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5,7-Dimethyl-8-quinolinol as a Specific Non-extracting Reagent for Lanthanide Ions at Usual pH Region

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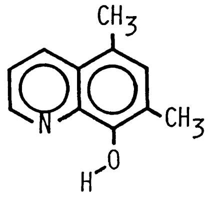
Lanthanide ions were not extracted with 5,7-dimethyl-8-quinolinol in the wide pH region of less than 11, even though other metal ions of Al^{3+}, and the first transition metal ions were extracted at ordinary pH conditions. To realize this specificity, the presence of both of alkyl groups at 5- and 7- positions was essential. The possibility of application of this finding to the separation and purification of lanthanide is discussed.

Many types of reagents have been used for the extraction and separation of lanthanide ions, such as 8-quinolinol derivatives,$^{1-4)}$ acethylacetone derivatives, and phosphate esters. Derivatives of 8-quinolinol have sometimes showed unusual specific extraction behavior for metal ions. For example, 2-methyl-8-quinolinol can not extract aluminium ion from aqueous solution, which had been explained based on the steric effect of 2-methyl group.$^{5)}$ But this explanation can not be accepted because it forms 1:3 chelate in non-aqueous solution.$^{6)}$ Therefore, the role of 2-methyl group became obscure. Thus, the solvent effect on complexation equilibria and the substituent effect for controlling the solubility and basicity of the ligand in aqueous solution have been discussed.$^{7)}$

On the course of our systematic studies on the substituent effect of 8-quinolinol derivative, 5,7-dimethyl-8-quinolinol was found to show a non-extraction specificity for the lanthanide ions at the usual pH region. However, it can normally extract aluminium and some of the first transition metal ions, except for iron(III), which showed two extraction zones at an acidic pH region and at a strongly alkaline region. The effect of methyl groups at 5- and 7- positions is discussed compared with that of bromo groups and with non-substituted 8-quinolinol.



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A Hitachi model 200-10 spectrophotometer equipped with 1 cm quartz cells was used for absorbance measurement. A Seiko plasmaspectrometer SPS-1200 (ICP-AES) was applied for the determination of metal ions in the aqueous phase. A Hitachi Horiba M-7E pH meter, calibrated daily with standard pH solution, was used. 5,7-Dimethyl-8-quinolinol (5,7-Me_2-Ox, HL, **1**) was synthesized by Skraup reaction with 2-amino-4,6-dimethylphenol and glycerol. The purified product was assigned by elemental analysis, ^1H-NMR, and UV-vis spectra. Distribution constant ($K_{D,HL}$) and acid dissociation constants ($K_{a,NH}$ and $K_{a,OH}$) of the reagent were determined as $10^{3.38}$, $10^{-4.45}$, and $10^{-12.1}$, at I = 0.1 (NaCl) and 25 ^{o}C, respectively, from pH - distribution ratio curves between water and chloroform by UV spectrophotometry.

Extraction procedure is as follows: an aliquot of 10 cm^3 of aqueous solution containing $1x10^{-4}$ mol dm^{-3} of metal ion was taken in a 30 cm^3 extraction vial. The ionic strength and pH of the solution were adjusted to 0.1 with sodium chloride and with appropriate buffer solution. The solution was shaken for 2 h with a 10 cm^3 of chloroform solution containing $1x10^{-2}$ mol dm^{-3} of reagent. Chloroform used was saturated with water just before the preparation of the reagent solution. After phase separation, absorbance of the organic phase was measured. Concentration of lanthanide ions in the aqueous phase was determined by ICP-AES. The lanthanide chelates were back-extracted with acidic aqueous solution and their concentrations were determined by ICP-AES, in order to confirm the material balance of the extraction system.

The pH - extraction efficiency plots of lanthanide ions are shown in Fig.1. Lanthanide ions were not extracted at all below pH 11, but are extracted at highly alkaline region. The efficiency reached to 80% for Yb^{3+} in 1.5 - 4 mol dm^{-3} sodium hydroxide solution, and those for Pr^{3+} and Eu^{3+} were 10 - 20%. As the hydrolysis of lanthanides occurs, the extraction proceeds via hydrolyzed lanthanide species, which react rather slowly with the reagent, and 2 h shaking was required to reach the equilibrium. An extraction is also made in the presence of 0.01 mol dm^{-3} sodium tartrate to avoid the formation of lanthanide hydroxides. But, the extraction curves are not so much different from those without tartrate. Synergistic effect of 1,10-phenanthroline (its concentration was $1x10^{-3}$ mol dm^{-3}) was also examined at the all pH region and strongly

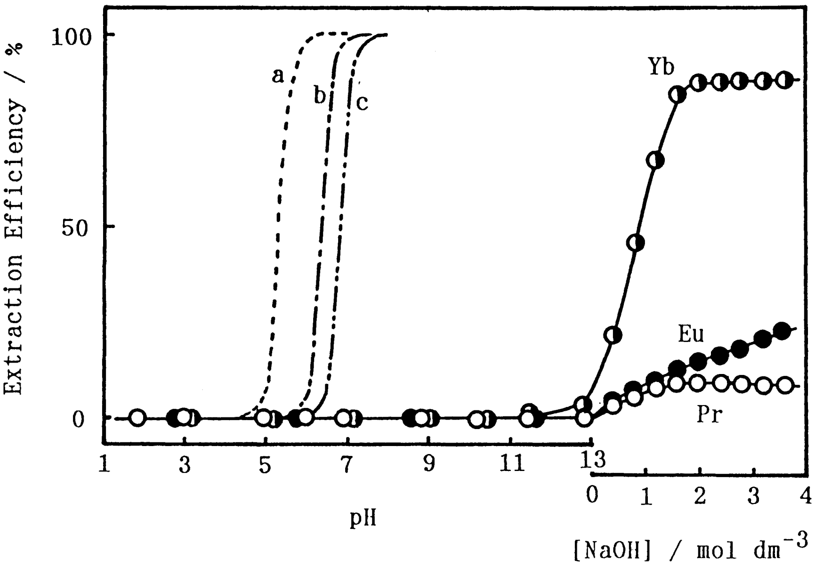

Fig.1. Extraction efficiency - pH or - [NaOH] curves for lanthanide ions with 8-quinolinol derivatives at $[HL]_o$ = $1x10^{-2}$ mol dm^{-3} and $[M^{3+}]$ = $1x10^{-4}$ mol dm^{-3}, a) Yb^{3+} with 5,7-dibromo-8-quinolinol (Ref.2), b) Yb^{3+} with 8-quinolinol, c) Yb^{3+} with 5-methyl-8-quinolinol.

alkaline region, but the extraction curves did not show any changes. As shown in lines a, b, and c in Fig.1, 8-quinolinol and 5-methyl-8-quinolinol extracted Yb^{3+} at neutral pH region and 5,7-dibromo-8-quinolinol extracted it at weakly acidic conditions.2) These data clearly show that the introduction of two methyl groups at 5- and 7- positions have produced an unusual pH shift in the extraction region to alkaline side in the order of 6 - 8 pH units. Unfortunately, 7-methyl-8-quinolinol is hard to synthesize, therefore, its extraction properties could not be evaluated. However, Kelex-100, having very large alkenyl group at 7-position but without 5-methyl group, extracted lanthanide ions at normal pH condition of 7.3 - 8.5. This fact indicates that, in addition to 7-methyl group, 5-methyl group plays an important role for the specificity. Thus, the steric effect concept in ordinary sense should be ruled out, since the location of 5- and 7-position seems to be hard to give steric effect on complexation. Such extraction behavior of 5,7-dimethyl-8-quinolinol was quite an unexpected finding. The stoichiometry of the extracted species, however, is expected to be normal one, $[ML_3(HL)_n]$, based on the following facts.

Other metal ions, Al^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} are extracted with 5,7-dimethyl-8-quinolinol (Fig.2). Iron(III) ion was also extracted at strongly alkaline region as found for lanthanides, and the extracted species showed the same absorption spectra (λ_{max} = 498 nm) as that of the chelate $[FeL_3]$ extracted at acidic pH region. This fact indicates that the same species was extracted at the both conditions. Therefore, very similar situation will be taken place for the stoichiometry of lanthanides.

The values of half extraction pH ($pH_{1/2}$) are summarized in Table 1, together with those of 8-quinolinol, estimated from the reported data.8) Compared with $pH_{1/2}$ values of Al^{3+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions, those of Ni^{2+} and Zn^{2+} ions showed significant shifts of $pH_{1/2}$ to the alkaline side. Thus, the shift is not specific for lanthanide ions. However, the amount of the shift for lanthanide ions is unusually large.

In order to confirm the role of alkyl group at 7-position, more bulky t-buthyl group was introduced. As expected, 7-t-buthyl-5-methyl-8-quinolinol did not extract lanthanide ions over the all pH region and alkaline

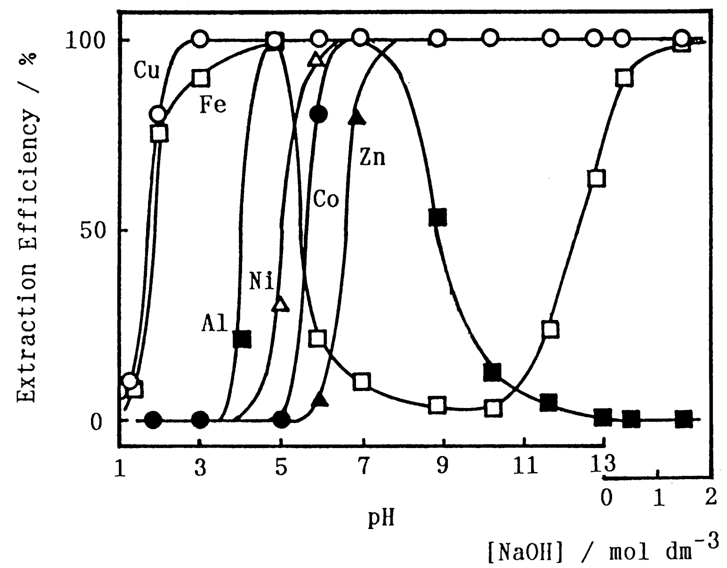

Fig.2. Extraction efficiency - pH or - [NaOH] curves for metal ions with 5,7-dimethyl-8-quinolonol at $[HL]_0$ = $1x10^{-2}$ mol dm^{-3} and $[M^{n+}]$ = $1x10^{-4}$ mol dm^{-3}.

conditions. The reagent, however, did extract copper(II) ion quantitatively from pH 2 to 1.5 mol dm^{-3} sodium hydroxide solution by the use of the same conditions as shown in Fig.2. In the case of iron(III) ion, this reagent also showed two extraction zones at pH 2 - 4 and pH > 12. Presence of the extraction zone in strongly alkaline condition is similar to that found for 5,7-dimethyl-8-quinolinol.

Table 1. Half extraction pH values of metal ions with 8-quinolinol or 5,7-dimethyl-8-quinolinol[a)]

M^{n+}	$pH_{1/2}$ 5,7-Me_2-Ox	 8-quinolinol	$\Delta pH_{1/2}$
Yb^{3+}	14	6.4	7.6
Cu^{2+}	1.5	1.5	0.0
Fe^{3+}	1.5	1.5	0.0
Al^{3+}	4.2	3.8	0.4
Co[b)]	5.8	5.2	0.6
Ni^{2+}	5.2	3.1	2.1
Zn^{2+}	6.4	3.3	3.1

a) $[HL]_o = 10^{-2}$ mol dm^{-3},
b) Co^{III} in the chelate.

Thus, 5,7-dimethyl-8-quinolinol can be used for the purification of lanthanides by removing other common metal ions from aqueous phase at acidic or neutral pH region. This specificity should be explained in terms of the basicity of the ligand, and formation of hydroxo-complexes of lanthanides. The $pH_{1/2}$ values for Yb^{3+} are shifted to the alkaline side by the increase in the basicity of the ligand as shown in Fig.1; curve a ($pK_{a,OH}$ = 7.3, $pH_{1/2}$ = 5.44), curve b (9.7, 6.38), and curve c (10.99, 6.78), respectively. Therefore, $pH_{1/2}$ value of Yb^{3+} with 5,7-dimethyl-8-quinolinol ($pK_{a,OH}$ = 12.1) is expected to be 7.4. Its $pH_{1/2}$ value, however, was 14 as shown in Fig.1. This result should be attributed to the hydrolysis of Yb^{3+} taking place over pH 7, in addition to the $pK_{a,OH}$ shift effect on $pH_{1/2}$. Details of such studies are now under way.

References

1) T.Hori, M.Kawashima, and H.Freiser, Sep.Sci.technol., 15, 861(1980).
2) O.Tochiyama and H.Freiser, Anal.Chem. ,53, 874(1981).
3) S.Taguchi and H.Freiser, Solv.Extr.Ion Exch., 4, 275(1986).
4) E.Yamada and H.Freiser, Anal.Chem., 53, 2115(1981).
5) H.Irving, E.J.Butler, and M.F.Ring, J.Chem.Soc., 1949, 1489.
6) P.R.Scherer and Q.Fernando, Anal.Chem., 40, 1938(1968).
7) T.Yotsuyanagi, Y.Katsura, and T.Kudoh, International Congress on Analytical Sciences (1991)Abst., p51.
8) K.L.Chang, K.Ueno, and T.Imamura, "Handbook of Organic Analytical Reagent," CRC Press (1982), pp.253-267.

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