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Ion-Associate Solvent Extraction of Gallium(III) from Aqueous Sodium Hydroxide Solution

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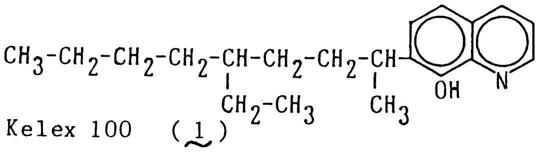
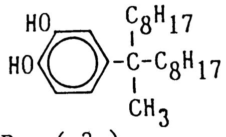
Gallium(III) was extracted as $Q_3[GaL_3]$ from 1 - 4 mol/dm^3 NaOH solutions by the combined use of o-dihydroxy derivatives of benzene or naphthalene (H_2L) and asymmetric quaternary ammonium ions (Q^+) having at least one methyl-group. Hydrophobic large alkyl groups are an essential constituent of the extractant, while disposition of them is not necessarily restricted on the ligands (H_2L), but on the counter ions (Q^+). These findings provide a new basis for designing the reagent suitable for the ion-association extraction of metal ion from the strongly alkaline media.

Solvent extraction of metal ions from alkaline media is an attractive method for the purification and recovery of them. However, hydrolysis of metal species seems to prevent to realize it. Recently, such extraction methods were reported by the use of extractants having large alkyl groups. Helgorsky$^{1)}$ found that 7-alkyl-8-quinolinol (Kelex 100, HR (1)) can extract gallium(III) from 3 mol/dm^3 aqueous sodium hydroxide solution, and the stoichiometry of the extracted species was reported to be GaR_3.$^{2)}$ Russian chemists have demonstrated that 4-(1,1-dioctylethyl)pyrocatecohol (DOP, H_2A (2)) can extract aluminum$^{3)}$ and actinide$^{4)}$ ions from sodium hydroxide solution as $Na_3[MA_3]$. In these works, the stoichiometry of the extraction is quite understandable. The role of the alkyl groups in the extractants, however, remains equivocal, even though Freiser et al.$^{5)}$ have discussed the surface active nature of Kelex 100 in the kinetic aspects of the extraction at the alkaline pH region. Originally, introduction of such long alkyl groups on the extractants was made in order to reduce the loss of the extractant due to its solubility in water.

We have found that the large alkyl group is not necessarily placed on the chelating ligand, but it can be placed on the counter ions, in the case of ion-associate extraction system. In addition, the forms of the quaternary ammonium ion play an important role in these extraction systems, that is, asymmetric ones having at least one methyl-group are the most effective, which enable the closest



Kelex 100 (1)



DOP (2)

approach between the charge centers in their ion-associate formation. Thus, we can obtain a new method for designing the extraction system, which works in very alkaline media, without the special extractant having a long alkyl group on it.

Aqueous gallate solution was prepared by dissolving freshly precipitated gallium hydroxide in 3 mol/dm^3 sodium hydroxide solution. Pyrocatecohol (PC) and 4-tert-butyl derivative (PC-4 or H_2pc-4) were used without further purification (Kanto Chemical Co.,Inc.). 2,3-Dihydroxynaphtalene (DHN or H_2dhn) was obtained from Lancaster Synthesis Ltd., and purified by recrystallization from methanol-water mixture. Other reagents used were of analytical reagent grade. Equal volumes (10 cm^3) of an organic solvent containing quaternary ammonium salt(QX) and an aqueous sodium hydroxide solution containing metal ion and extractant were shaken with a mechanical shaker with 330 strokes per min. The pH of the aqueous phase was adjusted with borax and sodium hydroxide solution. After equilibration, the mixture was centrifuged for 10 min at 2000 rpm. The metal concentration of the aqueous phase was measured by a Hitachi model 180-80 polarized Zeeman atomic absorption spectrophotometer. All the extraction experiments were carried out at 20 °C by using 30 cm^3 polyethylene vials fitted with polypropylene caps.

The extraction efficiency of Ga(III) with PC, PC-4, and DHN is shown in Fig.1 as a function of pH and sodium hydroxide concentration. In the case of PC, Ga(III) was not extracted with sodium ion as a counter cation, although Tarnopol'skii et al.$^{3)}$ reported the extraction of aluminum(III) with DOP as an ion-associate of $Na_3[Al(dop)_3]$. On the other hand, Ga(III)-PC chelate was extracted with benzyldimethyltetradecylammonium chloride (Z^+Cl^-) even from 4 mol/dm^3 sodium hydroxide solution. These results indicate that in the case of ion-association extraction system, the long alkyl-groups are not necessarily placed on the ligands, but they can be placed on the counter cations.

The extraction efficiency curves 2 and 3 in Fig.1 for PC and PC-4 with Z^+Cl^- show dips around pH 13, but curve 4 for DHN with trioctylmethylammonium chloride ($TOMA^+Cl^-$) did not show any dip. Furthermore, the depth of the dip depends on the kinds of organic solvents used, as shown in Fig.2. Toluene is the most effective one. The forms of the ion-associate extracted were $Z_3[Ga(pc\text{-}4)_3]$ and $(TOMA)_3[Ga(dhn)_3]$ at the lower pH side of the dip (pH 4 - 11). At the strongly alkaline media, the quantitative studies on PC system

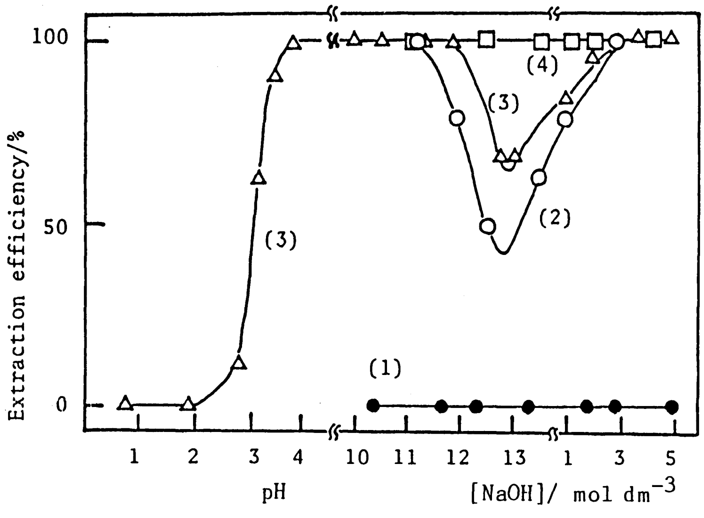


Fig.1. Extraction efficiency vs. pH or sodium hydroxide concentration curve for 10^{-3} mol/dm^3 Ga(III) with PC (1,2), PC-4 (3), and DHN (4) into cyclohexane (1,2) and toluene (3,4). Concentration (mol/dm^3) of extractant: (1-3) 3 X 10^{-2}, (4) 10^{-2}, and of counter ions: (1) $[Z^+]_t$ = 0, (2,3) $[Z^+]_t$ = 6 X 10^{-2}, (4) $[TOMA^+]_t$ = 10^{-2}. Subscript t indicates the total concentration of the species in the blanket.

was difficult due to its aerial oxidation, while DHN was stable enough to confirm its stoichiometry to be $Q_3[GaL_3]$ in 3 mol/dm^3 sodium hydroxide by the molar ratio method. DHN itself was also extracted as Q(HL).

$$Ga(OH)_4^- + 3Q(HL)_o \rightleftharpoons Q_3[GaL_3]_o + 3H_2O + OH^- \qquad (1)$$

$$K_{ex} = [Q_3[GaL_3]]_o[OH^-][Ga(OH)_4^-]^{-1}[Q(HL)]_o^{-3} \qquad (2)$$

where the subscript o indicates the species in the organic phase. The concentration extraction constant, K_{ex}, for DHN-TOMA$^+$-aqueous 3 mol/dm^3 sodium hydroxide-toluene system was estimated to be $10^{10.0 \pm 0.5}$ at 20 °C from the log D vs. log $[Q(HL)]_o$ plots. Thus, the species having the same stoichiometry of $Q_3[GaL_3]$ was extracted at the both side of the dip. Aluminum(III) ion can also be extracted as $Q_3[AlL_3]$ and its extraction behavior is very similar to that of gallium(III).

The extraction behaviors around the dips in Figs.1 and 2 can be explained as follows: the decrease in the efficiency at pH 11 - 13 can be rationalized by the competitive co-ordination of hydroxide ion with the chelating ligands. The use of a more hydrophobic ligand such as DHN (Fig.1, curve 4) and the use of richer organic solvent such as toluene promote the extraction so that the depth of the dip was diminished (increase in the extraction efficiency, see Fig.2, curve 3). Therefore, the increase in the efficiency at 0.1 - 2 mol/dm^3 sodium hydroxide solution should be attributed to the change in the relative decrease of the affinity of the aqueous phase to the metal chelate anion, owing to the sodium hydroxide-assisted strong salting out effect. A similar effect was reported in the phase-transfer phenomena of quaternary onium salts from aqueous sodium

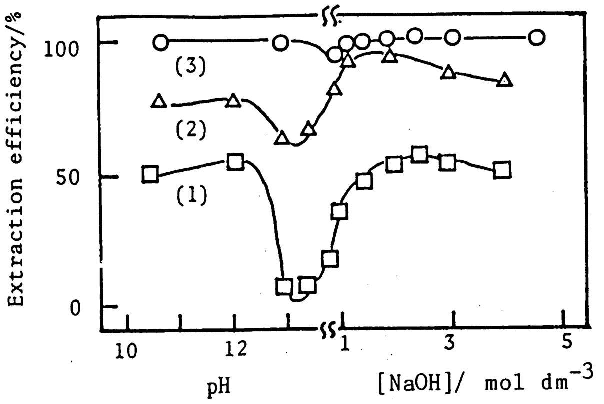


Fig.2. Ion-association extraction behavior of Ga(III) - PC - TOMA$^+$ with (1): Nitorobenzene, (2):1,2-Dichloroethane, (3): Toluene. $[Ga(III)]_t = 10^{-3}$ mol/dm^3, $[PC]_t = 3 \times 10^{-3}$ mol/dm^3, $[TOMA^+]_t = 6 \times 10^{-3}$ mol/dm^3.

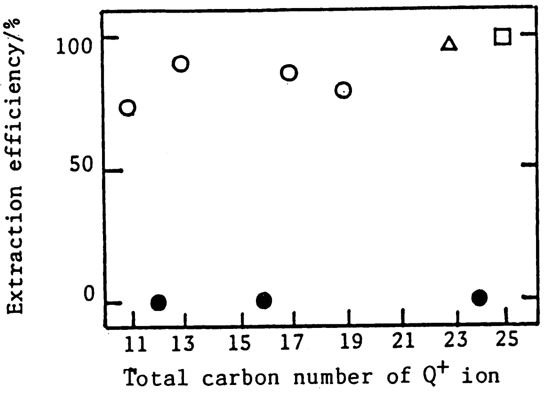


Fig.3. Relationship between total carbon number of quaternary ammonium ion and extraction efficiency of gallium(III) - PC-4 chelate from 2 mol/dm^3 aqueous sodium hydroxide solution with toluene. $[Ga]_t = 10^{-3}$ mol/dm^3, $[PC\text{-}4]_t = 3 \times 10^{-3}$ mol/dm^3, $[Q^+]_t = 6 \times 10^{-3}$ mol/dm^3.

○ : $R\text{-}N^+(CH_3)_3$ △ : $RR'\text{-}N(CH_3)_2$ (Z^+)
□ : $R_3\text{-}N^+CH_3$ ($TOMA^+$) ● : $R_4\text{-}N^+$

hydroxide solution to chlorobenzene.[6)] The reported second decrease at the higher sodium hydroxide concentration in $Na_3[Al(dop)_3]$ system[3)] should be again attributed to the effect of hydroxide ion to form hydroxo-complexes, which may overcome the strong salting-out effect brought about by the sodium hydroxide itself under those conditions.

It should be noted that the extraction efficiency, shown in Fig.3, seems to depend strongly on the symmetry of the cations. Tetrapropyl-, tetrabutyl-, and tetrahexyl-ammonium ions showed almost no extraction ability, while the ions having at least one methyl-group gave the higher efficiency. In order to understand this findings, the efficiency was also measured by the use of quarternary ammonium ions which have three hexyl-groups and one alkyl-group of various carbon numbers, $(C_6H_{13})_3N^+C_nH_{2n+1}$ (n = 2 - 6). The results shown in Table 1 demonstrate that the efficiency clearly increased as the alkyl- group on the cations are shortened, despite that the decrease in the chain length may cause the decrease in its molar volume and hydrophobicity. This finding is apparently against the empirical rule of the usual ion-association extraction systems in the pH region,[7,8)] as well as molar volume effect of the regular solution theory. These results suggest that the aqueous phase of the sodium hydroxide-assisted salting out system has a very different nature compared with that of the usual aqueous solution, and the distance of the closest approach between the charge centers in the ion-association may play an important role in the overall extraction process.

Table 1. Extraction efficiency of Ga-(PC-4) chelate from 3 mol/dm^3 NaOH solution to cyclohexane with alkyl-trihexylammonium ion

Alkyl chain	Extraction efficiency/%
$-CH_2CH_3$	66.2
$-CH_2CH_2CH_2CH_3$	50.3
$-CH_2CH_2CH_2CH_2CH_2CH_3$	4.8

$[Ga]_t = 1 \times 10^{-3}$ mol/dm^3
$[PC\text{-}4]_t = 3 \times 10^{-2}$ mol/dm^3
$[Q^+]_t = 1 \times 10^{-2}$ mol/dm^3

The results obtained here will provide a new concept for designing the extraction system of metal ions from the alkaline media, and especially "overall hydrophobic properties can be shared between the metal chelates and the counter ions" is noteworthy, because the tedious preparation of the ligand having a long alkyl groups is saved.

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