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The Back-extraction Behavior of Chelate Compounds. III.† The Extraction and the Back-extraction of the Metal (II) Diethyldithiocarbamates

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Synopsis. The behavior of trace amounts of cadmium(II), cobalt(II), copper(II), iron(II), mercury(II), manganese (II), nickel(II), lead(II), and zinc(II) in backextraction has been examined in order to establish the basic conditions for the separation of metals as their diethyldithiocarbamates by back-extraction.

A number of papers and reviews concerning the solvent extraction of metal diethyldithiocarbamates have been presented, but scarcely no back-extraction techniques have been examined and applied to the separation of metals.$^{1)}$ In the present work, the behavior of trace amounts of cadmium(II), cobalt(II), copper(II), iron(II), mercury(II), manganese(II), nickel(II), lead(II), and zinc(II) in back-extraction has been examined in order to establish the basic conditions for the separation of metals as their diethyldithiocarbamates by back-extraction.

Experimental

Extraction. Extraction was carried out with a buffered solution containing a radioactive tracer; the pH was adjusted to the desired value by mixing an appropriate amount of 10^{-2} M (1M=1 mol dm^{-3}) of hydrochloric acid, acetic acid, sodium acetate, and sodium hydroxide. A solution of 5×10^{-3} M of DDDC (diethylammonium diethyldithiocarbamate) in carbon tetrachloride (10 cm^3) was shaken by means of a mechanical shaker (340 strokes/min) with an equal volume of an aqueous solution containing 10^{-4} M of each metal for 5 min at room temperature (20—25 °C). After centrifugation, a 3-cm^3 portion of each phase was pipetted out into a test tube, after which the radioactivity was counted with a NaI(Tl) scintillation counter. The distributions of Cu(II) and Ni(II) were spectrophotometrically determined by measuring the absorbance of $\mathrm{Cu(DDC)_2}$ at 436 nm and that of $\mathrm{Ni(DDC)_2}$ at 440 nm respectively. The concentration of uncomplexed DDDC in the organic phase was spectrophotometrically determined as a copper chelate in carbon tetrachloride. The pH of the aqueous phase was measured again after extraction by means of the pH meter.

Back-extraction. Since an organic phase which had been prepared by the standard extraction procedure contained an uncomplexed DDDC in a different quantity because of its decomposition, the organic phase was shaken with a buffered solution of pH 8—9 in order to remove the uncomplexed DDDC just before the back-extraction procedure. Then a 5-cm^3 aliquot of the organic phase was shaken with a 5-cm^3 portion of an aqueous solution adjusted to the desired pH or acidity for 5 min at room temperature. The distribution was determined as in the case of the extraction.

Percent Extraction. The percentage of extraction, %E, and the percentage of back-extraction, $\%\,E_{\mathrm{back}}$ can be calculated by means of these equations: $\%E=D(1+D)\times100$ and $\%E_{\mathrm{back}}=D^*(1+D^*)\times100$, where D and D^* are the net distribution ratios of a metal in the extraction and the back-extraction respectively.

Results and Discussion

The shaking time of 5 min was preferred in the extraction process, because the decomposition of DDDC and its metal chelates seems quite small within this time, as is shown in Fig. 1. The Mn–DDC chelate extracted was the most unstable among all the metal–DDC chelates in carbon tetrachloride, and decomposed gradually just after the extraction. The extraction of 10^{-4} M of 9 divalent metals was carried out with 5×10^{-3} M of DDDC in carbon tetrachloride for each, while the back-extraction of the metal diethyldithiocarbamates extracted was done with various acidic and basic aqueous solutions. The results are shown in Fig. 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,

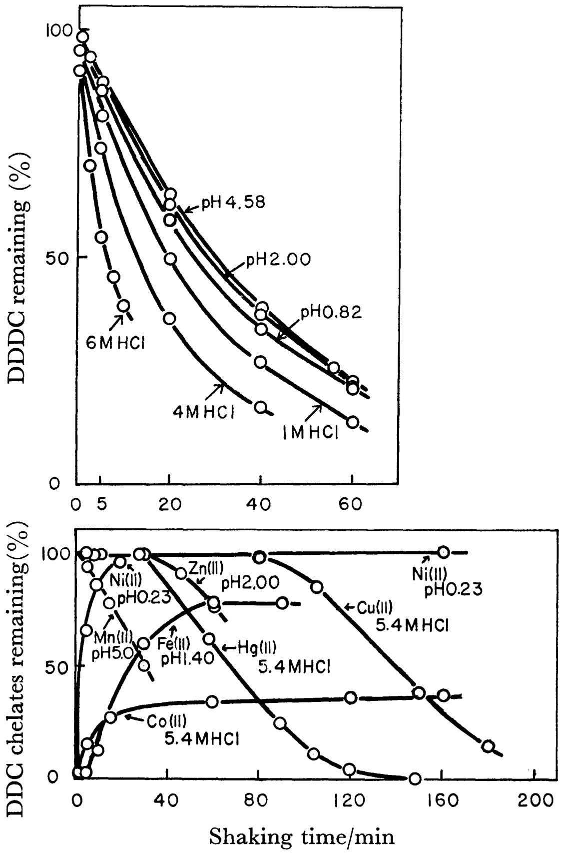

Fig. 1. Percentage of remaining of 10^{-3} -10^{-2} M of DDDC and its metal chelates in carbon tetrachloride on continuous shaking with an aqueous solution of various pH or various concentration of hydrochloric acid.

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† Part II: T. Honjo*, T. Unemoto, and T. Kiba, *Bull. Chem. Soc. Jpn.*, **48**, 1651 (1975).

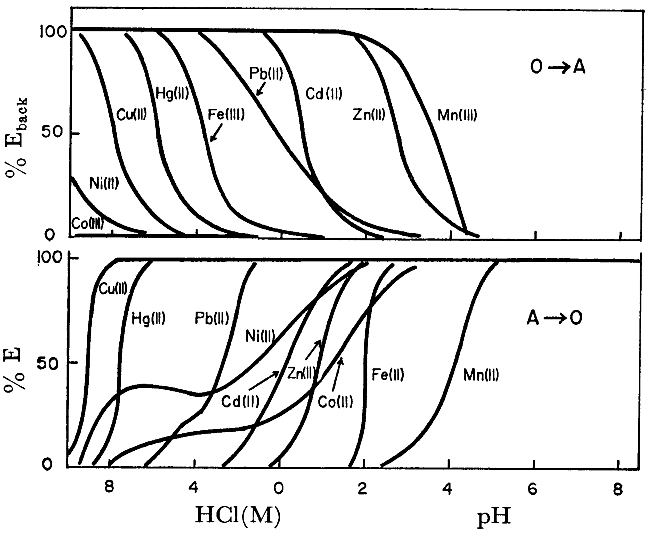

Fig. 2. Extraction and back-extraction curves of metal–5×10^{-3} M of DDDC–carbon tetrachloride systems.

denote the extraction and the back-extraction of the chemical species respectively. The data on the $pH_{1/2}$ values (the pH of the half-extraction) and the $HCl_{1/2}$ (the concentration of hydrochloric acid of the half-extraction of metal diethyldithiocarbamates) obtained in the present extraction system are summarized in Table 1. The disagreement of the $pH_{1/2}$ and the $HCl_{1/2}$ values appearing in the liquid-liquid extraction of Cu(II), Hg(II), Pb(II), Cd(II), and Zn(II) with DDDC may be due to the fact that the concentration of DDDC is equivalent to those of metals in carbon tetrachloride in the back-extraction. The curves of Mn(II), Fe(II), Co(II), and Ni(II) in the extraction and the back-extraction give asymmetrical forms, suggesting an irreversible extraction process, *i.e.*, the oxidation of the metals or a slow rate of chelate formation during extraction. However, the curves of Zn(II) and Hg(II) in the extraction and the back-extraction became exactly symmetrical when the back-extraction was carried out with 5.0×10^{-3} M of DDDC in carbon tetrachloride. The solvent effect on the extractions of Zn(II) and Mn(II) with DDDC has also been investigated. As is shown in Fig. 3, Zn(II) and Mn(II) are readily extracted with non-polar solvents, such as benzene and carbon tetrachloride. The extractability of Zn(II) and Mn(II) with DDDC in nitrobenzene was found to be enhanced. The unstable $Mn(DDC)_3$ in carbon tetrachloride after extraction was not decomposed for at least 15 min with 12% nitrobenzene and not for 1 h with 80% nitrobenzene. This fact may result from the solvation effect of nitrobenzene, which has polarity; this polarity decreases the decomposition of DDDC and its metal chelates.

TABLE 1. $pH_{1/2}$ AND $HCl_{1/2}$ VALUES DETERMINED BY THE EXTRACTION AND THE BACK-EXTRACTION OF METALS WITH 5×10^{-3} M OF DDDC IN CARBON TETRACHLORIDE

Metal	$pH_{1/2}$ or $HCl_{1/2}$	
	Extraction	Back-extraction[a]
Cd(II)	0.1	0.4
Co(II)	1.2	>10 M[b]
Cu(II)	9.0 M	7.8 M
Fe(II)	2.1	3.8 M[b]
Hg(II)	7.5 M	5.8 M
Mn(II)	4.3	3.6[b]
Ni(II)	1.3 M	>10 M
Pb(II)	2.6 M	0 M
Zn(II)	1.0	2.7

a) Without uncomplexed DDDC. b) The (III) valent metals of the extract ascertained by means of mass spectrometry. Conditions: electron energy, 75 eV; current, 200 μA; temperature, 140—160 °C; parent peaks (m/e): 503 for $Co(DDC)_3^+$, 450 for $Fe(DDC)_3^+$, and 499 for $Mn(DDC)_3^+$.

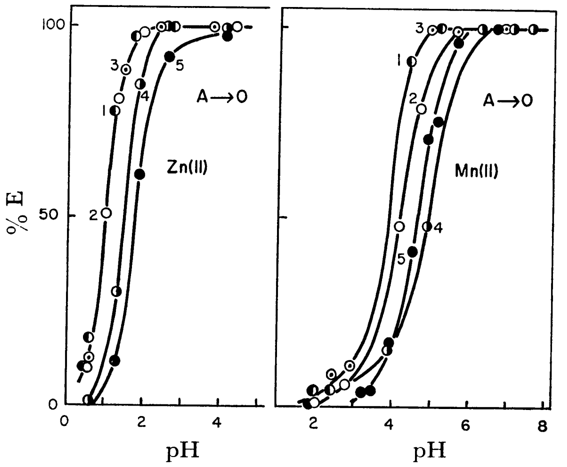

Fig. 3. Effect of diluent on the extraction of Zn(II) and Mn(II) with DDDC in various organic solvents.
1 —◐— Nitrobenzene, 2 —○— carbon tetrachloride, 3 —⊙— benzene, 4 —◑— chloroform, 5 —●— methyl isobutyl ketone.

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References

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