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

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Kazushige Nishizawa[a]; Tetsurou Nishida[a]; Takahito Miki[a]; Tadashi Yamamoto[a]; Morikazu Hosoe[b]
[a] DEPARTMENT OF NUCLEAR ENGINEERING, OSAKA UNIVERSITY, SUITA, OSAKA, JAPAN [b] DEPARTMENT OF GEOSCIENCE, NATIONAL DEFENSE ACADEMY, YOKOSUKA, KANAGAWA, JAPAN

To cite this Article Nishizawa, Kazushige , Nishida, Tetsurou , Miki, Takahito , Yamamoto, Tadashi and Hosoe, Morikazu(1996) 'Extractive Behavior of Magnesium Chloride and Isotopic Enrichment of Magnesium by a Crown Ether', Separation Science and Technology, 31: 5, 643 — 654

To link to this Article: DOI: 10.1080/01496399608000709

URL: http://dx.doi.org/10.1080/01496399608000709

SEPARATION SCIENCE AND TECHNOLOGY, 31(5), pp. 643–654, 1996

Extractive Behavior of Magnesium Chloride and Isotopic Enrichment of Magnesium by a Crown Ether

KAZUSHIGE NISHIZAWA, TETSUROU NISHIDA,
TAKAHITO MIKI, and TADASHI YAMAMOTO
DEPARTMENT OF NUCLEAR ENGINEERING
OSAKA UNIVERSITY
2-1, YAMADAOKA, SUITA, OSAKA 565, JAPAN

MORIKAZU HOSOE
DEPARTMENT OF GEOSCIENCE
NATIONAL DEFENSE ACADEMY
1-10-20, HASHIRIMIZU, YOKOSUKA, KANAGAWA 239, JAPAN

ABSTRACT

Magnesium chloride was extracted into an organic phase including dicyclohexano-18-crown-6 (DC18C6). The partition coefficient showed its highest value for a liquid–liquid extraction system of 3.5 M $MgCl_2$ aqueous phase. Magnesium isotopes ^{24}Mg, ^{25}Mg, and ^{26}Mg were enriched in the system with their respective enrichment factors. The enrichment factor for $^{24}Mg/^{26}Mg$ was $\epsilon = 0.0112$ as a maximum value. The enrichment factors for a unit difference of mass numbers varied depending on the $MgCl_2$ concentrations in the aqueous phase. The isotope-recognizing ability of DC18C6 was $K_c = 1.0016$, which is smaller than the separation factor due to an exchange of the aqua/dichloro complex of Mg^{2+}, $K_p = 1.0040$. An odd/even isotope effect was observed, and it was assigned to nuclear properties other than mass difference. Odd/even staggering associated with the optical transition of electrons offers a consistent explanation to the different behaviors of isotopes with odd or even mass numbers.

Key Words. Magnesium isotope; Crown ether; Isotope separation; Enrichment factor; Odd/even mass number

INTRODUCTION

Magnesium has a small ionic radius as a bivalent cation in an aqueous solution. It is known that hydration energy is larger for a smaller ionic radius (1). When a magnesium ion is extracted into an organic phase including a neutral carrier such as crown ether, the magnesium ion should exchange from the aqua-complex to a dichloro-complex, being neutral species. One interest is whether it is possible for the small magnesium ion to make a crown ether complex.

In previous papers (2, 3) we showed that the strontium ion is extracted into an organic phase including dicyclohexano-18-crown-6 (DC18C6), and strontium isotopes are enriched in the liquid–liquid extraction system. Isotope enrichment factors have been observed to vary with salt concentration in the aqueous phase (3). Chloride salts of bivalent cations exist as two different chemical species in the aqueous solution; an aqua-complex and a dichloro-complex. Some isotope is enriched in one of the species. Furthermore, cationic isotopes are enriched in a process of complex formation with the crown ether. In the liquid–liquid extraction system, the isotope separation factors are the sum of both effects mentioned above. The isotope effect associated with the exchange between the aqua-complex and the dichloro-complex is large for the magnesium ion because of its large hydration energy.

For liquid–liquid extraction systems using DC18C6, we have shown that isotopes of odd mass numbers of zinc (4), strontium (2), and barium (2), behave differently from those of even mass numbers. Magnesium is composed of three naturally occurring isotopes, ^{24}Mg, ^{25}Mg, and ^{26}Mg, whose abundances are 78.6, 10.1, and 11.3%, respectively. This isotopic composition is suitable for the study of the isotope effect assigned to the odd mass number or the even mass number (odd/even isotope effect) because ^{25}Mg is in relatively high abundance. This effect will be discussed as it relates to the salt concentrations in the aqueous phases.

An isotope shift between two isotopes due to optical transition has been recognized for many years (5). The nuclear properties, which are now generally assumed to be the major causes of the isotope shift, are the mass and the distribution of electric charge. The odd/even isotope staggering (5) assigned to the odd mass number or the even mass number is also recognized, especially for the field effect. It is of interest to study the connection between the isotope shift of optical transition and the isotope effect due to complex formation.

A sodium isotope, ^{22}Na, is one of the rare β^+ emitters. This isotope is used in various scientific fields as a source of annihilation radiation. One of the isotopes, ^{24}Mg, is a precursor of ^{22}Na through ^{24}Mg(d,α)^{22}Na. In this sense, the production of isotopically pure ^{24}Mg is important.

EXPERIMENTAL

Dicyclohexano-18-crown-6 (DC18C6) was a product of Nisso Chemical Company. Hexahydrate magnesium chloride was of reagent grade from Wako Pure Chemical Industry, guaranteed to be 99.9%. It was used without further purification. Chloroform was of reagent grade from Nakarai Tesque.

An organic phase was prepared by dissolving DC18C6 in chloroform whose concentration was 0.2 M. Before use for extraction, this organic phase was scrubbed with a large amount of demineralized water, in order to eliminate such water-soluble impurities in the solution as photolysis products of $CHCl_3$ and ethanol mingled as a stabilizer of $CHCl_3$. An aqueous phase was prepared by dissolving $MgCl_2{\cdot}6H_2O$ in demineralized water at various concentrations. Twenty milliliters each of the aqueous phase and the organic phase were shaken together for extraction. The extraction was made at 293.2 ± 0.5 K. The detailed procedure is found elsewhere (3).

The concentration of magnesium was analyzed by an atomic absorption spectrophotometer (Shimadzu-AA-640-12). The isotopic composition of magnesium was measured with a surface ionization mass spectrometer (MAT 261. Finnign MAT). Before charging a magnesium salt on the mass spectrometer, a sample solution of $MgCl_2$ was passed through into a cation exchanger column. The column was purged with methanol to remove organic impurities, and then magnesium was eluted with HNO_3 solution in order to obtain magnesium nitrate. The $Mg(NO_3)_2/HNO_3$ solution was dried in a vial made from a fluoro resin.

RESULTS AND DISCUSSION

Partition Coefficient

The relationship between a partition coefficient and the concentration of magnesium chloride in the aqueous phase is illustrated in Fig. 1. The partition coefficient (D) is defined as the ratio of magnesium transferred into an organic phase to that in an initial aqueous phase. Since the amount of magnesium chloride extracted into the organic phase is small comparing with that remaining in the aqueous phase, the equilibrium concentration in the aqueous phase is almost equal to the initial concentration. The abscissa of Fig. 1 is a linear scale of logarithms of the $MgCl_2$ activity

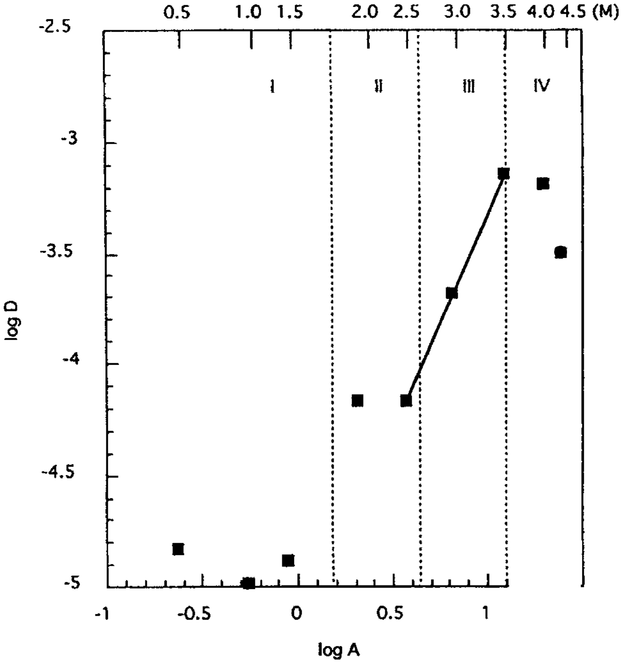

FIG. 1 Logarithms of distribution coefficient (D) against logarithms of $MgCl_2$ activity (A) in the aqueous phase. The $MgCl_2$ activities in the aqueous phases are defined for $MgCl_2$ concentrations of 0.5 to 3.5 M.

(0–3.5 M) which is calculated through activity coefficients (6). The concentrations of $MgCl_2$ corresponding to the measured points are shown in an upper scale.

The log D values are grouped into four regions of the concentrations (I, II, III, and IV). In region I, log D values are small relative to the other regions and they change little depending on the concentrations. In the most diluted aqueous phase, magnesium chloride dissociates completely, existing as the aqua-complexes of Mg^{2+} and Cl^-. Since Pauling's ionic radius of Mg^{2+} is small and its hydration energy is high, it is hard to extracted into the organic phase through exchanging water molecules to the crown ether. While relatively high partition coefficients are observed in region II, they do not change depending on the concentrations. Magnesium exists more popularly as a monochloro-complex $(MgCl)^+$ in these concentrations. In region III, including 2.5 M, log D values increase linearly with logarithms of the activity of $MgCl_2$. Since the slope of this straight line is 2.0, stoichiometric equilibrium is realized in the extraction of $MgCl_2$ from these aqueous phase concentrations, as shown in the following equation:

$$(Mg^{2+})_{aq} + 2(Cl^-)_{aq} + (L)_{org} \overset{K_{ex}}{=} (MgLCl_2)_{org} \qquad (1)$$

where suffixes aq and org indicate the chemical species in parenthesis found in the aqueous phase and in the organic phase, respectively. The crown ether complex of magnesium chloride is shown as $MgLCl_2$. The equilibrium constant, K_{ex} of Eq. (1), is shown in the following equation:

$$K_{ex} = [MgLCl_2]_{org}/([Mg^{2+}]_{aq}[Cl^-]^2_{aq}[L]_{org}) \qquad (2)$$

where $[MgLCl_2]_{org}$ and $[L]_{org}$ are the concentrations of the magnesium-crown-complex and the crown ether in the organic phase, respectively. The magnesium and chloride concentrations in the aqueous phase are shown as $[Mg^{2+}]_{aq}$ and $[Cl^-]_{aq}$, respectively. The partition coefficient is

$$D = [Mg]_{org}/[Mg]_{aq} \qquad (3)$$

From Eq. (2) and Eq. (3), we can get

$$\log D = 2 \log[Cl^-]_{aq} + \log[L]_{org} + \log K_{ex} \qquad (4)$$

The concentration of chloride ions in the aqueous phase is two times larger than that of $MgCl_2$, and $[L]_{org}$ is constant at 0.2 M. Equation (4) is rewritten to Eq. (5):

$$\log D = 2 \log A + C \qquad (5)$$

where A is the activity of $MgCl_2$ and C is a constant. In region IV the D values decrease with the concentration and are due to the increasing viscosity of the aqueous phase. A dichloro-complex of magnesium would first be produced in the 2.5 M aqueous phase and would grow with an increase of the concentration. In a 4.5 M aqueous phase, the dichloro-complex is the only species of magnesium.

Isotopic Equilibrium

Isotopic equilibrium is expressed by the following equation:

$$({}^{l}MgCl_2)_{aq} + ({}^{26}MgLCl_2)_{org} \overset{K}{=} ({}^{l}MgLCl_2)_{org} + ({}^{26}MgCl_2)_{aq} \qquad (6)$$

where ${}^{l}Mg$ indicates a lighter isotope, ${}^{24}Mg$ or ${}^{25}Mg$. The equilibrium constant, K, is

$$\begin{aligned} K &= [({}^{l}MgLCl_2)_{org}({}^{26}MgCl_2)_{aq}]/[({}^{l}MgCl_2)_{aq}({}^{26}MgLCl_2)_{org}] \\ &= ([{}^{l}Mg]/[{}^{26}Mg])_{org}/([{}^{l}Mg]/[{}^{26}Mg])_{aq} \end{aligned} \qquad (7)$$

where $([^{1}\mathrm{Mg}]/[^{26}\mathrm{Mg}])_{\mathrm{org}}$ and $([^{1}\mathrm{Mg}]/[^{26}\mathrm{Mg}])_{\mathrm{aq}}$ represent the isotopic ratios found in the organic and in the aqueous phases, respectively. The equilibrium constant K of Eq. (7) is identical with the separation factor, α, of the present extraction system. An enrichment factor, ϵ, is defined as $\epsilon = \alpha - 1$.

The enrichment factors observed in the present extraction system are illustrated in Fig. 2 as functions of the mass number. From the definition of ϵ, it is 0.0000 at mass number 26. As is shown in Fig. 2, the straight lines joining the ϵ values at mass numbers 24 and 26 deviate from the ϵ values at mass number 25. The deviation is either positive or negative depending on the $MgCl_2$ concentrations in the aqueous phase. This effect is assigned to the odd/even mass number, as will be discussed below.

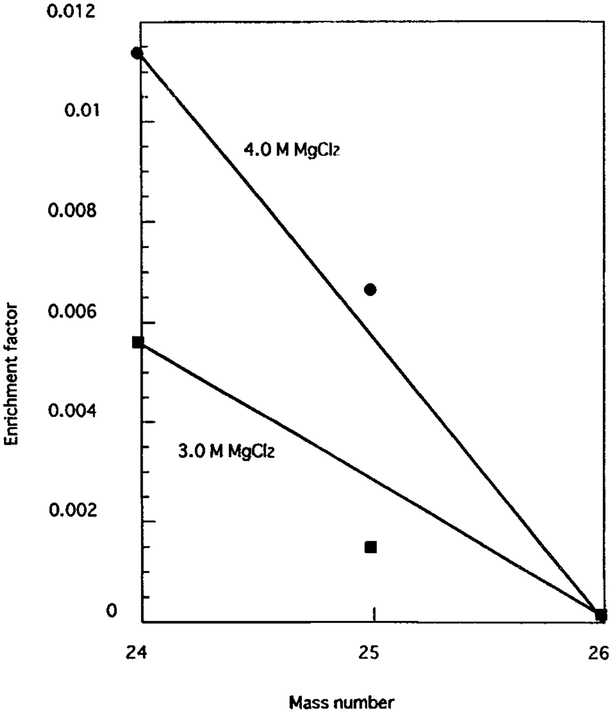

FIG. 2 Enrichment factor as a function of mass number. The relationships of enrichment factor to mass number are illustrated for extraction from 3.5 and 4.0 M aqueous phases as examples. The odd/even isotope effect is shown as a deviation of the enrichment factor at mass number 25 from a straight line.

The enrichment factor (ϵ_u) for a unit difference of mass numbers is defined as follows:

$$\epsilon_u = \epsilon_{24}/2 \tag{8}$$

where ϵ_{24} is the enrichment factor observed at mass number 24. The ϵ_u values correspond to the inclination of the straight lines in Fig. 2. They are illustrated in Fig. 3 as a function of $MgCl_2$ concentrations in the aqueous phase of the extraction. They vary with the concentration in the aqueous phase as does the lithium (7) and strontium (3) isotope effect. If isotopic enrichment is realized by the simple chemical exchange reaction described by Eq. (6), the enrichment factors should be constant and independent of the concentrations. Otherwise, isotopic enrichment should be the sum of two or more processes. These enriching processes can be

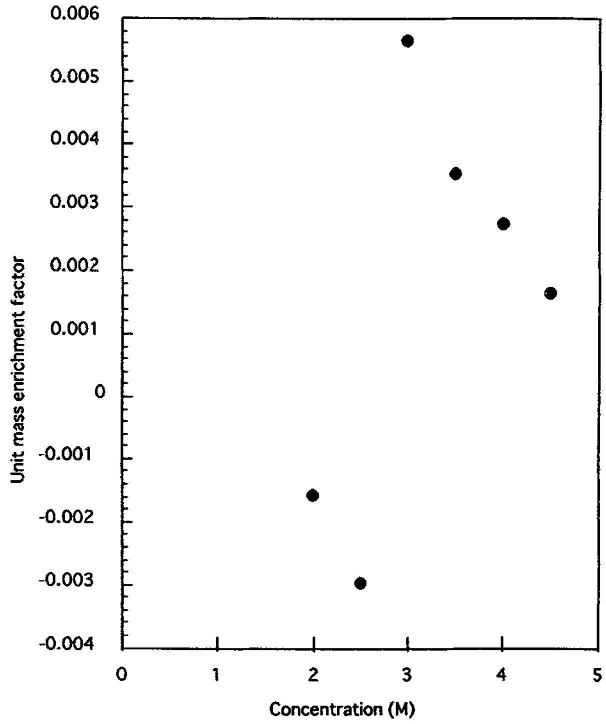

FIG. 3 Unit mass enrichment factors obtained at representative $MgCl_2$ concentrations. The definition of the unit mass enrichment factor will be found in the text.

estimated separately by introducing ϵ dependency on the concentration in the aqueous phase.

In a dilute solution of magnesium chloride, magnesium ions and chloride ions hydrate with some water molecules, and so exist as the aqua-complexes. In a more concentrated solution, the population of dichloro-complexes will be large compared with that of aqua-complexes, and in the most concentrated solution (4.5 M), all magnesium ions would be in dichloro-complexes. The isotopes should be distributed unevenly in the aqua-complexes or in the dichloro-complexes. An isotopic equilibrium is described by the following equation, as simplified for ^{24}Mg and ^{26}Mg:

$$^{24}\mathrm{Mg}^{2+}_{(\mathrm{aqua})} + {}^{26}\mathrm{Mg}^{2+}_{(\mathrm{dichloro})} \overset{K_p}{=} {}^{26}\mathrm{Mg}^{2+}_{(\mathrm{aqua})} + {}^{24}\mathrm{Mg}^{2+}_{(\mathrm{dichloro})} \tag{9}$$

where $\mathrm{Mg}^{2+}_{(\mathrm{aqua})}$ and $\mathrm{Mg}^{2+}_{(\mathrm{dichloro})}$ represent the aqua-complex and the dichloro-complex of magnesium, respectively. Although both complexes have different chemical properties in the aqueous phase, they cannot be easily isolated from each other. Therefore, the equilibrium constant, K_p, which corresponds to the separation factor between ^{24}Mg and ^{26}Mg, is not directly observable.

We can express the isotope exchange equilibrium of magnesium by the following equation when it forms a complex with DC18C6:

$$[^{24}\mathrm{Mg}^{2+}(\mathrm{dichloro})]_{\mathrm{aq}} + [^{26}\mathrm{MgLCl_2}]_{\mathrm{org}} \overset{K_c}{=} [^{24}\mathrm{MgLCl_2}]_{\mathrm{org}} + [^{26}\mathrm{Mg}^{2+}(\mathrm{dichloro})]_{\mathrm{aq}} \tag{10}$$

where $[\mathrm{Mg}^{2+}(\mathrm{dichloro})]_{\mathrm{aq}}$ and $[\mathrm{MgLCl_2}]_{\mathrm{org}}$ are the dichloro-complex of magnesium in the aqueous phase and the crown-ether-complex of that in the organic phase, respectively. The equilibrium constant of Eq. (10) is represented by K_c.

In the case of the two enriching processes shown in Eqs. (9) and (10), the observable isotope separation factor, α_{obs}, has the following relationship (7) to K_p and K_c:

$$\ln \alpha_{\mathrm{obs}} = \ln K_c + (\ln K_p)/(1 + w) \tag{11}$$

where w is the ratio of the dichloro-complex to the aqua-complex of magnesium. All the magnesium ions would be in the dichloro-complex in the most concentrated solution, 4.5 M, in the present experiment; that is, $w_{4.5} \rightarrow \infty$. On the other hand, in the 3.0 M solution, where ϵ has a discontinuous large value compared with the less concentrated aqueous phase (stoichiometric equilibrium is attained at this point), the population of the dichloro-complex of magnesium is small; $w \approx 0$. Thus, we can rewrite Eq. (11) as Eqs. (12) and (13) for the 3.0 and 4.5 M aqueous phases, respectively:

$$0.0056 = \ln K_c + \ln K_p \tag{12}$$

$$0.0016 = \ln K_c \tag{13}$$

The K_c and K_p values are obtained from Eqs. (12) and (13): $K_c = 1.0016$ and $K_p = 1.0040$. Since the isotope abundance ratio of magnesium in the dichloro-complex in the 4.5 M solution is identical with that in the aqueous phase, the K_c value is attributed to an intrinsic separation factor associated with the complex formation for the dichloro-complex of magnesium with the crown ether.

The ϵ_u values at 2.0 and 2.5 M are discontinuously low relative to the more concentrated aqueous phases. As mentioned above, no dichloro-complexes of magnesium exist in these aqueous phases, that is, the aqua-complex and the monochloro-complex of magnesium coexist. Although the exact abundance of these species is not known, the isotopic ratio (^{24}Mg/^{26}Mg) in aqua-complexes decreases with an increase of monochloro-complexes. The unit mass enrichment factors obtained at these extraction conditions should be small, because the isotopic component of magnesium ions extractable from the dilute aqueous phase is ^{24}Mg-depleted relative to ^{26}Mg.

Isotope Effect Induced by the Odd/Even Mass Number

When the isotope enrichment factor at mass number 24 and that at mass number 26 ($\epsilon = 0.0000$) are joined by a straight line, the ϵ value observed at mass number 25 is not on this line, as can be seen in Fig. 2. The deviation of ϵ_{25} from the straight line is defined as the odd/even isotope effect ($\epsilon_{O/E}$). It has either a positive or a negative value according to the initial $MgCl_2$ concentrations in the aqueous phase of the extraction. The odd/even isotope effect is illustrated in Fig. 4 as a function of the concentrations in the aqueous phase. It is common with the unit mass enrichment factor that the $\epsilon_{O/E}$ values will change depending on the concentrations in the aqueous phase. The $\epsilon_{O/E}$ values decrease with $MgCl_2$ concentrations, except for 4.0 M. They show discontinuous changes between 2.5 and 3.0 M.

As can be seen from the definition of the $\epsilon_{O/E}$ value, it expresses a component of isotope effects other than that induced by the mass difference. It shows almost the same order of magnitude as the ϵ_u value. Since all magnesium ions exist as the dichloro-complex in the 4.5 M aqueous

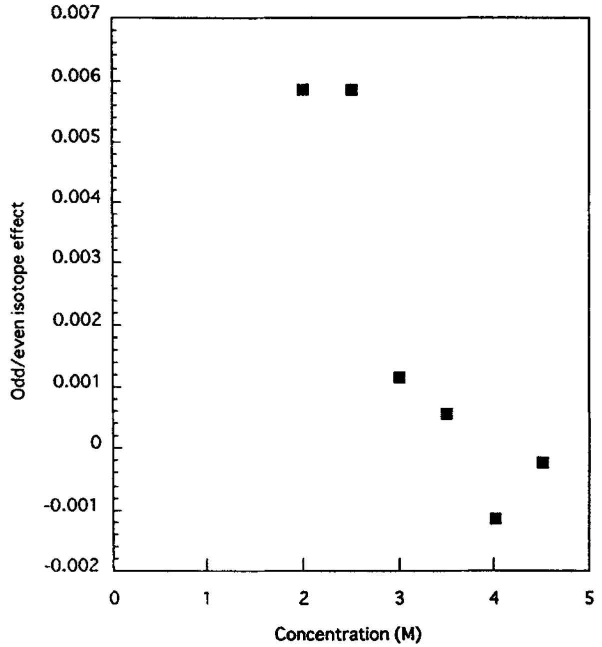

FIG. 4 Odd/even isotope effects obtained at various $MgCl_2$ concentrations in the aqueous phase.

phase, a true odd/even isotope effect induced by complex formation with the crown ether is revealed at this concentration; $\epsilon_{O/E} = -0.0003$. The absolute value of this $\epsilon_{O/E}$ is small compared with the $\epsilon_{O/E} = 0.0058$ obtained in the less concentrated regions. This shows that the odd/even isotope effect is more conspicuous in the exchange between the aqua-complex and the dichloro-complex than during coordination of the crown ether to the magnesium ion.

The isotope effect formerly accepted in the chemical exchange reaction has been reduced to the difference of vibrational energies in the chemical bonds between the isotope and the legand due to the mass difference of the isotopes. The odd/even isotope effect cannot be explained by this theory.

Isotope Effect Associating with Complex Formation

It is not clearly known that any kind of molecular orbital is formed when a ligand such as a water molecule, a chloride ion, or the crown ether coordinates to the magnesium ion. However, we can presume that the lone pair electrons of the ligand coordinate to a vacant 3s orbital of the magnesium ion and an sp hybrid orbital is formed. The 3s orbital of magnesium is in different energy states for individual isotopes, that is, in the 3s3p → $3s^2$ transition, the isotope shift between ^{24}Mg and ^{26}Mg has been identified, and its value is 46 mK (8). This isotope shift can be assigned to a specific mass shift because it is prominent in a light element like magnesium. For the odd mass number isotope ^{25}Mg, the value for the isotope shift is not known. It is assumed (9) that a decrease in angular momentum of the nucleus caused by the existence of an unpaired neutron yields an odd/even staggering of the energy state. It produces a change in the energies of intramolecular bonds of the complex.

CONCLUSIONS

(1) Magnesium is extracted into the organic phase in a liquid–liquid extraction system using DC18C6. Magnesium ions are distributed stoichiometrically between the aqueous phase and the organic phase when the concentration of the aqueous phase is between 2.5 and 3.5 M.

(2) Magnesium isotopes ^{24}Mg, ^{25}Mg, and ^{26}Mg can be enriched in the present system. The enrichment factor for ^{24}Mg/^{26}Mg is $\epsilon = 0.0112$, the maximum value.

(3) The enrichment factors for a unit difference of mass number vary depending on the $MgCl_2$ concentrations in the aqueous phases. The ability of isotope recognition assigned to DC18C6 is $K_c = 1.0016$, which is smaller than the separation factor, $K_p = 1.0040$, due to the exchange between the aqua-complex and the dichloro-complex.

(4) The odd/even isotope effect which is observed is assigned to nuclear properties other than the mass difference. The odd/even isotope staggering associated with the transition of the electrons would produce a consistent explanation to the $\epsilon_{O/E}$ values observed in the present experiment.

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Received by editor July 3, 1995