Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Enrichment of Zinc Isotopes by a Liquid Membrane System Using a Crown Ether

Kazushige Nishizawa; Takahito Miki; Tomonori Satoyama; Toshiyuki Fujii; Tadashi Yamamoto; Masao Nomura

To cite this Article Nishizawa, Kazushige , Miki, Takahito , Satoyama, Tomonori , Fujii, Toshiyuki , Yamamoto, Tadashi and Nomura, Masao(1998) 'Enrichment of Zinc Isotopes by a Liquid Membrane System Using a Crown Ether', Separation Science and Technology, 33: 7, 991 — 1002

To link to this Article: DOI: 10.1080/01496399808545003

URL: http://dx.doi.org/10.1080/01496399808545003

SEPARATION SCIENCE AND TECHNOLOGY, 33(7), pp. 991–1002, 1998

Enrichment of Zinc Isotopes by a Liquid Membrane System Using a Crown Ether

---

KAZUSHIGE NISHIZAWA,* TAKAHITO MIKI, TOMONORI SATOYAMA, TOSHIYUKI FUJII, and TADASHI YAMAMOTO
DEPARTMENT OF NUCLEAR ENGINEERING
OSAKA UNIVERSITY
2-1, YAMADA-OKA, SUITA, OSAKA, JAPAN

MASAO NOMURA
RESEARCH LABORATORY FOR NUCLEAR REACTORS
TOKYO INSTITUTE OF TECHNOLOGY
2-12-1, OOKAYAMA, TOKYO, JAPAN

ABSTRACT

A liquid membrane system to enrich zinc isotope was investigated. The liquid membrane was composed of a solution of dicyclohexano-18-crown-6 in chloroform. Zinc chloride dissolved in diluted hydrochloric acid was used as a feed phase. A receiving phase was made of a 0.001 M HCl solution. The zinc isotopes were enriched (1) at the interface of the liquid-membrane/feed-phase and (2) at that of the liquid-membrane/receiving-phase. The separation factor attained in the system was α = 1.049 for the separation of ^{64}Zn and ^{66}Zn. The enrichment factor of ^{66}Zn relative to ^{67}Zn was $\epsilon = -0.053$, which is in the inverse direction of enrichment by a liquid–liquid extraction. The enrichment factor of ^{64}Zn to ^{66}Zn showed a different value from that of ^{66}Zn to ^{68}Zn, regardless of their similar mass difference. The isotope effects in the Zn–crown complex were dominated by the field shift of electronic energy in the isotope atom. This is in contrast to the Bigeleisen–Mayer approximation for a chemical exchange reaction.

Key Words. Zinc isotopes; Separation of ^{64}Zn from ^{66}Zn; Separation of ^{67}Zn from ^{66}Zn; Isotope shift; Crown ether; Liquid membrane

---

* To whom correspondence should be addressed.

INTRODUCTION

In isotopic enrichment studies by a liquid–liquid extraction system using a crown ether, it has been reported that odd atomic mass isotopes are enriched by quite different separation factors from even atomic mass isotopes. This effect has been observed for magnesium (1), zinc (2, 3), strontium (4, 5) and barium (5) isotopes. The odd atomic mass isotopes enrich preferentially in the aqueous phase of liquid–liquid extraction. On the basis of these experimental evidences, Nishizawa and coworkers (1, 2, 4) explained that the odd/even isotope effect in the chemical exchange separation of isotopes is brought about by the isotope shift in the orbital electron energy of the isotope atom, especially from the even–odd staggering which has been recognized for many years (6). Bigeleisen (7, 8) showed theoretically in his recent papers that the field shift of the isotope shift results in an anomalous enrichment factor of ^{235}U in the U(IV)–U(VI) exchange reaction (9).

Even for the even atomic mass isotopes of the even atomic numbered elements, the enrichment factors have exhibited a nonlinear dependence on the mass difference in isotope separation by the use of macrocyclic ligands; for instance, the enrichment factor of ^{44}Ca to ^{40}Ca was reported to show a different value from that of ^{48}Ca to ^{44}Ca, but the authors did not define the cause (10, 11). One of our present purposes is to accumulate experimental evidence of the chemical isotope shift induced by the isotope shift of the electronic energy of the isotope atom.

We reported in previous papers (2, 3) that we obtained in a liquid–liquid extraction system a large enrichment factor, $\epsilon_u = 0.018$, for a unit difference of mass numbers of zinc isotopes. Because of its high ionization potential, however, zinc is one of the most difficult metals for isotopic analysis by a surface ionization mass spectrometer. The precision of the isotope ratio was limited. In the present study this is somewhat improved by an additive effect of the enrichment factors in a liquid membrane system. We examine the isotope separation efficiency of a continuous process system using a liquid membrane of dicyclohexano-18-crown-6.

The distribution coefficient of zinc in a liquid–liquid extraction system using dicyclohexano-18-crown-6 (2) is reported to be larger than that of lithium (12); that is, the stability constant of the zinc–crown complex is larger than that of the lithium–crown complex. The flux of metal ions transported in the liquid membrane must depend on the amount of complex formed at the interfaces between the aqueous phases and the liquid membrane. The enriched isotopes of zinc would be obtained at a higher rate than that of lithium in a liquid membrane system.

In order to suppress ^{60}Co build-up in a primary coolant of a boiling water reactor, injection of trace amounts of soluble zinc was recently tried (13). This approach was shown to be effective for the reduction of gamma-ray radiation on the piping system carrying the coolant. This method of reducing the radiation field has been successfully put to practical use in several nuclear reactors used for power generation. There is, however, a problem contingent on the use of zinc which has an isotope, ^{64}Zn, of almost 49% as a naturally occurring abundance. Thermal neutron absorption of ^{64}Zn yields a radioactive isotope, ^{65}Zn, in the vicinity of reactor core, and its half-life is relatively long (245 days). In order to suppress the occupational radiation dose to workers involved in the inspection and maintenance of the reactor subsystem, ^{64}Zn-depleted zinc is desirable. To obtain ^{64}Zn-depleted zinc, an effective isotope separation technique should be developed.

Another application of zinc isotopes is for biomedical use; for instance, ^{68}Zn is the precursor of radioactive ^{67}Ga, which is widely used in clinical medicine for tumor localization (14). At present, zinc isotopes are enriched in electromagnetic separators. Their production is limited, and the cost is quite high. One of the purposes of the present study is to examine an alternative isotope separation technique.

EXPERIMENTAL

The dicyclohexano-18-crown-6 (DC18C6) used is a product of Nisso Chemical Company. Zinc chloride is of reagent grade from Wako Pure Chemical Industry, guaranteed to be 99.9%, and hydrochloric acid is of reagent grade from the same company. They were used without further purification. Chloroform is of reagent grade from Nakarai Tesque.

A liquid membrane was prepared by dissolving DC18C6 in chloroform whose concentration was 0.2 mol·dm^{-3} (M). Before using it for the liquid membrane, this solution was scrubbed with a large amount of demineralized water in order to eliminate water-soluble impurities in the solution such as photolysis products of $CHCl_3$ and ethanol mingled as a stabilizer of $CHCl_3$. A feed phase was prepared by dissolving $ZnCl_2$ in solutions of various concentrations of HCl to obtain 2.0 M $ZnCl_2$. The receiving phase was a 0.001 M HCl solution.

An experimental apparatus for the liquid membrane system was made of a glass tube of the U-type, as schematically shown in Fig. 1. Two branches were used as part of feed phase as inlets for a fresh solution of 2.0 M $ZnCl_2$ and some concentration of HCl, and as an outlet for the solution depleted of $ZnCl_2$ and HCl which entered the liquid membrane. The concentrations of $ZnCl_2$ and HCl in the feed phase solution were kept constant by circulating a large amount of the solution with the fixed component.

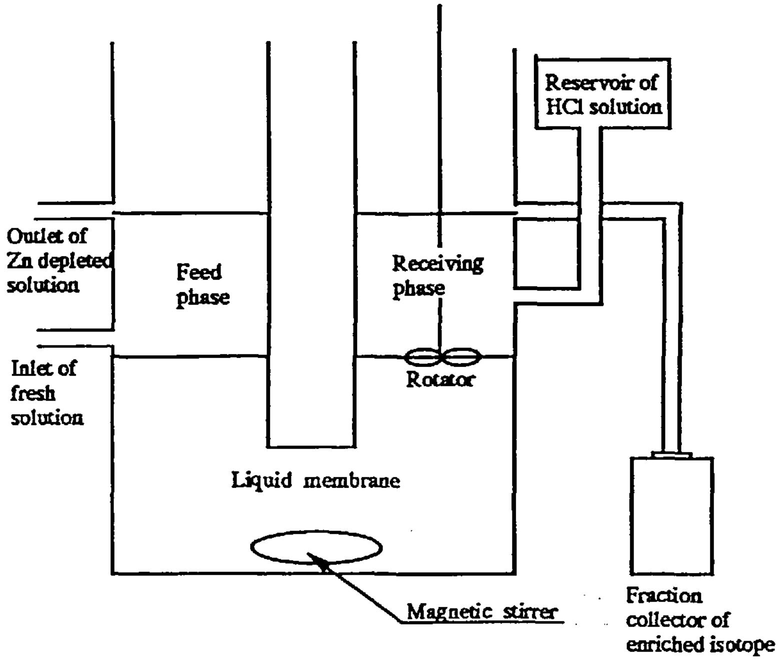

FIG. 1 Schematic diagram of liquid membrane system.

The liquid membrane was placed at the bottom of the U-tube. The liquid for the feed phase composed of 2.0 M $ZnCl_2$ and some concentration of HCl had a smaller specific gravity than the liquid membrane whose main component was chloroform. The feed phase and the receiving phase were placed on either surface of the liquid membrane. The entire system was dipped in a water and ethanol bath, so all the liquids were kept at 273.2 ± 0.5 K.

The liquid membrane was stirred by a magnetic stirrer in order to keep the concentration of zinc and the isotopic composition homogeneous throughout the membrane. Care was taken that the speed of the stirrer did not intermix liquids of the feed phase and the receiving phase. The interface between the liquid membrane and the receiving phase was stirred by a rotator. Fresh HCl solution (0.001 M) was continuously supplied near the bottom of the receiving phase, and the solution containing $ZnCl_2$ was removed to a fraction collector by overflow, so the zinc concentration of the receiving phase was both constant and low.

The zinc chloride solution was analyzed by an atomic absorption spectrophotometer (Shimadzu AA-640-12). Before analyzing isotopic abundance by the mass spectrometer, the $ZnCl_2$ solution was passed through a cation exchanger column and then the column adsorbing Zn^{2+} was purged with methanol to remove any organic impurity. The column was then eluted with nitric acid solution to obtain $Zn(NO_3)_2$. The $Zn(NO_3)_2/HNO_3$ solution was dried in a vial made from fluoro resin.

Isotopic abundance ratios of Zn were measured by a surface ionization mass spectrometer (MAT 261, Finigan Mat). A single filament method was adopted. Almost 5 μg of Zn was loaded onto the filament, together with a small amount of fine powder of silica gel and phosphoric acid. The filament was heated by an electric current in the atmosphere to convert zinc nitrate to zinc oxide on the filament. The filament set in the ion source of the mass spectrometer was slowly heated by an electric current because some organic ion current appeared at about 0.7 A, and we waited for 1.5 hours in that condition until it disappeared. It took about 4.5 hours in order to raise to 2.4 A the filament current to obtain enough ion current to measure the zinc isotope ratios. The ion current was detected by a single secondary electron multiplier, and the signals were registered in an analog recorder. It took about 5 minutes to scan one block of zinc isotopes from ^{64}Zn to ^{68}Zn. Measurement of the zinc isotope group was repeated more than 10 times. An averaged value of 6 or 7 measurements was adopted for the isotope ratios. The decrease of the total ion current was compensated for on the recorder chart. The precision of the present measuring system was ±0.5% for $^{64}Zn/^{66}Zn$, ±1.9% for $^{67}Zn/^{66}Zn$, and ±0.9% for $^{68}Zn/^{66}Zn$ in one sigma.

RESULTS AND DISCUSSION

The enrichment factors (ϵ's) for zinc isotopes of ^{64}Zn, ^{66}Zn, ^{67}Zn, and ^{68}Zn obtained by liquid membrane separation are illustrated in Fig. 2 as a function of mass numbers, together with those obtained by liquid–liquid extraction for reference. While the enrichment factors of zinc isotopes vary with the concentrations of $ZnCl_2$ and HCl in the feed phase, these values are obtained for 2.0 M $ZnCl_2$ and 1.0 M HCl. An isotope separation factor (α) for the liquid membrane system is defined as α = (isotopic ratio in receiving phase)/(isotopic ratio in feed phase). In the present study the isotopic ratio (R) is determined by using ^{68}Zn as a base; $R = {}^{m}Zn/{}^{68}Zn$, where ^{m}Zn represents ^{64}Zn, ^{66}Zn, or ^{67}Zn. The enrichment factor is $\epsilon = \alpha - 1$. Since the absolute value of ϵ is commonly small compared with unity in the chemical exchange reaction; $\ln \alpha = \epsilon$. As seen in Fig. 2, even for ϵ's of the even atomic mass isotopes, they do not have a linear dependency to the mass number. In our recent studies on the isotope separations of zinc (15), nickel (16), iron (17), and chromium (18) by the chemical exchange reaction using the macro cyclic ligands, we found that the separation is largely influenced

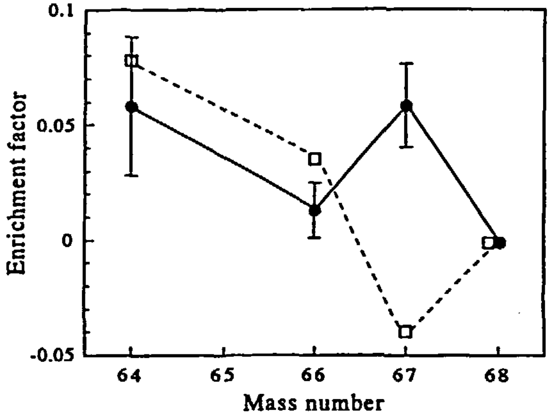

FIG. 2 Enrichment factors of zinc isotopes. The enrichment factors obtained by liquid membrane system are shown as solid circles with error bars. The enrichment factors obtained by liquid–liquid extraction are shown as squares for reference.

by the isotope shift of the electronic energy of the isotope atom. The field shift or the nuclear size and shape of the isotope atom in the isotopomer dominates the enrichment factors of the isotopes. Consequently, even for isotopes of the same element, the separation factors differ for every isotope pair. In the present study we use the enrichment factor for each isotope pair: for instance, $\epsilon_{64,66}$ means the enrichment factor of ^{64}Zn relative to ^{66}Zn. Either magnitude of $\epsilon_{64,66}$ or direction (positive or negative of ϵ) of the liquid membrane is almost identical with that of liquid–liquid extraction. However, the direction of $\epsilon_{67,66}$ is opposite; the cause will be discussed below.

For isotope separation by means of liquid–liquid extraction, the isotope separation factor changes depending on an existing condition of the metal ions in the aqueous phase (1, 2, 4, 12). The cations in the diluted solution dissociate from the counteranions, existing as aqua complex ions. In the concentrated solution, in turn, they form complexes with some counteranions, and apparently exist as neutral species or anionic ions. Since the zinc ion incorporated in the aqua complex or in the complex with the counteranions is classified in different chemical species, the isotopic abundance of zinc in either species must have an individual value. Therefore, in the complexes extracted into the organic phase, isotopic ratios must show different values between those extracted from the diluted aqueous phase and those from the concentrated one.

In the liquid membrane system the feed phase is usually composed of a more concentrated salt solution than the receiving phase. In this case the enrichment occurs at the interface between the feed phase and the liquid membrane, and it is followed at the interface between the receiving phase and the liquid membrane. If the liquid membrane is fully stirred to avoid local condensation of the salt, the isotopic ratio is kept homogeneous in the membrane.

Assigning the isotopic ratios to be R_f, R_m, and R_r in the feed phase, in the liquid membrane, and in the receiving phase, respectively, the isotope separation factors are shown to be $\alpha_f = R_m/R_f$ and $\alpha_r = R_m/R_r$ at the interfaces of the liquid-membrane/feed-phase and of the liquid-membrane/receiving-phase. Since the isotope separation factor of the liquid membrane system is defined as $\alpha_m = R_r/R_f$, the following equations are derived:

$$\alpha_m = \alpha_f/\alpha_r \qquad \text{and} \qquad \epsilon_m = \epsilon_f - \epsilon_r \tag{1}$$

where ϵ_m is the enrichment factor of the whole system of the liquid membrane. The enrichment factor at the interface of the liquid-membrane/feed-phase and that of the liquid-membrane/receiving-phase are shown as ϵ_f and ϵ_r, respectively.

The enrichment factor $\epsilon_{64,66}$ of the liquid membrane system is illustrated in Fig. 3 as a function of HCl concentration in the feed phase, together with that of liquid–liquid extraction. Since the enrichment of isotopes by the liquid membrane system is performed at both interfaces, and the enrichment factor of ϵ_f or ϵ_r corresponds to that of liquid–liquid extraction carried out at that concentration in the initial aqueous phase.

The liquid volume in the receiving phase is kept constant by a continuous supply of 0.001 M HCl solution and overflowing the exhaust of the solution reacted with the liquid membrane. Zinc chloride and hydrochloric acid are also transported at a constant rate into the receiving phase through the liquid membrane about 4 hours after the system is run. Thus, the concentrations of HCl and $ZnCl_2$ result in equilibrium in the receiving phase. The equilibrium concentrations are shown in Fig. 4. Both HCl and $ZnCl_2$ concentrations are low in the receiving phase relative to those in the feed phase. In the liquid–liquid extraction, the enrichment factor cannot be observed in such a diluted aqueous phase, but it can be estimated from the enrichment factor of the whole system of the liquid membrane, $\epsilon_{64,66}$(m), and that of the feed membrane interface, $\epsilon_{64,66}$(f), using the relationship shown in Eq. (1). In these, $\epsilon_{64,66}$(f) is identical with the enrichment factor obtained in the corresponding concentration of HCl in the initial aqueous phase of liquid–liquid extraction. Consequently, ϵ_r is given by the difference between the enrichment factor of liquid–liquid extraction and ϵ_m. The values of $\epsilon_{64,66}$(r)'s are shown in the 4th column of Table 1, where $\epsilon_{64,66}$(r) in parentheses at 0.01 M HCl of the feed phase is estimated to be similar with that at 0.1 M HCl of the feed phase,

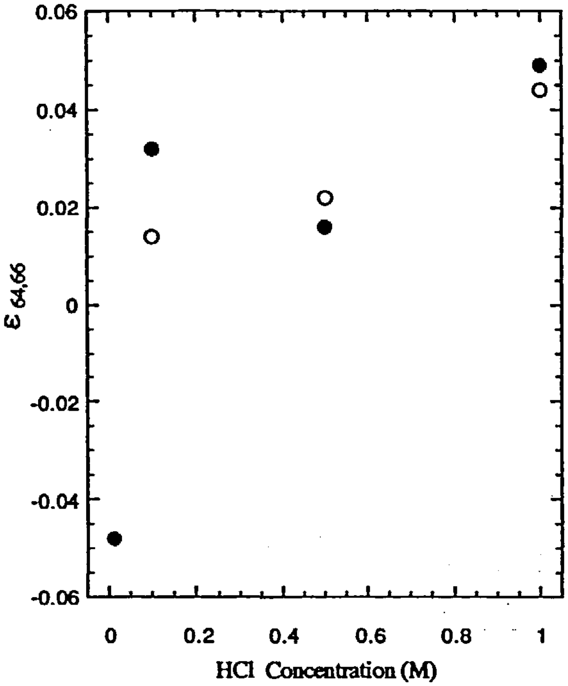

FIG. 3 Enrichment factors of ^{64}Zn relative to ^{66}Zn. Enrichment factors obtained by the present liquid membrane system are shown as solid circles, and those by liquid–liquid extraction as open circles for reference.

because the concentrations of HCl and $ZnCl_2$ are almost the same for both cases, as seen in Fig. 4.

The values of $\epsilon_{64,66}(r)$ in the present system correspond to the enrichment factors obtained by liquid–liquid extraction undertaken in the extremely diluted aqueous phase; for example, even in 1.0 M HCl of the feed phase, the concentrations of HCl and $ZnCl_2$ in the receiving phase result in 0.0051 and 0.0043 M, respectively. In the concentration region of HCl in the feed phase from 0.01 to 1.0 M, except for 0.5 M, the $\epsilon_{64,66}(r)$'s show a negative value, meaning that the enriching direction of the isotopes in the diluted aqueous phase is opposite to that in the concentrated aqueous phase.

As shown in Fig. 2, the odd mass number isotope, ^{67}Zn, gives a different isotope effect from the even mass number isotopes in the isotope separation system of the liquid membrane. The direction of enrichment by the liquid membrane system is opposite to that by liquid–liquid extraction. In our previ-

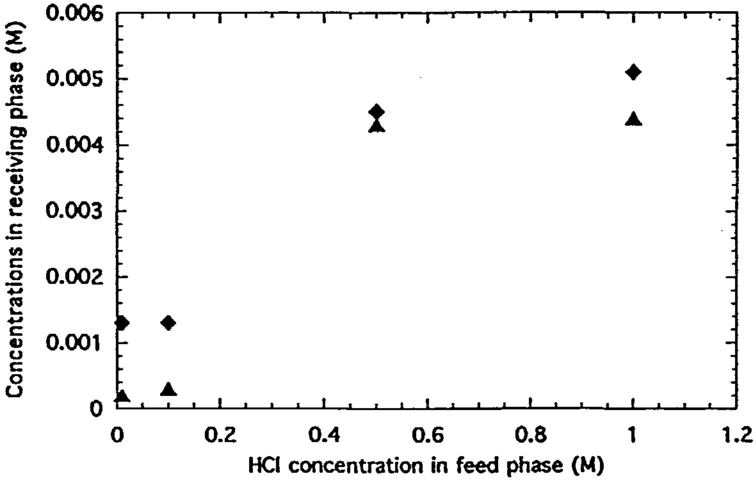

FIG. 4 Concentrations of Zn^{2+} (▲) and of H^+ (◆) in the receiving phase after equilibrium.

ous study (2) on the isotope separation of zinc, we defined an odd/even atomic mass effect, $\epsilon_{O/E}$. Since the enrichment factor differs for every isotope pair as mentioned above, the unit mass enrichment factor and the odd/even separation factor do not have any meaning in isotope separation for some transition elements using a macro cyclic ligand. In the present study we use $\epsilon_{66,67}$, which means the enrichment factor of ^{66}Zn relative to ^{67}Zn.

Figure 5 shows $\epsilon_{66,67}$'s as a function of the concentration of HCl in the feed phase, along with those obtained by liquid–liquid extraction. Like $\epsilon_{64,66}(r)$ at the interface of the liquid-membrane/receiving-phase, $\epsilon_{66,67}(r)$'s at the inter-

TABLE 1
Enrichment Factors of ^{64}Zn to ^{66}Zn of the Liquid Membrane System

C_f (M)[a]	$\epsilon_{64,66}(m)$[b]	$\epsilon_{64,66}(f)$[c]	$\epsilon^{64,66}(r)$[d]
0.01	−0.048	(−0.066)	(−0.018)
0.1	0.032	0.014	−0.018
0.5	0.016	0.022	0.006
1.0	0.049	0.044	−0.005

[a] HCl concentration in feed phase.
[b] Enrichment factor of liquid membrane system for ^{64}Zn to ^{66}Zn.
[c] Enrichment factor at feed–membrane interface for ^{64}Zn to ^{66}Zn.
[d] Enrichment factor at receiving–membrane interface for ^{64}Zn to ^{66}Zn.

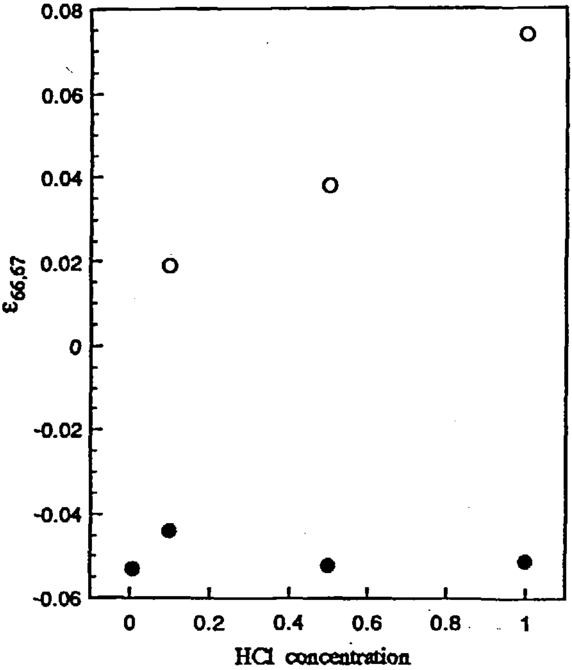

FIG. 5 Enrichment factors of ^{66}Zn relative to ^{67}Zn. Enrichment factors obtained by the present liquid membrane system are shown as solid circles, and those by liquid–liquid extraction as open circles for reference.

face can also be calculated using Eq. (1). These values, $\epsilon_{66,67}(r)$'s, appear in the 4th column of Table 2. They are positive and large for all concentrations of HCl in the feed phase, being opposite to $\epsilon_{66,67}(m)$'s which are given by both enriching processes of the feed-phase/membrane and the receiving-phase/membrane. The isotopic enrichment given by the interface between the receiving phase and the liquid membrane corresponds to that given by liquid–liquid extraction undertaken at the extremely diluted aqueous phase, as mentioned above. If the liquid–liquid extractive separation of isotopes could be carried out under extremely low concentrations of HCl and $ZnCl_2$ (0.0051 and 0.0043 M, respectively), the $\epsilon_{66,67}$ value would therefore be positive and large.

Hydrochloric acid is also transported from the feed phase to the receiving phase through the liquid membrane. This transport is thought to be carried out in two ways. The first is that hydrogen ions coordinate directly to the crown ether, and the chloride ions are accompanied by H^+–crown complexes

TABLE 2
Enrichment Factors of ^{66}Zn Relative to ^{67}Zn, $\epsilon_{66,67}$, of the Liquid Membrane System

C_f (M)[a]	$\epsilon_{66,67}$(m)[b]	$\epsilon^{66,67}$(f)[c]	$\epsilon^{66,67}$(r)[d]
0.01	−0.053	(0.010)	(0.063)
0.1	−0.044	0.019	0.063
0.5	−0.052	0.038	0.090
1.0	−0.051	0.074	0.125

[a] HCl concentration in feed phase.
[b] $\epsilon^{66,67}$ of the liquid membrane system.
[c] $\epsilon^{66,67}$ at feed–membrane interface.
[d] $\epsilon^{66,67}$ at receiving–membrane interface.

to neutralize the charge of complex ions. This method of transport is assumed to be negligible because in the experiment carried out on the feed phase without zinc salt, HCl is not transported. The second is that $(ZnCl_3)^-$ or $(ZnCl_4)^{2-}$ coordinates to the crown ether, and H^+ ion(s) is added for neutralization of the complex ion. The ratio of HCl to $ZnCl_2$ carried into the receiving phase is 0.83, meaning that 0, 1, or 2 H^+ ions are accompanied by a Zn–crown complex.

The rate of transport of zinc salt from the feed phase into the receiving phase varies with the concentrations of $ZnCl_2$ and HCl in the feed phase, with the vigor of a magnetic stirrer placed in the liquid membrane, and with the speed of a rotator placed near the interface of the membrane/receiving-phase. It is desirable to obtain as large an amount of enriched isotope as possible, but care is necessary to avoid intermixing both liquids of the feed phase and receiving phase.

CONCLUSIONS

1. Zinc isotopes are firstly enriched at the interface between the liquid membrane, including DC18C6, and the feed phase of zinc chloride solution in hydrochloric acid, and second at the interface between the liquid membrane and the receiving phase.
2. The separation factor attainable in the present system is $\alpha = 1.049$ for ^{64}Zn/^{66}Zn.
3. The isotope of ^{67}Zn is observed to behave differently from the even mass number isotopes. The direction of enrichment is the inverse to that observed in liquid–liquid extraction. The enrichment factor of ^{66}Zn relative to ^{67}Zn is $\epsilon_{66,67} = -0.053$.

4. The even atomic mass isotopes ^{64}Zn, ^{66}Zn, and ^{68}Zn also exhibit individual enrichment factors upon the isotope pair, regardless of the similar mass difference. The enrichment factor for ^{64}Zn to ^{66}Zn is $\epsilon_{64,66} = 0.049$, and that for ^{66}Zn to ^{68}Zn is $\epsilon_{66,68} = 0.011$.
5. The isotope effect in the chemical exchange reaction using DC18C6 is dominated by the isotope shift of the electronic energy in the isotope atom. This is in contrast to the isotope effect predicted by the Bigeleisen–Mayer approximation (18) on the chemical exchange reaction.

REFERENCES

1. K. Nishizawa, T. Nishida, T. Miki, T. Yamamoto, and M. Hosoe, *Sep. Sci. Technol.*, *31*, 643 (1996).
2. K. Nishizawa, T. Satoyama, T. Miki, T. Yamamoto, and M. Nomura, *Ibid.*, *31*, 2831 (1996).
3. K. Nishizawa, K. Nakamura, T. Yamamoto, and T. Masuda, *Solv. Extr. Ion Exch.*, *11*, 389 (1993).
4. K. Nishizawa, T. Satoyama, T. Miki, T. Yamamoto, and M. Hosoe, *J. Nucl. Sci. Technol.*, *32*, 1230 (1995).
5. K. Nishizawa, K. Nakamura, T. Yamamoto, and T. Masuda, *Solv. Extr. Ion Exch.*, *12*, 1073 (1994).
6. L. Wilets, D. L. Hill, and K. W. Ford, *Phys. Rev.*, *91*, 1488 (1958).
7. J. Bigeleisen, *J. Am. Chem. Soc.*, *118*, 3676 (1996).
8. J. Bigeleisen, *Proc. Natl. Acad. Sci. USA*, *93*, 9393–9396 (September 1996) Chemistry.
9. Y. Fujii, M. Nomura, M. Okamoto, H., Onitsuka, F. Kawakami, and K. Takeda, *Z. Naturforsch.*, *44a*, 395 (1989).
10. K. G. Heumann and H. P. Schiefer, *Angew. Chem.*, *92*, 406 (1980).
11. K. G. Heumann and H. P. Schiefer, *Naturforsch.*, *36b*, 566 (1981).
12. K. Nishizawa, T. Takano, I. Ikeda, and M. Okahara, *Sep. Sci. Technol.*, *23*, 333 (1988).
13. W. J. Marble and R. L. Cowan, *Proc. 1991 JAIF Int. Conf. Water Chem. Nucl. Plants*, Tokyo (1996), p. 55.
14. M. Janghorbani, B. T. G. Ting, and U. R. Young, *Clin. Chim. Acta*, *108*, 9 (1980).
15. K. Nishizawa et al., To be published.
16. K. Nishizawa, T. Miki, R. Ikeda, T. Fujii, T. Yamamoto, and M. Nomura, *J. Mass Spectrom. Soc. Jpn.*, *45*, 521 (1997).
17. T. Fujii, F. Kawashiro, T. Yamamoto, M. Nomura, and K. Nishizawa, Submitted to *J. Mass Spectrom. Soc. Jpn.*,
18. K. Nishizawa et al., To Be Published.
19. J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.* *15*, 261 (1947).

Received by editor August 1997
Revision received September 1997