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Effect of the Poly(oxyethylene) Chain Length of Ionic Surfactants on the Extraction of Alkali Metal Ions

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Synopsis. The following three extractants were synthesized: $C_{12}H_{25}\text{–O}\!\left(CH_2CH_2O\right)_n CH_2\text{–}C_6H_3(OH)(NO_2)$ ($n=$ 3, 6, 9). The extraction constants for alkali metal ions were also determined. The extractability with an extractant having three oxyethylene units decreases in the order $Li^+ > K^+ > Na^+ > Cs^+ \gtrsim Rb^+$; for other extractants, $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$.

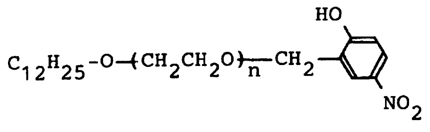
Nonionic surfactants having a poly(oxyethylene) (POE) chain are known to coordinate to the alkali and alkaline earth metal ions through oxygen atom to form a helical configuration.[1,2] The resultant cationic complexes are readily extractable into suitable organic solvents by forming ion-pairs with hydrophobic anions.[3] In a previous study,[4] a new extractant (TP) was synthesized from Triton X-100 by introducing a proton-dissociable dye at the terminal hydroxyl group of the POE chain. Since TP is a monobasic acid, alkali metal ions are extracted into 1,2-dichloroethane by forming 1:1 complexes. The extractability was found to decrease in the order $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. This selectivity can be related to the complex-stability characteristic inherent to the POE-type ligand.

The present study was undertaken in order to clarify the effect of the POE chain length on the extraction of alkali metal ions. Three analogous extractants to TP have been newly synthesized using monodisperse POE-type surfactants and a proton-dissociable dye. The structures and abbreviations of the synthesized extractants are as follows (Chart 1):

Experimental

Reagents. The extractants were synthesized from monodisperse surfactants, ethylene glycol and 2-hydroxy-5-nitro benzyl bromide (known as Koshland-I reagent, Dojin Labs., Inc.), as described before.[4] The product was identified by means of NMR spectrometry. The monodisperse surfactants employed were dodecylethers of diethylene glycol, pentaethylene glycol and octaethylene glycol; these were purchased from Wako Pure Chemical Industries, Ltd.

All of the chemicals were of analytical-reagent grade and were used as received.



$n = 3$ (3EP)
$n = 6$ (6EP)
$n = 9$ (9EP)

Chart 1.

Extraction Study. Five milliliters of an aqueous solution containing 0.10 mol dm^{-3} alkali metal chloride and a pH buffer were placed in a 50-ml centrifuge tube. To this was added the same volume of 1,2-dichloroethane containing $3\times10^{-5}-5\times10^{-4}$ mol dm^{-3} extractant. The aqueous and organic solutions were equilibrated by shaking for 15 min at 25 °C. After centrifuging for phase separation, the absorbances of both the aqueous and organic phases at 300—450 nm and the pH of the aqueous phase were measured. In the extraction of barium perchlorate, the pH was adjusted with borate buffer, which was effective in preventing precipitation of barium carborate at a higher pH.

Results and Discussion

Since these extractants are monobasic acids, the extraction equilibrium may be represented by the following equation:

$$M^+ + (HL)_o \rightleftharpoons (ML)_o + H^+, \qquad (1)$$

where M^+ and HL represent the alkali metal ion and the extractant, respectively, and the subscript "o" refers to the species in the organic phase. The extraction constant (K_{ex}) can be defined as

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

and, thus,

$$-\log K_{ex} = -\log D + pH + \log[(HL)_o], \qquad (2)$$

where D stands for the conventional distribution ratio of the metal ion between the two phases.

Since the complexed metal is quantitatively extracted, the distribution ratio of the metal ion can easily be determined spectrophotometrically. In addition, since the free extractant remains in the organic phase, $[(HL)_o]$ can be calculated by the difference. It is thus possible to check the validity of Eq. 1 by plotting $\log D$ against $\log[(HL)_o]$ at constant pH. The aqueous solution is initially adjusted at around pH, where $[(ML)_o]$ is approximately equal to $[(HL)_o]$. Some typical plots for sodium and potassium are shown in Fig. 1. As expected, a linear relationship with a slope of 1.0 was obtained in every case, indicating the validity of the extraction equilibrium of Eq. 1. Similar relationships between $\log D$ and $\log[(HL)_o]$ hold for each alkali metal ion with all of the extractants. The extraction constants evaluated by Eq. 2 are summarized in Table 1 together with those of TP.

Table 1. Extraction Constants ($-\log K_{ex}$[a)]) for Alkali Metal Ions at 25 °C

M^+	3EP	6EP	9EP	TP[b)]
Li	11.32 (0.07)[c)]	10.75 (0.07)	10.74 (0.05)	10.36
Na	11.57 (0.03)	10.45 (0.07)	10.31 (0.03)	10.08
K	11.49 (0.08)	9.59 (0.07)	9.42 (0.08)	9.15
Rb	11.72 (0.09)	9.70 (0.10)	9.73 (0.07)	9.26
Cs	11.68 (0.10)	9.90 (0.05)	9.86 (0.05)	9.28

a) According to Eq. 2. b) Ref. 4. c) Standard deviation.

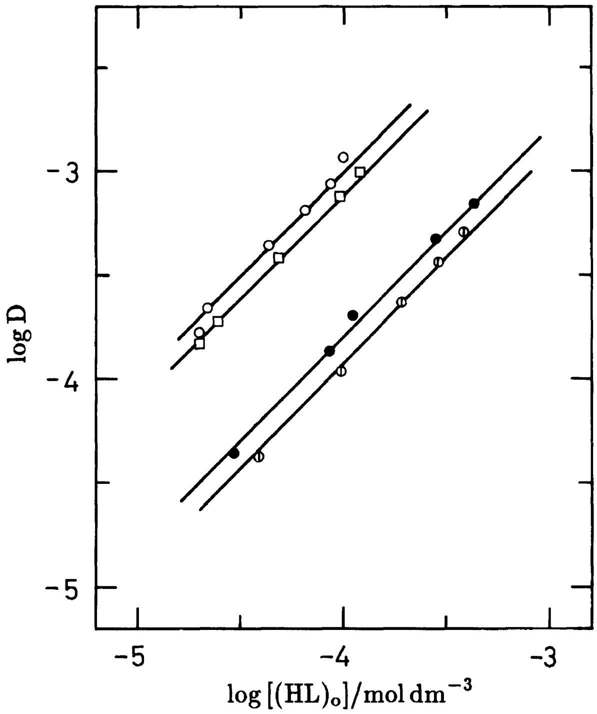


Fig. 1. Plots of the distribution ratio ($\log D$) against $\log[(HL)_o]$ at constant pH. aqueous phase, $[MCl] = 0.10$ mol dm^{-3}. ⦶: KCl with 3EP (4.28×10^{-5}—4.28×10^{-4} mol dm^{-3}) at pH = 11.60, ○: KCl with 6EP (6.34×10^{-5}—2.18×10^{-4} mol dm^{-3}) at pH = 10.65, ●: KCl with 9EP (3.28×10^{-5}—5.47×10^{-4} mol dm^{-3}) at pH=9.68, □: NaCl with 6EP (6.34×10^{-5}—2.18×10^{-4} mol dm^{-3}) at pH=11.38.

It can be clearly seen that 3EP is very different from the other extractants regarding both the extraction efficiency and the extraction selectivity. The extraction constants with 3EP decreases in the order Li^+ ($10^{-11.32}$) > K^+ ($10^{-11.49}$) > Na^+ ($10^{-11.57}$) > Cs^+ ($10^{-11.68}$) $\gtrsim$ Rb^+ ($10^{-11.72}$). The difference between the largest extraction constant (Li^+) and the smallest one (Rb^+) is only 0.4 in the log unit, showing the poor selectivity of 3EP for alkali metal ions. The same trend in the extractability is observed for extraction with the lipophilic anion, 2,6-dinitro-4-*t*-octylphenolate (A^-).[4)] The extraction constants defined as $[(MA)_o]/[M^+][A^-]$ decrease in the order Li^+ ($10^{-0.62}$) > K^+ ($10^{-0.94}$) > Na^+ ($10^{-1.01}$). The agreement in the extractability for both cases strongly suggests that the extraction is mainly governed by an ionic–ionic attraction between the cation and the terminal *p*-nitrophenolate anion of 3EP. This in turn suggests that complexation between the cation and 3EP is not important in the extraction. It is generally accepted that small-size metal ions, such as lithium and sodium, are difficult to form POE complexes, because of their strong hydration in water. In addition, 3EP has only three oxyethylene units in the POE chain, whose length is not sufficiently long for complexation. More than six or seven oxyethylene units are said to be needed for complexation.[1,3)]

Unlike 3EP, 6EP exhibits the highest selectivity for potassium, whereas lithium, which is most easily extractable with 3EP, is most difficult to extract. The extractability decreases in the order $\mathrm{K}^+ > \mathrm{Rb}^+ > \mathrm{Cs}^+ > \mathrm{Na}^+ > \mathrm{Li}^+$. The extraction constant for potassium ($10^{-9.59}$) is fifteen-times larger than that for lithium ($10^{-10.75}$). This fact indicates that 6EP is a more effective extractant for the mutual separation of alkali metal cations than is 3EP. A similar selectivity to that of 6EP is also observed for the 9EP and TP systems. In order to clarify the difference in selectivity, the separation factors (the ratio of extraction constants) between potassium and lithium with 9EP and TP were calculated to be $10^{1.32}$ and $10^{1.21}$, respectively. These factors are about twenty-times larger than that ($10^{-0.17}$) with 3EP.

In contrast to extraction with 3EP, the extraction behaviors with 6EP and 9EP seem to be largely dependent on the complexation characteristic between the cation and the POE chain. Ono et al.[5,6)] reported that the stability constant of the potassium complex ($10^{2.72}$) with POE in methanol is by one order of magnitude larger than that for sodium ($10^{1.42}$). On the other hand, the separation factors between potassium and sodium with 6EP and 9EP are $10^{0.86}$ and $10^{0.89}$, respectively. The decrease in the selectivity may be attributable to an ionic interaction in the complex, i.e., an ionic interaction between the sodium and anion-site of the extractant is stronger than that for potassium, resulting in a net decrease in the separation factor for these cations.[7)]

With regard to the extraction constants with 6EP and 9EP, it can be seen from Table 1 that the constants with 9EP are somewhat larger than those with 6EP. Okada[8)] estimated the formation constants between potassium and various long-size POEs in meth-

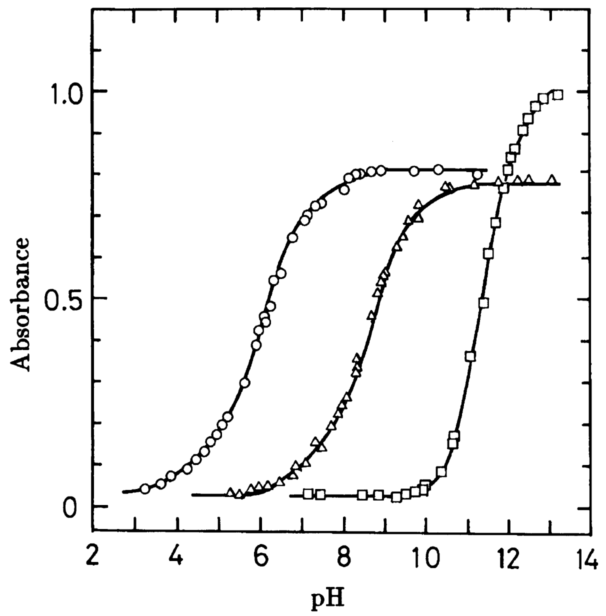


Fig. 2. Extraction of $Ba(ClO_4)_2$. aqueous phase; $[Ba(ClO_4)_2]=0.10$ mol dm^{-3}. organic phase; □ : $[(3EP)_o]=4.28\times10^{-4}$ mol dm^{-3} (411 nm), △: $[(6EP)_o]=3.95\times10^{-4}$ mol dm^{-3} (395 nm), ○: $[(9EP)_o]=3.28\times10^{-4}$ mol dm^{-3} (401 nm).

anolic solution by means of HPLC. The constants increase by 0.069 in the log unit as one oxyethylene unit is added to the POE chain. Thus, the expected difference between 6EP and 9EP is about 0.21 in the log unit, while the observed one is 0.17 in the log unit. The similarity also indicates the importance of complexation between the cation and the POE chain in the extraction system.

The larger difference in the extractability among 3EP, 6EP, and 9EP is observed in the extraction of barium perchlorate. Figure 2 shows the dependence on the pH for extraction. The pH values at which extraction takes place are 3.5, 6.0, and 10 for 9EP, 6EP, and 3EP, respectively. An increase in the POE chain length of the extractant leads to extraction at a lower pH region. In each case, a large excess of $Ba(ClO_4)_2$, compared with the extractant, was employed. In addition, since the extractability was considerably affected by the nature of the inorganic anion in the aqueous phase, the extracted complex seems to have a composition of $Ba^{2+}:ClO_4^-:L^-=1:1:1$, like that of the TP complex.[4] A detailed study concerning the extraction of alkaline earth metal ions will appear in the near future.

Since the overall extraction constant can generally be related to the acid dissociation constant and distribution ratio of the extractant, as well as the distribution ratio and stability constant of the complex, these constants must be determined in order to clarify details concerning the extraction mechanism; such a study is in progress.

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