

The Solvent Extraction of Alkali and Alkaline Earth Metal Ions with Nonionic and Ionic Surfactants Having Poly(oxyethylene) Chain

Yukio SAKAI,^{*,†} Masahiro SHINMURA,[†] Hajime OTSUKA,^{††} and Makoto TAKAGI^{††}

[†]Faculty of Education, Miyazaki University, Funatsuka, Miyazaki 880

^{††}Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812
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Extraction behavior of alkali and alkaline earth metal cations was investigated with a new extractant derived from polyethylene glycol mono[4-(1,1,3,3-tetramethylbutyl)phenyl]ether (Triton X-100; average number of oxyethylene group, 10) by introducing a phenolic(2-hydroxy-5-nitrobenzyl) group at the hydroxyl terminal of the polyethylene glycol chain. Alkali metal cations were extracted into 1,2-dichloroethane by forming 1:1 complex with the extractant. The overall extraction constant sequence was $K^+(10^{-9.15}) > Rb^+(10^{-9.26}) > Cs^+(10^{-9.28}) > Na^+(10^{-10.08}) > Li^+(10^{-10.36})$. The selectivity for K^+ , Na^+ , and Li^+ was discussed by comparing the extraction behavior with a mixture of nonionic surfactant or dicyclohexano-18-crown-6 and a proton-dissociable lipophilic dye. For alkaline earth metal cations, the extractability decreased in the order $Ba^{2+} > Sr^{2+} > Ca^{2+} \gg Mg^{2+}$. The metal extractability strongly depended on the nature of the anion in the aqueous phase.

In a previous paper,¹⁾ we have reported the extraction behavior of alkaline earth metal cations with nonionic surfactants having a poly(oxyethylene) chain in the presence of lipophilic anions. Alkaline earth metal cations form cationic complexes with a poly(oxyethylene) chain, and the complexes are easily extractable into 1,2-dichloroethane together with lipophilic anions. The lipophilicity of the surfactant complexes seems to arise from the formation of a lipophilic shell around the cation. The extraction efficiency is strongly dependent on the lipophilicity of the counter anion.

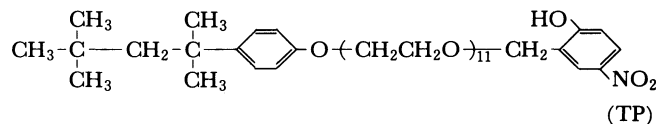
Similar to alkaline earth metal cations, alkali metal cations also form cationic complexes with a poly(oxyethylene) chain.^{2–4)} Yanagida et al.⁵⁾ reported that potassium ions were extracted with poly(oxyethylene) compounds together with an anion in the aqueous phase and the extractability depended on the nature of the counter anion. The interaction between the poly(oxyethylene) chain and cations has been applied not only to the photometric determination of the nonionic surfactant using the potassium ion and such a colored lipophilic anion as picrate,^{6,7)} but also to the sensors based on ionic-selective electrodes.^{8,9)}

From the standpoint of metal separation, the introduction of an anionic group into a poly(oxyethylene) chain can be expected to give a new series of extractants similar to those reported for crown ethers.¹⁰⁾ Yamazaki et al.¹¹⁾ synthesized some poly(oxyethylene) derivatives with a hydroxyl group and a carboxyl group at each end of the poly(oxyethylene) chain and studied a carrier mediated transport of alkali metal ions.

In the present study, an integration of a nonionic surfactant (Triton X-100) and a proton-dissociable dye is attempted in the hope to obtain a new extraction-photometric reagent for alkali and alkaline earth metal cations. The basic features of the metal extraction with the extractant have been investigated.

Experimental

Reagent. The extractant (TP) which contains both Triton X-100 and phenolic structures was synthesized from Triton X-100, ethylene glycol, and 2-hydroxy-5-nitrobenzyl bromide (known as Koshland-I reagent, Dojin Labs. Inc.) as described below.



Nonionic surfactants, Triton X-100 and polyethylene glycol mono(*p*-nonylphenyl)ethers (5PEGP, 10PEGP; 5 and 10 indicate the number of oxyethylene groups) were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. Dicyclohexano-18-crown-6 (DCH18C6) was purchased from Nakarai Chemicals Co., Ltd. 2,5-Dinitro-4-(1,1,3,3-tetramethylbutyl)phenol (DNP) was synthesized by the method described in the preceding paper.¹⁾ 1,2-Dichloroethane and metal salts were purchased from Wako Pure Chemical Industries, Ltd.. These reagents used were of best available grade.

2-(2-Hydroxy-5-nitrobenzyloxy)ethanol. 2-Hydroxy-5-nitrobenzyl bromide (3g, 13 mmol) was dissolved in 60 ml of ethylene glycol and stirred for 5 h at 60 °C. After the unreacted ethylene glycol was removed under reduced pressure, the resulting precipitates were recrystallized from a water-methanol mixture to give white crystals. The product was identified by means of IR and NMR spectrometry. Yield 2.53 g (93%), mp=132–133 °C. ¹H NMR (CDCl₃), 7.8–8.2 (2H, m, aromatic H), 6.9 (1H, s, aromatic H), 4.4 (2H, s, ArCH₂–), 3.6 (4H, s, OCH₂CH₂).

Synthesis of TP. Triton X-100 tosylate (6.5 g, 10 mmol), which was synthesized from tosyl chloride and Triton X-100 in a usual manner, was added to a suspension of sodium hydride (60% in oil; 1 g, 25 mmol) in DMF (13 ml) under nitrogen. To this solution, the DMF solution (13 ml) of 2-(2-hydroxy-5-nitrobenzyloxy)ethanol (2.1 g, 10 mmol) was slowly added at 0 °C and stirred for 24 h at room temperature. The temperature was then raised to 50–58 °C and after 2 h stirring, the mixture was concentrated under reduced pressure. The residue was taken up into chloroform and washed with water. The chloroform solution was con-

centrated and the residue was purified by column chromatography on silica gel (Wakogel C-200) with chloroform. Yield 57%. Yellow viscous oil. Found: C, 61.17; H, 8.95; N, 1.13%. Calcd for $C_{43}H_{71}O_{15}N$: C, 61.33; H, 8.50; N, 1.66%. 1H NMR ($CDCl_3$), 8.0–8.2 (2H, m, aromatic H), 6.8–7.4 (5H, m, aromatic H), 4.8 (2H, s, $ArCH_2-$), 4.1–4.4 (2H, m, $ArOCH_2-$), 3.7–3.9 (44H, m, OCH_2CH_2), 1.85 (2H, s, $-CH_2-$), 1.5 (6H, s, $-C(CH_3)_2-$), 0.9 (9H, s, $-C(CH_3)_3$).

Determination of Acid Dissociation Constant of TP. The acid dissociation constant of TP in 20% dioxane was determined photometrically. An aliquot (20 ml) of dioxane solution of TP (4.0×10^{-4} mol dm^{-3}) was transferred to a 100 ml standard flask and an aliquot (7–10 ml) of aqueous alkali metal hydroxide or tetraethylammonium hydroxide solution (1.0 mol dm^{-3}) was added. After the mixture was diluted to 100 ml with water, the whole solution was transferred to a beaker and titrated with 1.0 mol dm^{-3} hydrochloric acid. The pH and the optical absorbance at 412 nm which corresponded to the absorption maximum of deprotonated TP were measured at 25 °C. The ionic strength was in the range 0.07–0.1.

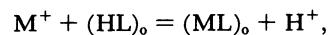
Extraction Study. A pH-buffered aqueous solution (6 ml) of alkali or alkaline earth metal salt (0.1 mol dm^{-3}) was equilibrated with 1,2-dichloroethane solution (6 ml) of TP (10^{-4} mol dm^{-3}) or of mixture of PEGP and DNP by shaking mechanically for 20 min at 20 °C using a 50-ml centrifuge tube. After centrifuging for phase separation, the absorbances of both organic and aqueous phases at 300–450 nm and the pH of the aqueous phase were measured. When necessary, the concentration of metal ion in organic phase was determined by flame photometry (Nippon Jarrell Ash Co. Ltd., model AA-855) after back extraction with dilute hydrochloric acid.

Results and Discussion

The solubility of TP in 20% dioxane was so small that there appeared faintly milky turbidity even at 8×10^{-5} mol dm^{-3} TP concentration. The solubility increased with increasing pH of the solution. The increase is due to the proton dissociation of TP. On the other hand, TP was readily soluble in ordinary water-immiscible organic solvents. The distribution ratio of TP between water and 1,2-dichloroethane was more than 200. The deprotonated TP anion in 20% dioxane showed an absorption maximum at 412 nm, where a molar absorptivity was $14000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The acid dissociation constant was photometrically determined to be $10^{-6.90 \pm 0.05}$. The effect of a variety of alkali metal cations, including lithium, sodium and potassium, on the constant was investigated. However, the values obtained were similar to each other, suggesting that there were not appreciable interactions between TP (or TP anion) and alkali metal cations in this medium.

Alkali metal cations were extracted with TP into 1,2-dichloroethane. The extractability decreased in the order $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. In preliminary experiments, it was found that the extraction was dependent only little on the concentration as well as the nature of the anion in the aqueous phase. Hence,

the extraction equilibrium can be represented by the following equation:



where M^+ and HL represent alkali metal cation and TP, respectively, and the subscript "o" refers to the species in the organic phase. The extraction constant K_{ex} is defined by

$$K_{ex} = \frac{[ML]_o[H^+]}{[HL]_o[M^+]}. \quad (1)$$

In the present study, since a large excess of alkali metal cations is used as compared with the amount of the extractant, the concentration of M^+ in the aqueous phase remains constant before and after the extraction. In addition, the ratio of the concentration of complexed TP (TP anion) to that of free TP in the organic phase can be readily obtained from spectrophotometrical data. Under these conditions, it is possible to establish the stoichiometry of metal extraction by looking at the dependence of the ratio $[ML]_o/[HL]_o$ on pH, which also allows the evaluation of the extraction constant defined by Eq. 1.

The spectral parameters of alkali metal cation-TP complexes used for the calculation of extraction constants are summarized in Table 1. The molar absorptivities were calculated from the absorbance of organic phase and the concentration of extracted metal ion, which was obtained by flame photometry. All of these values, except for lithium, are similar to each other. The plots of logarithmic value of the ratio ($\log [ML]_o/[HL]_o$) against pH (which was assumed to be equal to $-\log [H^+]$) are shown in Fig. 1. Linear relationships with a slope of about 1 were obtained, indicating the validity of the proposed extraction equilibrium.

The validity of the proposed extraction reaction was also justified from the experiment on the effect of TP concentration on the metal distribution ratio (D = total concentration of metal in organic phase / total concentration of metal in aqueous phase). The results obtained are shown in Fig. 2. The plots of $\log D$ against $\log [TP]_o$ under constant pH conditions show a linear relationship with a slope of about 1.0, which indicates that TP extracts alkali metal ions by forming 1 : 1 complexes as assumed before.

Based on these results, the extraction constants were calculated and summarized in Table 1. It is noticeable that the extraction constants for potassium, rubidium and cesium are almost the same at about $10^{-9.2}$, while those of sodium and lithium are lower by one order at $10^{-10.08}$ and $10^{-10.36}$, respectively.

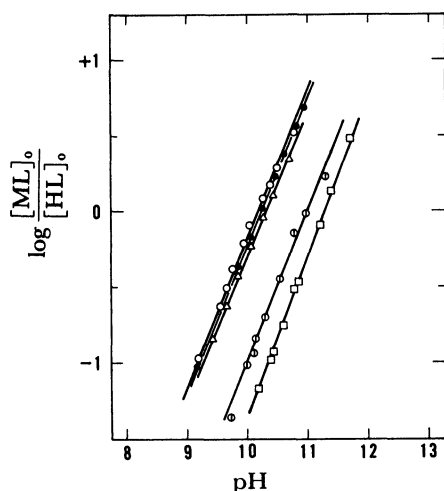
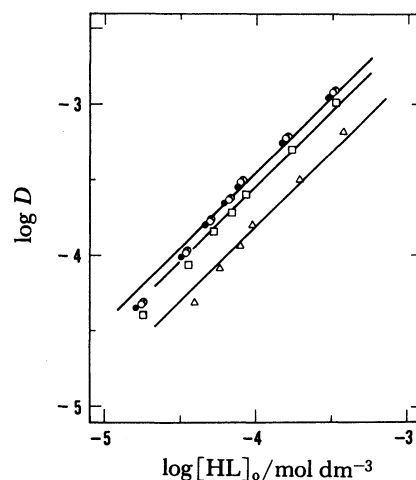
A similar selectivity for alkali metal cations was observed for the ion-pair extraction with noncyclic linear poly(oxyethylene) ligands and lipophilic anionic dye. Table 2 indicates the extraction constants for potassium and sodium with a combined use of such neutral ligands (5PEGP, 10PEGP, and DCH18C6) and

Table 1. Spectral Characteristics of Alkali Metal Complexes of TP and Extraction Constants (1,2-dichloroethane, 20°C)

Salts	Max. Wavelength	Molar absorptivity	$-\log K_{\text{ex}}^{\text{a)}}$
	nm	$\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	
LiCl	406	14300	10.36
NaCl	413	16200	10.08
KCl	418	16400	9.15
RbCl	418	16400	9.26
CsCl	418	16400	9.28

a) K_{ex} according to Eq. 1.Table 2. Extraction of Potassium and Sodium with Neutral Ligand and DNP. Extraction Constants ($\log K_{\text{ex}}^{\text{a)}$, 1,2-dichloroethane, 20°C)

Salts	5PEGP	10PEGP	DCH18C6	DCH18C6 ^{b)}	DCH18C6 ^{c)}
NaCl	4.06	4.64	4.34	3.97	4.20
KCl	4.67	5.55	6.33	6.00	6.36

a) K_{ex} in $\text{mol}^{-2} \text{dm}^6$ according to Eq. 2. b) With picrate in chloroform at 25°C (Ref. 12). c) With picrate in dichloromethane at 20°C (Ref. 13).Fig. 1. Plots of $\log [\text{ML}]_0 / [\text{HL}]_0$ against pH. Concentration before equilibration: Organic phase, $[\text{HL}]_0 = 1.09 \times 10^{-4} \text{ mol dm}^{-3}$. Aqueous phase, $[\text{MCl}] = 0.100 \text{ mol dm}^{-3}$. ○: KCl, ●: RbCl, △: CsCl, ◐: NaCl, □: LiCl.Fig. 2. Plots of distribution ratio ($\log D$) against $\log [\text{HL}]_0$ at constant pH. Concentration before equilibration: organic phase, $[\text{HL}]_0 = 2.18 \times 10^{-5} - 4.36 \times 10^{-4} \text{ mol dm}^{-3}$. Aqueous phase, $[\text{MCl}] = 0.100 \text{ mol dm}^{-3}$. KCl(pH=9.79), ●: RbCl(9.88), △: CsCl(9.44), ◐: NaCl(10.73), □: LiCl(10.91).

DNP. The extraction constants are given by the following equation;

$$\text{M}^+ + (\text{E})_0 + \text{A}^- = (\text{MEA})_0$$

$$K_{\text{ex}} = \frac{[\text{MEA}]_0}{[\text{M}^+][\text{E}]_0[\text{A}^-]}, \quad (2)$$

where $(\text{E})_0$ and A^- represent the neutral ligand in organic phase and DNP anion in aqueous phase, respectively.

From Table 2, the extraction constant of potassium with DCH18C6 is about hundred times larger than that for sodium. This difference in the constants does not seem to depend much on the nature of anion and solvent used.^{12,13)}

As to PEGP system, Table 2 shows that the differ-

ence in extraction constant between potassium and sodium increases with increasing number of oxyethylene unit of nonionic surfactants. The constant with 10PEGP for potassium ($10^{5.55}$), for which the length of poly(oxyethylene) chain is close to that of TP, is by about one order of magnitude larger than that for sodium ($10^{4.64}$). The difference (0.91 in log unit) is consistent with that (0.93) of TP. Thus, it may be concluded from the comparison that an extractant having noncyclic-poly(oxyethylene) chain has inherently higher extraction preference toward potassium over sodium and that the selectivity constant (the ratio of extraction constant) between of potassium and

sodium with 10PEGP and TP is one tenth of that with DCH18C6.

If the acid dissociation constant and distribution ratio of the extractant remain the same on change in extractant structure, a selectivity of metal extraction can generally be related to both the stability constant of the complex formation in aqueous phase and the distribution ratio of the resultant complex between aqueous and organic phases.

Ono et al.^{3,4)} investigated the complexation between alkali metal cations and open-chain poly(oxyethylene) conductometrically in methanol and found that the stability constants for sodium ($10^{1.43}$) are by one order of magnitude smaller than that for potassium ($10^{2.72}$). The difference in the stability constants is close to those of the extraction constants in the present study, which suggests that the difference in sodium- and potassium-extractability is related to the complex-stability characteristics inherent to poly(oxyethylene) type ligands. This in turn suggests that the difference in distribution ratio among the alkali metal complexes of PEGP and TP is rather small. This seems reasonable, since a poly(oxyethylene) chain adopts a helical conformation^{14,15)} in its complex with alkali metals and such a solvation shell-type around the cation is thought to show similar lipophilicity.

It is generally accepted that small-size cations such as sodium and lithium are strongly hydrated in water, which makes it difficult to form stable complexes with PEGP. It is also reported that lithium ion does not bind with poly(oxyethylene) chain in methanol because of its strong solvation.^{3,4)} However, lithium was considerably extracted with TP in the present study. The extractability can be interpreted by a strong ionic interaction between lithium and *p*-nitrophenolate anion of TP. The extraction of potassium, sodium, and lithium with DNP was studied in strongly alkaline media (alkali metal hydroxide solution) to give the metal extraction constant in the absence of a neutral ligand; the constants ($K'_{ex} = [MA]_o/[M^+][A^-]$) obtained were $10^{-0.62}$, $10^{-0.94}$ and $10^{1.01}$, respectively. The extractability decreases in the following order; $Li^+ \gg K^+ > Na^+$. Takagi et al.¹²⁾ reported that the crown ether compounds having an anionic side chain interact favorably with sodium and lithium ions through ionic interaction, resulting in a net decrease in the alkali metal extraction selectivity based on the "size effect" of crown ethers. The same trend obviously holds for the extraction with the present noncyclic poly(oxyethylene) extractant having a proton dissociable site within the molecule.

Unlike the extraction of alkali metal cations, the extraction of alkaline earth metals by TP is considerably affected by the nature of inorganic anions present in the aqueous phase (Fig. 3). As shown in Fig. 3, the extractability of barium decreases with anions in the order, $ClO_4^- > SCN^- > Cl^-$. The sequence of the anions is compatible with the hydrophobicity of these anions.

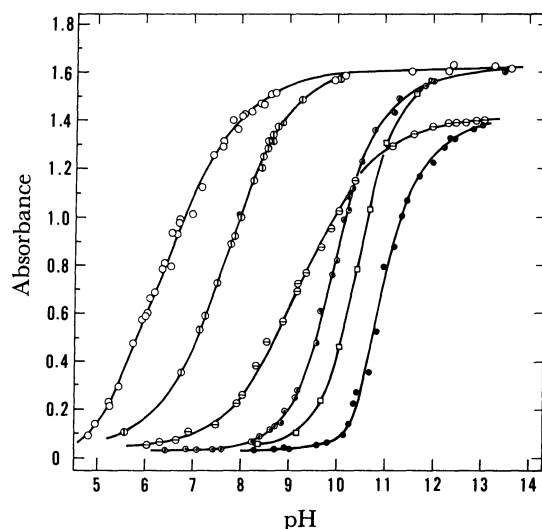


Fig. 3. Influence of pH on the extraction of alkaline earth metal ions with TP.

Concentration before equilibration:

organic phase, $[HL]_o = 1.00 \times 10^{-4} \text{ mol dm}^{-3}$

aqueous phase, $[MX_2] = 0.10 \text{ mol dm}^{-3}$

○: $Ba(ClO_4)_2$ (absorbance measured at 403 nm), ◻: $Ba(SCN)_2$ (405 nm), ●: $BaCl_2$ (410 nm), ◻: $SrCl_2$ (407 nm), ◻: $Ca(ClO_4)_2$ (388 nm), ●: $CaCl_2$ (400 nm).

A similar effect was observed in the extraction of barium with a mixture of PEGP and DNP.¹⁾ In the previous study, it was described that barium was extracted by forming a complex having a composition of $Ba^{2+} : PEGP : DNP^- : \text{inorganic anion} = 1 : 1 : 1 : 1$. In the present system, it is also possible that the TP anion extracts barium together with an inorganic anion in order to neutralize the charge on barium ion. However, there is a difference between the two systems ($Ba^{2+} - PEGP - DNP^- - X^-$ and $Ba^{2+} - TP^- - X^-$) with regard to the effect of the inorganic anion on the distribution ratio of barium ion, i.e., the dependence of the extraction on the nature of the inorganic anion is much larger in the TP system than in the PEGP-DNP system. As shown in Fig. 3, the extractions of barium perchlorate and chloride with TP take place at pH 5.0 and 8.5, respectively, while corresponding pHs with PEGP and DNP were 6.0 and 7.0 (the ratio of extraction constants for barium perchlorate and barium chloride was about ten for the PEGP-DNP system¹⁾). This appears to arise from the dissociation of barium complex to the inorganic anion and the cationic barium complex in the organic phase, which is favorable for improving the extractability. This presumption is partly supported from the result of electric conductivity measurement on a barium-loaded organic phase. The apparent conductivity of organic phase increases in the order, $ClO_4^- > SCN^- > Cl^-$. This suggests that the dissociation constant of the barium complexes in the organic phase increases in the same order for these anions.

As to the selectivity of TP among alkaline earth metal cations, the following sequence was observed as

shown in Fig. 3: $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} \gg \text{Mg}^{2+}$. The extraction of magnesium ion is negligibly small and hence is not shown in Fig. 3. A detailed study on the extraction equilibrium and related constants is in progress.

In conclusion, the introduction of a proton-dissociable group into a poly(oxyethylene)-type surfactant molecule gave an efficient extractant for alkali and alkaline earth metal ions. The metal ions could be extracted into and back-extracted from organic solvents simply by changing the pH of the contacting aqueous solution, while the extractant stayed essentially in organic solution. This makes the extractant useful both in ordinary solvent extraction and in carrier-mediated liquid membrane separation processes. Unlike crown ether-based reagents, poly(oxyethylene)-based extractants are easy to prepare at low costs, and could be a candidate for a large scale separation of certain alkali metals in the future. On the other hand, poly(oxyethylene)-based extractants obviously can not be expected to offer a variety of metal extraction selectivity as has been proved possible with crown ether-based reagents. However, it is becoming increasingly clear that the extraction of alkali and alkaline earth metal ions depends remarkably on the nature of the incorporated anionic group (which is to make a direct interaction with the extracted metal ion), basicity and the extent of anionic charge delocalization within the proton-dissociating functional group.¹⁶⁾ In this sense, it would deserve further study to look at the effect of the nature of the anionic group on the extraction selectivity of metal ions.

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