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Extraction of Alkali Metal Ions and Tetraalkylammonium Ions with Ionic Surfactants Containing a Poly(oxyethylene) Chain

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The effect of the poly(oxyethylene) (POE) chain length of ionic surfactants, expressed as $C_{12}H_{25}(OCH_2CH_2)_n OCH_2C_6H_3(OH)(NO_2)$ (n = 2—9), on the extraction of monovalent cations, including alkali metal and tetraalkylammonium (TAA) ions, was investigated. The extraction constants (K_{ex}) with surfactants having a POE chain of $n \geqq 6$ were almost constant for each alkali metal ion. The K_{ex} sequence was $Li^+ < Na^+ < Cs^+ \leqq K^+ = Rb^+$. The extractability and selectivity largely decreased as n in the surfactant decreased ($n < 6$). The effect of the POE chain length was related to the stability of the alkali metal–POE complex. Unlike an alkali metal ion, the K_{ex} values for all TAA ions were almost constant with surfactants of n = 2—8. These facts indicated that the surfactant extracts alkali metal ions by both complex formation with its POE chain and ion-pair formation with a terminal *p*-nitrophenolate anion. On the other hand, TAA ions were extracted simply by ion-pair formation with a *p*-nitrophenolate anion of the surfactant. The proposed structures are discussed from the viewpoint of the spectrum shift of the extracted species.

The poly(oxyethylene) (POE) chain forms complexes with a so-called hard metal cation, such as alkali, alkaline earth and lanthanide metal ions.[1—3] This complex formation has been utilized not only for the separation of these cations, but also for the determination of POE-type nonionic surfactants.[4,5] Most of these applications are based on the extraction of an ion-pair formation between the POE-cationic complex and a coexisting lipophilic anion into a water-immiscible organic solvent. When an anionic dye is used as a counter anion, the concentration of the extracted metal ions as well as that of the surfactants can be determined photometrically. From the standpoint of the extraction of metal ions, the integration of a nonionic surfactant having a POE chain and a chromoionophore is expected to be entropically advantageous compared with the combined use of a surfactant and a chromoionophore.

In a previous paper,[2] we reported on novel extractants derived from monodisperse POE-dodecyl ethers and 2-hydroxy-5-nitrobenzyl bromide and their basic features of the metal extraction of alkali and alkaline earth cations. As a result, it has been shown that an increase in the oxyethylene (OE) number in the hydorophilic group leads to an improvement in the extractability of these metal ions. The effect of the OE number on the extractability was interpreted as an increase in the stability of the complex formed; that is, the longer the POE chain, the higher the stability. However, it was observed that the extraction constants did not increase linearly with the number of OE units in ionic surfactants.

In the present study, a series of surfactants in which the number of OE units was varied from two to nine, were synthesized and used for the extraction of alkali metal ions with the aim of clarifying the relationship between the extractability of alkali metal ions and the POE chain length. In addition, the surfactants were applied to the extraction of tetraalkylammonium (TAA) cations. A comparison of these results reveals a difference in the extraction mechanisms between the alkali metals and the TAA cations. The difference is also discussed from the standpoint of the spectral shift of the extracted species.

Experimental

Reagents: The structures and abbreviations (*n*EP; *n* indicates the number of OE units of POE chain in surfactant) of the ionic surfactants synthesized are as follows (Chart 1).

These surfactants were synthesized from monodisperse polyethylene glycol dodecyl ethers (Wako Pure Chemical Industries, Ltd.) and 2-hydroxy-5-nitrobenzyl bromide (Tokyo Kasei Organic Chemical Co., Inc) by the following procedure. The surfactant (1.4 mmol) was dissolved in 100 ml of benzene. To this solution was added sodium hydride (20 mmol). The mixture was stirred and cooled in an ice-water bath. Then, 2-hydroxy-5-nitrobenzyl bromide (1.6 mmol) dissolved in 100 ml of benzene was added to the mixture using a syringe at a 0.3 ml min^{-1} flow rate under a nitrogen atmosphere. The mixture was stirred at 60 °C for 1 h. Then, sodium hydride was removed by filtration and benzene was evaporated

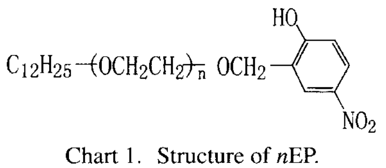

Chart 1. Structure of *n*EP.

using an evaporator. After the residue had been dissolved in 100 ml of chloroform, the chloroform phase was washed with a 2 M (1 M = 1 mol dm^{-3}) potassium hydroxide solution and water alternately. The washing procedures were repeated until the aqueous phase was not colored, and then the solvent was removed. Finally, the product was purified by passing through a silica gel column (Wakogel C-200) with chloroform as the eluent. The product was identified by means of NMR spectrometry (Bruker AC 250P spectrometer). The 9EP was synthesized by a previously described procedure.[1]

Extraction Study: The extraction procedure was as follows. An aqueous solution (5 ml) of 0.1 M alkali metal chloride or 0.1 M TAA chloride, whose pH was adjusted with a small amount of 1.0 M diethanolamine or with alkali metal or TAA hydroxide solution, was transferred to a 50-ml centrifuge tube. Then, the same volume of chloroform solution containing 4.0×10^{-5} M *n*EP was added to the tube and shaken for 30 min at 25 °C. After phase separation by centrifuging, the spectra of both the aqueous and chloroform phases were measured at 300—450 nm using a Hitachi M-6000 UV-vis spectrophotometer. The pH of the aqueous phase was also measured using a Toa HM-40s pH meter.

Results and Discussion

When an alkali metal or TAA cation was extracted with *n*EP into chloroform, the color of the organic phase changed to yellow. The maximum wavelengths ($\lambda_{\max}$) and the molar absorptivities for *n*EP and their alkali metal complexes are summarized in Table 1. It can be clearly seen from Table 1 that the wavelengths of the complexes are shifted to a shorter wavelength range as the radius of metal ion as well as the length of the POE chain of the surfactant decreases.

The extraction equilibrium for alkali metal ions can be represented by the following equation:

$$\mathrm{M^+ + (HL)_o = (ML)_o + H^+},$$

where M$^+$ represents the alkali metal or TAA cations, and HL represents the surfactant (*n*EP). The parentheses with subscript "o" refer to species in the chloroform phase. Thus, the extraction constant, K_{ex}, can be defined as

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

In this study, the extracted cations concentration ([(ML)$_o$]) was calculated from the absorbance at $\lambda_{\max}$ using the molar absorptivity (Table 1) of the complex, which was obtained by mixing a known amount of surfactant in chloroform with a high concentration solution (4 M) of the alkali metal hydroxide. The free surfactant concentration ([(HL)$_o$]) could also be calculated from the absorbance at 325 nm or from the mass balance equation of the surfactant, because the concentration of ML or HL in the aqueous solution was ascertained to be negligibly small. The concentration of the alkali metal ion ([M$^+$]) in the aqueous phase is considered to be nearly constant (0.1 M) before and after the extraction, because a large excess of metal ion was used compared with the amount of the surfactant. Thus, the extraction constants could be calculated from a plot of log ([(ML)$_o$])/[(HL)$_o$]) vs. pH. Figure 1 shows plots calculated from the data with 6EP. Linear relationships with a slope of about 1 for each alkali metal ion and TAA ion were obtained, indicating the validity of the proposed equation.

The log K_{ex} values for alkali metal ions are plotted against the number of OE units (*n*) of *n*EP in Fig. 2 together with

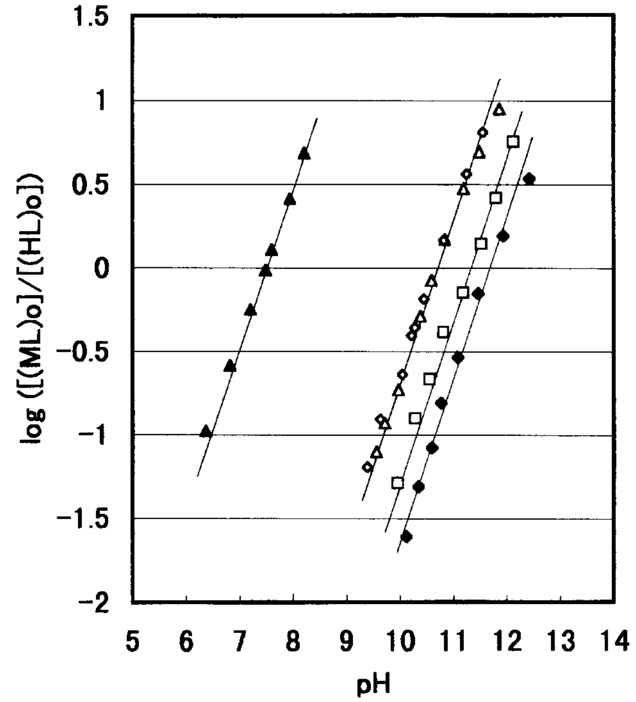

Fig. 1. Plots of log [(ML)$_o$]/[(HL)$_o$] against pH. ◆ Li$^+$, □ Na$^+$, △ K$^+$, ◇ Rb$^+$, ▲ TBA.

Table 1. Maximum Wavelength ($\lambda_{\max}$) and Molar Absorptivity (ε)[a] of Surfactant and Extracted Species

	log ε	Li$^+$		Na$^+$		K$^+$		Rb$^+$		Cs$^+$		TEA		TBA	
Surfactant	at 315 nm	$\lambda_{\max}$	log ε	$\lambda_{\max}$	log ε	$\lambda_{\max}$	log ε	$\lambda_{\max}$	log ε	$\lambda_{\max}$	log ε	$\lambda_{\max}$	log ε	$\lambda_{\max}$	log ε
2EP	4.01			398	4.25	398	4.22	401	4.25	403	4.25	424	4.32	428	4.40
3EP	3.97	398	4.30	405	4.28	405	4.28	405	4.29	407	4.29				
4EP	4.00	400	4.26	408	4.31	409	4.31	410	4.32	410	4.31	424	4.32	429	4.37
5EP	4.01	402	4.25	413	4.31	413	4.32	412	4.31	412	4.31				
6EP	4.01	403	4.24	413	4.30	417	4.32	417	4.30	417	4.30	424	4.35	430	4.43
7EP	3.99	403	4.24	413	4.29	418	4.31	418	4.31	418	4.30				
8EP	4.00	403	4.24	413	4.29	418	4.32	419	4.32	418	4.31	424	4.31		
9EP	4.01	403	4.32	413	4.37	418	4.37	419	4.38	419	4.37				

a) Molar absorptivity was calculated from the absorbance at $\lambda_{\max}$ of $CHCl_3$ after mixing 4 M alkali hydroxide solution.

those for the TAA ions. Figure 2 clearly shows that there is a large difference in the extractability between alkali metal ions and TAA ions with regard to the dependence on the POE chain length. In contrast to that the extractability for the TAA ions are almost constant from 2EP to 8EP, the extraction of alkali metal ions is largely affected by the length of the POE chain in the surfactant.

The effect of the POE chain length on the extractability on alkali metal ions may be summarized as follows:

1) The K_{ex}s using surfactants from 2EP to 4EP increase by about one order of magnitude with each oxyethylene unit increase. In addition, the constants for the alkali metal ions are similar to one another, except for the lithium ion.

2) Some differentiation between the constant for the sodium ion and the other ions occurs when the surfactants have POE chains comprising more than five EO units. The extractability of alkali metal ions with 5EP increases in the order Li^+ ($10^{-10.9}$) < Na^+ ($10^{-10.4}$) < Cs^+ ($10^{-10.2}$) < K^+ ($10^{-9.9}$) $\fallingdotseq$ Rb^+ ($10^{-9.95}$). The extraction constant for the sodium ion becomes almost constant from 5EP to 9EP.

3) When the surfactants with 6EP—9EP are used, the extractability for each alkali metal ion becomes almost constant. The K_{ex} value increases in the order Li^+ ($10^{-10.7}$) < Na^+ ($10^{-10.3}$) < K^+ ($10^{-9.6}$) $\fallingdotseq$ Rb^+ ($10^{-9.6}$) $\fallingdotseq$ Cs^+ ($10^{-9.7}$) in this region.

In a study of the extraction of potassium thiocyanate with POE-dodecyl ether into dichloromethane, Yanagida et al.[6] found that the extractability increased remarkably when a surfactant having a POE chain with more 7OE units was used. The strong interaction between the potassium ion and heptaethylene glycol in an acetone or methanol medium was observed by means of NMR spectrometry.[7] Okada[8] has suggested that 5—6 OE units are necessary for complexation with K^+ and Rb^+, and 6—7 OE units with Cs^+. These numbers are very similar to the minimum number of OE units of the *n*EP showing constant K_{ex} values, as seen in Fig. 2.

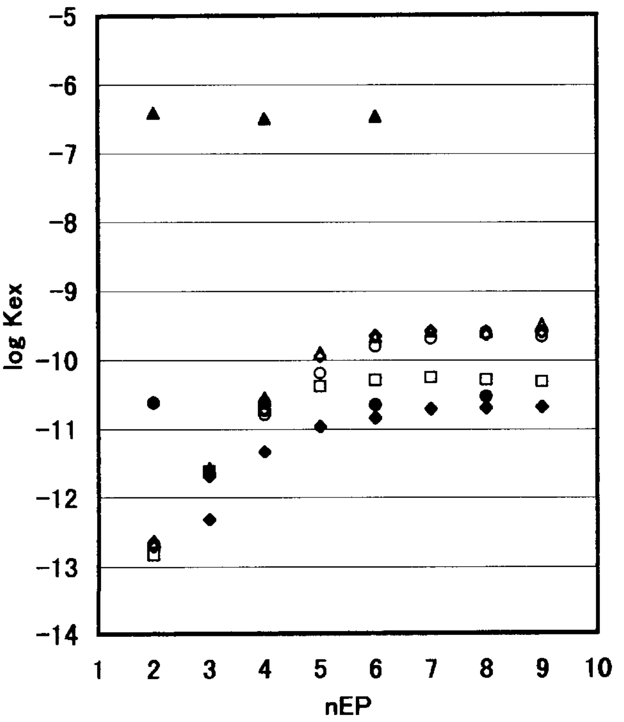

Fig. 2. Extraction constant for monovalent cation with surfactants. ◆ Li^+, □ Na^+, △ K^+, ◇ Rb^+, ○ Cs^+, ● TEA, ▲ TBA.

The POE chain length of 2EP—4EP is obviously too short to form a stable cyclic complex with alkali metal ions. It has been clearly shown that the formation constant of a potassium complex with POE chain in methanol drastically decreased as the EO number of POE chain decreased from seven to six.[8] In addition to the instability of the complex, all of the water molecules coordinated to the alkali metal ion cannot be replaced by the oxygen atoms of such a short POE chain of the surfactants; thus, the distribution of the complex into chloroform is lowered. Further, the metal ions with the short POE surfactant may be extracted mainly by a strong ionic interaction with a *p*-nitrophenolate anion, which results in a decrease in the selectivity.[9] The poor extractability and the poor selectivity with such a short POE chain were also observed at a picric acid/nonionic surfactant extraction system.[10]

Unlike an extraction system with 2EP—4EP, the extraction constants with 6EP—9EP are almost constant for each alkali metal ion. The extractability increases in the order Li^+ ($10^{-10.7}$) < Na^+ ($10^{-10.3}$) < Cs^+ ($10^{-9.7}$) < K^+ ($10^{-9.6}$) = Rb^+ ($10^{-9.6}$), which is the same order as has been reported.[1,2] To elucidate the selectivity in detail, it is necessary to know the acidity constant and the distribution ratio of the surfactant, as well as the stability constant and distribution ratio of the complex. At this stage, the only thing to declare is that the selectivity for alkali metal ions in this extraction system does not arise from the difference in the acidity constants of the surfactants. The pK_{a} values of the surfactants determined in 60% methanol lie between 7.53±0.06 at the 99% confidence level.[11] Considering that the surfactants have two hydrophobic groups at both sides of the POE chain and that their metal complex may have a hydrophobic shell of ethylene units as a result of a bond between the oxygen of the POE chain and a metal ion, the distribution ratio of the surfactant as well as that of the complex seems to remain the same upon a change in the length of the POE chain in the surfactants. The formation constants of K^+, Rb^+, and Cs^+ complexes with POE-dodecyl ether containing 11EO units in methanol are reported to be $10^{3.08}$, $10^{3.05}$, and $10^{2.93}$ respectively.[8] Ono et al.[12] also reported that the formation constant of a sodium ($10^{1.43}$) complex with a POE chain is by one order of magnitude smaller than those of potassium ($10^{2.72}$), rubidium ($10^{2.77}$), and cesium ($10^{2.58}$) in methanol. Taking the values of the formation constants into consideration, it may be concluded that the selectivity of the surfactants (6EP—9EP) for alkali metal ions is governed by the stability of the POE complexes with the metal ions. Although it was reported that lithium ion as well as sodium ion are difficult to form a POE complex in methanol, because of strong hydration,[12] it is considerably extracted with surfactants. The extractability can be attributable to a strong ionic interaction between a lithium ion and a *p*-nitrophenolate anion of *n*EP, as reported before.[1]

One basic feature of this method, in which the K_{ex}s with 6EP—9EP shows a constant value for each alkali metal ion, is different from a picric acid/nonionic extraction system.[10] This suggests that the position of an alkali metal ion in the complex is fixed near to the *p*-nitrophenolate anion, as discussed below.

In contrast to the alkali metal ions, the extractability of TAA is independent on the POE chain length of the surfactant; that is, the K_{ex} value for the tetraethylammonium (TEA) ion is around $10^{-10.6}$, and that for the tetrabutylammonium (TBA) ion is around $10^{-6.5}$ from 2EP to 8EP. The difference between two K_{ex} values for TEA and TBA ions is $10^{4.1}$. Some researchers have proposed how to predict the extraction constant for an ion-pair extraction system by assigning the individual extraction constants to the cation and anion. The assigned values to the TEA and TBA cations by Yotsuyanagi et al.[13] for an extraction system with a picrate anion into chloroform are $10^{1.99}$ and $10^{5.75}$, respectively. The calculated values by a simple equation proposed by Motomizu[14] for TEA and TBA ions are $10^{3.5}$ and $10^{8.2}$, respectively. The difference between the K_{ex} values for the TEA and TBA cations obtained in this study is nearly equal to an intermediate value of $10^{3.76}$ and $10^{4.7}$. Considering this fact, in addition to the independence of the extraction constant on the POE chain length, the TAA cations are probably extracted simply by forming ion-pairs with the anionic surfactants.

In this study, it was observed that a shift in the maximum wavelength (λ_{max}) of the extracted complex depends on the cation (Table 1). Figure 3 shows the λ_{max}s of the *n*EP complexes for each of the cations, from which halochromism[15] can be seen. The λ_{max} decreases as the ionic size of the cation decreases in the order $TBA^+ > TEA^+ > Cs^+ = Rb^+ > K^+ > Na^+ > Li^+$. In addition, the shorter is the POE chain of the surfactants, the lower is the λ_{max} for each of the alkali metal complexes. Kitadani et al.[16] reported about the solvent effect on the electronic absorption spectrum of sodium *p*-nitrophenolate in the presence of 15-crown-5 ether. The shift in the λ_{max} of sodium *p*-nitrophenolate in the nonhydroxylic solvent was correlated with a charge separation between the sodium cation and the phenolate anion. Reichardt et al.[15] have reported that the hypochromic band shifts were proportional to the charge-to-size ratio of the cations from a study of the spectrum change of pyridinium *N*-phenolate betaine dye. Thus, the shifts of λ_{max} in this study can be correlated with the strength of the ionic interaction between the *p*-nitrophenolate anion and the alkali metal cation in the complex. The λ_{max} of *p*-nitrophenolate anion of the surfactant is expected to be at 430 nm inherently without a salt, because the λ_{max} of the free anion of a betaine dye is reported to be very close to that in the presence of TBA.[15] The hypsochromic band shift becomes larger as the size of the monovalent cation decreases. This trend is the same as that observed in the betaine system. In other words, the distance between the alkali metal cation and the phenolate anion of the surfactant becomes shorter as the size of the cation becomes smaller, which results in a strong ionic interaction.

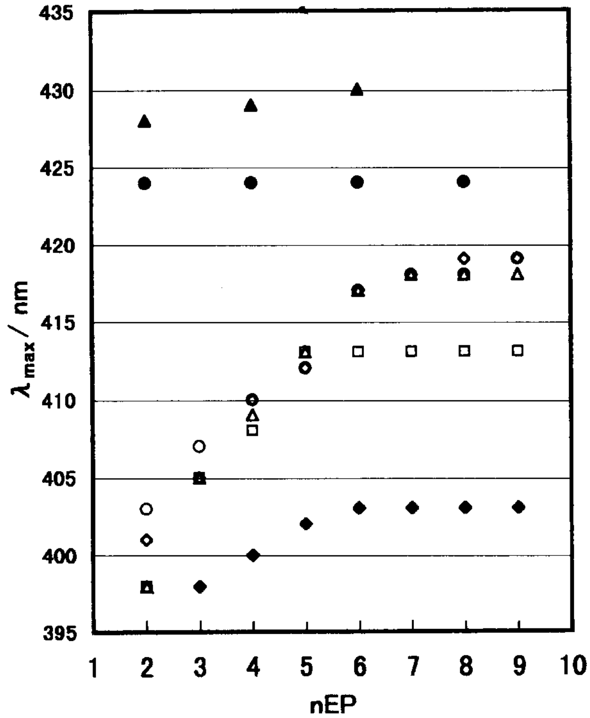

Fig. 3. Maximum wavelength of monovalent cations extracted with surfactants. ◆ Li^+, □ Na^+, △ K^+, ◇ Rb^+, ○ Cs^+, ● TEA, ▲ TBA.

The influence of the POE chain length in the surfactant on λ_{max} can be interpreted by considering the change in distance between the cation and the phenolate anion in the complex. As shown in Fig. 3, the λ_{max} of the alkali metal complex with 2EP—5EP decreases as the number of OE units in *n*EP decreases. This means that the alkali metal cation and the phenolate anion come nearer and nearer to each other as the number of OE units in the surfactant decreases. In spite of this stronger interaction, the K_{ex} value decreases as the POE chain becomes shorter, as shown in Fig. 2. On the other hand, the constant λ_{max} values of sodium complex with 5EP—9EP and of other alkali metal complexes with 6EP—9EP indicate that the distance between the alkali metal cation and the phenolate anion becomes constant when the POE chain in the surfactants consists of more than 5—6EO units.

In contrast to the metal cations, the λ_{max} values for the extracted TEA and TBA are about 424 and 429 nm, respectively, even for 2EP and the extraction constants for TEA and TBA are almost constant for 2EP—8EP and 2EP—6EP, respectively. This supports the supposition that the extraction of the TAA ions occurs simply by forming ion pairs with the *p*-nitrophenolate anion of the surfactant, as stated above. Figure 4 shows two different models for the alkali metal complex and the TEA ion-pair with 4EP.

A comparison of the present result with a crown compound is thought to be meaningful to point out the feature of acyclic and cyclic effects of the POE chain. The extraction constants for alkali metal ions with *N*-(2-hydroxy-5-nitrobenzy)-aza-

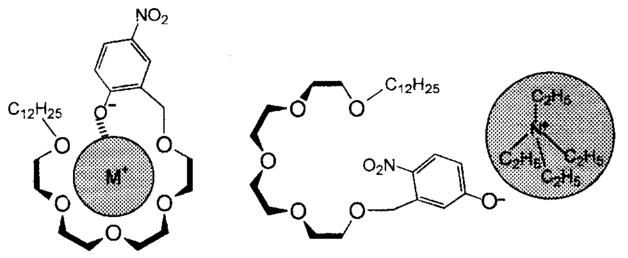

Fig. 4. Model of the extracted species of alkali metal ion (M^+) and TEA ion with 4EP.

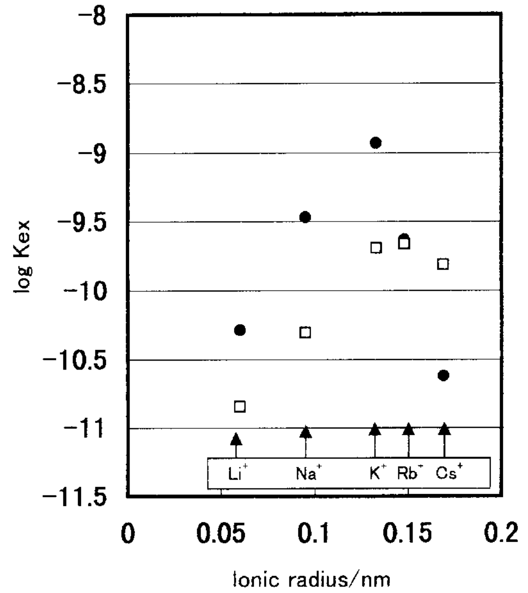

Fig. 5. Comparison of extraction constants with 6EP and *N*-(2-hydroxy-5-nitrobenzyl)-aza-18-crown-6. □ 6EP, ● *N*-(2-hydroxy-5-nitrobenzyl)-aza-18-crow-6.

18-crown-6 (A18C6)[17] are shown in Fig. 5 together with those obtained with 6EP. Although one nitrogen atom is included in the crown ether ring in place of one oxygen atom, the number of EO units and the structures of proton-dissociable dyes are the same in both extractants. From Fig. 5, following points can be seen:

1) The extraction constants for Li^+, Na^+, and K^+ increase almost linearly in both extraction systems. The slope of the line from Li^+ to K^+ with A18C6 is almost parallel with that of 6EP. The logarithmic values of K_{ex} for these metal ions with A18C6 are larger by 0.6—0.8 than those of 6EP. The difference can be attributable to an increase in the stability of the complex between these metal ions and the POE ring of A18C6. However, it is noticeable that the selectivities for these metal ions are similar in both cases. Considering the difference in the extractability and the selectivity between Triton X-100/picrate and the usual 18-crown-6/picrate systems,[18] the similarity suggests that the strong ionic interaction between the cation and the *p*-nitrophenolate anion plays an important role in the extraction of alkali metal ions in both extractants. Such an interaction improves the extractability, but, at the same time, results in a decrease of the selectivity.[9]

2) The extraction constants for Rb^+ and Cs^+ with A18C6 drastically decrease because of the "size-effect" of A18C6. Unlike A18C6, the extractability of Rb^+ with 6EP is comparable to that of K^+. Obviously, the flexibility of an acyclic POE chain prevents a decrease in the extractability. However, the K_{ex} value of Cs^+ with 6EP is somewhat smaller than that of Rb^+. This is probably due to an insufficient length of the POE chain of 6EP to form a stable cyclic complex with Cs^+. In other words, it is with 5EP or 6EP that a remarkable difference in size of alkali metal ions can be observed as the difference of the extractability (Fig. 2).

In conclusion, studies on the extraction constants and the shift of the maximum wavelength using a series of surfactants with different POE chains reveal that alkali metal ions are complexed with the POE chain through the oxygen atoms to form a cyclical configuration,[19] and are capped with the terminal phenolate anion of the surfactants. On the other hand, TAA ions are extracted by ordinary ion-pair formation with the surfactant anion.

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