Studies of the Solvent Extraction of Niobium-95 in the Tribenzyl Amine-Hydrochloric Acid System

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There are many reports on the solvent extraction of metals, but these extraction methods are only applicable to the particular cases described in these papers. The present authors have undertaken a quantitative investigation of solvent extraction and have made an effort to elucidate the chemical behavior of metals in the case of solvent extraction. One of the authors has already reported the quantitative treatment of the solvent extraction of ^{144}Ce with acetylacetone[1]. Recently, we both reported the mutual separation of ^{95}Zr and ^{95}Nb with acetylacetone[2].

Since about 1958 there has been a rapid developement in amine extraction, particularly for uranium extraction[3]. It has been reported that the mechanism of amine extraction is similar to that of anion exchange[3-5]. However, phenomena which can not be completely explained as anion exchange mechanism have been found in a few reports[6-8].

In the present paper, the distribution coefficients of ^{95}Nb between hydrochloric acid and amine are investigated. Based on the results, the mechanism of amine extraction and the species of niobium in hydrochloric acid are discussed.

Experimental

Reagents.—Carrier-free ^{95}Nb was separated from ^{95}Zr(^{95}Nb) by the anion exchange method and was stored in 18 N sulfuric acid, as has been described in a previous paper[2]. Before being used for experiments, ^{95}Nb was extracted with acetylacetone and was converted into the chloride form by back-extraction with hydrochloric acid.

Tribenzylamine (TBA) obtained from the Tokyo Kasei Co., Ltd. was of a high purity as indicated by melting point measurement and was used without further purification. A standard solution of TBA was prepared by dissolving TBA in chloroform. TBA was converted into the hydrochloride form (TBA-Cl) before being used for experiments by shaking the TBA solution in chloroform with 6 M hydrochloric acid for 30 min.

E. P. grade chloroform was treated with concentrated sulfuric acid and then purified by distillation.

All other chemicals were of guaranteed reagent grade.

Distribution Measurement. — All equilibrations were carried out in glass-stoppered tubes. These tubes were shaken with a mechanical shaking device in a constant temperature bath. The experiments were carried out at 25±0.5°C unless otherwise stated. The distribution coefficients, *D*, were determined as follows: ^{95}Nb was previously extracted from concentrated hydrochloric acid with TBA-Cl in chloroform. An aliquot of this organic solution, containing ^{95}Nb, was shaken for one hour with aqueous solutions of various conditions. After the phases had disengaged, the phases were transferred into two test tubes and the γ-activities of both tubes were measured with a scintillation counter. Studies of the equilibration rate have shown that complete equilibration was attained in less than 30 min.; however, the shaking time of one hour was chosen for this work.

The determination of the acidity of both phases was necessary. The aqueous phase was titrated with a standard solution of sodium hydroxide, using methyl orange as the indicator. The acid in the organic phase was titrated with a stadard sodium hydroxide solution in ethanol by the aid of a pH meter.

Results and Discussion

Extraction Mechanism and Some Related Equations. — The authors consider that the anionic species of niobium in the aqueous phase is transferred to the organic phase as follows:

$$\mathrm{Nb(OH)}_p\mathrm{Cl}_q{}^{+5-p-q} + (p+q-5)\mathrm{RCl} \rightleftharpoons \mathrm{R}_{p+q-5}\mathrm{Nb(OH)}_p\mathrm{Cl}_q + (p+q-5)\mathrm{Cl}^- \tag{1}$$

followed by the reaction of the above species with TBA-Cl in the organic phase, containing large amounts of TBA-Cl:

$$\mathrm{R}_{p+q-5}\mathrm{Nb(OH)}_p\mathrm{Cl}_q + i\mathrm{RCl} \rightleftharpoons \mathrm{R}_{p+q-5}\mathrm{Nb(OH)}_p\mathrm{Cl}_q\cdot i\mathrm{RCl} \tag{2}$$

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1) N. Suzuki and S. Oki, This Bulletin, 35, 233, 237 (1962).

2) N. Suzuki and T. Omori, ibid., 35, 595 (1962).

3) C. F. Coleman, K. B. Brown, J. G. Moore and K. A. Allen, A/Conf. 15/P/510 (1958); C. F. Coleman, K. B. Brown, J. G. Moore and D. J. Crouse, *Ind. Eng. Chem.*, **50**, 1756 (1958), W E. Keder, J. C. Sheppard and A. S. Wilson, *J. Inorg. Nucl. Chem.*, **12**, 327 (1960).

4) J. Y Ellenburg, G. W. Ledicotte and F. L. Moore, *Anal. Chem.*, **26**, 1045 (1954).

5) G. E. Boyd and Q. V. Larson, *J. Phys. Chem.*, **64**, 988 (1960).

6) K. A. Allen, *J. Am. Chem. Soc.*, **80**, 4133 (1958).

7) W. J. McDowell and C. F. Baes. Jr., *J. Phys. Chem.*, **62**, 777 (1958).

8) S. Matsuo, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 458 (1961).

where RCl indicates TBA-Cl and $6 \leq (p+q) \leq 8$.

The extraction constant for Eq. 1 and the formation constant for Eq. 2 are:

$$K_{p,q} = \frac{(\mathrm{R}_{p+q-5}\mathrm{Nb(OH)}_p\mathrm{Cl}_q)_\mathrm{o}(\mathrm{Cl}^-)_\mathrm{a}{}^{p+q-5}}{(\mathrm{Nb(OH)}_p\mathrm{Cl}_q{}^{+5-p-q})_\mathrm{a}(\mathrm{RCl})_\mathrm{o}{}^{p+q-5}} \quad (3)$$

$$K_i = \frac{(\mathrm{R}_{p+q-5}\mathrm{Nb(OH)}_p\mathrm{Cl}_q \cdot i\mathrm{RCl})_\mathrm{o}}{(\mathrm{R}_{p+q-5}\mathrm{Nb(OH)}_p\mathrm{Cl}_q)_\mathrm{o}(\mathrm{RCl})_\mathrm{o}{}^i} \quad (4)$$

where the subscripts a and o detote the aqueous and organic phases respectively.

On the other hand, the next reaction can be considered with respect to the formation of an anionic complex of niobium in the aqueous solution. For the sake of simplicity, it is reasonable to consider the typical form of $\mathrm{Nb(OH)_2Cl_4}^-$ as the predominant species based on the following experimental results:

$$\begin{aligned} &\mathrm{Nb(OH)}_m\mathrm{Cl}_n{}^{+5-m-n*} \\ &\quad + (m-2)\mathrm{H}^+ + (4-n)\mathrm{Cl}^- \\ &\quad \rightleftharpoons \mathrm{Nb(OH)_2Cl_4}^- + (m-2)\mathrm{H_2O} \end{aligned} \quad (5)$$

The equilibrium constant for Eq. 5 is defined as

$$\begin{aligned} \beta_{m,n} = &\frac{(\mathrm{Nb(OH)}_m\mathrm{Cl}_n{}^{+5-m-n})_\mathrm{a}}{(\mathrm{Nb(OH)_2Cl_4}^-)_\mathrm{a}} \\ &\times (\mathrm{H}^+)_\mathrm{a}{}^{m-2}(\mathrm{Cl}^-)_\mathrm{a}{}^{4-n} \end{aligned} \quad (6)$$

The solubility of TBA-Cl in the aqueous solution can be ignored. The distribution coefficient for niobium, D, therefore, is derived in terms of activities from Eqs. 3, 4 and 6:

$$\begin{aligned} D &= \frac{\sum\limits_p\sum\limits_q\sum\limits_i(\mathrm{R}_{p+q-5}\mathrm{Nb(OH)}_p\mathrm{Cl}_q \cdot i\mathrm{RCl})_\mathrm{o}}{\sum\limits_m\sum\limits_n(\mathrm{Nb(OH)}_m\mathrm{Cl}_n{}^{+5-m-n})_a} \\ &= \frac{(\mathrm{Cl}^-)_\mathrm{a}{}^5}{\sum\sum(\beta_{m,n} \cdot (\mathrm{H}^+)_\mathrm{a}{}^{-m}(\mathrm{Cl}^-)_\mathrm{a}{}^n)} \\ &\quad \times [\sum\sum\sum(K_{p,q} \cdot K_i \cdot \beta_{p,q} \cdot (\mathrm{H}^+)_\mathrm{a}{}^{-p} \\ &\qquad \times (\mathrm{Cl}^-)_\mathrm{a}{}^{-p}(\mathrm{RCl})_\mathrm{o}{}^{p+q+i-5}] \end{aligned} \quad (7)$$

On the basis of the above equations, it is possible to indicate the factors which influence the extractability of niobium. The dependence of the hydrogen ion activity on D is given by the differentiation of Eq. 7 with respect to the hydrogen ion activity at a constant chloride level. Thus,

$$\frac{\partial \ln D}{\partial \ln (\mathrm{H}^+)_\mathrm{a}} = \overline{m} - \overline{p} \quad (8)$$

Proceeding as above, we obtain

$$\frac{\partial \ln D}{\partial \ln (\mathrm{Cl}^-)_\mathrm{a}} = 5 - \overline{p} - \overline{n} \quad (9)$$

where $\overline{m}$ and $\overline{n}$ denote, respectively, the average number of hydroxide and chloride groups per Nb in the aqueous phase, and $\overline{p}$, the average number of hydroxide groups per Nb in the organic phase.

In this experiment it is difficult to maintain the ionic strength constant; the analysis of the results obtained at such higher ionic strengths is possible only by the use of "activity" instead of "molar concentration". Therefore, the results are shown in terms of the activity. The activities for the hydrogen ion and the chloride ion are assumed to be:

$$\begin{aligned} (\mathrm{H}^+)_\mathrm{a} &= [\mathrm{H}^+]_\mathrm{a}\gamma_{\pm\mathrm{HCl}} \\ (\mathrm{Cl}^-)_\mathrm{a} &= [\mathrm{Cl}^-]_\mathrm{a}\gamma_{\pm\mathrm{LiCl}} \end{aligned} \quad (10)$$

where brackets are used to indicate the molar concentrations. The mean activity coefficients for hydrochloric acid, $\gamma_{\pm\mathrm{HCl}}$, and lithium chloride, $\gamma_{\pm\mathrm{LiCl}}$, are calculated from the data listed in Harned and Owen[9]. For the sake of simplicity, is assumed that the species in the organic phase are monomeric and that their activity coefficients are equal to 1.

Distribution of Hydrochloric Acid.—Hydrochloric acid of various acidities ranging from 1 M to 11.4 M were shaken with a 0.1 M TBA solution in chloroform. As is shown in Fig. 1, the acid concentration in the organic phase abruptly increases with the increasing acidity of hydrochloric acid, but the difference in the acid concentration between the cases of TBA and pure chloroform is just 0.1 M, equivalent to the TBA concentration.

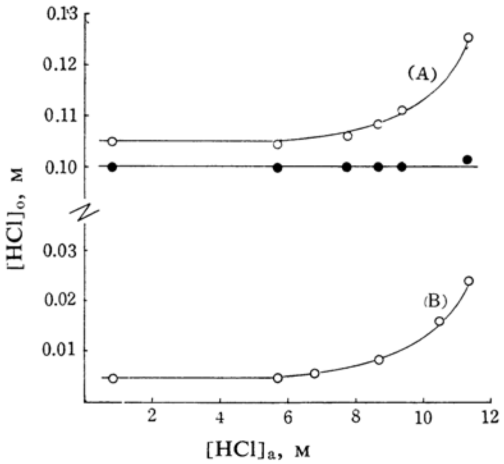

Fig. 1. Distribution of hydrochloric acid at 25°C.

○, (A) 0.100 M TBA in $\mathrm{CHCl_3}$; (B) pure $\mathrm{CHCl_3}$

●, Difference between curve (A) and curve (B)

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* $\mathrm{Nb(OH)}_m\mathrm{Cl}_n{}^{+5-m-n}$ shows the general form of the niobium chloro-complex in the aqueous solution.

[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd. Ed., Reinhold Pub. Co., New York (1950).

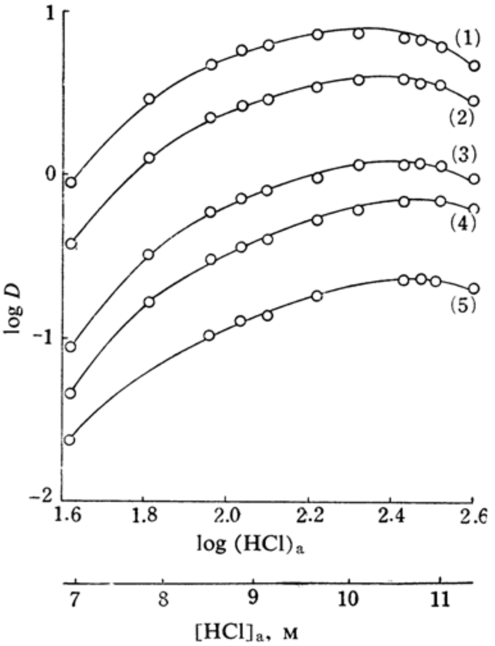

Fig. 2. Distribution of niobium between hydrochloric acid and TBA-chloroform at 25°C.

(1) (2) (3) (4) (5)
[RCl]$_o$: 0.200, 0.150, 0.100, 0.075, 0.050 M

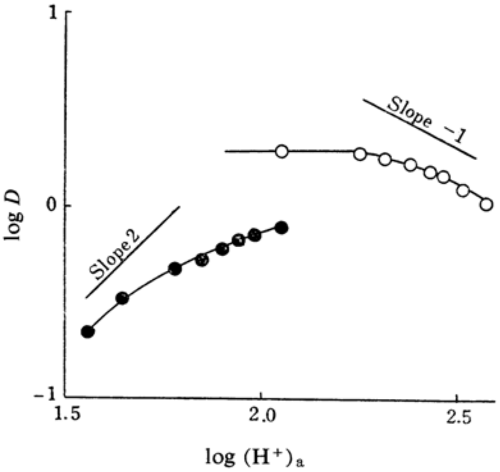

Fig. 3. Acid dependence of D values for niobium at 25°C.

○, $[\mathrm{Cl}^-]_{a,\ \mathrm{total}}=11.4$ M
●, $[\mathrm{Cl}^-]_{a,\ \mathrm{total}}=8.85$ M

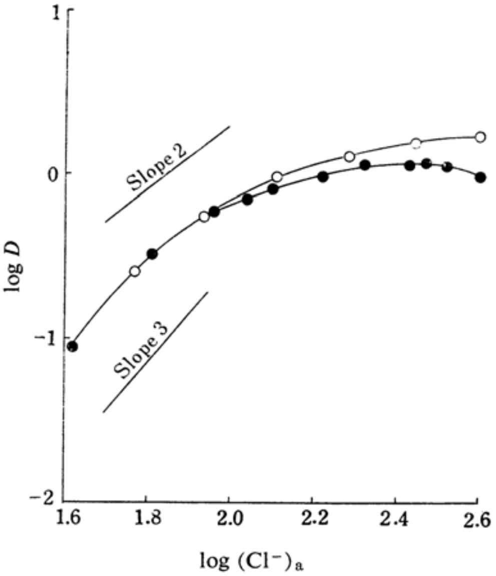

Fig. 4. Chloride dependence of D values for niobium at 25°C.

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

Dependence of the Extractability of ^{95}Nb on Hydrochloric Acid.—The distribution of ^{95}Nb between hydrochloric acid and a TBA-Cl chloroform solution was determined. As is shown in Fig. 2, the distribution of ^{95}Nb increases with an increase in the concentration of TBA-Cl, and there is a maximum at about 10.5 M of hydrochloric acid. In this experiment, of course, the results are influenced by the concentration of hydrogen and chloride ions.

Dependence on Chloride Ion Activity. — To examine the effect of the chloride ion activity, a series of experiments were carried out. By using hydrochloric acid-lithium chloride mixtures, 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 slope of the curve varies from 0.5 to 2.5. According to Eq. 9:

$$\frac{\partial \log D}{\partial \log (\mathrm{Cl}^-)_a}=5-\bar{p}-\bar{n}\simeq 0.5\sim 2.5 \qquad (9')$$

Dependence on Hydrogen Ion Activity.—The details of these experiments were similar to those of the above experiment, but in this case the chloride levels were held at 8.85 M and 11.4 M while the hydrogen ion activity was varied. At constant chloride levels, D is not so much affected by the hydrogen ion activity, as may be seen in Fig. 3. Although D remains constant at high chloride levels, 11.4 M, D decreases with a slope of −1 as the hydrogen ion activity increases. According to Eq. 8:

$$\frac{\partial \log D}{\partial \log (\mathrm{H}^+)_a}=\bar{m}-\bar{p}\simeq 0\sim -1.2 \qquad (8')$$

At low chloride levels, the decrease in D is suspected as being due mainly to the hydrolysis of niobium, i.e., $\bar{m}>\bar{p}$.

From Eqs. 8′ and 9′, we find:

$$1.2 \leq \bar{p} \leq 2.5$$

It seems reasonable, however, to consider that p ($=\bar{p}$) is constant in these conditions, probably equal to two, because the values of D are constant in the $\bar{m}=\bar{p}$ region and decrease gradually for $\bar{m} \lessgtr \bar{p}$. Thus, the decrease of the D values with a slope of -1 may be explained by the following reaction (cf. the following paragraph):

$$Nb(OH)_2Cl_4^- + H^+ \rightleftharpoons Nb(OH)Cl_4 + H_2O \qquad (11)$$

Species and Reaction in the Organic Phase.—In order to estimate the niobium species in the organic phase, ^{95}Nb was extracted from 10 M hydrochloric acid with various concentrations of TBA-Cl solutions in chloroform. There was no difference between the two cases of D values; viz., in one case D values were obtained by direct extraction of ^{95}Nb in hydrochloric acid with TBA-Cl, and in another case D values were obtained by the backward equilibration of the organic phase containing ^{95}Nb with hydrochloric acid. The resulting plot shown in Fig. 5 has a slope of 3.0 above 0.1 M TBA-Cl and of 2.1 below 0.1 M, indicating that one molecule of the niobium complex associates with up to three molecules of amine.

When the aqueous phase conditions are held constant, Eq. 7 can be replaced by:

$$D = A(RCl)_o + B(RCl)_o^2 + C(RCl)_o^3 \qquad (12)$$

where A, B and C are the constants. Therefore, if a plot of $D/(RCl)_o$ against $(RCl)_o$ fits the quadratic curve and if the intercept is not equal to zero, i. e., $K_{p,q(p+q=6)} \neq 0$, it can be considered that one molecule of amine exchages with the niobium chloro-complex.

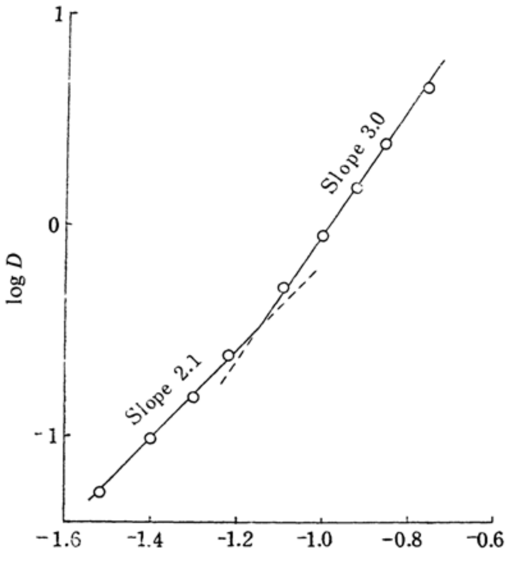

Fig. 5. TBA dependence of D values for niobium at 25°C.

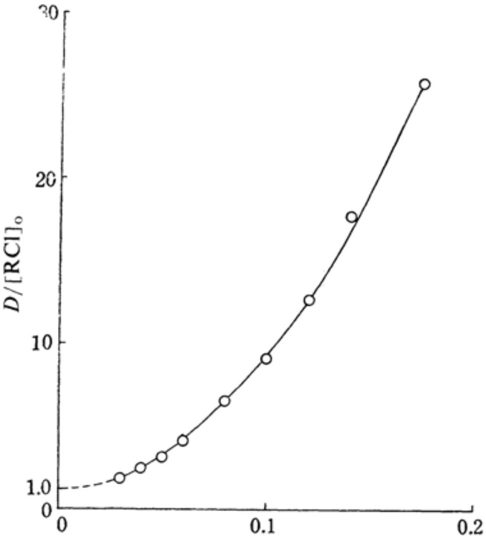

Fig. 6. Plot of $D/[RCl]_o$ vs. $[RCl]_o$.

The resulting curve is shown in Fig. 6, which indicates that the charge number of the niobium chloro-complex extracted is probably -1. It was found that the p value in the formula of $Nb(OH)_pCl_q^-$ was equal to two; therefore, this would mean that the complex in the organic phase is $RNb(OH)_2Cl_4 \cdot iRCl$ ($i=1$ and 2).

These considerations lead to the conclusion that the typical extractable species of niobium is $Nb(OH)_2Cl_4^-$. Other extractable species [i. e., $Nb(OH)_3Cl_3^-$, $Nb(OH)_2Cl_5^{-2}$, $Nb(OH)Cl_5^-$, etc.] will be present in very small amounts if such species exist at all. The species of niobium in hydrochloric acid have been investigated by the anion exchange method$^{10)}$ and by the spectrophotometric method, indicating the presence of $Nb(OH)_2Cl_4^-$ in a 10.5 M hydrochloric acid solution$^{11)}$.

From a plot of $D/(RCl)_o$ vs. $(RCl)_o$, $K_{i=1}$ and $K_{i=2}$ can be obtained as 4.4 and 786 respectively. If it is assumed that only $Nb(OH)_2Cl_4^-$ is the extractable species, $K_{p=2,\,q=4}$ can be calculated as about 940.

Temperature Effect.—There are few papers which have investigated the effect of temperature in a solvent extraction, but the authors consider that temperature is one of the most important factors. Equilibration experiments were carried out at 10 and 40°C. These results are shown in Fig. 7. At a low temperature,

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10) E. H. Huffman, *J. Am. Chem. Soc.*, **74**, 4714 (1952); K. A. Kraus, ibid., **71**, 3885 (1949).

11) J. H. Kanzelmeyer, J. Ryan and H. Freund, ibid., **78**, 3020 (1956).

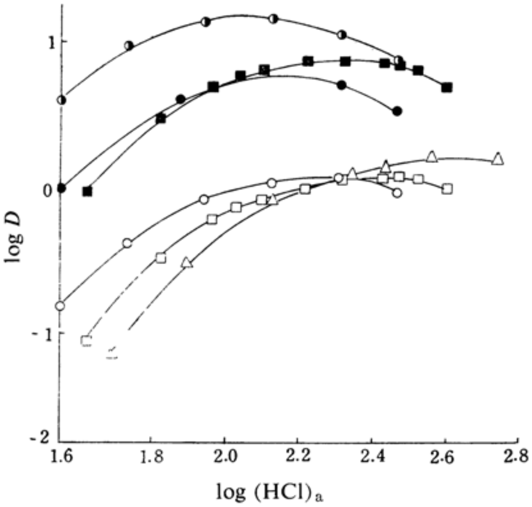


Fig. 7. Temperature dependence of D values for niobium.

○, 40±0.5°C ; □, 25±0.5°C ; △, 10±0.5°C
◑, $[RCl]_o = 0.30$ M ; ●, 0.20 M ; ■, 0.10 M

the extraction curve is similar to that shown in Fig. 4 (chloride dependence). The solubility of TBA-Cl in chloroform* is relatively small, so it is better to raise the temperature in order to use a high concentration of the TBA-Cl solution. The shapes of extraction curves are not equal to each other at different temperatures. At lower temperatures D shows a maximum in the region of higher acidity. The acidity at which it shows a maximum of D shifts to a lower acidity with an increase in the temperature. These results suggest that the reaction expressed in Eq. 11 and the formation of the niobium chloro-complex are promoted with an increase in the temperature.

Conclusion

The extraction processes of ^{95}Nb from hydrochloric acid with tribenzyl amine are shown by the following reactions:

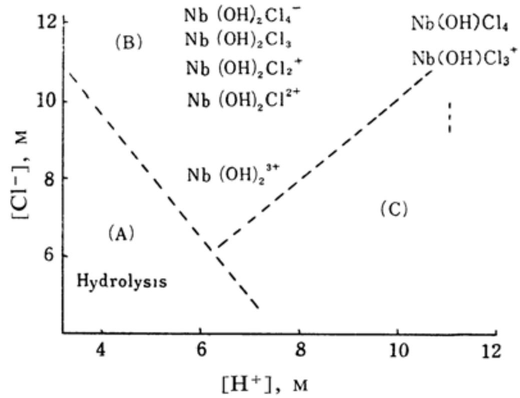
$$Nb(OH)_2Cl_4^- + RCl \rightleftharpoons RNb(OH)_2Cl_4 + Cl^- \qquad K_{p=2,\ q=4}=940$$

$$RNb(OH)_2Cl_4 + RCl \rightleftharpoons RNb(OH)_2Cl_4 \cdot RCl \qquad K_{i=1}=4.4$$

$$RNb(OH)_2Cl_4 \cdot RCl + RCl \rightleftharpoons RNb(OH)_2Cl_4 \cdot 2RCl \qquad K_{i=2}=786$$

The $K_{p=2,\ q=4}$ value is comparatively small, but it is interesting that the apparent D values are large. This fact suggests that the secondary reaction, as shown in Eq. 2, occurs in the organic phase; therefore, the overall extraction ratio increases. The formation constants for niobium chloro-complexes cannot be obtained owing to their complexity, but the authors present in Table I a scheme concerning the niobium species in the chloride system. In region A, the hydrolysis (and/or polymerization) of niobium may occur; $Nb(OH)_2Cl_n^{+3-n}$ species exist in region B and C, and $Nb(OH)Cl_n^{+4-n}$ may exist in region C only. As the temperature rises, the formation of niobium chloro-complexes will be promoted, but dehydroxylation may occur simultaneously; therefore, the situation is not simple.

TABLE I. NIOBIUM SPECIES IN HYDROCHLORIC ACID-LITHIUM CHLORIDE SOLUTIONS AT 25°C



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* The maximum concentration is about 0.2M TBA-Cl at 25°C.