The Solvent Extraction of Alkaline Earth Metal Ions
with Nonionic Surfactants

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The extraction of alkaline earth metal ions has been investigated using a mixture of polyethylene glycol mono-p-nonylphenyl ether (PEGP; average number of oxyethylene group, 10) and 4-(1,1-dimethyl-3,3-dimethylbutyl)-2,5-dinitrophenol (2,5-dinitro-4-t-octylphenol, DNP; HL) in 1,2-dichloroethane. The metal extraction takes place with one molecule of deprotonated DNP (L^-) and an extraneous monoanion (X^-) for neutralization of the dicationic charge of the metal ion. The ease of extraction generally follows the order, $Ba^{2+} > Sr^{2+} > Ca^{2+} \gg Mg^{2+}$. The nature of the anion present in the aqueous phase strongly affects the extractability. For barium, the extractability decreases in the order $ClO_4^- > SCN^- > I^- > Cl^- > NO_3^-$. The composition of the extracted complexes for barium and strontium ions proportional to the metal is metal : PEGP : $L^- : X^- = 1 : 1 : 1 : 1$. The overall extraction constants were estimated.

Nonionic surfactant molecules with noncyclic poly-(oxyethylene) chains are known to form cationic complexes with alkali and alkaline earth metal ions. The complexes can be extracted into organic solvents by forming ion pairs with suitable counter anions. Such extractions have successfully been applied to the evaluation of complexation equilibrium constants between metal ions and poly(oxyethlene) derivatives[1–3] as well as to the determination of poly(oxyethlene)-chain-containing nonionic surfactants.[4,5] The nature of the counter anion strongly influences the extractablity of such cationic complexes. Yanagida et al.[1] investigated the extractability of potassium complexes from poly(oxyethylene) derivatives and showed that the extractability varies with the anion in the order $SCN^- > I^- \gg Br^- > NO_3^- > Cl^-$.

For the extraction of alkaline earth metal ions, however, only a few systematic investigations on the effect of anion have been reported.

On the other hand, a carrier mediated transport of metal ions through membranes continues to be a major concern in biological cell membrane studies as well as in industrial metal separation technology.[6] For alkaline earth metal ions, so far a combination of a lipophilic (counter) anion such as picrate and a lipophilic neutral complexing ligand such as poly(oxyethylene)-chain-containing surfactant or crown ether has been a preferred method, and few systems have a potential for the selective separation of alkaline earth metal ions on a large scale.

In the present study, a proton dissociable lipophilic molecule, 4-(1,1-dimethyl-3,3-dimethylbutyl)-2,5-dinitrophenol(2,5-dinitro-4-t-octylphend, DNP; HL) is used in combination with a poly(oxyethylene)-chain-containing, surfactant type neutral ligand (polyethylene glycol mono-p-nonylphenyl ether, PEGP; average number of oxyethylene group, 10) for the extraction alkaline earth metals. The basic features in the metal extraction equilibrium has been elucidated.

Experimental

Reagent. p-tert-Octylphenol was purchased from Wako Pure Chemicals Co. LTD., and dicyclohexano-18-crown-6 (DCH18C6) from Nakarai Chemicals Co. LTD. DNP was synthesized as described below. 1,2-Dichloroethane was of analytical reagent grade and used as received. Other reagents used were of the best available quality.

Synthesis of DNP. p-tert-Octylphenol (5.0 g) was dissolved in a mixture of chloroform (25 ml) and acetic acid (25 ml). Concentrated nitric acid (4 ml) was added dropwise with stirring at room temperature. The mixture was stirred for 30 min, then diluted with 50 ml of chloroform and washed with distilled water. The chloroform layer was dried and evaporated, and the residue was purified by passage through a silica gel column with chloroform as eluent. Yellow crystals yield 4.8 g (67%), mp 48—49 °C. Found: C, 56.76; H, 6.73; N, 9.41%. Calcd for ($C_{14}H_{20}N_2O_5$): C, 56.75; H, 6.80; N, 9.45%. H NMR (CDCl₃) δ=0.80 (9H, CH₃), 1.45 (6H, CH₃), 1.78 (2H, -CH₂-), 8.18 (2H, aromatic H).

Properties of DNP.   DNP is sparingly soluble in water and readily soluble in organic solvents. The absorption spectrum of DNP in 1,2-dichloroethane shows a maximum at 360 nm, with a molar absorptivity at this wavelength of 6500 $dm^3 mol^{-1} cm^{-1}$. The deprotonated anion in dichloroethane shows an absorption maximum at 460 nm with a molar absorptivity of 8500 $dm^3 mol^{-1} cm^{-1}$. The proton dissociation constant of DNP (HL) was determined photometrically to be $10^{-4.5}$ in a 1: 3 (v/v) dioxane: water mixture.

Extraction Study.   An aqueous solution (7 ml) containing 0.10 mol dm^{-3} alkaline earth metal salt and a pH buffer (diethanolamine-HCl) was placed in a 50-ml glass stoppered centrifuge tube. To this was added 7 ml of 1,2-dichloroethane containing 6×10^{-6}—1×10^{-4} mol dm^{-3} PEGP (or DCH18C6) and 5×10^{-6}—1×10^{-4} mol dm^{-3} DNP. The aqueous and organic solutions were equilibrated by shaking for 20 min at 25 °C. The tube was centrifuged for phase separation (3000 rpm for 15 min). The absorbances of both the organic and the aqueous phases were measured at 300-450 nm on a double beam spectrophotometer (Hitachi UV-200 type) in a 10 mm quartz cell.

Results and Discussion

The extraction equilibrium may be formulated by the following general reaction:

$$M^{2+} + n(PEGP)_o + m(HL)_o + (2-m)X^-$$
$$\rightleftharpoons (M(PEGP)_nL_mX_{2-m})_o + mH^+ \qquad (1)$$
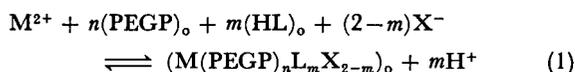
where the suffix "o" refers to the species in the organic phase. The overall extraction constant K_{ex} is then defined by Eq. 2, which can be rewritten in a logarithmic form by Eq. 3, where D stands for the conventional distribution ratio of the metal ion between the two phases.

$$K_{ex} = \frac{[M(PEGP)_nL_mX_{2-m}]_o[H^+]^m}{[M^{2+}][PEGP]_o^n[HL]_o^m[X^-]^{2-m}} \qquad (2)$$

$$\log D = n \log [PEGP]_o + m \log [HL]_o - m \log [H^+]$$
$$+ (2-m) \log [X^-] + \log K_{ex} \qquad (3)$$

The special case where $m=1$, the ratio (Q) of the dissociated (L^-) and undissociated (HL) phenol concentrations in the organic phase is given by Eq. 4 in logarithmic form.

$$\log Q = \log \frac{[M(PEGP)_nLX]_o}{[HL]_o}$$
$$= - \log [H^+] + n \log [PEGP]_o + \log [X^-]$$
$$+ \log [M^{2+}] + \log K_{ex}. \qquad (4)$$

Both the D and Q values are readily obtained experimentally under various extraction conditions.

Figure 1 shows the dependence of the log Q values on the pH. As the pH of the aqueous phase is increased, the fraction of the L^- species or the extent of metal extraction increases, due to the facilitated dissocitation of HL. The extractability among alkaline earth metal ions decreases in the order $Ba^{2+} > Sr^{2+} > Ca^{2+} \gg Mg^{2+}$. The extraction of magnesium ion is negligibly small and hence is not shown in Fig. 1. In accordance with Eq. 4, all plots in Fig. 1 give straight lines having a slope of 1.0. This means that only one molecule of L^- is involved in the metal species extracted.

The dashed line in Fig. 1 indicates the extraction of calcium chloride with DNP alone (i.e., in the absence of PEGP). In this case, it is probable that DNP anion L^- acts as a bidentate chelating ligand to occupy the two coordination sites on calcium. It is interesting that here again the slope of the plot is 1.0, indicating that an anionic species (most probably Cl^-) other than L^- is involved in the extracted calcium species. This is probably related to the present extraction conditions, i.e., the presence of a large excess of metal chloride salt in aqueous solution as compared with a spectrometric concentration of the extractant phenol in the organic phase. The metal extraction ability of DNP when used by itself
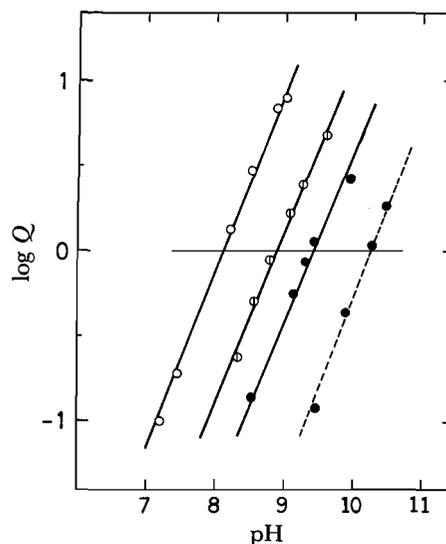

Fig. 1. Influence of pH on log Q for extraction of alkaline earth metal ions. Concentrations before equilibration: organic phase, [PEGP]$_o$=5.0×10⁻⁴ mol dm⁻³, [DNP]$_o$=6.9×10⁻⁵ mol dm⁻³; aqueous phase, [MCl₂]=0.12 mol dm⁻³.
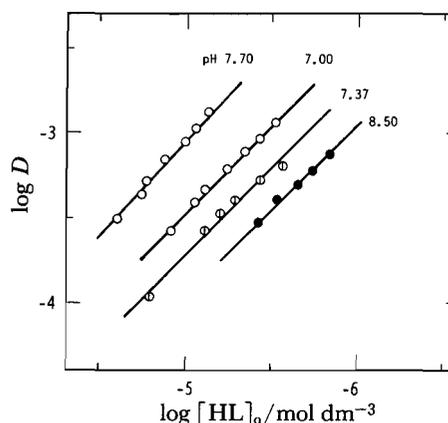O, Ba²⁺; ⊕, Sr²⁺; ●, Ca²⁺; dashed line, Ca²⁺ in the absence of PEGP.

Fig. 2. Plots of distribution ratio (log D) against log [HL]$_o$ at constant pH. [HL]$_o$ stands for free DNP in organic phase. Concentrations before equilibration: organic phase, [PEGP]$_o$=0.005 mol dm⁻³, [DNP]$_o$=5.0×10⁻⁶—1×10⁻⁴ mol dm⁻³; aqueous phase, [M(ClO₄)₂]=0.10 mol dm⁻³.
O, Ba²⁺; ⊕, Sr²⁺; ●, Ca²⁺.

is poor, and calcium shown in Fig. 1 is the most easily extractable among the alkaline earth metals.

That the extracted species contain equimolecular amounts of metal ion and DNP anion has also been confirmed by the metal extraction at varying DNP concentration and constant pH. The results are shown in Fig. 2, where log D is plotted against log [DNP]$_o$. A linear relationship with a slope of 1.0 was obtained in every case.

Figure 3 shows the dependence on the concentration of PEGP for the extraction of alkaline earth metal ions.
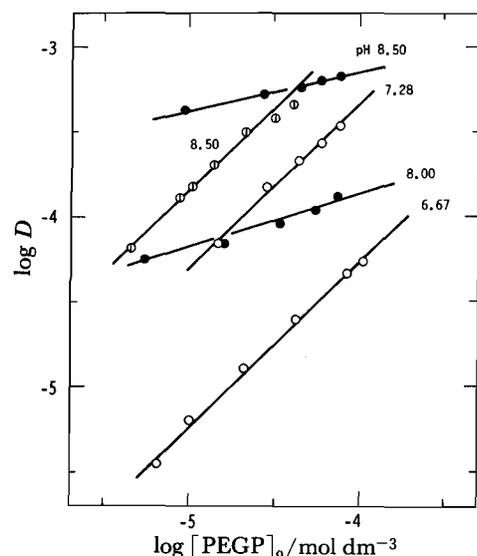
Fig. 3. Plots of distribution ratio (log D) against log [PEGP]$_o$ at constant pH. Concentrations before equilibration: organic phase, [DNP]$_o$=5.0×10^{-4} mol dm^{-3}, [PEGP]$_o$=6.0×10^{-6}—10^{-4} mol dm^{-3}; aqueous phase, [MCl$_2$]=0.10 mol dm^{-3}.
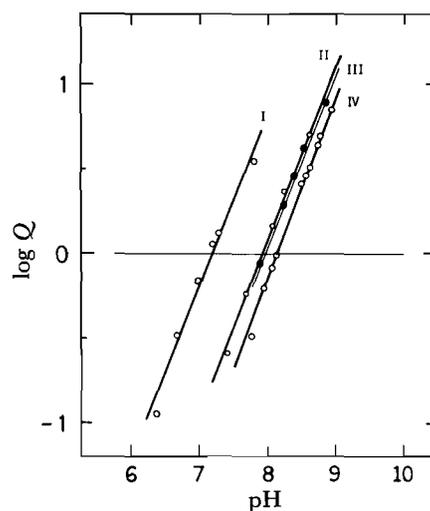O, Ba^{2+}; ⊕ Sr^{2+}; ●, Ca^{2+}.

Fig. 4. Influence of pH on log Q for extraction of barium salts. Concentrations before equilibration: organic phase, [PEGP]$_o$=5.0×10^{-4} mol dm^{-3}, [DNP]$_o$=6.9×10^{-5} mol dm^{-3}; aqueous phase, [Ba(ClO$_4$)$_2$]=0.10 mol dm^{-3} (I), [Ba(SCN)$_2$]=0.087 mol dm^{-3} (II), [BaI$_2$]=0.103 mol dm^{-3} (III), [Ba(NO$_3$)$_2$]=0.101 mol dm^{-3} (IV).

The distribution of metal ions increases linearly with an increase in the concentration of PEGP. The slope of the plot of log D against log [PEGP]$_o$ gives a value for n in Eq. 3. As can be seen in Fig. 3, the values of the slopes for barium and strontium ions are 1.0, which indicates that both ions react with PEGP to form complexes having a composition of metal ion to PEGP ratio of 1 to 1. Considering the conformation suggested for the polyethylene glycol complex,[7,8] it is possible that the complexes in the present study assume a similar helical conformation.

On the other hand, the dependence of the calcium extraction on the PEGP concentration is different from that of barium and strontium ions; the slopes for calcium ion are 0.32 and 0.23 at pH 8.0 and 8.5 respectively (Fig. 3). The difference seems to arise from the difference in solvation by water for these ions. The calcium ion is strongly hydrated, so that the water molecule coordinated to the calcium ion are not replaced effectively by PEGP molecules, while both barium and strontium ions are easily encircled by the oxygen atoms of the poly(oxyethylene) chain in PEGP by replacing the hydration water molecules.

Finally, the effect of inorganic anions was investigated for the extraction of barium. The results are shown in Fig. 4, where log Q is plotted against pH. The extraction is influenced by the nature of the inorganic anion present in the aqueous phase. The extractability decreases in the order ClO$_4^-$>SCN$^-$>I$^-$>Cl$^-$>NO$_3^-$. The sequence is comparable with that observed for the extraction of alkali metal ions with poly (oxyethylene) derivatives[1] and DCH18C6.[9] The sequence is also compatible with the crystal ionic radius for these

anions.[10] As may be expected, the bulkier anions are less hydrophilic and therefore promoted to be transferred into the organic phase. The effect of pH on log Q for various barium salts are similar, and a good linear relationship between pH and log Q (slope, 1.0) holds for each metal salt, as is expected from Eq. 4. This fact indicates that a barium ion is accompanied by an in oganic anion as well as by a DNP anion when extracted into the organic phase.

Based on the experimental results obtained above, the overall extraction constants for alkaline earth metal ions were calculated. The results are summarized in Table 1. Recently, Motomizu et al.[11] reported the extraction constants of inorganic anions with the Zephilamine cation. By comparing the extraction constants obtained in the present study with those reported, it is revealed that the difference among the extraction constants for the accompanied inorganic anions (in barium extraction) is very small in this study. The separation factor between perchlorate and chloride is only 6.3 in the present study, in contrast to about 1000 in the extraction with Zephilamine. From the investigation on the effect of organic anion on the extractability of sodium, potassium and calcium ions with DCH18C6, Jawaid et al.[12] concluded that the efficiency of the extraction increases with the hydrohobicity of the counter anion, while the selectivity among the accompanied anions decreases. The low anion selectivity in the present study is probably due to the high lipophilicity of DNP anion which plays a dominant role on the nature of the ion-pair complex formed in the organic phase.

In contrast to the ion-pair complex with the quater-

Table 1.   Extraction of Alkaline Earth Metal Salts by DNP at 25°C. $-\log K_{ex}$[a]

Neutral extractant	Ba(ClO$_4$)$_2$	Ba(SCN)$_2$	BaI$_2$	Ba(NO$_3$)$_2$	BaCl$_2$	SrCl$_2$	Sr(ClO$_4$)$_2$	CaCl$_2$
PEGP	2.2	2.8	2.9	3.1	3.0	3.6	3.1	(7.6)[b]
DCH18C6	—	—	—	—	3.1	3.6	—	4.4

a) K_{ex} in mol^{-2}dm^6 according to Eq. 2. b) Composition of extracted species is Ca^{2+}:10PONPE:DNP:X$^-$=1: (0.2—0.3):1:1.

nary ammonium ion where there can be no direct chemical bond between the cationic center and anion, it is also possible that ion-pair complex in the present study can involve some kind of direct coordinate bond between the metal center and the accompanied anion X$^-$. Such a bond formation would be favored between a hard acid (alkaline earth metal ion) and a hard base (Cl$^-$), and helps to enhance the extractability of a chloro complex rather than an iodo or thiocyanato complex. This leads to a lowered extraction selectivity between lipophilic and hydrophilic anions. The importance of direct interaction between the alkali metal cation and the anionic group is well documented in the extraction of crown ether complexes.[13]

In Table 1, the extraction constants with DCH18C6 are also shown. These constants were calculated on the assumption that the extraction of alkaline earth metal ions with the crown ether proceeds by the same mechanism as the extraction with PEGP. The validity of the assumption was partly justified by the plots of log Q against pH, which indicated linear relationships with a slope of 1.0 (Eq. 4). It can be seen that the extraction constants for barium and strontium ions with PEGP are close to those with DCH18C6. The similarity suggests that the extraction is governed by the nature of the counter anion rather than that of the neutral ligand, PEGP. An extracted metal species contains generally

In summary, DNP is an effective extractant for alkaline earth metal ions when used in combination with PEGP. An extracted metal species contains generally one molecule each of deprotonated DNP, inorganic monoanion, and PEGP. The extractability of the metal complex follows the order of the lipophilicity of the ions: Ba^{2+}>Sr^{2+}>Ca^{2+}≫Mg^{2+} and ClO$_4$$^-$> SCN$^-$>I$^-$>Cl$^-$>NO$_3$$^-$. The present study, however, is limited by the use of a spectrophotometric concentra-

tion measurement ($<5\times10^{-4}$ mol dm^{-3}) of DNP and a similar concentration of PEGP. Extraction at much higher reagent concentration is still open to further research.

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