

Dipyridinium-Type Anion-Exchange Extractants for Anionic Metal Complexes and Disulfonate Anions

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A new series of anion-exchange extractants, polymethylenebis[3-(*N,N*-dioctylcarbamoyl)pyridinium]s (abbreviated as C_n BPY; $n=3,4,6,8,10$) were synthesized; they are lipophilic dipyridinium ions bearing two cationic centers at various separations within a molecule. The extraction behavior of metal ions from aqueous hydrohalic acid was investigated. The extractability of divalent metal ions (zinc(II) and cadmium(II)) decreased in the order: $C_{10}>C_8>C_6>C_4>C_3$ BPY > monocationic extractant (1-butyl-3-(*N,N*-dioctylcarbamoyl)pyridinium, abbreviated as BuMPY). However, in the extraction of trivalent metal ions (iron(III) and indium(III)), the extraction ability of extractants decreased in the order: BuMPY \approx $C_{10}>C_8>C_6>C_4>C_3$ BPY. These orders were analogous to those observed in the previously reported extractions using diphosphonium extractants. The extraction of organic dianionic substrates, 1,5- and 2,6-naphthalenedisulfonates (abbreviated as NDS²⁻) was also investigated. The extraction of 1,5-NDS²⁻ decreased in the order: $C_{10}\approx C_8\approx C_6>C_4>C_3$ BPY, while that of 2,6-NDS²⁻ decreased in the order: $C_{10}>C_8>C_6>C_4>C_3$ BPY. There were no distinct maxima in the plot of extraction constant ($\log K_{ex}$) vs. n -value; such behavior was considerably different from that of diphosphonium extractants reported previously. The structural aspects of extractants and their relation to extraction selectivity are discussed.

Keywords Anion-exchange extraction, lipophilic dipyridinium salt, anionic metal complex, disulfonate anion

In recent works¹⁻³, we prepared a series of lipophilic diphosphonium ions, polymethylenebis(trioctylphosphonium)s ($R_3P^+-(CH_2)_n-P^+R_3$; $R=$ octyl; $n=2,3,4,6,10$) as anion-exchange extractants, and investigated the extraction of metal ions and that of organic disulfonate anions. The following results were obtained: (i) dicationic extractants have an enhanced extraction ability toward doubly charged anionic species such as $M^{II}X_4^{2-}$ (M^{II} : divalent metal ion; X^- : halides) compared with monocationic extractants ($R_3R'P^+$; $R=$ octyl, $R'=$ methyl or butyl) ("multiple charge compatibility")⁴, (ii) the extraction ability of dicationic extractants increases with an increase in the distance between two cationic centers within the extractants ("ion-chelation-like mechanism"), (iii) in the extraction of organic disulfonate anions (naphthalenedisulfonates), the extractability of the anions was very dependent on the nature of the bridging methylene chain which connects the two cationic centers, indicating the compatibility of the distances between the two ionic centers in both the extractant and the disulfonate anion when they form an ion-association complex in organic solution ("geometrical charge distribution compatibility").

In the present work, we synthesized a series of lipophilic dipyridinium ions, polymethylenebis(3-(*N,N*-dioctylcarbamoyl)pyridinium)s (abbreviated as C_n BPY, $n=3,4,6,8,10$) as dicationic extractants; the structures of dipyridinium extractants as well as diphosphonium extractants are summarized in Fig. 1. The extraction of metal-halide complex anions and of organic disulfonate anions by the dipyridinium extractants was studied and compared with that by the diphosphonium extractants previously reported.¹⁻³ The special features of dicationic extractants mentioned above were further

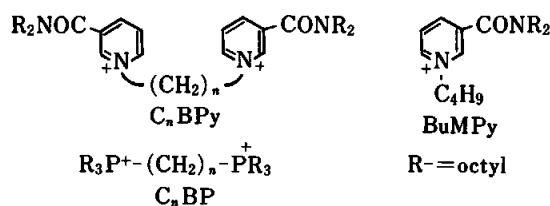


Fig. 1 Pyridinium extractants (C_n BPY and BuMPY; $n=3,4,6,8,10$) and phosphonium extractants (C_n BP; $n=2,3,4,6,10$). Counter-anion of these salts is bromide.

discussed. From the viewpoint of practical use, the dipyridinium extractants are inferred to be of greater advantage than such dicationic extractants hitherto reported as diammoniums ($R_3N^+-(CH_2)_n-N^+R_3$; R =alkyl)^{5,6} and diphosphoniums.¹⁻³ The diammoniums (especially having long alkyl groups and short methylene chains) are difficult to synthesize because of the low reactivity of amines in nucleophilic reactions.⁶ On the other hand, starting materials for the synthesis of the phosphoniums are very expensive.

Experimental

Reagents

Pyridinium extractants were synthesized from *N,N*-dioctylnicotinamide and corresponding bromoalkanes. Sodium salts of naphthalenedisulfonates (1,5- and 2,6-isomers; abbreviated as NDS²⁻) were commercial products and recrystallized twice from methanol. Other chemicals were of reagent grade and were used as received.

Synthesis of pyridinium extractants

N,N-Dioctylnicotinamide: A modification of the method of preparation reported by Dalton *et al.*⁷ was used. Nicotinic acid (19 g, 0.15 mol) and thionyl chloride (56 g, 0.47 mol) were stirred and heated under reflux for 3 h. The excess thionyl chloride was evaporated and the residue was dissolved in dry THF (tetrahydrofuran, 50 ml)+DMF (*N,N*-dimethylformamide, 5 ml). To the solution, dioctylamine (38 g, 0.16 mol) and triethylamine (48 g, 0.47 mol) were added dropwise (1 h) with cooling by ice under nitrogen atmosphere, and the mixture was stirred and heated (90 °C) for 10 h. After removal of THF and DMF by evaporation, the residue was dissolved in chloroform, and the solution was washed with water, aqueous sodium bicarbonate solution, and water again, and then dried (magnesium sulfate). The solvents were then evaporated, the residue was molecular-distilled under high vacuum (0.02 Pa), and the fraction (bath temperature 150–160 °C) was collected. A yellow viscous oil was obtained. Yield (42 g, 77%). ¹H NMR (CDCl₃, δ from TMS) δ =8.7–8.5, 7.7–7.1 (4H, m, aromatic H),

3.6–3.0 (4H, br, NCH₂), 1.7–0.7 (30H, br, CCH₂C, CH₃). Anal. Calcd. for C₂₂H₃₈N₂O: C, 76.24; H, 11.05; N, 8.08%. Found: C, 75.90; H, 11.08; N, 8.08%.

Decamethylenebis[3-(*N,N*-dioctylcarbamoyl)pyridinium]dibromide (C₁₀BPY-Br₂): *N,N*-Dioctylnicotinamide (7.2 g, 0.021 mol), 1,10-dibromodecane (1.6 g, 0.0053 mol), and DMF (15 ml) were stirred and heated (85 °C) for 25 h under nitrogen atmosphere. The removal of DMF by evaporation gave a reddish viscous oil, which was purified by column chromatography on silica gel first with ether and then with a methanol solution containing 1% ammonium bromide as eluents. The main band was collected. After the removal of eluents by evaporation, the residue was dissolved in benzene, filtered to remove insoluble materials, evaporated to remove benzene, and dried *in vacuo*. A brown amorphous solid was obtained. Yield (3.6 g, 65%). ¹H NMR (CDCl₃) δ =10.0–9.7, 8.7–8.2 (8H, br, aromatic H), 5.4–4.9 (4H, br, N⁺CH₂), 3.8–3.0 (8H, br, NCH₂), 2.5–0.5 (76H, br, CCH₂C, CH₃). Other polymethylenebis[3-(*N,N*-dioctylcarbamoyl)pyridinium]dibromides (C_{*n*}BPY-Br₂, *n*=3,4,6,8) and 1-butyl-3-(*N,N*-dioctylcarbamoyl)pyridinium bromide (abbreviated as BuMPY-Br) were prepared in a similar manner to C₁₀BPY-Br₂ synthesis. All the products were obtained in the form of a brown amorphous solid (BuMPY-Br was a reddish viscous oil) and were identified by ¹H NMR. Table 1 summarizes the yields and the results of elemental analysis.

Extraction of anionic metal complexes

An aqueous hydrochloric acid or hydrobromic acid solution (1 M, 1 M=1 mol/dm³, 10 ml) containing 0.2 mM metal salt was shaken with a 1,2-dichloroethane solution containing an extractant (0.5 mM for C_{*n*}BPY-Br₂; 1 mM for BuMPY-Br) in a stoppered centrifuge tube at 25 °C for 20 min. After phase separation, the metal concentration in the aqueous phase was determined by atomic absorption spectrophotometry by using a Nippon Jarrel Ash AA-1 instrument. The amount of metal ion extracted into organic phase was taken as the difference between the amount initially added and that determined after equilibrium in the aqueous phase. In each run, the material balance on the metal distribution between the

Table 1 Elemental analyses and yields of pyridinium extractants

Pyridinium extractant	Elemental analysis, %						Yield, %	
	C		H		N			
	Found	Calcd	Found	Calcd	Found	Calcd		
C ₃ BPY	C ₄₇ H ₈₂ N ₄ O ₂ Br ₂ ·4.2H ₂ O	58.12	58.16	8.98	9.39	5.88	5.77	27
C ₄ BPY	C ₄₈ H ₈₄ N ₄ O ₂ Br ₂ ·3H ₂ O	57.13	57.11	8.98	8.99	5.73	5.55	74
C ₆ BPY	C ₅₀ H ₈₈ N ₄ O ₂ Br ₂ ·3H ₂ O	60.28	60.59	9.11	9.15	5.61	5.65	65
C ₈ BPY	C ₅₂ H ₉₂ N ₄ O ₂ Br ₂ ·1.8H ₂ O	62.72	62.61	9.65	9.70	5.65	5.62	71
C ₁₀ BPY	C ₅₄ H ₉₆ N ₄ O ₂ Br ₂ ·2.8H ₂ O	62.30	62.15	9.57	9.81	5.63	5.37	69
BuMPY	C ₂₆ H ₄₇ N ₂ OBr·H ₂ O	62.64	62.26	9.71	9.85	5.68	5.59	70

aqueous and organic phases was confirmed by back-extraction experiments, as mentioned in the previous paper.¹

The extraction of NDS^{2-} was carried out at 25 °C in a similar way to that described in the previous paper.²

Results and Discussion

Synthesis of dipyridinium extractants

Dipyridinium extractants (C_nBPy ; $n=3,4,6,8,10$) were easily prepared from *N,N*-dioctylnicotinamide and the corresponding dibromoalkanes. Table 1 summarizes the results of elemental analysis. A back-extraction experiment confirmed that each dipyridinium extractant prepared possessed two bromide counter anions; when an organic solution containing a given amount of the extractant was treated with an aqueous perchlorate stripping solution, bromide ion was completely back-extracted into the aqueous solution. The bromide ion was determined potentiometrically by using a bromide-selective electrode (BR-125, Toa Denpa Kogyo Co., Ltd.) to confirm the theoretical amount of bromide ion released into the aqueous solution (exactly twice as much as the molar quantity of extractant initially added). Under the synthetic reaction conditions mentioned above, where an excess of nicotinamide over dibromoalkane was present, the bifunctional substrate (the latter) was allowed to fully react, so that only dipyridinium salt was obtained.

We could not synthesize the dipyridinium extractant having ethylene chain (C_2BPy), probably because 1,2-dibromoethane is much more subject to elimination (rather than nucleophilic substitution reaction) during the reaction with *N,N*-dioctylnicotinamide than other dibromoalkanes. C_3BPy was obtained in a low yield (see Table 1), which may be ascribed to a similar synthetic problem.

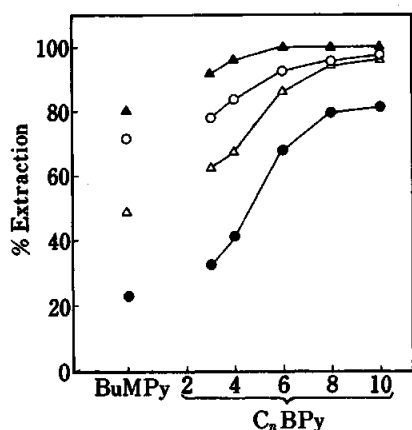


Fig. 2 Extraction of divalent metal ions (Zn^{2+} and Cd^{2+}) from aqueous hydrochloric acid or hydrobromic acid: O, Zn-HCl; ●, Zn-HBr; △, Cd-HCl; ▲, Cd-HBr. ZnSO_4 and CdSO_4 were used as metal salts.

Extraction of anionic metal complexes

Figure 2 shows the extraction of divalent metal ions such as zinc(II) and cadmium(II) by use of the pyridinium extractants from aqueous hydrohalic acid. These divalent metal ions can form an extractable complex ($\text{M}^{\text{II}}\text{X}_4^{2-}$ type; M^{II} : Zn^{2+} , Cd^{2+} ; X^- : Cl^- , Br^-) which is a doubly charged anionic species. The concentration of monopyridinium extractant (BuMPy) used in the organic phase was twice that of dipyridinium extractant, so that the cationic charge concentration in the organic phase was the same for the monopyridinium and dipyridinium extractants.

For all of the extraction systems shown in Fig. 2 (Zn-HCl , Zn-HBr , Cd-HCl , and Cd-HBr), the extractability of dipyridinium extractants increased with an increase in the length of bridging methylene chain connecting the two pyridinium cationic centers, *i.e.*, the extraction ability of extractants decreased in the order: $\text{C}_{10}\text{BPy} > \text{C}_8\text{BPy} > \text{C}_6\text{BPy} > \text{C}_4\text{BPy} > \text{C}_3\text{BPy}$. The extractability of monopyridinium extractant (BuMPy) was inferior to that of C_3BPy , which was the least effective among the dipyridinium extractants. Accordingly, the dipyridinium extractants have an enhanced extraction ability for the dianionic metal complexes compared with the monopyridinium extractants.

On the other hand, in the extraction of trivalent metal ions such as iron(III) and indium(III), which can form singly charged anionic complexes ($\text{M}^{\text{III}}\text{X}_4^-$ type), the extraction ability of extractants decreased in the order: $\text{BuMPy} \approx \text{C}_{10}\text{BPy} > \text{C}_8\text{BPy} > \text{C}_6\text{BPy} > \text{C}_4\text{BPy} > \text{C}_3\text{BPy}$ (Fig. 3). The monopyridinium extractant showed a higher extraction ability; the behavior is much different from that observed in the extraction of divalent metal ions.

These results suggest that the functions of dicationic extractant previously described, *i.e.*, "multiple charge compatibility" and "ion-chelation-like mechanism", are at work as well in the extraction system using

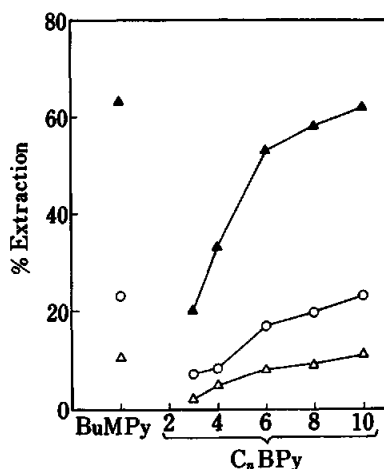


Fig. 3 Extraction of trivalent metal ions (Fe^{3+} and In^{3+}) from aqueous hydrochloric acid or hydrobromic acid: O, Fe-HCl; △, In-HCl; ▲, In-HBr. FeCl_3 and $\text{In}_2(\text{SO}_4)_3$ were used as metal salts.

dipyridinium extractants. Consequently, it now seems to be verified that such unique properties of anion-exchange extractants can be expected not only for diphosphonium extractants but also for any other anion-exchange extractants possessing two cationic centers. The enhanced extraction of dianionic metal complexes by dicationic extractants is due to the simultaneous interaction of two cationic centers with the dianionic metal complex species ($M^{II}X_4^{2-}$). On the other hand, the higher extraction ability of "long bridge-chain" extractants ($C_{10}BPy$, C_8BPy , etc.) is explained by the model that the dianionic metal complexes can more effectively interpose between the two cationic centers of these extractants (somewhat like a chelation by cationic extractants), leading to the formation of more fully dehydrated and readily extractable ion-pair association complexes.

The extraction ability of pyridinium extractants was roughly comparable to that of the phosphonium extractants which have the corresponding methylene chain bridges. Small differences in the ability were observed in the individual cases, which may be ascribed to the difference in the structures of cationic centers in these extractants.

Extraction of organic disulfonate anions

One can assume that the extraction of dianionic substrate NDS^{2-} involves the formation of a 1:1 ion-pair complex between the dicationic extractant and the dianion as follows:



$$K_{ex} = [Q \cdot NDS]_o [Br^-]_w^2 / [Q \cdot Br_2]_o [NDS^{2-}]_w \quad (2)$$

where $Q \cdot Br_2$ represents the bromide salt of dipyridinium extractants C_nBPy , and subscripts w and o denote the aqueous and organic phases, respectively. Equation (2) can be rewritten logarithmically as follows:

$$\log D = \log K_{ex} + \log [Q \cdot Br_2]_o - 2 \log [Br^-]_w \quad (3)$$

where

$$D = [Q \cdot NDS]_o / [NDS^{2-}]_w \quad (4)$$

The dipyridinium extractants $Q \cdot Br_2$ and complex $Q \cdot NDS$ are highly lipophilic and do not appreciably dissolve in aqueous phase. Further, NDS^{2-} alone did not distribute to the organic phase under the relevant pH conditions ($pH > 2$). Thus, the values of D are easily obtained from NDS^{2-} concentration in the aqueous phase after equilibrium.

Figures 4 and 5 show the plots of $\log(D/[Q \cdot Br_2]_o)$ against $-\log[Br^-]_w$ for the extraction of 1,5- NDS^{2-} and 2,6- NDS^{2-} , respectively. All of the plots in the figures gave a straight line with slope 2, suggesting that the reaction depicted in Eq. (1) in fact took place. Thus, the extraction constants of the 1:1 ion-pair complex $Q \cdot NDS$ can be derived from Eq. (3). Figure 6 shows graphical representations of the extraction constants

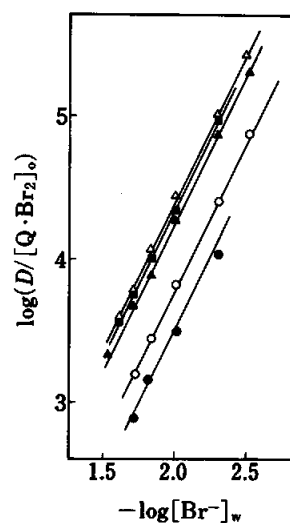


Fig. 4 Plot of $\log(D/[Q \cdot Br_2]_o)$ vs. $-\log[Br^-]_w$ in the extraction of 1,5- NDS^{2-} by C_3BPy (●), C_4BPy (○), C_6BPy (▲), C_8BPy (△) and $C_{10}BPy$ (■).

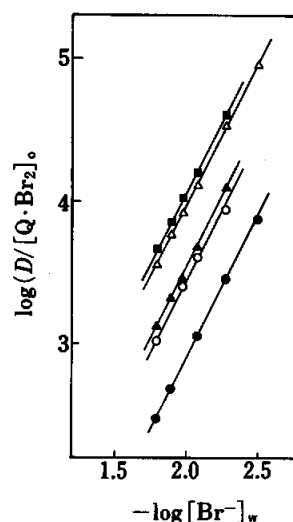


Fig. 5 Plot of $\log(D/[Q \cdot Br_2]_o)$ vs. $-\log[Br^-]_w$ in the extraction of 2,6- NDS^{2-} . Symbols are the same as those used in Fig. 4.

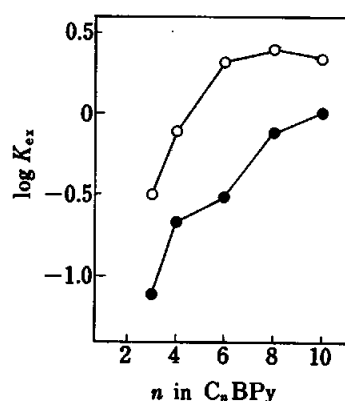


Fig. 6 Dependence of $\log K_{ex}$ value on the structure of extractants. Extraction of 1,5- NDS^{2-} (○) and 2,6- NDS^{2-} (●).

($\log K_{ex}$) as a function of methylene-chain length (n in C_n BPy) in the extraction of 1,5- and 2,6-NDS²⁻.

The $\log K_{ex}$ value in the extraction of 1,5-NDS²⁻ decreased in the order: $C_{10} \approx C_8 \approx C_6 > C_4 > C_3$ BPy. As reported in the previous paper², in the extraction of 1,5-NDS²⁻ by diphosphonium extractants (C_n BP) ($\log K_{ex}$ - n in C_n BP plot), the $\log K_{ex}$ value decreased on going from C_6 BP to C_{10} BP (structures are seen in Fig. 1), i.e., the maximum value of $\log K_{ex}$ was observed at $n=6$. However, the extraction by dipyrindinium extractants showed no distinct maximum; among the "long bridge-chain" extractants (C_6 -, C_8 -, C_{10} BPy), the extractability was almost the same. Accordingly, it is obvious that the dipyrindinium extractants do not possess the same substrate (anion) recognition ability that the diphosphonium extractants exhibited.

It is well-known that 1-alkylpyridinium iodides form charge-transfer complexes between their pyridinium nucleus and iodide anion⁸, which suggests that in the pyridinium nucleus, the cationic charge is fairly delocalized. On the contrary, in the case of phosphonium salts, the cationic charge is localized at the phosphonium phosphorous atom. It is reasonable to suppose that in the extraction using dipyrindinium extractants, the compatibility of ionic center separations between the extractant cation and the disulfonate anion is not so effectively at work because of the delocalization of cationic charge; such compatibility is seen in the extraction using diphosphonium extractants as mentioned above.² The charge distribution and extractability may be not so influenced by the carbamoyl group of dipyrindinium extractants.

The extraction of 2,6-NDS²⁻ decreased in the order: $C_{10} > C_8 > C_6 > C_4 > C_3$ BPy; the situation is somewhat different from that in the 1,5-NDS²⁻ extraction. The extraction optimum appears to shift toward longer methylene-chain bridged extractants such as C_{10} BPy. This may be attributed to the fact that the distance between the two terminal anions ($-\text{SO}_3^-$) of 2,6-NDS²⁻ is 2 Å longer than that of 1,5-NDS²⁻.

In the extraction using diphosphonium extractants², the extraction ability drastically increased at C_3 BP \rightarrow C_4 BP for 1,5-NDS²⁻ extraction ($\Delta \log K_{ex} = ca. 1.1$) and at C_4 BP \rightarrow C_6 BP for 2,6-NDS²⁻ extraction ($\Delta \log K_{ex} = ca. 0.7$). However, in the present extraction system using dipyrindinium extractants, such a large change in $\log K_{ex}$ value was not observed, and the $\log K_{ex}$ value increased only gradually with an increase in the methylene chain length (n). This is ascribed to a reason similar to that mentioned above, that the dipyrindinium extractants have rather delocalized cationic charges.

The features of the extraction of monoanionic substrate, 1-naphthalenesulfonate (abbreviated as NS⁻), were similar to those in the case of diphosphonium extractants (the extraction constants gradually decreased with an increase in the methylene-chain length (n) in the extractants and the variation range is 0.3–0.4 in log unit).²

In the extraction of NDS²⁻, one of the two cationic

centers of extractants interacts with a terminal sulfonate anion of the disulfonate substrate while the other cationic center binds the residual anionic site of the substrate, so that the compatibility of the distances between the ionic charges in both the extractant and the substrate becomes a dominant factor in determining the extractability. However, such a situation does not hold in the extraction of NS⁻, and hence the extraction is not much influenced by the structure of cationic centers within the extractants (localized charge or delocalized charge).

Special feature of dicationic extractants

In the extraction of dianionic metal complexes ($M^{II}X_4^{2-}$), the dipyrindinium extractants (especially "long bridge-chain" extractants) serve as an effective extractant, in analogy with the diphosphonium extractants previously reported.³ Nicotinamides with long alkyl chain act as an efficient extractant for copper from concentrated aqueous chloride solutions.⁷ Therefore, such nicotinamides may become commercially available in the future; from these, the dipyrindinium extractants can then be easily derived. Consequently, the dipyrindinium extractants may be profitable for practical use.

In the extraction of organic dianionic substrates, the dipyrindinium extractants do not afford the same high substrate (anion) recognition ability that the diphosphonium extractants possess. In other words, as for the extraction of NDS²⁻ (the two anionic charges are separately present within a molecule), the extraction behavior of two types of extractants (dipyrindinium extractants and diphosphonium extractants) is considerably different. On the contrary, in regard to the extraction of monoanionic substrate NS⁻ as well as in regard to the extraction of anionic metal complexes ($M^{II}X_4^{2-}$ and $M^{III}X_4^{-}$)³, there are no significant differences between the two types of extractants. Thus, where the substrates having separated multi-charges are concerned, the structure of cationic centers within dicationic extractants can be the critical factor influencing the extractability.

Anion-exchange extractions (ion-pair or ion-association extractions) have been hitherto discussed mostly in terms of lipophilicity, molar volume, and charge density of the ionic species involved. We have now verified the importance of the structural aspect of ion-association complexes. The concept presented by us can hopefully be extended to the development of more sophisticated systems in order to more effectively recognize and more selectively separate the desired substrates.

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