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The Separation of Aluminium(III) and Chromium(III) as Their AcAc(acetylacetone)-Complexes, and of Cobalt(II), Copper(II), Magnesium(II), Manganese(II), Nickel(II), and Lead(II) as Their TTA(thenoyltrifluoroacetone)-Complexes, by Extraction Chromatography

Takaharu HONJO, Yoshio HONDA, Tetsu MATSUMOTO, Ryumon HONDA, and Toshiyasu KIBA
Department of Chemistry, Faculty of Science, Kanazawa University, Marunouchi, Kanazawa 920

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Synopsis. The liquid-liquid extraction behavior of the Al(III) and Cr(III)–AcAc(acetylacetone)–$CHCl_3$ system and of the Mg(II), Pb(II), Mn(II), Co(II), Ni(II), and Cu(II)–TTA(thenoyltrifluoroacetone)–MIBK (isobutyl methyl ketone) system have been studied, and the results have been applied to the separation of these metals as their AcAc- and TTA-complexes by extraction chromatography.

The systematic and quantitative group separation of nineteen common cations by extraction chromatography has been devised in the authors' laboratory using the following six columns, in which the organic solvents were adsorbed on Kel-F(poly(chlorotrifluoroethylene)):[1)]

	Stationary phase (5.5 g Kel-F)	Mobile phase (HCl(M) or pH)	Metal ions retained (each 0.5 mg)
1	100% TBP(1)	2M HCl	Fe(III), Hg(II), Sn(IV)
2	20% TOA-CCl_4	2M HCl	Ag(I), Bi(III), Cd(II), Zn(II)
3	100% TBP(2)	6M HCl	Sb(III)
4	50% AcAc-$CHCl_3$	pH 5.0	Al(III), Cr(III)
5	1.5M TTA(1)-MIBK	pH 5.0	Co(II), Cu(II), Mg(II), Mn(II), Ni(II), Pb(II)
6	1.5M TTA(2)-MIBK	pH 7.0	Ca(II), Ba(II), Sr(II)

The mutual separation of the metal ions retained on each column has already been attempted by passing a suitable eluting solution through columns of TBP (tributyl phosphate) (1),[2)] TOA(trioctylamine)–CCl_4,[3)] and TTA(2)–MIBK(isobutyl methyl ketone).[4)] In this investigation, the extraction behavior of the Al(III) and Cr(III)–50% AcAc–$CHCl_3$ system and of the Co(II) Cu(II), Mg(II), Mn(II), Ni(II), and Pb(II)–0.2 M TTA–MIBK system have been examined, and the results have been applied to the mutual separation by extraction chromatography of the metals retained on the columns of the 50% AcAc–$CHCl_3$ system, and the 1.5 M TTA (1)–MIBK system.

Experimental

The experimental procedures were almost the same as those previously described.[1–6)] Into a 50-ml centrifuge tube, 50% AcAc in chloroform(10-ml) and an aqueous solution (10-ml) containing 0.5 mg each of Al(III) and Cr(III), 10-ml of 0.2 M TTA in MIBK, and 10-ml of an aqueous solution containing 10 ppm each of Co(II), Cu(II), Mg(II), Mn(II), Ni(II), and Pb(II) were put together, and the contents for each of the metal ions were agitated with a mechanical shaker for 30—40 min at room temperature (20—23 °C). The pH of the solution was adjusted to a desired value by using 0.5 M acetic acid or an aqueous ammonia solution. The pH was checked again after every extraction by means of the pH meter. In the case of Cr(III), the mixture was heated gently for 1 h until the completion of the formation of the AcAc-chelate of Cr(III) with or without Al(III), because the quantitative extraction of Cr(III) with 50% AcAc in chloroform was impossible at room temperature.[1,7)] The back extraction was carried out by shaking a 5-ml or 10-ml portion of the organic phase containing the extracted metal chelates with an aqueous solution of the desired acidity. The distribution ratios of the metals were determined radiometrically with Co-60, Cr-51, Mn-54, Ni-63, and Pb-210, colorimetrically for Al oxinate at 390 nm, or atomic absorptiometrically for Cu(II) and Mg(II). The extraction chromatography was carried out by using a glass chromatographic column (10 mm in diameter and 30 cm long, with a course frit at the bottom) containing a 5.5 g portion of Kel-F(40—80 mesh), a definite volume of 50% AcAc in chloroform (5.0-ml) and 1.5 M TTA in MIBK (6.5-ml) which had been pre-equilibrated with the eluting solution of pH 5.0, and a definite volume of the eluting solution(5.0—6.5 ml). A 50-ml sample solution containing 0.5 mg each of Co(II), Cu(II), Mg(II), Mn(II), Ni(II), and Pb(II), adjusted to pH 5.0, was passed through the column at the rate of 0.03—0.3 ml per minute, and then an eluting solution of a suitable pH, which had previously been pre-equilibrated with the organic solution of the stationary phase, was passed through at the flow rate of 0.4—0.5 ml per minute. The effluent was taken up in a fraction collector. In the case of the Al(III) and Cr(III)–50% AcAc–$CHCl_3$ system, a 100-ml sample solution of pH 5.0 containing acetylacetonates of Al(III) and Cr(III)(each 0.5 mg), which had been prepared by heating for an hour, was percolated through the column at the rate of 0.2-ml per minute, and then an eluting solution of a definite acidity was passed through at the flow rate of 0.5-ml per minute, as has previously been reported.[1)]

Theoretical

The percentage of extraction, % E, and the percentage of back extraction, % E_{back}, can be calculated by means of the following equations: % $E=D/(1+D)\cdot 100$, % $E_{\mathrm{back}}=D^*/(1+D^*)\cdot 100$, where D and D^* are the net distribution ratios of a metal in the extraction and in the back extraction respectively. The % E and the % E_{back} of metals in the column can be expressed by the following equation[5)]: % $E=(1-V^*/V_{\mathrm{m}})\cdot 100$, where V^* is the volume of the mobile phase and where V_{m} is the volume of the eluate relative to the maximum of the eluted metal concentration.

Results and Discussion

The symbols in Fig. 1 A→O and O→A denote the extraction and the back extraction of chemical species

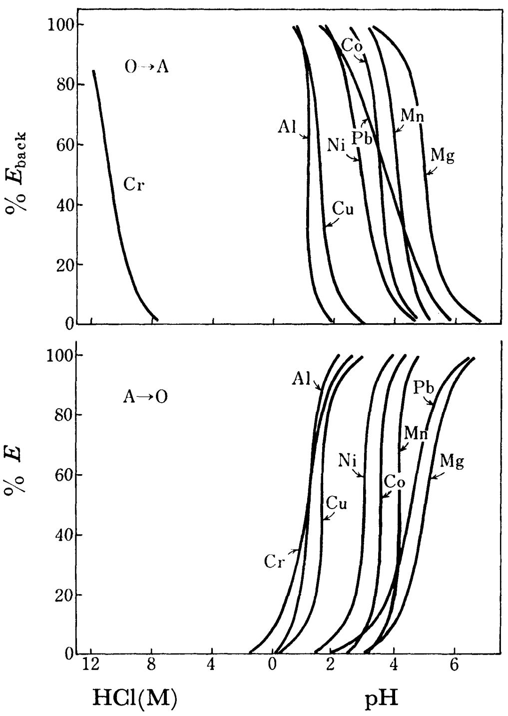

Fig. 1. The effect of pH or HCl(M) on the extraction and the back extraction of Al(III) and Cr(III)-50% AcAc-$CHCl_3$ system, and Co(II), Cu(II), Mg(II), Mn(II), Ni(II), and Pb(II)-0.2 M TTA-MIBK system.

respectively. The extraction and the back extraction are repeated in the column many times during the process of the extraction chromatography, which is closely related to the batch extraction; therefore, the optimum pH or acidity of the eluting solution can be predicted from the distribution ratios of the metals obtained by the ordinary extraction.[1-6] When the results of the batch extraction of metals with 0.2 M TTA in MIBK are applied by extraction chromatography to the mutual separation of metals retained on the column of the 1.5 M TTA-MIBK system, the eluting solution with every pH lower by 0.88 than that predicted from the batch extraction with the 0.2 M TTA-MIBK system was adopted, because the shift of the pH of the extraction curves to the lower pH region was assumed to be 0.87 when the concentration of TTA was changed from 0.2 M to 1.5 M. An optimum mutual separation of Al(III) and Cr(III) in the 50% AcAc-$CHCl_3$ system and of Co(II), Cu(II), Mg(II), Mn(II), Ni(II), and Pb(II) in the 1.5 M TTA-MIBK system was established by using the eluting solutions given in Fig. 2. The recovery of the metals was about 70—100 %. The deposit of some chelate in the column due to the loss of the stationary solvent phase was observed during the course of loading; this phenomenon may cause the lower recovery. The values of the distribution ratios of the metals obtained by the batch extraction and the extraction chromatography are summarized in Table 1. The main discrepancy between the two values may be caused by the differences in the contact times of the two phases and/or by the time-lag in the complex formation in the extraction and the back extraction, as has previously been pointed out by the present authors.[3-6]

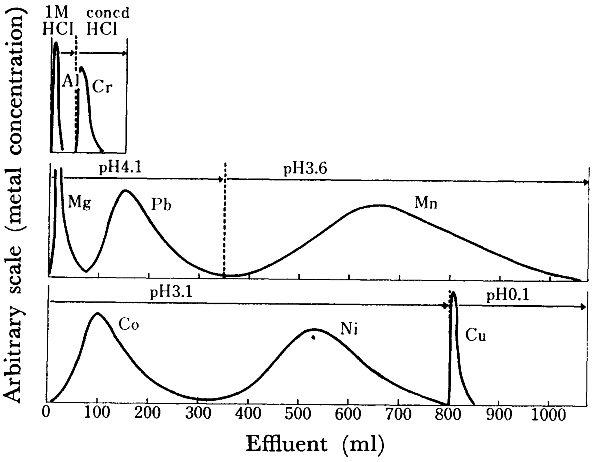

Fig. 2. The mutual separation of Al(III) and Cr(III) on a 50% AcAc-$CHCl_3$-Kel-F column, and Co(II), Cu(II), Mg(II), Mn(II), Ni(II), and Pb(II) on a 1.5 M TTA-MIBK-Kel-F column from a mixed solution.

TABLE 1. % E AND % E_{back} OF Al(III), Cr(III), Mg(II), Pb(II), Mn(II), Co(II), Ni(II), AND Cu(II) OBTAINED FROM THE EXTRACTION AND ELUTION CURVES

Metal	Acidity	Liquid-liquid extraction[a)]			Acidity	Extraction chromatography[b)]
		% E	% E_{back}			%
			Found	Calcd		
Al(III)	1M HCl	0	90	100	1M HCl	58
Cr(III)	concd HCl	0	85	100	concd HCl	55
Mg(II)	pH 5.0	50	50	50	pH 4.1	62
Pb(II)	pH 5.0	74	13	26	pH 4.1	96
Mn(II)	pH 4.5	94	18	6	pH 3.6	98
Co(II)	pH 4.0	94	13	6	pH 3.1	94
Ni(II)	pH 4.0	100	8	0	pH 3.1	99
Cu(II)	pH 1.0	8	90	92	pH 0.1	7

a) Al(III) and Cr(III) (each 0.5 mg)-50% AcAc-$CHCl_3$, Mg(II), Pb(II), Mn(II), Co(II), Ni(II), and Cu(II) (each 10 ppm)-0.2M TTA-MIBK systems. b) Al(III) and Cr(III) (each 0.5 mg)-50% AcAc-$CHCl_3$, Mg(II), Pb(II), Mn(II), Co(II), Ni(II), and Cu(II) (each 0.5 mg)-1.5 M TTA-MIBK systems.

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