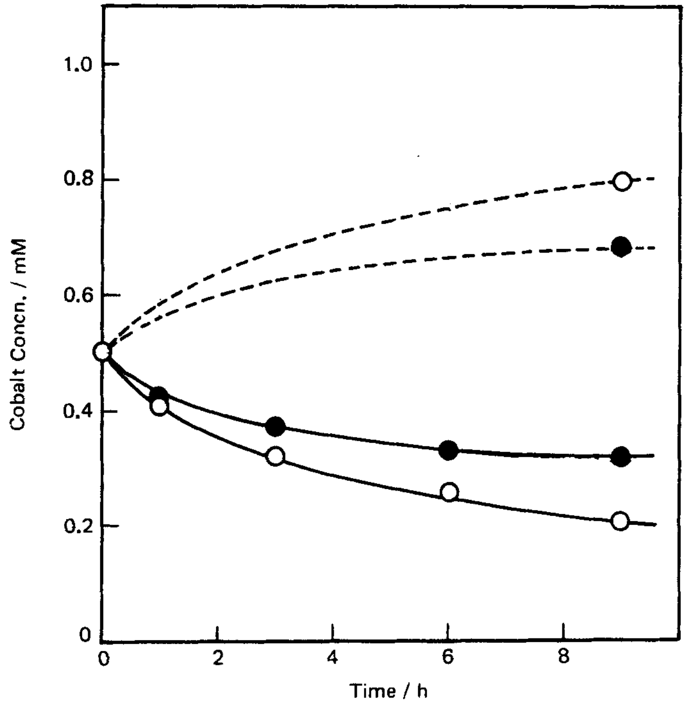

FIG. 5. Photo-assisted transport of cobalt ion. Change in the cobalt concentration in the W_{ox} phase (full line) and in the W_{red} phase (dotted line) against time under two initial conditions. (○) W_{ox} contained 0.5 m*M* $Co(NO_3)_2$, 1 m*M* NTA, 0.02% H_2O_2, 10 m*M* KCl, and 20 m*M* Bicine–NaOH buffer (pH 7.9), while W_{red} (150 mL) contained 0.5 m*M* $Co(NO_3)_2$, 1 m*M* NTA, 15 m*M* glucose, 100 mg TiO_2, 10 m*M* KCl, and 20 m*M* Bicine–NaOH buffer (pH 7.9); W_{red} was irradiated by a 500-W xenon lamp without filter. 0.2 *M* MTOA · chloride was present in the membrane. (●) The conditions were the same as the former except that the reaction was carried out in the dark. The dotted line represents the estimated value of cobalt concentration in the W_{red} phase, the determination of cobalt being difficult because of the suspended titanium oxide. After 9 h reaction, the suspension was removed by filtration and the cobalt concentration was determined.

CONCLUSION

Transport of iron and cobalt ions through liquid membrane was attained by use of a lipophilic quaternary ammonium ion, MTOA, as a carrier. The metal ions formed extractable anionic complexes with appropriate ligands, chloride and NTA, respectively, and the transport system utilized the extractability difference of the metal complexes on each side of the membrane with the aid of a redox reaction. Iron ion was transported through a supported liquid membrane as well as through a liquid surfactant membrane, and the transport was almost selective to coexisting metal ions such as cobalt, nickel, and copper. Cobalt ion was similarly transported via a NTA complex, and the transport could be coupled with a photo-induced redox reaction. Thus, in this paper, a new type of liquid membrane separation system assisted by a redox reaction was presented. In the future it is hoped that more extended studies will be made to more general transition metals and help solve problems in practical metal separation and concentration.

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