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EXTRACTION OF METAL IONS FROM TRICHLOROACETIC ACID SOLUTIONS TO POLAR SOLVENTS

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Cs(I),Ca(II),Ba(II),Co(II),Mn(II),Hg(II), Al(III), Cr(III), Fe(III), Tm(III),Bi(III) and Th(IV) in trichloroacetic acid-sodium trichloroacetate buffer solutions have been readily extracted with polar solvents which have donor oxygen atom, e.g. alcohols,ketones,esters and ethers, without any additional extracting reagent.

It is well known that chromium(III) is not extracted with acetylacetone(AA) into chloroform from its aqueous solution at room temperature[1,2], because of an extremely slow rate of substitution of the hydrated water in $Cr(H_2O)_6^{3+}$ with AA, but the extraction can be achieved by refluxing the aqueous solution with AA[3] or by adding organic base such as amines[4] or pyridine[5] into the aqueous solution. In chelate extraction the pH of the aqueous phase is usually adjusted with acetic acid-sodium acetate buffer solution. The present authors tried to employ trichloroacetic acid, dichloroacetic acid and monochloroacetic acid to adjust the pH of the aqueous solution in place of acetic acid. It was found that the extraction of Cr(III) with AA was achieved readily at room temperature and the ability of enhancing the extraction was higher in the following order; monochloroacetic acid<dichloroacetic acid<trichloroacetic acid. In addition, Cr(III) was readily extracted into isopentyl alcohol in the absence of AA when a series of buffer solutions prepared by mixing 2M CCl_3COOH and 2M NaOH in various ratios was employed. This has not been found in the literature on the extraction of metals with carboxylic acids[6]. The present authors further investigated the extraction behavior of twelve cations in the same buffer solutions as above with various organic solvents which have donor oxygen atom.

The series of buffer solutions(pH 0-8) was prepared by mixing 2M trichloroacetic acid and 2 M sodium hydroxide in varying ratio and the solution was saturated with the solvent to be used. Hereafter, this series of buffer solutions will be noted as 2M trichloroacetic acid buffer solution in this letter. In a 50 ml centrifuge tube 10 ml of an organic solvent and 10 ml of an aqueous solution containing a metal ion at 10^{-3} to 1 mole/l were put together, and the content was vigorously shaken by a shaking machine for a definite interval(1-60 minutes). After centrifugation an aliquot of each phase was taken out and the percent extraction(%E) of the metal was determined. A tracer method was applied by using ^{137}Cs, ^{51}Cr, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{170}Tm, ^{203}Hg or ^{207}Bi as the tracer. On the other hand, colorimetry was adopted for Al by measuring the absorption of 8-hydroxyquinolinate at 390 nm, and titration with a standardized EDTA solution was done for Ca, Ba and Th respectively. The pH of the aqueous solution was measured after the extraction equilibrium was established in all cases.

The first finding was that a remarkable increase of the extractability of Cr(III) was obtained when the extraction was carried out with 1:1 mixture of AA and isopentyl alcohol from an aqueous solution of Cr(III) of 2x10^{-4}mole/l containing trichloroacetate,monochloroacetate or perchlorate as buffer. The results are shown in Table I, in which the easiness of the extraction may be appreciated from the lowering in the pH value of the half extraction, $pH_{1/2}$.

Table I. The extraction of Cr(III) from aqueous solution containing various salts in various concentration.

Buffer salt solution	CCl_3COO^-			CH_2ClCOO^-		CH_3COO^-		ClO_4^-	
concentration(mole/l)	2.0	0.5	0.1	2.0	0.1	2.0	0.1	1.2	0.1
$pH_{1/2}$	1.6	2.3	3.5	5.1	5.5	6.3	6.0	2.8	3.8

After the extraction most of Cr(III) in the organic phase was certified as being $Cr(AA)_3$ chelate from the absorption spectrum of the organic phase.

The second finding was that Cr(III) could be extracted into the organic phase in the absence of AA from buffer solutions each containing one of the chloroacetic acids and their sodium salt. This fact can be seen from the results shown in Table II.

Table II. Extraction of Cr(III) with 10 ml of isopentyl alcohol from 10 ml of various buffer solutions at pH 4.0 without AA. Cr(III): 2x10^{-4}mole/l, Buffer soln.: 2 mole/l, Shaking: 20 min.

Buffer salt solution	CCl_3COO^-	$CHCl_2COO^-$	CH_2ClCOO^-	CH_3COO^-	ClO_4^-
%E	93	57	6	∿0	∿0

It was also found that when the pH of 2M trichloroacetic acid buffer solution was 3.9, the %E of Cr(III) reached as high as 93 only by shaking the both phases for 1 minute.

The extraction of Cr(III) was tried from 2M trichloroacetic acid buffer solution at pH 4.0 with ninteen kinds of organic solvent. Table III shows the %E obtained under the same conditions as shown in Table II.

Table III. Extraction of Cr(III) with various organic solvents.

Solvent	%E	Solvent	%E
Benzene	∿ 0	4-Methyl-2-pentanone	67
Toluene	∿ 0	Ethyl acetate	67
Cyclohexane	∿ 0	Butyl acetate	23
Chloroform	∿ 0	Isopentyl acetate	8
Carbon tetrachloride	∿ 0	Diethyl ether	34
1-Pentanol	96	Dibutyl ether	∿ 0
Isopentyl alcohol	93	Nitrobenzene	∿ 0
1-Hexanol	96	Tributyl phosphate	∿100
Benzyl alcohol	87	0.25 M TOPO* in benzene at pH 5.0	∿100
2-Octanol	56		

*Trioctyl phosphine oxide

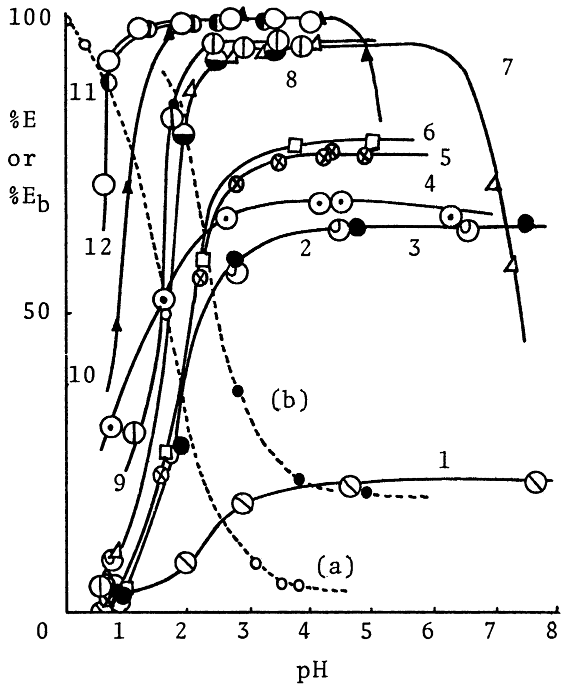

Fig.1. Extraction and back-extraction of various metal ions with isopentyl alcohol from 2M trichloroacetic acid buffer solution. Shaking: 1-15 min. Concn.of metal: 10^{-3}-10^{-4}mole/l.

1.Cs, 2.Ca, 3.Ba, 4.Hg, 5.Mn, 6.Co(II), 7.Cr, 8.Tm, 9.Al, 10.Fe, 11.Bi, 12.Th.

(a): back-extraction of Cr,

(b): back-extraction of Co(II).

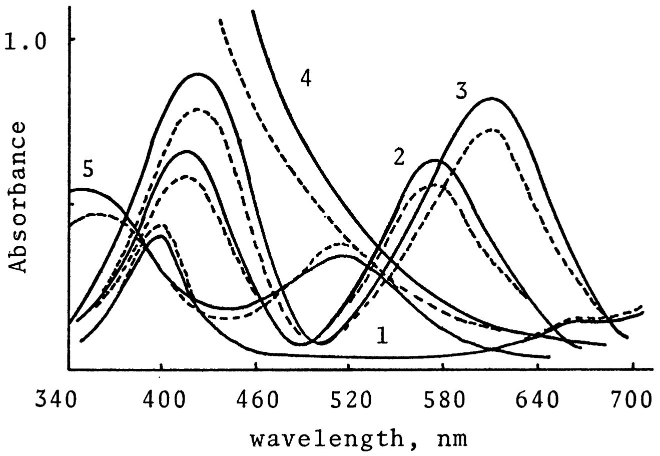

Fig.2. Absorption spectra of organic phase(——) after the extraction and of aqueous phase(---) before the extraction.

1: aqua complex of Ni(II).

2: aqua complex of Cr(III).

3: chloro complex of Cr(III).*

4: hydroxo complex of Fe(III).

5: ammine complex of Co(III).**

* $CrCl_3 \cdot 6H_2O$ was freshly dissolved in 0.1 M HCl

** Co(II) was oxidized with H_2O_2 in 1 M NH_3-NH_4Cl.

From the results obtained the extraction of Cr(III) from 2M trichloroacetic acid buffer solution seems to be attributted to the donor property of oxygen atom in the solvent molecules.

As one of the representatives of these polar solvents isopentyl alcohol was chosen and further extraction experiments of other metal ions were carried out. The results are shown in Fig.1. The absorption spectra of the isopentyl alcohol phase after the extraction and those of the aqueous phase before the extraction are shown in Fig.2. The similitude of the spectra of the organic phase and the aqueous phase of each metal species suggests that the inner solvation sphere of a metal does not alter before and after the extraction.

In order to certify this assumption a small portion of liquid taken from each phase was submitted to paper electrophoresis (applied potential: 14.9 V/cm, current: 9-10 mA, time; 180 min., base solution: 0.1 mole/l LiCl and 10^{-3}mole/l $HClO_4$ in 50 % ethanol.). The migration distance of each species can be seen from Table IV. In this test all species taken from both phases migrated toward the cathode and the migration distance of the same metal species was identical with each other.

The distribution of trichloroacetate anion between isopentyl alcohol and the aque-

Table IV. Migration distance of metal species.

Metal	Distance travelled, cm		Relative migration rate	
	hydrated ion in aq.phase(a)	extracted species in org.phase(o)	(a)	(o)
K	5.5(as reference)		1.0(as reference)	
Mn	4.2	4.4	0.76	0.84
Co	4.6	4.8	0.84	0.87
Cu	4.2	3.5	0.76	0.64
Al	4.3	4.2	0.78	0.76
Cr	3.8	3.8	0.69	0.69
Fe	0	0	0	0
Bi	0	0	0	0
Th	0	0	0	0

ous phase was determined at a definite pH by measuring the concentration of the anion in the both phases by means of Fujiwara's pyridine-alkali reaction[7] and by titration with a standardized sodium carbonate solution.

The distribution of trichloroacetate anion depends upon pH of the aqueous phase as shown in Fig.3. From this fact the extraction of metal ions from 2 M trichloroacetic acid buffer solution with the polar organic solvents also depends upon the concentration of trichloroacetate anion in the aqueous phase.

Consequently, the extraction of metal ion from trichloroacetic acid buffer solution may be caused by the formation of ion-pair of a hydrated metal ion with trichloroacetate ion, followed by the solvation with the organic solvent which has a donor oxygen atom.

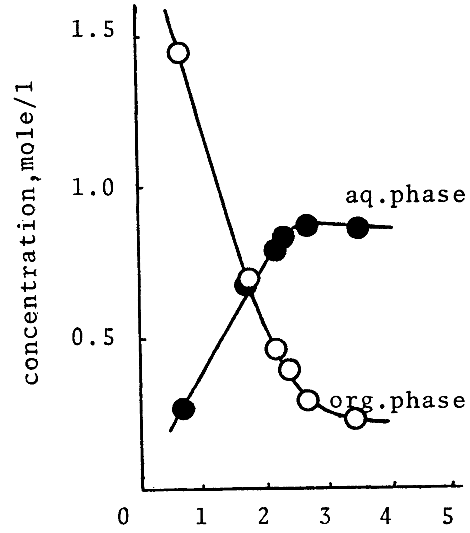

Fig.3. Distribution of CCl_3COO^- between isopentyl alcohol and aq.phase.

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