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Separation of Zinc Isotopes by Liquid–Liquid Extraction Using a Crown Ether

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ABSTRACT

The zinc isotope effect in a liquid–liquid extraction system using dicyclohexano-18-crown-6 was investigated. The enrichment factor for a unit difference of mass number was $\epsilon_u = 0.018$ as a maximum, which is greater than that for magnesium isotopes. The enrichment factor to eliminate ^{64}Zn from ^{66}Zn, ^{67}Zn, ^{68}Zn, or ^{70}Zn is over 0.036. The isotope with an odd mass number, ^{67}Zn, behaved differently from those with even mass numbers. This odd/even isotope effect was $\epsilon_{O/E} = 0.056$. From the values of ϵ_u and $\epsilon_{O/E}$, it was found that the crown ether separated the zinc isotopes more effectively on the basis of an odd or an even mass number than of mass difference. The separation factors vary with the concentrations of salt and/or conjugated acid in the initial aqueous phases of extraction. The optimal concentration necessary to obtain the largest separation factor had components of 2.0 M $ZnCl_2$ and 1.0 M HCl. The large value of ϵ_u for the high atomic number zinc and the notable $\epsilon_{O/E}$ make it clear that the vibration frequencies of the intramolecular bonds should have an isotope shift which is recognized in the orbital energy of the atoms.

Key Words. Zinc isotopes; Unit mass enrichment factor; Odd/even isotope effect; Isotope shift; Crown ether; Liquid–liquid extraction

INTRODUCTION

In order to suppress ^{60}Co buildup in a primary coolant of a boiling water reactor, injection of trace amounts of soluble zinc has recently been tried (1). This approach was shown to be effective in the reduction of gamma-ray radiation on the piping system carrying the coolant. This method to reduce the radiation field has been successfully put into practical use in several nuclear reactors used for power generation. There is, however, a problem with the use of zinc. It has an isotope, ^{64}Zn, which is almost 50% of the naturally occurring abundance ratio. Thermal neutron absorption of ^{64}Zn in the vicinity of the reactor core yields a radioactive isotope, ^{65}Zn, whose half-life is relatively long at 245 days. In order to suppress the occupational radiation dose of workers who inspect and maintain the reactor subsystem, ^{64}Zn-depleted zinc is desirable. To obtain ^{64}Zn-depleted zinc, an effective isotope separation technique has to be developed.

Another application of zinc isotopes is for biomedical use (2), for instance, ^{68}Zn is the precursor of radioactive ^{67}Ga, which is widely used in clinical medicine for tumor localization. At present, zinc isotopes are enriched in electromagnetic separators. Their production is limited, and the costs are quite high. One purpose of the present study is to examine an alternative isotope separation technique.

In a previous paper (3) we reported that the enrichment factor of zinc isotopes for unit atomic mass difference is $\epsilon_u = 0.013$ in the liquid–liquid extraction system using a crown ether of dicyclohexano-18-crown-6 (DC18C6). From the viewpoint of elimination of ^{64}Zn, since the mass difference between ^{64}Zn and ^{66}Zn is two atomic mass units, the enrichment factor is larger than 0.026. This enrichment factor is extremely large compared with $\epsilon = 0.0007$ (4), which was calculated for the chemical exchange reaction between 6-hydrated zinc ion and 4-iodinated complex. The zinc isotopes were separated by a liquid-phase thermal diffusion technique (5). While it seems to be effective, it is impossible to compare it with the present study since the separation factor cannot be deduced from the system itself.

In the chemical exchange reaction, it is formerly recognized (6) that the isotope effect is inversely proportional to the square of the mass and proportional to the mass difference. Urey (7) noted that chemical methods are promising only for elements with atomic weights not greater than 40.

In our previous study, several new facts for enriching medium and heavy isotopes have been found: 1) the unit mass separation factor, ϵ_u, for zinc isotopes of atomic number 30 is larger than that for magnesium (8) of atomic number 12; 2) ϵ_u for zinc isotopes (3) is greater than for their mass numbers; 3) ϵ_u for barium of atomic number 56 is greater than that

for strontium (9) of atomic number 38; and 4) ϵ_u for zinc is greater than that for nickel (10) of atomic number 28. The chemically different behaviors between the odd mass number isotopes and the even mass number isotopes were found for various elements, including magnesium, nickel, zinc, strontium, and barium, by liquid–liquid extraction using DC18C6. For most of these elements the isotope effects assigned to odd or even mass numbers are greater than those assigned to the unit difference of mass numbers. These facts indicate that the isotopic enriching mechanism in a chemical exchange reaction should be reexamined.

EXPERIMENTAL

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

An organic phase was prepared by dissolving DC18C6 in chloroform whose concentration was 0.2 mol·dm^{-3} (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 $ZnCl_2$ into of HCl solution, of fixed concentration. Each 20 mL of the aqueous phase and the organic phase were shaken together for the extraction. Then the solution mixture was transferred to a separating funnel and rested for 30 minutes so the phases could disengage. These shaking and standing processes were carried out at 293 ± 0.5 K by means of a water and ethanol bath. The organic phase was isolated from the aqueous phase and then scrubbed with 20 mL pure water for backextraction of $ZnCl_2$ into the water. The zinc chloride solution thus obtained was analyzed by an atomic absorption spectrophotometer (Shimadzu AA-640-12).

The $ZnCl_2$ solution was passed into 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 a fluoro resin.

The isotopic abundance ratios of Zn were measured by a surface ionization mass spectrometer (MAT 261, Finigan Mat). A single filament method was used. Almost 5 μg of Zn was charged on the filament together with a small amount of silica gel powder and phosphoric acid. The filament was electrically heated in air to obtain zinc oxide on the filament. The

precision of the present measuring system was less than 0.5% in one sigma for the isotopic ratio of $^{64}Zn/^{66}Zn$.

RESULTS AND DISCUSSION

The separation factor of zinc isotope in the liquid–liquid extraction system is defined as

$$\alpha = ([^{L}Zn]/[^{68}Zn])_{org}/([^{L}Zn]/[^{68}Zn])_{aq} \quad (1)$$

where ^{L}Zn indicates isotopes of zinc lighter than ^{68}Zn, and $([^{L}Zn]/[^{68}Zn])_{org}$ and $([^{L}Zn]/[^{68}Zn])_{aq}$ denote the isotopic ratios found in the organic phase and in the aqueous phase after completion of the isotopic equilibrium, respectively. ^{70}Zn is the heaviest naturally occurring isotope, but its abundance ratio is too low (0.62%) to measure with a mass spectrometer equipped with a surface ionization ion source. Therefore, we omitted ^{70}Zn in the present experiment. An enrichment factor, ϵ, is defined as $\epsilon = \alpha - 1$, and in general, α is small compared with unity: $\epsilon = \ln \alpha$. In order to compare the isotope enrichment factors of other elements, or to separate them from an odd/even isotope effect, the unit mass enrichment factor ϵ_u is defined as

$$\epsilon_u = \epsilon/(A_{68} - A_L) \quad (2)$$

where A_{68} and A_L show the mass numbers of ^{68}Zn and ^{L}Zn, respectively.

Figure 1 illustrates ϵ values for ^{64}Zn, ^{66}Zn, ^{67}Zn, and ^{68}Zn. From the definition, ϵ at $A = 68$ is always zero. As with lithium (11), magnesium (8), and strontium (12) isotope separations, zinc isotope enrichment factors also vary depending on the salt concentrations of the aqueous phases of the liquid–liquid extraction systems. The ϵ values taken from salt concentrations of 0.5 M and 2.0 M in the 1.0 M HCl aqueous solution are shown in Fig. 1 as examples. The ϵ values at mass number 67 deviate from the lines for both 0.5 and 2.0 M zinc concentrations. The deviation is defined as the odd/even isotope effect.

Unit Mass Enrichment Factor

When ϵ_u is defined according to Eq. (2), the value at mass number 67 is so far from the straight line, that it is eliminated from the calculation of ϵ_u. The ϵ values which vary with the salt concentrations in the initial aqueous phase are shown in Fig. 2(a) as a function of the salt concentrations in 1.0 M HCl solution. The ϵ_u values are always positive, which shows that the lighter isotope are enriched in the organic phase; that is, the stability constant of the complex of the lighter isotope with DC18C6

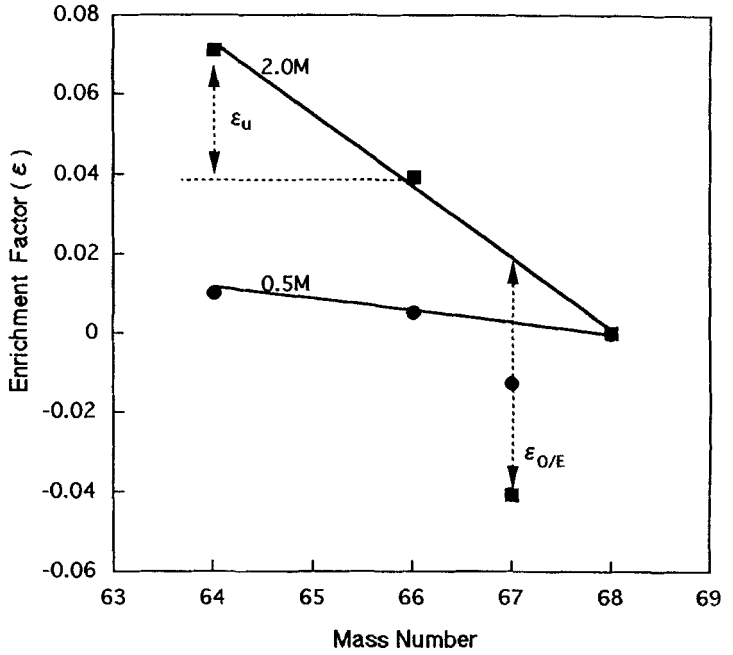

FIG. 1 Isotopic enrichment factor of zinc for each mass number. Unit mass enrichment factor ε_u and odd/even isotope effect $\varepsilon_{O/E}$ are defined in the text.

is larger than that of the heavier one. Since Pauling's ionic radius of Zn(II) is 74 nm, and in general it is larger for the lighter isotope, the lighter isotope is a good fit to DC18C6 whose radius is relatively large (260–320 nm). The larger stability constants for the lighter isotopes can be explained by this fit of the ion to the hole size of the crown ether.

In Fig. 2(b), ϵ_us are illustrated as a function of HCl concentrations in the initial aqueous phase of the fixed zinc concentration of 2.0 M. Except for the most diluted HCl, ϵ_us increase with HCl concentration. The is identical with lithium, magnesium, and strontium isotope separations carried out by the present authors.

A bivalent zinc ion in the aqueous solution can be dealt with like those of magnesium and strontium. The zinc ion exists in the aqueous solution as the aqua complex $Zn^{2+}(OH_2)_n$ or the dichloro complex $Zn^{2+}Cl_2^-$. The former is more popular in the system of a diluted aqueous solution rich of water molecules, and the latter is more popular in a solution of stronger ionic strength. Since each complex is counted as a different chemical

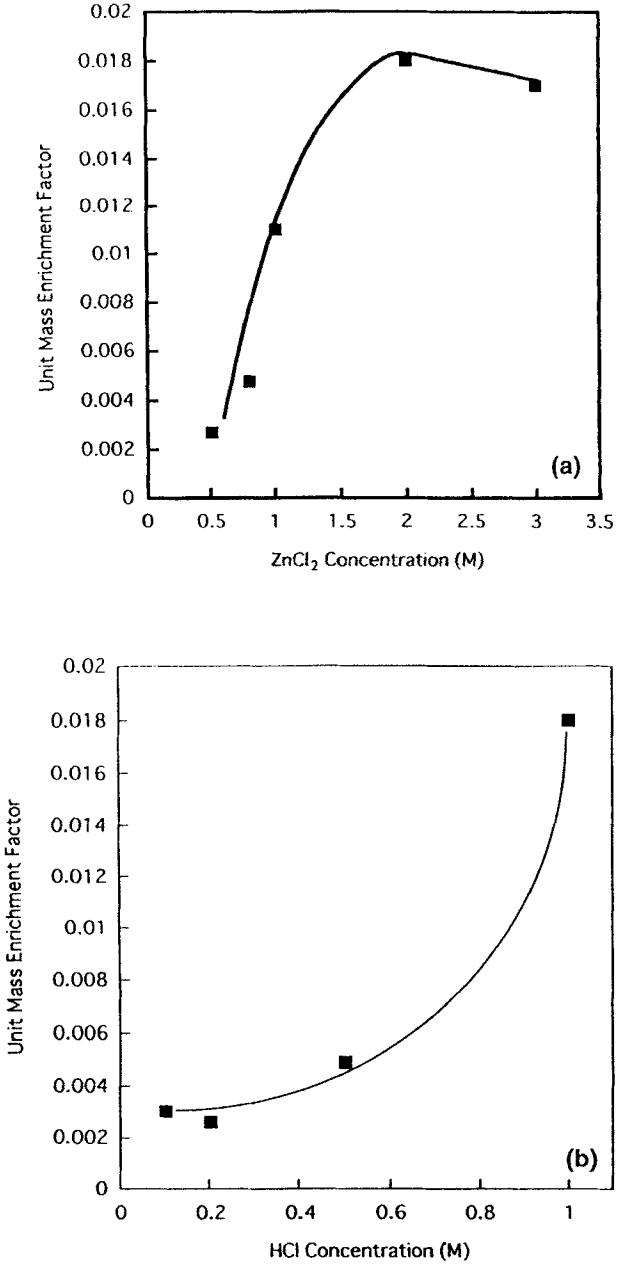

FIG. 2 Unit mass enrichment factors as a function of (a) $ZnCl_2$ concentration and (b) HCl concentration in the initial aqueous phase.

species, the isotopic composition of zinc in each species is not identical. The isotopic equilibrium in both species is as follows (if ^{64}Zn and ^{68}Zn are used as the isotopic composition for simplification):

$$^{64}Zn^{2+}(OH_2)_n + {}^{68}Zn^{2+}Cl_2^- \overset{K_p}{\rightleftharpoons} {}^{64}Zn^{2+}Cl_2^- + {}^{68}Zn^{2+}(OH_2)_n \quad (3)$$

The zinc ion complex with the neutral carrier DC18C6 has to be a neutral molecule accompanying counteranions to be extracted into the organic phase. The isotopic equilibrium between the dichloro complex in the aqueous solution and the crown complex in the organic phase is:

$$^{64}Zn^{2+}Cl_2^- + {}^{68}ZnLCl_2 \overset{K_c}{\rightleftharpoons} {}^{64}ZnLCl_2 + {}^{68}Zn^{2+}Cl_2^- \quad (4)$$

where L represents crown ether and $ZnLCl_2$ is the crown complex of zinc in the organic phase.

The equilibrium constants, K_p in Eq. (3) and K_c in Eq. (4) have the following relationship (8):

$$\ln \alpha = \ln K_c + (\ln K_p)/(1 + W) \quad (5)$$

where W is the ratio of the chloro complex to the aqua complex of zinc in the aqueous solution: $W = [Zn^{2+}Cl_2^-]/[Zn^{2+}(OH_2)_n]$.

Because of the relatively high salt concentration and some other different conditions in the present experiment, we cannot find the stability constants of zinc chloro complex formation in the aqueous solution in the literature. Since the enrichment factors measured in salt concentrations of 2.0 M and 3.0 M are almost parallel, as shown in Fig. 2, and the distribution coefficients shown in Fig. 6 are almost identical in more concentrated aqueous solution to 2.0 M zinc in the aqueous solution, the W value is almost zero: all zinc ions exist as the aqua complex. Equation (5) is rewritten as

$$\begin{aligned} \ln \alpha(0.5) &= \ln K_c + \ln K_p \\ \ln \alpha(2.0) &= \ln K_c \end{aligned} \quad (6)$$

where $\alpha(0.5)$ and $\alpha(2.0)$ show the separation factors given by 0.5 M and 2.0 M zinc solutions, respectively. Since ϵs at 0.5 and 2.0 M are $\epsilon_u = 0.011$ and $\epsilon_u = 0.072$ as shown in Fig. 1, respectively, we can calculate $K_c = 1.072$ and $K_p = 0.941$. The equilibrium constant K_c of Eq. (4) is for ^{64}Zn and ^{68}Zn, and it shows the intrinsic isotope separation ability of DC18C6 between ^{64}Zn and ^{68}Zn.

Zinc required for the water chemistry of a nuclear reactor has to have ^{64}Zn depleted from its isotopic composition. The largest unit mass enrichment factor obtained in the present experiment is $\epsilon_u = 0.018$. Since natu-

rally occurring zinc includes ^{64}Zn, ^{66}Zn, ^{68}Zn, and ^{70}Zn, the enrichment factor to eliminate ^{64}Zn is $0.018 \times 2 = 0.036$.

Odd/Even Isotope Effect

The ϵ value at mass number 67 differs from those expected from the straight line linking the ϵs of even mass numbers. This deviation from the line is $\epsilon_{O/E}$, as mentioned above. If the enrichment factors are determined unconditionally by the mass of isotopes, the ϵs of ^{67}Zn should be on the straight line. The significantly large value of $\epsilon_{O/E}$ relative to ϵ_u suggests the existence of some other factors determining the chemical behavior of the isotope rather than the mass difference.

The $\epsilon_{O/E}$ values also increase with the concentration of salt in the initial aqueous phase, except for 0.8 M, as shown in Fig. 3(a). By applying the identical calculation with ϵ_u to the $\epsilon_{O/E}$, we obtain the following equations:

$$\begin{aligned} \ln \alpha_{O/E(0.5)} &= \ln K_{O/E(c)} + \ln K_{O/E(p)} \\ \ln \alpha_{O/E(2.0)} &= \ln K_{O/E(c)} \end{aligned} \tag{7}$$

where $\alpha_{O/E(0.5)}$ and $\alpha_{O/E(2.0)}$ denote the separation factors obtained in 0.5 and 2.0 M aqueous solution; $\alpha_{O/E(0.5)} = 1.015$ and $\alpha_{O/E(2.0)} = 1.058$, respectively. From Eq. (7), the ability of DC18C6 to distinguish the isotope of the odd mass number or the even mass number ($K_{O/E(c)}$) and the equilibrium constant ($K_{O/E(p)}$) of isotope exchange between dichloro and aqua complexes are calculated; $K_{O/E(c)} = 1.056$ and $K_{O/E(p)} = 0.960$, respectively. The absolute value of the enrichment factor of $\epsilon_{O/E}$ is over 3 times larger than that of ϵ_u. The fact suggests that some other chemical property of the isotope has a larger effect than the mass difference for enrichment.

The addition of conjugated acid to zinc chloride solution gives rise to an increase of counteranions to the zinc ions. Consequently, the ratio of chloro complex to aqua complex is increased, leading to a large W value in Eq. (5). The odd/even isotope effects are illustrated in Fig. 3(b) as a function of HCl concentration. The absolute values of $\epsilon_{O/E}$ increase with HCl concentration, except at 0.2 M HCl. It is obvious that an increase in the HCl concentration causes the population of the dichloro complex of zinc in the aqueous phase to increase.

Isotope Effect Induced by Isotope Shift of Orbital Energy

For the chemical exchange reactions, the enrichment factors can be estimated through the partition functions of the isotopic compounds (6). The separation factor for isotope exchange between two compounds of a given element is described as the ratio of the partition function ratios (f_1,

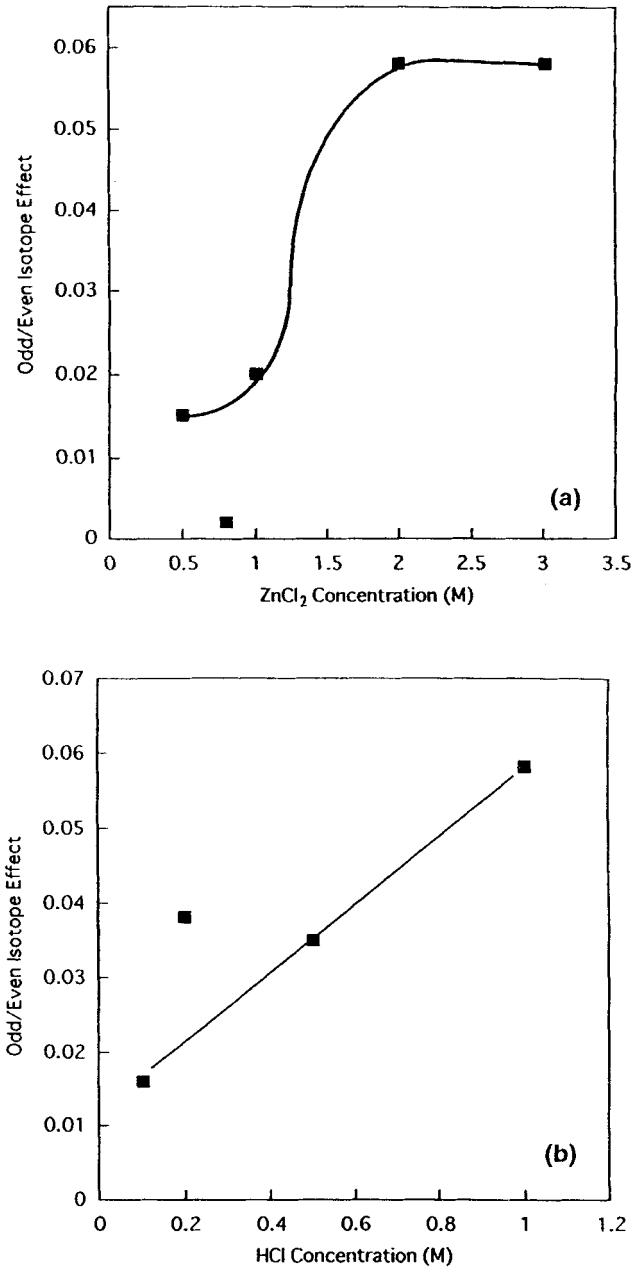

FIG. 3 Odd/even isotope effects as a function of (a) $ZnCl_2$ concentration and (b) HCl concentration in the initial aqueous phase.

f_2) if the symmetric configuration is neglected:

$$\alpha = f_1/f_2 \tag{8}$$

The partition function ratios are related to the vibrational frequencies of the isotopic molecules. The vibrational frequency is a function of the force constants of the bonds in the molecule, especially of those between the isotope and the other atoms. For the coordinate bond between the isotope atom and the ligand, the force constants are dependent on the orbital energy of the isotope atom, which is known to show an isotope shift. In this sense the isotopes which show a greater isotope shift in the orbital energy give a greater difference of the force constants in the coordinate bond, leading to the large separation factor.

The specific mass shift of the 3d-orbital of zinc is said to be excessively large (13) for its larger atomic mass. The molecular orbital of the zinc–crown ether complex is not precisely known, but it is assumed to be composed of hybrid orbital associated with the 3d, 4s, and 4p orbitals of zinc. Since a nucleus composed of an even numbers of protons and an odd numbers of neutrons possesses a smaller angular momentum relative to that of an even–even configuration, the s-orbital energy is higher for

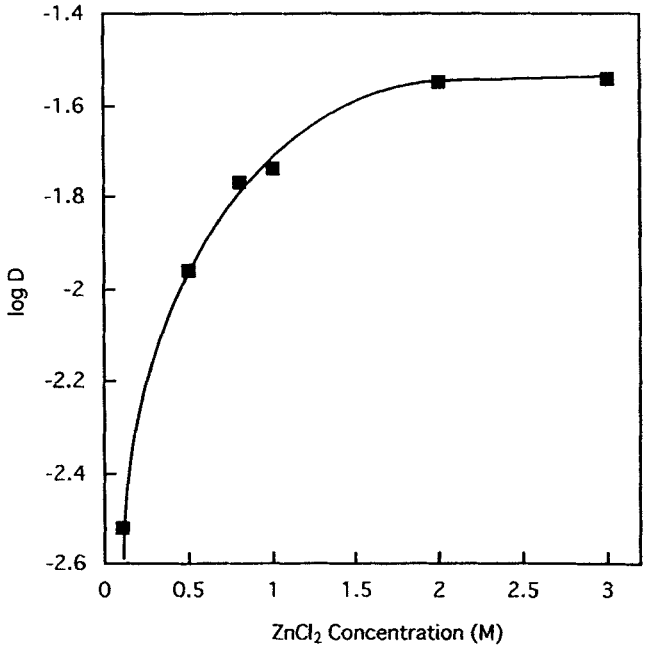

FIG. 4 Logarithmic distribution coefficient to salt concentration in the aqueous phase.

the odd mass number isotope of zinc, ^{67}Zn, compared with those of the even mass numbers. Thus, the extremely different behavior of ^{67}Zn from ^{64}Zn, ^{66}Zn, and ^{68}Zn is assumed to be due to the isotope shift of orbital energy.

Distribution Coefficient

The distribution coefficients are illustrated in Fig. 4 as a function of the Zn concentrations in the aqueous phase of the extraction. In a simple extraction system which can be described as in Eq. (9), log D has to have linear dependency to log [Cl], and its slope should be 2.0 because $D/K_{ex} = [Cl^-]^2[L]$:

$$Zn^{2+} + 2Cl^- + L \overset{K_{ex}}{=} ZnLCl_2 \quad (9)$$

where K_{ex} is the equilibrium constant, D is the distribution coefficient, and $[Cl^-]$ and [L] are the activity of Cl^- in the aqueous phase and the concentration of DC18C6 in the organic phase, respectively. As the ionic strengths in the aqueous phase are not always constant in the present experiment, the linear dependency between log D and log[Cl] is distorted. This is caused by the increase of the chloro complex of zinc with the increase of the concentration of Zn salt in the aqueous phase.

REFERENCES

1. W. J. Marble and R. L. Cowan, *Proc. 1991 JAIF Int. Conf. Water Chem. Nucl. Pow. Plants, Tokyo*, 1966, p. 56.
2. M. Janghorbani, B. T. G. Ting, and U. R. Young, *Clin. Chim. Acta*, *108*, 9 (1980).
3. K. Nishizawa, K. Nakamura, T. Yamamoto, and T. Masuda, *Solv. Extr. Ion Exch.*, *11*, 389 (1993).
4. N. M. Zhavoronokov, D. A. Knyazev, A. A. Ivlev, and G. D. Klinskii, *Russ. J. Phys. Chem.*, *51*, 1 (1977).
5. W. M. Rutherford, *Ind. Eng. Chem., Process Des. Dev.*, *25*, 855 (1986).
6. J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, *15*, 261 (1947).
7. H. G. Urey and L. Greif, *J. Am. Chem. Soc.*, *57*, 321 (1935).
8. K. Nishizawa, T. Nishida, T. Miki, T. Yamamoto, and M. Hosoe, *Sep. Sci. Technol.*, In Press.
9. K. Nishizawa, K. Nakamura, T. Yamamoto, and T. Masuda, *Solv. Extr. Ion Exch.*, *12*, 1073 (1994).
10. K. Nishizawa, Unpublished Data.
11. K. Nishizawa and T. Takano, *Sep. Sci. Technol.*, *23*, 751 (1988).
12. K. Nishizawa, T. Satoyama, T. Miki, T. Yamamoto, and M. Hosoe, *J. Nucl. Sci. Technol.*, *32*, 1230 (1995).
13. C. J. Foot, D. N. Stacey, V. Stacey, R. Kloch, and Z. Les, *Proc. R. Soc., London, A384*, 205 (1982).

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