BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(7), 1799—1800 (1974)

The Back-extraction Behavior of Chelate Compounds. I. The Extraction and the Back-extraction of the Metal Oxinates

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(Received November 15, 1973)

Synopsis. The behavior of trace amounts of silver, bismuth, cadmium, cerium, cobalt, europium, iron, mercury, indium, manganese, lead, scandium, and zinc in back-extraction have been examined in order to ascertain the basic conditions for the mutual separation of metals as their oxinates by back-extraction.

In recent years a number of investigations concerning the liquid-liquid extraction of metal oxinates have been reported and reviewed, but only a few back-extraction techniques have been treated and applied to the separation of metals.[1,2] In this investigation, the behavior of trace amounts of silver(I), bismuth(III), cadmium(II), cerium(III), cobalt(II), europium(III), iron(III), mercury(II), indium(III), manganese(II), scandium(III), and zinc(II) in back-extraction have been examined in order to ascertain the basic conditions for the mutual separation of metals as their oxinates by back-extraction. The results have then been applied to the separation of cobalt from mixtures of iron radioisotopes by means of back-extraction.

Experimental

Extraction. Extraction was carried out for a buffered solution containing a radioactive tracer; the solution was made to have 0.1 M acetic acid (in the acidic region) or 0.1 M boric acid (in the basic region), and its pH was adjusted to an appropriate value. A solution of 0.01—0.1 M oxine in chloroform (5 ml) was shaken by means of a mechanical shaker with an equal volume of an aqueous solution containing each metal for 30 min at room temperature (20—25 °C). After centrifugation, a 3 ml portion of each phase was pipetted out into a test tube, and the radioactivity was counted with the NaI(Tl) scintillation counter. The pH of the aqueous phase was measured again after extraction by means of the pH meter.

Back-extraction. A 5 ml aliquot of an organic phase which had been prepared by the standard extraction procedure was shaken with a 5 ml portion of an aqueous solution adjusted to a desired pH for 30 min at room temperature. The distribution was determined as in the case of the extraction.

Theoretical

The percentage of extraction, $\% E$, and the percentage of back-extraction, $\% E_{\mathrm{back}}$, can be calculated by means of the following equations:

$$\%E = D/(1+D)\cdot 100 \tag{1}$$

$$\%E_{\mathrm{back}} = D^*/(1+D^*)\cdot 100 \tag{2}$$

where D and D^* are the net distribution ratios of a metal in the extraction and in the back-extraction respectively.

Results and Discussion

The extraction of trace amounts of 13 metals was carried out with 0.01—0.1 M oxine in chloroform for each, while the back-extraction of the metal oxinates was done with various acidic and basic aqueous solutions.

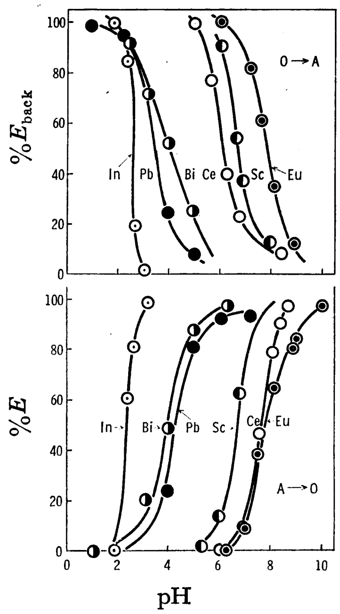

Fig. 1. The effect of pH or HCl(M) on the extraction and the back-extraction of trace amounts of Ag(I), Cd(II), Co(II), Fe(III), Hg(II), Mn(II), and Zn(II)-0.01—0.1 M oxine-chloroform system.

The results are shown in Figs. 1—2 as a function of the pH or HCl(M) of the aqueous phase. The symbols in the two figures, A→O and O→A, denote the extraction and the back-extraction of chemical species respectively.

The data on the $\mathrm{pH}_{1/2}$ values of metal oxinates obtained in the present extraction system are summarized in Table 1. The difference in $\mathrm{pH}_{1/2}$ gaves larger in the order of Fe(III), Sc(III), Zn(II)<Cd(II), Eu(III)<Bi(III)<In(III)<Hg(II)<Ce(III)<Ag(I)<Pb(II)<Mn(II)<Co(II). The disagreement of the $\mathrm{pH}_{1/2}$ values appearing in the liquid-liquid extraction of the chelates indicates that the extraction equilibrium is not strictly reached under the present conditions. The fact that the extraction and the back-extraction curves of cobalt oxinate are quite different, *i.e.*, the nonequilibrium nature of the process, may be useful for the back-extraction separation of metals.

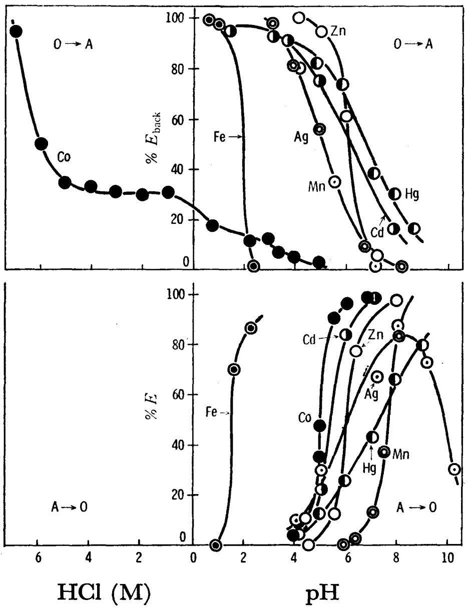

Fig. 2. The effect of pH on the extraction and the back-extraction of trace amounts of Bi(III), Ce(III), Eu(III), In(III), Pb(II), and Sc(III)-0.01—0.1 M oxine-chloroform system.

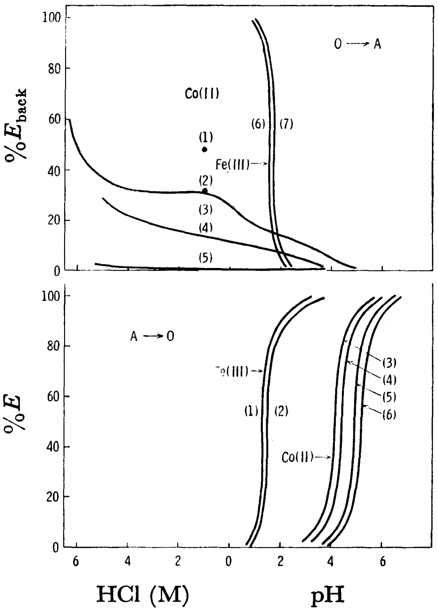

Fig. 3. The extraction and the back-extraction of Co(II) and Fe(III) with 0.01 M oxine in chloroform under various conditions.

Extraction:

	(1)	(2)	(2)	(3)	(4)	(5)	(5)	(6)
Co(II) (M)	None	None	10^{-3}	Trace	Trace	Trace	10^{-3}	Trace
Fe(III) (M)	10^{-3}	Trace	Trace	10^{-3}	10^{-4}	10^{-5}	None	None

Back-extraction:	(1)	(2)	(3)	(4)	(5)
Extraction pH	6.0	6.0	6.0	8.0	6.0
Shaking time (min)	30	5	30	30	90
Co(II) (M)	10^{-1}	Trace	Trace	Trace	Trace
Fe(III) (M)	None	None	None	None	None

	(5)	(6)	(6)	(8)
Extraction pH	6.0	3.5	3.5	3.5
Shaking time (min)	90	30	30	30
Co(II) (M)	Trace	None	10^{-3}	None
Fe(III) (M)	10^{-3}	Trace	Trace	10^{-3}

As can been seen in Fig. 3, the back-extractability of cobalt decreases as the shaking time becomes longer, and the pH values increase.

This abnormal behavior of cobalt oxinates seems to be caused by the transformation of $Co(Ox)_2$ into a certain inert complex such as $Co(Ox)_3$.3)

The range of the extraction of cobalt shifts to a lower pH as the concentration of the coexisting iron increases; that is, the mutual separation of cobalt and iron with oxine in chloroform seems to be unattainable in the regular extraction. When a sample solution the pH of which had been adjusted to 6.0 was shaken with a 0.01 M oxine-chloroform solution for 90 min, the extraction of cobalt and iron proceeded quantitatively. Iron, however, could be stripped out of the organic phase by shaking it with an aqueous solution of a 1 M HCl solution for 30 min, while all cobalt remained in the organic phase. Thus, the data on metal oxinates in the extraction and the back-extraction may give valuable hints for finding the best conditions for the mutual separation of other metals as their oxinates by back-extraction, as has already been reported by the present authors for the Co(II)-Ni(II)-STTA-cyclohexane system.4)

TABLE 1. $pH_{1/2}$ DETERMINED BY THE EXTRACTION AND THE BACK-EXTRACTION OF METALS WITH 0.01—0.1 M OXINE IN CHLOROFORM

Metal	HOx (M)	$pH_{1/2}$	
		Extraction	Back-extraction
Ag(I)	0.1	6.10	5.10
Bi(III)	0.01	4.20	4.05
Cd(II)	0.1	5.40	5.50
Ce(III)	0.01	7.68	6.70
Co(II)	0.01	5.10	5 M HCl
Eu(III)	0.01	7.85	7.75
Fe(III)	0.01	1.50	1.50
Hg(II)	0.01	7.80	7.50
In(III)	0.01	2.35	2.60
Mn(II)	0.01	7.70	5.35
Pb(II)	0.01	4.45	3.00
Sc(III)	0.01	6.67	6.67
Zn(II)	0.01	6.10	6.10

We would like to thank the Ministry of Education for its Scientific Research Grant to one of us (T.H.).

References

1) K. Motojima and H. Hashitani, *Bunseki Kagaku*, **9**, 151 (1960).
2) J. Stary, *Anal. Chim. Acta*, **28**, 132 (1963).
3) S. Oki, *ibid.*, **50**, 465 (1970).
4) T. Honjo, T. Unemoto, and T. Kiba, *Bunseki Kagaku*, **23**, 203 (1973).