Metal-ion Complexation of Noncyclic Poly(oxyethylene) Derivatives. I. Solvent Extraction of Alkali and Alkaline Earth Metal Thiocyanates and Iodides*

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The reaction of noncyclic poly(oxyethylene) derivatives with alkali and alkaline earth metal ions was investigated by means of the solvent extraction of their thiocyanates or iodides. Polyethylene glycols with more than 23 oxyethylene units showed a strong extracting power comparable to those of the crown ethers, and the power increased with the increasing number of oxyethylene units in them. Extraction studies using homogeneous poly(oxyethylene) monododecyl ethers revealed that more than 7 oxyethylene units were necessary to bind the potassium ion in the water phase and to transfer the complexed salt to the organic phase, and that the extracting ability of octa(oxyethylene) monododecyl ether was about one sixth of that of 18-crown-6. The monododecyl ether is fairly effective as a complexing agent for potassium picrate even below its critical micelle concentration; the stoichiometry of the extractable complex was found to be 0.8: 1 with respect to the ether and the picrate. There was no remarkable difference in the selectivity for alkali metal ions between noncyclic poly(oxyethylene) derivatives and 18-crown-6.

In comparison with cyclic polyethers, noncyclic polyethers seemed extraordinarily weak in ability of metal ion complexation,[1–3] while a search of the literature revealed that, before Pedersen's discovery of macrocyclic polyethers,[4] high-molecular-weight polyethylene glycols had been reported to form complexes with mercuric chloride[5] and with alkaline earth metal salts, especially in the presence of tetraphenylborate.[6–8]

Recently, in connection with the progress of the chemistry of macrocyclic polyethers, the interaction of open-chain poly(oxyethylene) derivatives with metal ions has attracted special interest; the unusual reaction of alkali metal in the presence of polyethylene glycol,[9] octopus molecules, and related compounds,[10,11] the isolation of the complexes with metal salts,[12,13] the crystalline structures of the complexes with mercuric and cadmium chlorides,[14–16] and solvent extraction using poly(oxyethylene) derivatives (POE) as extractants[17] are noteworthy.

The purpose of the present investigation is to clarify the effectiveness of noncyclic poly(oxyethylene) derivatives as complexing agents for metal ions. At first, solvent extraction was undertaken, because it is very convenient for the rapid screening of the complexing efficiency.

As regards the extraction of metal salts with cyclic polyethers, large hydrophobic anions such as picrate[18–21] and dipicrylaminate,[22] have been used as counter anions, since the ion-paired complexes formed are more extractable and can be easily determined colorimetrically. It has now been found, however, that thiocyanate and iodide salts form extractable salt-polyether complexes. Further, because they are stable and neutral in their aqueous solution, the thiocyanates and iodides were used in this extraction study.

Experimental

Materials. The following chemicals were obtained in the best available purity from the sources indicated: KSCN, $Ba(SCN)_2 \cdot 2H_2O$, $Ca(SCN)_2 \cdot 3H_2O$ (Pr. G. grade) NH_4SCN (G. R. grade), CsI (reagent grade) (Wako Pure Chemicals Industries, Ltd.); NaSCN, KI (G. R. grade), NH_4I, $Mg(SCN)_2 \cdot 4H_2O$ (E. P. Grade) (Nakarai Chemicals, Ltd.); LiI (G. R. grade) (Mitsuwa's Pure Chemicals), polyethylene glycols** 300 ($n=7$), 400 ($n=9$), 600 ($n=14$), 1000 ($n=23$), 4000 ($n=90$), 6000 ($n=140$), 20000 ($n=450$), polypropylene glycols** 1000; (diol type, $n=17$), 3000 (triol type, $n=52$), (Wako Pure Chemicals Industries, Ltd); penta(oxyethylene), hexa(oxyethylene), and octa(oxyethylene) monododecyl ethers (Tokyo Kasei Kogyo Co., Ltd.) (The purity was ascertained by NMR); and dicyclohexyl-18-crown-6 (Nakarai Chemicals, Ltd.). Block copolymers of propylene oxide (PO) and ethylene oxide (EO) (Pluronics), $PO_{34}EO_5$, $PO_{34}EO_{11}$, $PO_{34}EO_{45}$, and $PO_{34}EO_{232}$ were obtained from the Daiichi Kogyo Seiyaku Co., Ltd. The mole ratios of PO to EO were determined by means of both NMR and the molecular weight. Dibenzo-18-crown-6 and 18-crown-6 were prepared according to the methods of Pedersen[23] and Cram[24] respectively. Poly(oxyethylene) monododecyl ether with an average of 25 oxyethylene units was prepared by the reaction of dodecyl alcohol with ethylene oxide in the presence of sodium hydroxide. The average number of oxyethylene units was ascertained by NMR spectrometry.

Extraction Procedure. By preliminary experiments, halogenated solvents, such as dichloromethane, chloroform, and carbon tetrachloride, were found to be preferable, since other solvents, such as hexane and benzene, are readily emulsified in the presence of POE and are difficult to separate from the water phase. Considering the efficiency of dichloromethane for the extraction with cyclic polyethers,[19] we chose it as the solvent. An aqueous POE solution (0.02 M***, 25 cm^3), 25 cm^3 of a thiocyanate solution (1.0 M), and 50 cm^3

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** The figures indicate the nominal average molecular weight. The figures (n) in parentheses are the average numbers of oxyethylene units, calculated from the average molecular weight.

*** Throughout this paper, 1 M=1 mol dm^{-3}.

of dichloromethane saturated with water were transferred into 250-cm^3 Erlenmeyer flask equipped with a well-grounded stopper. The mixture was placed in a thermostated water bath (25±0.5 °C) for ten minutes, and then shaken 200 times vigorously; this was found to be sufficient for equilibration. The stopper was replaced by the separation cock so as to use this Erlenmeyer flask as a separatory funnel in succession, and then the flask was turned upside down. With few exceptions, the phases separated clearly on standing. The dichloromethane layer was separated. After removing the dichloromethane by means of a rotary evaporator, the thiocyanate ion in the residue was determined by Volhard's method. In the extraction of potassium nitrate, the potassium ion in the residue was determined by means of Nippon Jarrell Ash Atomic Absorption Spectrometer AA-1. Duplicates agreed, usually to less than 5% from the mean, and were averaged for use in the calculation of the degree of extraction (Figs. 1, 2, 5, and 6.).

Percent Extraction of POE. According to the above-mentioned procedure, the extraction of the POE by dichloromethane was carried out in the absence of any salts. The residue of the dichloromethane layer was kept standing under a vacuum to a constant weight. The weight thus obtained was used in the calculation of the percentage of extraction (Table 1).

Extraction of Potassium Picrate. The extraction was worked out according to the procedure outlined by Frensdorf.[19] The picrate concentration in the water phase was measured by means of a Shimadzu Double-beam Spectrometer, UV-200, using as the extinction coefficient (λ=357 nm, ε=1.46×10^4 in water).

Results and Discussion

The degree of extraction of potassium thiocyanate and the degree per oxyethylene unit are plotted against the number of oxyethylene units in each extractant in Figs. 1 and 2. Polyethylene glycols with more than about 23 oxyethylene units were found to have a strong power of extracting the potassium ion, one which was comparable to those of the macrocyclic polyethers. In addition, the extractability per oxyethylene unit was almost constant. The same is true of the poly(oxyethylene) monododecyl ethers with more than seven oxyethylene units (Fig. 2). While polypropylene glycols showed a low extracting power, a series of block copolymers of propylene oxide and ethylene oxide increased in their extracting power with the increase in the number of oxyethylene units (Fig. 1). The slope of the extraction curve was almost the same as that of polyethylene glycols, suggesting that the repeating oxyethylene is a factor governing the extraction. These facts indicate that even noncyclic poly(oxyethylene) derivatives have a remarkable complexing power for the potassium ion, even in an aqueous phase, if they have more than a definite number of oxyethylene units, and that the strength increases linearly with the number of repeating oxyethylenes.

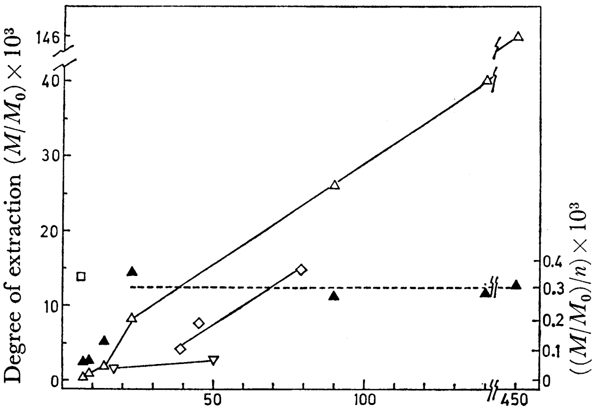

Fig. 1. Extraction of potassium thiocyanate into dichloromethane by poly(oxyethylene) derivatives. Thiocyanate concentration [M_0]=0.5 M. POE concentration: 0.01 M. △, Polyethylene glycols; ▽, polypropylene glycols; ◇, the block copolymers of PO and EO (Pluronics); □, 18-crown-6; ▲, the degree of extraction per one oxyethylene unit by polyethylene glycols. ----: Average value.

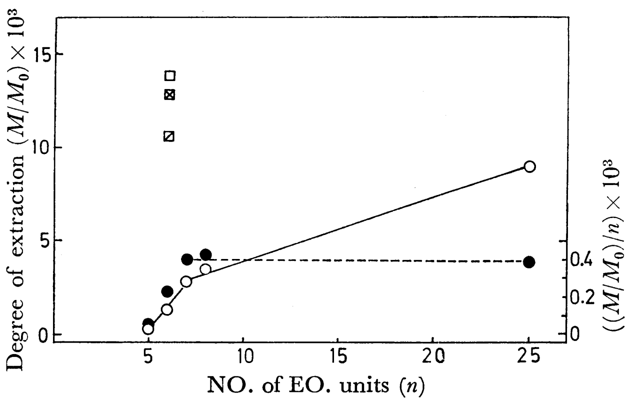

Fig. 2. Extraction of potassium thiocyanate into dichloromethane by homogeneous poly(oxyethylene) monododecyl ethers. Thiocyanate concentration [M_0] =0.5 M. Polyether concentration: 0.01 M. ○, homogeneous poly(oxyethylene) monododecyl ethers (The ether having 25 EO units is not homogeneous.); ●, the degree of extraction per one oxyethylene unit. ----: Average value; □, 18-crown-6; ▨, dicyclohexyl-18-crown-6; ☒, dibenzo-18-crown-6.

As is shown in Table 1, the affinity of PEG to dichloromethane increased with the number of oxyethylene units. The rather hydrophobic property of the high-molecular-weight POE is worth noting.

Extraction properties are governed not only by the strenght of complex formation, but also by the solubility

Table 1. Percentage of extraction of poly(oxyethylene) derivatives by dichloromethane

Polyethylene glycols	Percentage of extraction	Pluronics of alkylated ether	Percentage of extraction
PEG 400 (n=9)[a]	6%	$PO_{34}EO_{11}$	91%
PEG 600 (n=14)[a]	14%	$PO_{34}EO_{45}$	95%
PEG 1000 (n=23)[a]	27%	$PO_{34}EO_{282}$	93%
PEG 4000 (n=90)[a]	*ca.* 100%	$C_{12}H_{25}EO_{25}$-H	93%

a) The figures indicate the nominal average molecular weight. The figures(n) in parentheses are the average numbers of oxyethylene units, calculated from the average molecular weight.

relation of the extractant and the formed complex.[19] The less efficient extraction of the short-chain polyethylene glycols is, thus, apparently due to their hydrophilic character.

The extraction using homogeneous poly(oxyethylene) monododecyl ethers as extractants has made it clear that seven repeating oxyethylenes are the minimum number to bind the potassium ion effectively in the water phase and to transfer the complexed salt to the dichloromethane phase (Fig. 2). This finding quite agreed with that of Liu,[25] who observed that the interaction of polyethylene glycols with potassium iodide in methanol became distinguished above heptaethylene glycol.[28]

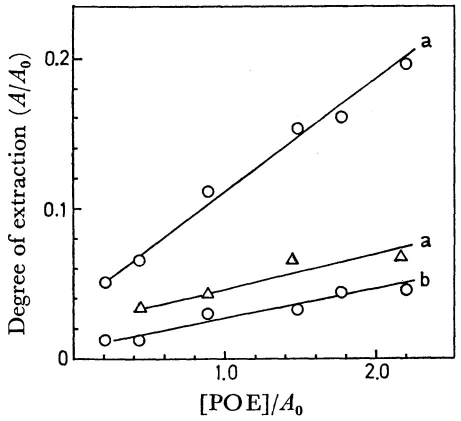

Fig. 3. Extraction of potassium picrate into dichloromehtane by homogeneous poly(oxyethylene) monododecyl ethers. Picrate concentration $[A_0]=7\times10^{-5}$ M. Potassium ion concentration $[M_0]=10^{-1}$ for a; 5×10^{-3} M for b.
○, Octa(oxyethylene) monododecyl ether;
△, hexa(oxyethylene) monododecyl ether.

However, the poly(oxyethylene) monododecyl ethers examined were all typical nonionic surfactants, and the effect of the micelle formation was conceivable under the conditions thus far discussed. To eliminate the influence of the micelle on the extracting properties as much as possible, the extraction of potassium picrate was undertaken when the extractants were diluted to around their critical micelle concentration.[26] Figure 3 shows that, even below the CMC, the extracting ability is fair for octa(oxyethylene) monododecyl ether, but very poor for the hexa(oxyethylene) ether. Compared with the results with dicyclohexyl-18-crown-6 under the same conditions,[19] the extracting ability of the octa(oxyethylene) ether was about one-sixth of that of the crown ether. This approximation is consistent with the results shown in Fig. 2. As expected, the extractability by the octa(oxyethylene) ether decreased much more drastically with a decrease in the potassium-ion concentration than by the crown ether.[19]

Assuming from the results shown in Table 1 that there is no complication due to the distribution of the ether between the two phases, the logarithm of the distribution ratio calculated from the degree of extraction by the octa(oxyethylene) ether was plotted against the logarithm of the total concentration of the ether (Fig. 4). This plot gave a straight line with a slope of about 0.8 : 1 in respect to the ether and the picrate. The deviation from 1 : 1 is probably due to a partial micelle formation, since the CMC's of these types of nonionic surfactants are generally lowered by the presence of an electrolyte.[27]

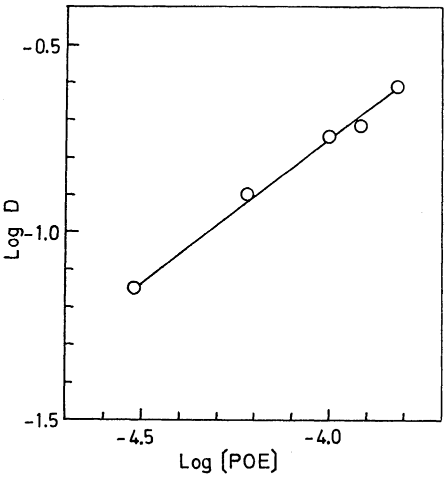

Fig. 4. Distribution ratio of potassium picrate *vs.* concentration of octa(oxyethylene) monododecyl ether. The conditions used are identical with those in Fig. 3. POE: Octa(oxyethylene) monododecyl ether.

Calzolari *et al.*[12] recently reported the isolation of the complex formed by hexa(oxyethylene) diphenyl ether and sodium cobalt(II) thiocyanate. The composition of the complex indicates that the hexa(oxyethylene) coordinates with one sodium ion. Considering our result and this earlier finding, six to seven oxyethylene units seem critical for the complexation with alkali metal ions.[28] This conclusion contrasts with the 1 : 2 and 1 : 4 compositions needed in the $HgCl_2$–POE complexes.[14,15]

The extraction was also extended to other potassium salts. The iodide was found extractable to the same extent as the thiocyanate by both 18-crown-6 and noncyclic poly(oxyethylene) derivatives (Fig. 5). How-

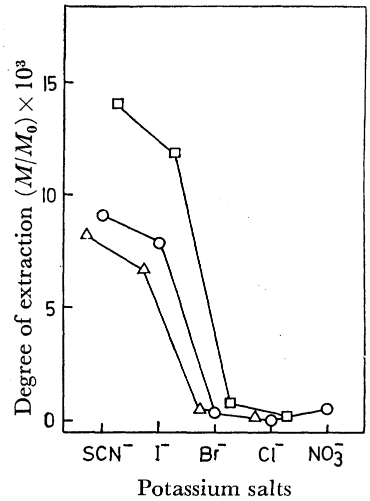

Fig. 5. Extraction of potassium salts into dichloromethane by poly(oxyethylene) derivatives. Concentration of each salt $[M_0]=0.5$ M. POE concentration: 0.01 M. □, 18-Crown-6; ○, $C_{12}H_{25}EO_{25}$–H; △, PEG 1000.

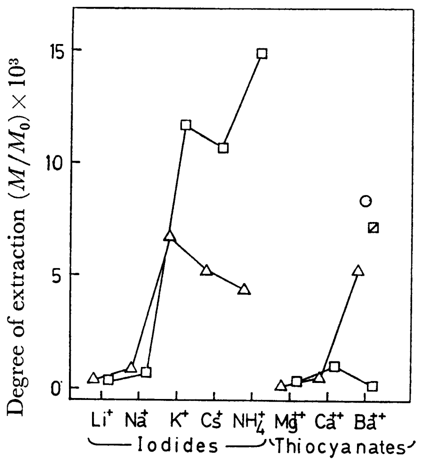

Fig. 6. Extraction of alkali metal iodides and alkaline earth metal thiocyanates into dichloromethane by poly(oxyethylene) derivatives. The conditions and symbols used are identical with those in Figs. 2 and 5.

ever, the nitrate, bromide, and chloride could not be extracted effectively by either of the extractants. The formation of extractable complexes with the thiocyanate and iodide may well be explained by the concept of water structure-enforced ion pairing.[29)]

Figure 6 shows the extractions of other alkali and alkaline earth metal salts by polyethylene glycols (PEG) 1000 ($n=23$) and 18-crown-6. It is interesting to note that the selectivities for alkali metal ions are very similar to one another. On the other hand, ammonium iodide was found to be less extractable by PEG 1000.

As for barium thiocyanate, PEG 1000 was more effective than 18-crown-6. However, when dicyclohexyl-18-crown-6 was employed, the 1: 1 complex[4)] was precipitated during the extraction. The degree of extraction was found to be 7.2×10^{-3}, which corresponds to more than four times as much as that of 18-crown-6; it went up to 17.2×10^{-3} when the complex precipitated was included in the calculation of the degree of extraction. It should also be noted that 18-crown-6 extracted slightly more calcium thiocyanate than the barium salt; this is in contrast with their large differences in complexing stability constants reported by Izatt *et al.*[30)] Recently, Rais *et al.* observed the synergistic effect of PEG in the extraction of alkaline earth metal ions by nitrobenzene.[31)] In view of these findings, the solubility relation might exert much influence on the extraction of alkaline earth metal salts.

It was once concluded that the poly(oxyethylene) chain existed in a zigzag conformation at a low degree of polymerization and in a meander conformation at a high degree of polymerization.[32)] Recently Tadokoro *et al.*[33)] have established that the structure of poly(oxyethylene) in the crystalline state has a distorted helical structure containing seven oxyethylene units and two turns, and that it takes a planar zigzag structure only when it is elongated.[34)] The molecular model (Corey-Pauling-Koltum model) based on this fact indicates that the helical structure is convenient for disposing the oxygen atoms of poly(oxyethylene) to the cationic species and can easily take a conformation very similar to 18-crown-6 by a slight rotation of each bonding. The hydrophobic property of high-molecular-weight poly(oxyethylene) derivatives, proved by the high-percent extraction by dichloromethane, implies that the helical conformation is energetically favorable in an organic solvent. In view of these points, noncyclic poly(oxyethylene) derivatives may take, on the average, a helical conformation even in the liquid state and may favorably complex with cations, or the cations may induce an energetically favorable helical structure and, as a result, show a fair extracting power for the cationic species. Polypropylene glycols were confirmed to have a nonplanar zigzag chain because of the steric effect of the methyl groups.[35)] Their low extracting ability may be attributable to their nonplanar zigzag conformation.

A further investigation based on these results is now in progress.

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