Studies of the Solvent Extraction of Zirconium-95 in the Tribenzylamine-Hydrochloric Acid System

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(Received December 17, 1962)

In a previous paper[1], the mechanism of the amine extraction of niobium-95 was reported on and the niobium species in a hydrochloric acid solution were estimated. If the zirconium species in the same medium were known, the separation of zirconium and niobium could be carried out successfully. Although a number of investigations have been carried out on the zirconium species in a hydrochloric acid solution, the results reported are not in satisfactory agreement with each other[2-4].

In the present paper, the distribution of carrier-free zirconium-95 between hydrochloric acid and tribenzylamine is investigated.

Experimental

Carrier-free zirconium-95 was prepared from zirconium-niobium-95 by the anion-exchange resin method and was stored in 9 N sulfuric acid. Before being used for each experiment, zirconium-95 was extracted with acetylacetone from an aqueous solution containing hydrogen peroxide[5]. The zirconium-95, being free from niobium-95, was then converted

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[1] T. Omori and N. Suzuki, This Bulletin, 35, 1633 (1962).

[2] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal Ion Complexes, Part II: Inorganic Ligands", The Chemical Society, London (1958), p. 94.

[3] B. A. J. Lister and L. A. McDonald, *J. Chem. Soc.*, **1952**, 4315.

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into the chloride form by back extraction with concentrated hydrochloric acid. The experiments were carried out within four hours to avoid the error due to the growth of niobium-95.

All the other chemicals and the techniques employed were similar to those described in the previous paper[1].

The experiments were carried out at 25±0.5°C unless otherwise stated.

Results and Discussion

The Distribution Mechanism and Some Related Equations.—It has been revealed that the anionic species in the aqueous phase are transferred to the organic phase in the amine extraction through the anion exchange mechanism and that, for the niobium-tribenzylamine system, the metal complexes in the organic phase form the more stable additive compounds with the amine. Thus, the distribution coefficient for zirconium, D_{Zr}, can be represented in terms of activities as follows:

$$D_{\mathrm{Zr}}=\frac{\sum\limits_{p}\sum\limits_{q}\sum\limits_{i}(\mathrm{R}_{p+q-4}\mathrm{Zr(OH)}_p\mathrm{Cl}_q\cdot i\mathrm{RCl})_{\mathrm{o}}}{\sum\limits_{m}\sum\limits_{n}(\mathrm{Zr(OH)}_m\mathrm{Cl}_n{}^{(4-m-n)+})_{\mathrm{a}}}$$

$$=\frac{(\mathrm{Cl}^-)_{\mathrm{a}}{}^4}{\sum\limits_{m}\sum\limits_{n}(\beta_{m,n}(\mathrm{H}^+)_{\mathrm{a}}{}^{-m}(\mathrm{Cl}^-)_{\mathrm{a}}{}^{n})}$$

$$\times\sum_{p}\sum_{q}\sum_{i}(K_{p,q}\cdot K_i\cdot\beta_{p,q}(\mathrm{RCl})^{p+q+i-4}$$

$$\times(\mathrm{H}^+)_{\mathrm{a}}{}^{-p}(\mathrm{Cl}^-)_{\mathrm{a}}{}^{-p})$$

$$(5\leq(p+q)\leq8) \qquad (1)$$

where the subscripts a and o denote the aqueous and organic phases respectively, and RCl represent the chloride form of tribenzyl amine (TBA-Cl). $K_{p,q}$, K_i and $\beta_{m,n}$ are defined as follows:

$$K_{p,q}=\frac{(\mathrm{R}_{p+q-4}\mathrm{Zr(OH)}_p\mathrm{Cl}_q)_{\mathrm{o}}(\mathrm{Cl}^-)_{\mathrm{a}}{}^{p+q-4}}{(\mathrm{Zr(OH)}_p\mathrm{Cl}_q{}^{(4-p-q)+})_{\mathrm{a}}(\mathrm{RCl})_{\mathrm{o}}{}^{p+q-4}} \qquad (2)$$

$$K_i=\frac{(\mathrm{R}_{p+q-4}\mathrm{Zr(OH)}_p\mathrm{Cl}_q\cdot i\mathrm{RCl})_{\mathrm{o}}}{(\mathrm{R}_{p+q-4}\mathrm{Zr(OH)}_p\mathrm{Cl}_q)_{\mathrm{o}}(\mathrm{RCl}_{\mathrm{o}})^{i}} \qquad (3)$$

$$\beta_{m,n}=\frac{(\mathrm{Zr(OH)}_m\mathrm{Cl}_n{}^{(4-m-n)+})_{\mathrm{a}}}{(\mathrm{ZrCl}_6{}^{2-})_{\mathrm{a}}}$$

$$\times(\mathrm{H}^+)_{\mathrm{a}}{}^{-m}(\mathrm{Cl}^-)_{\mathrm{a}}{}^{6-n} \qquad (4)$$

For the sake of simplicity it is assumed in these expressions that only mononuclear complexes exist in solutions. The activities of the species concerned have been employed in a way similar to that reported previously[1].

The Variation of the Distribution Coefficient with Hydrochloric Acid and TBA-Cl Concentrations.—The distribution of zirconium-95 between hydrochloric acid and a TBA-Cl solution in chloroform was determined. As is shown in Fig. 1, the distribution of zirconium-95 increases with an increase in the concentration of hydrochloric acid and TBA-Cl.

The Dependence of the Distribution Coefficient for Zirconium-95 on the Tribenzyl Amine Concentration.—A plot of log D_{Zr} against log$(\mathrm{RCl})_{\mathrm{o}}$ in Fig. 2 gives two straight lines with a slope of 2.8 up to 0.06 M TBA-Cl and of 3.8 above this point, indicating that one molecule of the zirconium complex associates with up to four molecules of TBA-Cl. At a constant acidity and chloride level, Eq. 1 can be written by:

$$D_{\mathrm{Zr}}=$$

$$\frac{\sum K_5\cdot(\mathrm{RCl})_{\mathrm{o}}+\{\sum K_6+\sum(K_5\cdot K_{i=1})\}(\mathrm{RCl})_{\mathrm{o}}{}^2+\cdots}{F(\mathrm{H,\ Cl})} \qquad (5)$$

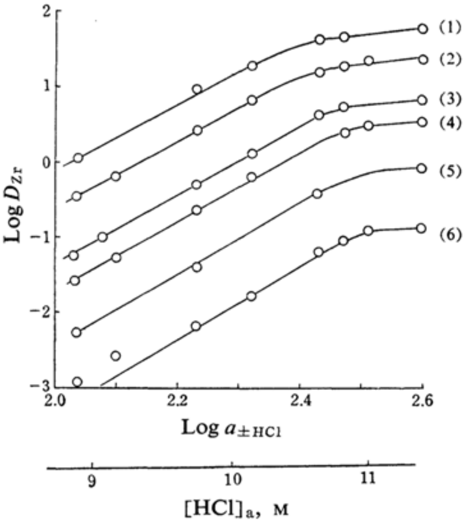

Fig. 1. Distribution of zirconium between hydrochloric acid and TBA-chloroform at 25°C.

	(1)	(2)	(3)	(4)	(5)	(6)
$[\mathrm{RCl}]_{\mathrm{o}}$, M:	0.200	0.150	0.100	0.075	0.050	0.025

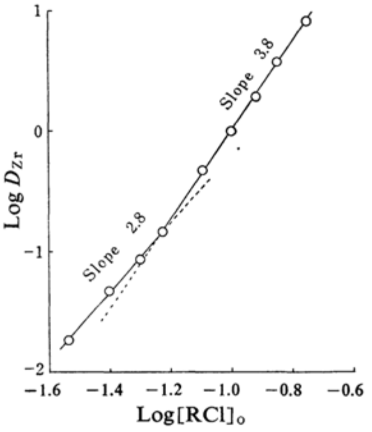

Fig. 2. TBA dependence of D_{Zr} values for zirconium at 25°C.

in which

$$F(\mathrm{H, Cl})=\frac{(\mathrm{Cl}^-)_\mathrm{a}{}^4}{\sum\sum\{\beta_{m,n}(\mathrm{H}^+)_\mathrm{a}{}^{-m}(\mathrm{Cl}^-)_\mathrm{a}{}^n\}}$$

$$K_5=K_{p,q(p+q=5)}\beta_{p,q(p+q=5)} \times(\mathrm{H}^+)_\mathrm{a}{}^{-p}(\mathrm{Cl}^-)_\mathrm{a}{}^{-p} \qquad (6)$$

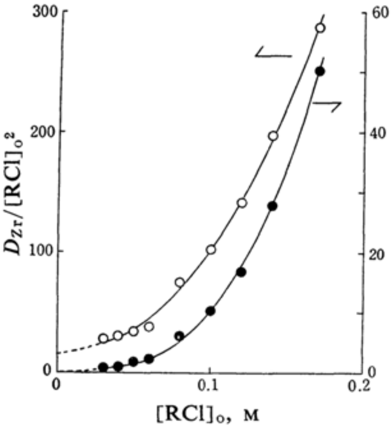

Fig. 3. Plot of $D_{\mathrm{Zr}}/[\mathrm{RCl}]_\mathrm{o}$ and $D_{\mathrm{Zr}}/[\mathrm{RCl}]_\mathrm{o}{}^2$ vs. $[\mathrm{RCl}]_\mathrm{o}$ for zirconium.

The plots of $D_{\mathrm{Zr}}/(\mathrm{RCl})_\mathrm{o}$ and $D_{\mathrm{Zr}}/(\mathrm{RCl})_\mathrm{o}{}^2$ against $(\mathrm{RCl})_\mathrm{o}$ are given in Fig. 3. The plot of $D_{\mathrm{Zr}}/(\mathrm{RCl})_\mathrm{o}$ against $(\mathrm{RCl})_\mathrm{o}$ provides a curve passing through the point of origin, showing that the values of $K_{p,q(p+q=5)}$ are equal to zero; i. e., the zirconium species with the charge of -1 are not extracted. The value of $\sum K_{p,q(p+q=6)}$ obtained by extrapolation of the plot of $D_{\mathrm{Zr}}/(\mathrm{RCl})_\mathrm{o}{}^2$ vs. $(\mathrm{RCl})_\mathrm{o}$ to a zero concentration of TBA-Cl is not equal to zero. Thus, one of the charge numbers of the zirconium chloro-complexes extracted is probably -2.

The Dependence on Chloride Ion and Hydrogen Ion Activities.—The dependence of the distribution coefficients on the chloride ion activities is given by the differentiation of Eq. 1 with respect to chloride ion activity at a constant acidity:

$$\frac{\partial \log D_{\mathrm{Zr}}}{\partial \log(\mathrm{Cl}^-)_\mathrm{a}}=4-\bar{p}-\bar{n} \qquad (7)$$

In this experiment, the concentration of hydrochloric acid was held at 7.62 M, while the chloride ion activity was varied by the addition of lithium chloride. As is shown in Fig. 4, the distribution coefficients in hydrochloric acid-lithium chloride mixed solutions are lower than those in a hydrochloric acid solution over the range of chloride ion activity investigated, because of the deficiency of the acidity.

The distribution curve has a slope of four at higher chloride ion activities. This suggests, according to Eq. 7, that the zirconium exists as Zr^{4+} in the aqueous phase, i. e., $\bar{p}+\bar{n}=0$, and that $\mathrm{ZrCl_6}^{2-}$ (viz., $\bar{p}=0$) is extracted to the organic phase; however, the existence of a zirconyl ion can not be ignored, as will be mentioned later.

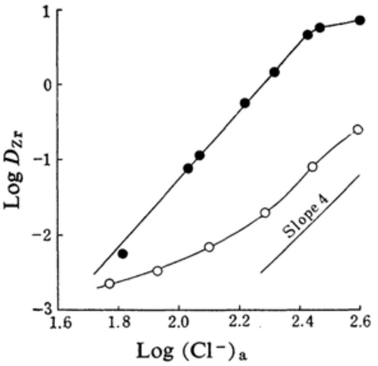

Fig. 4. Chloride dependence of D_{Zr} values for zirconium at 25°C.

○ HCl-LiCl mixture $[\mathrm{H}^+]_\mathrm{a}=7.62$ M
● Pure HCl

Proceeding as above, the following equation can be derived from Eq. 1 at a constant chloride level:

$$\frac{\partial \log D_{\mathrm{Zr}}}{\partial \log(\mathrm{H}^+)_\mathrm{a}}=\bar{m}-\bar{p} \qquad (8)$$

By using hydrochloric acid-lithium chloride mixtures, the chloride levels were held at 9.45 and 11.5 M, while the hydrogen ion activity was varied. The plot in Fig. 5 has a slope of ca. 2, i. e., $\bar{m}-\bar{p}=2$, when the chloride level was held at 11.5 M. Since $\bar{p}$ is equal to zero at a high chloride level, even in the region of relatively lower acidity (7.62 M), $\bar{m}$ should be equal to two. These suggest that the extractable species, $\mathrm{ZrCl_6}^{2-}$, can be formed by the action of hydrogen ions as follows:

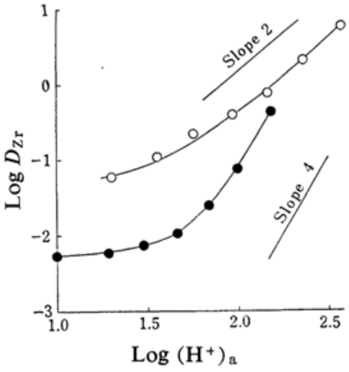

Fig. 5. Acid dependence of D_{Zr} values for zirconium at 25°C.

○ $[\mathrm{Cl}^-]_{\mathrm{a,total}}=11.5$ M
● $[\mathrm{Cl}^-]_{\mathrm{a,total}}=9.45$ M

$$Zr(OH)_2Cl_n^{(2-n)+} + 2H^+ + (6-n)Cl^- \rightleftharpoons ZrCl_6^{2-} + 2H_2O \quad (9)$$

Since the slope decreases as the acidity decreases, zirconium-95 may be partly extracted as $Zr(OH)_2Cl_4^{2-}$, which is formed from the zirconyl ion existing predominantly in the aqueous phase.

On the other hand, at a lower chloride level (9.45 M) such a plot shows a curve with a slope of four (Fig. 5), indicating the hydrolysis and/or the polymerization of the zirconium species. Thus, it should be recognized that hydrogen ions play a very important role in the zirconium extraction.

Temperature Effect.—It has been found that the extraction of the niobium with TBA-Cl is fairly much affected by the temperature[1]. Similar studies of the zirconium were carried out at 10±0.5 and 40±0.5°C. These results are shown in Fig. 6. There is an appreciable difference among the distribution curves obtained at different temperatures. At 40°C the distribution curve has a maximum in the region of higher acidity, whereas at 10°C it shows a straight line over the acidity range investigated. From the slope of the distribution curves in Fig. 6 it is concluded that the reaction expressed in Eq. 9 is promoted with an increase in the temperature.

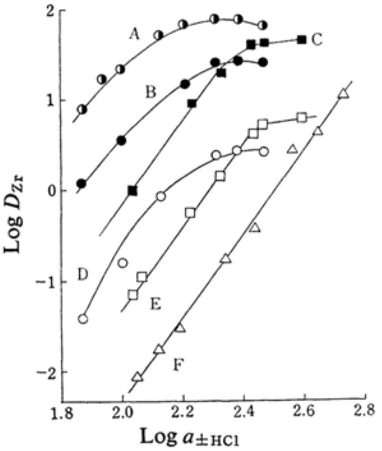

Fig. 6. Temperature dependence of D_{Zr} values for zirconium.

	$[RCl]_o$, M	Temp., °C
A	0.300	40
B	0.200	40
C	0.200	25
D	0.100	40
E	0.100	25
F	0.100	10

To judge from the above considerations, the extraction processes of zirconium-95 from hydrochloric acid solutions with tribenzylamine are presumably shown by the following reactions:

$$\begin{aligned} ZrCl_6^{2-} + 2RCl &\rightleftharpoons R_2ZrCl_6 + 2Cl^- \\ R_2ZrCl_6 + 2RCl &\rightleftharpoons R_2ZrCl_6\cdot 2RCl \end{aligned} \quad (10)$$

and partly

$$\begin{aligned} Zr(OH)_2Cl_4^{2-} + 2RCl &\rightleftharpoons R_2Zr(OH)_2Cl_4 + 2Cl^- \\ R_2Zr(OH)_2Cl_4 + 2RCl &\rightleftharpoons R_2Zr(OH)_2Cl_4\cdot 2RCl \end{aligned} \quad (11)$$

Although it is considered that the greater part of zirconium is extracted through the process expressed in Eq. 10, the $K_{p=0,q=6}$ value is relatively small in comparison with the $K_{i=2}$ value, as has been shown in the case of the niobium extraction[1]. The formation constants, $\beta_{m,n}$, for the zirconium chloro-complexes and the distribution constants, $k_{p,q}$, can not be obtained because of their complexity, but the authors have drawn up a scheme (Fig. 7) concerning the zirconium species in the chloride system. This includes the most probable species.

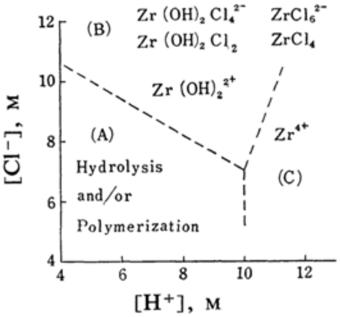

Fig. 7. Zirconium species in hydrochloric acid-lithium chloride solutions at 25°C.

The Possibility of the Mutual Separation of Zirconium-95 and Niobium-95.—In spite of the usefulness of the mutual separation of zirconium-niobium-95 in hydrochloric acid solutions, such a separation has not been carried out completely[6]. However, the more effective separation of zirconium and niobium can be expected, since there is an appreciable difference between the distribution coefficients of the zirconium and niobium with regard to the dependence of the distribution coefficient on the hydrogen ion concentration.

The separation factor, SF, under various conditions of a hydrochloric acid-lithium chloride solution at 25°C are tabulated in Table I. The separation factor increases up to 200 with a 7.6 M hydrochloric acid-0.8 M lithium chloride mixture, whereas it is 110 under optimum conditions for hydrochloric acid alone.

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[6] E. H. Huffman and R. C. Lilly, *J. Am. Chem. Soc.*, 73, 4474 (1951).

The separation factor as a function of temperature is also given in Table II. The separation factor is remarkably affected by the temperature and, even at 7.6 M hydrochloric acid, has a high value of 400 at 10°C. Since at a lower temperature the reaction expressed in Eq. 9 to zirconium is effectively restricted in comparison with the similar reaction to niobium, the higher separation factor is to be expected at lower temperature under suitable conditions, e. g., 7.5 M hydrochloric acid-1 M lithium chloride.

Table I. Separation factor, SF*, in hydrochloric acid-lithium chloride solution at 25°C ($[RCl]_o=0.100$ M)

[HCl] M	[LiCl] M	$\log D_{Nb}$	$\log D_{Zr}$	SF
7.6	—	−0.59	−2.64	110
8.0	—	−0.42	−2.20	62
9.0	—	−0.11	−0.98	7.4
2.5	9.0	0.28	−1.95	170
4.0	7.5	0.28	−1.67	89
7.6	0.3	−0.42	−2.64	166
7.6	0.8	−0.24	−2.54	200

* $SF=D_{Nb}/D_{Zr}$

Table II. Separation factor in hydrochloric acid solution as a function of temperature ($[RCl]_o=0.100$ M)

[HCl] M	$\log D_{Nb}$	$\log D_{Zr}$	SF	Temp. °C
7.6	−0.50	−2.52	100	40
7.6	−0.59	−2.64	110	25
7.6	−0.68	−3.28	400	10
8.0	−0.35	−2.08	54	40
8.0	−0.42	−2.20	62	25
8.0	−0.51	−2.90	310	10
9.0	−0.06	−0.89	6.8	40
9.0	−0.11	−0.98	7.4	25
9.0	−0.06	−1.58	33	10

In the TBA extraction, however, the distribution coefficients for both zirconium and niobium are relatively so small that it is desirable to use other amines, possessing a higher extractability for niobium.

Summary

The extraction process of zirconium-95 from hydrochloric acid solutions tribenzylamine is shown by the following reactions:

$$ZrCl_6^{2-} + 2RCl \rightleftharpoons R_2ZrCl_6 + 2Cl^-$$

followed by the reaction of the above species with TBA-Cl in a chloroform solution:

$$R_2ZrCl_6 + 2RCl \rightleftharpoons R_2ZrCl_6\cdot 2RCl$$

The main extractable species of zirconium, $ZrCl_6^{2-}$, is formed from the zirconyl ions:

$$Zr(OH)_2Cl_n^{(2-n)+} + 2H^+ + (6-n)Cl^- \rightleftharpoons ZrCl_6^{2-} + 2H_2O$$

On the basis of the present results and of previously reported data on niobium extraction, some information with respect to the optimum conditions for the separation of zirconium and niobium have been given.

The authors wish to express their hearty thanks to Professor Takanobu Shiokawa and Assistant Professor Kunio Seto for their kind suggestions made in the course of this work.

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