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Extraction of Metal Ions by Tri-Cationic Anion-Exchange Extractant

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Novel anion-exchange extractants were synthesized, which are lipophilic phosphonium ions bearing three cationic centers in a molecule. By using the tri-cationic extractants, the selectivity toward the extraction of triply charged anions such as hexacyanoferrate(III) was much increased.

Solvent extraction using anion-exchange extractant (liquid anion exchanger) is widely used in separation processes both in industry and in analytical chemistry, drawing much research efforts devoted to them.[1,2] In most of the studies hitherto reported, commercially-available long-chain quaternary ammonium ions and protonated tertiary amines are used as an anion-exchange extractant (mono-cationic extractant), and few attentions have been paid to the development of extractants whose extraction capability and selectivity are improved from such traditional mono-cationic extractants.

On the other hand, in the field of cation-exchange extractions, so-called chelate-forming extractions (proton - metal ion exchange), a variety of extractants have been synthesized, which can recognize various charge types and sizes of the metal ions of interest as well as the difference in stereochemistry of coordination around the metal. Accordingly, at present many excellent reagents are developed for practical uses.

In our previous studies,[3-5] we prepared a series of lipophilic diphosphonium ions, polymethylenebis(trioctylphosphonium)s, as a di-cationic anion-exchange extractant, and investigated the extraction of anionic metal complexes and organic anions; the extraction behaviors of di-cationic extractants were considerably different from those of conventional mono-cationic extractants. In the present study, we synthesized new extractants, 1,3,5-trimethylbenzenetriyltris(trioctyl phosphonium) tribromide (1,3,5-TP-Br_3) and 1,2,4-trimethylbenzenetriyltris-(trioctylphosphonium) tribromide (1,2,4-TP-Br_3), which possess three cationic centers in a molecule (tri-cationic extractant, Fig. 1). The extraction of anionic metal complexes showed that the triphosphonium salts served as an effective extractant for triply charged anions such as hexacyanoferrate(III), which are usually difficult to extract by using conventional mono-cationic extractants, especially in the presence of singly charged anions which are more

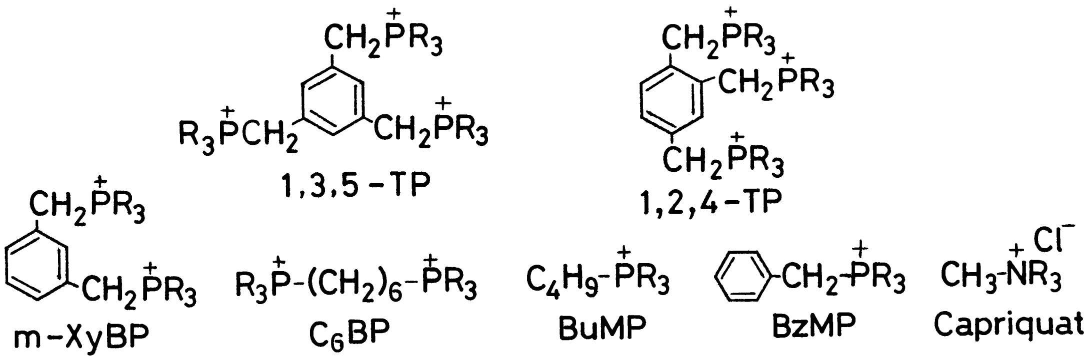

Fig. 1. Anion-exchange extractants (R = octyl). Counter-anion of these salts is bromide except for Capriquat (commercially-available product, Dojindo Lab.).

extractable.

Tri-cationic extractants, 1,3,5-TP-Br_3 and 1,2,4-TP-Br_3, were prepared[6] from the corresponding tris(bromomethyl)benzene[7] and trioctylphosphine in a similar manner to the synthesis of ethylenebis(trioctylphosphonium) dibromide described in the previous paper.[3] Extraction experiments were done as follows. An aqueous solution (10 mL) containing metal ion (anionic metal complex) was shaken with a 1,2-dichloroethane solution containing an extractant at 25 °C for 20 min. After phase separation, the metal concentration in the aqueous phase was determined by atomic absorption spectrophotometry; the concentration of hexacyanoferrate(III) was measured by absorption spectrophotometry at 420 nm. The amount of metal ion extracted into the organic phase was taken as the difference between the amount initially added and that determined after equilibrium in the aqueous phase. Material balance on the metal distribution between the aqueous and organic phases was confirmed by back-extraction experiments as mentioned in the previous paper.[3]

Table 1 shows the competitive extraction between triply negatively charged cyanometalate anion ($Fe(CN)_6^{3-}$) and singly charged anion ($Ag(CN)_2^-$) by use of various anion-exchange extractants. The concentration of extractant is 1.0 mM (1 M = 1 mol/dm^3) for tri-cationic extractant, 1.5 mM for di-cationic extractant, and 3.0 mM for mono-cationic extractant. Therefore, the concentration of cationic charge in the organic phase is 3.0 mM in any cases in the table.

It is well-known that qualitatively the extraction of anions should be favored by a decrease in hydrophilicity, i. e., by an increase in size and a decrease in charge. Irving and Damodaran[8] have examined the anion-exchange reactions of cyanometalate anion and a lipophilic anion, erdomanate ($Co(NH_2)_2(NO_2)_4^-$), using an anion-exchange extractant (tetrahexylammonium). They described that the extraction of singly charged anions ($Au(CN)_2^-$, $Ag(CN)_2^-$) greatly surpassed that of doubly charged anions ($Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, $Hg(CN)_4^{2-}$, etc.), the extraction constant for the former anions being higher than that for the latter ions by 3 or 4 logarithmic units. In addtion, the extraction constant for the reaction of more charged species ($Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, etc.) was too small to be measured. The situation appears to be similar to that observed in our extraction by mono-cationic extractant (BuMP, BzMP, Capriquat; Table 1); the extraction of singly charged anion ($Ag(CN)_2^-$) overwhelmed that of triply charged species ($Fe(CN)_6^{3-}$).

However, the use of tri-cationic extractants such as 1,3,5-TP and 1,2,4-TP brought about a great increase in the extraction of hexacyanoferrate(III); the extraction of triply charged anion was now comparable to that of singly charged anion, dicyanoargentate(I). Di-cationic extractants, C_6BP and m-XyBP, was also effective in the extraction of hexacyanoferrate(III), the preference however being considerably lower than the case of tri-cationic extractants. These results are understood by considering a concept of "multiple charge compatibility", i. e., the extractants bearing three cationic centers in a molecule have a greater ability to extract triply charged anionic species. The concept is supported by the fact that

Table 1. Competitive extraction of cyanometalate ions[a)]

Extractant[b)]	Number of cationic charge in a molecule	D[c)]	
		$Fe(CN)_6^{3-}$	$Ag(CN)_2^-$
1,3,5-TP	3	0.36	2.8
1,2,4-TP	3	0.27	3.5
C_6BP	2	0.10	9.1
m-XyBP	2	0.06	4.1
BuMP	1	<0.01	>100
BzMP	1	<0.01	>100
Capriquat	1	<0.01	8.4

a) Equal volumes (10 mL) of organic and aqueous solutions were equilibrated. The organic solution (1,2-dichloroethane) contained an extractant (1.0 mM for 1,3,5-TP-Br_3 and 1,2,4-TP-Br_3; 1.5 mM for C_6BP-Br_2 and m-XyBP-Br_2; 3.0 mM for BuMP-Br, BzMP-Br, and Capriquat) and the aqueous solution contained 1.0 mM $K_3Fe(CN)_6$ and 3.0 mM $KAg(CN)_2$; the anionic charge concentrations of these cyanometalates are the same (3.0 mM). Other conditions are seen in the text.

b) The structures are summarized in Fig. 1.

c) Distribution ratio. $D = [\text{metal}]_{org}/[\text{metal}]_{aq}$

Table 2. Extraction of anionic metal complexes[a)]

Aqueous phase conditions	Extracted anionic species	D		
		1,3,5-TP	C_6BP	BzMP
1.0 mM $K_3Fe(CN)_6$, 10 mM NaBr	$Fe(CN)_6^{3-}$	3.4	3.0	0.40
1.0 mM $K_3Cr(SCN)_6$, 1 M NaSCN	$Cr(SCN)_6^{3-}$	>100	>100	13
0.60 mM $Zn(NO_3)_2$, 0.36 M HCl	$ZnCl_4^{2-}$	2.0	3.3	0.33
0.60 mM $Zn(NO_3)_2$, 0.36 M HBr	$ZnBr_4^{2-}$	1.8	4.0	0.38
3.0 mM $KAg(CN)_2$, 10 mM NaBr	$Ag(CN)_2^-$	2.4	>100	>100
0.20 mM $FeCl_3$, 1 M HCl	$FeCl_4^-$	0.79	2.0	1.3
0.20 mM $In_2(SO_4)_3$, 1 M HBr	$InBr_4^-$	4.7	15	14

a) Conditions are the same as those in Table 1 except those of aqueous phase.

in the competitive extraction of hexacyanoferrate(III) and tetracyanozincate(II) ($Zn(CN)_4{}^{2-}$), the extraction of the triply charged anion by tri-cationic extractant (1,2,4-TP, D = 0.27) was superior to that by di-cationic extractant (m-XyBP, D = 0.04).9)

Table 2 shows the extraction of anionic metal complexes under various aqueous phase conditions. It is presumed that the anion-exchange reactions occur between the complex noted in the table and simple inorganic anion such as bromide, thiocyanate, and chloride. Although the feature of "multiple charge compatibility" is not so apparent as that observed in the competitive extraction between cyanometalates mentioned above, the tri-cationic extractant and di-cationic extractant are efficient in the extraction of triply and doubly charged anions, respectively.

In conclusion, it was proved that the multiplication of cationic center in a extractant molecule enabled to increase the extraction selectivity toward multi-charged anions. Obviously, this idea would be profitable not only in solvent extraction but also in sensing by liquid membrane electrode for various anionic substrates including multi-charged species of bioorganic interest such as ADP and ATP.

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6) 1,3,5-TP-Br_3: colorless amorphous solid. ^1H NMR ($CDCl_3$, δ form TMS) δ = 0.88 (27H, br, CH_3), 1.28 (108H, br, CCH_2C), 2.45 (18H, br, CCH_2P), 4.20 (6H, br, PCH_2Ar), 8.32 (3H, s, aromatic H). Found: C, 65.58; H, 11.24%. Calcd for $C_{81}H_{162}P_3Br_3 \cdot H_2O$: C, 65.44; H, 11.11%. 1,2,4-TP-Br_3: colorless amorphous solid. ^1H NMR δ = 0.88 (27H, br, CH_3), 1.28 (108H, br, CCH_2C), 2.55 (18H, br, CCH_2P), 4.40 (6H, br, PCH_2Ar), 8.16 (3H, br, aromatic H). Found: C, 65.05; H, 11.41%. Calcd for $C_{81}H_{162}P_3Br_3 \cdot H_2O$: C, 65.44; H, 11.11%. The presence of three cationic charge in an extractant molecule was confirmed by the following experiment. A 1,2-dichloroethane solution containing 1.0 mM 1,3,5-TP-Br_3 was shaken with an aqueous solution containing large excess (10 mM) of $K_3Fe(CN)_6$; the absorbance of the organic phase was determined at 420 nm, resulting in the detection of 1.0 mM $Fe(CN)_6{}^{3-}$. The fact suggests that 3.0 mM of cationic charge is present in the organic solution of 1.0 mM 1,3,5-TP-Br_3. The similar result was obtained with 1,2,4-TP-Br_3.

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9) Conditions are the same as those in Table 1 except that 1.2 mM $K_2Zn(CN)_4$ was added to the aqueous phase instead of $KAg(CN)_2$.

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