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Original Scientific Paper

Solvent Extraction of Niobium and Tantalum. V.* Separation of Niobium and Tantalum with TOA and Some N-Substituted Long Chain Amines

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Separation of niobium and tantalum by solvent extraction with di-*n*-octylamino ethanol (DOAE), di-*n*-octylamino propanol (DOAP), di-*n*-octylamino butanone (DOAB), di-*n*-octylamino acetic acid (DOAA), di-*n*-octylamine (DOA) and tri-*n*-octylamine (TOA) in chloroform is described, in the metal concentration range of 10^{-5} M. Separation can be achieved in 0.2 M HF metal solutions in the sulphuric acid concentration range of 1–5 M. Tantalum is extracted into the organic phase and can be stripped back easily with 1–6 M hydrochloric acid. Niobium and tantalum of radiochemical purity are obtained. The separation factors displayed by these extraction reagents are compared and discussed.

INTRODUCTION

Long chain aliphatic or aromatic amines in organic solvents have proved to be efficient extraction reagents for many metals. For niobium and tantalum they are of particular interest, because in the various aqueous systems these two metals are generally present in an anionic form. There is a vast literature describing different extraction systems of this type and some comprehensive reviews of the field¹⁻⁶. One of the first efficient separations of niobium and tantalum was achieved by extraction of strong hydrochloric acid solutions with MDOA in xylene⁷. Separations with TBA in methylene-chloride from sulphuric acid⁸ and TIOA in carbon tetrachloride from HF/H₂SO₄ solutions⁹ were reported subsequently.

In order to investigate the properties and extraction ability of the *N*-substituted long chain amines, we have studied the extraction behaviour of niobium and tantalum with di-*n*-octylamino ethanol (DOAE), di-*n*-octylamino propanol (DOAP), di-*n*-octylamino butanone (DOAB) and di-*n*-octylamino acetic acid (DOAA)^{10,11}. In these reagents one hydrogen of the secondary amine is replaced by 2-hydroxy-ethyl, 3-hydroxy-propyl, 3-oxo-butyl and -CH₂COOH group, respectively. Such *N*-substituted long chain amines have not yet been employed as extraction reagents and the effect of an additional functional group (hydroxy, oxo or carboxyl) presence in these amine type extractants, has not been reported. Significant changes in the extraction mechanism may be expected depending upon the character, electronegativity and position of

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these substituent groups as well as upon the solvent used. As a result, particularly in view of the different functional group affinity toward various metals, the selectivity of such extractants may be improved in comparison with simple long chain amines.

In the course of a systematic study of extraction behaviour of niobium and tantalum with these reagents in chloroform, from the aqueous phase containing different mineral acids¹², we have observed that in some systems, described below, an efficient separation of niobium and tantalum can be achieved. We now report results of these studies.

EXPERIMENTAL

Reagents

2-Di-*n*-octylamino-ethanol (1) (DOAE) and 3-di-*n*-octylamino propanol (1) were prepared from di-*n*-octylamine and 2-chlorethanol (1)¹³; di-*n*-octylamine and 3-chloropropanol (1)¹⁴ respectively.

4-Di-*n*-octylamino butanone (2) was prepared from di-*n*-octylamine and methyl vinyl ketone¹⁵. The preparation was carried out according to the procedure given for diethylamino butanone (2), with some minor modifications, which proved to be necessary for this homologue with a longer alkyl chain¹².

Di-*n*-octylamino acetic acid was prepared from di-*n*-octylamine and chloroacetic acid¹⁶.

Di-*n*-octylamine and tri-*n*-octylamine (Eastman Kodak Practical) were purified by distillation before use.

Chloroform (Merck *p. a.*) was used as the organic phase in all the experiments. Reagent concentration throughout the experiments was 1×10^{-2} M.

Radioactive Tracers

⁹⁵Nb was obtained from the Radiochemical Centre Amersham in the 0.5% oxalate solution. ¹⁸²Ta was obtained by irradiation of metal oxalate solutions in the reactor of the Institute »Boris Kidrič«, Vinča. Before use the tracers were transferred into the hydrofluoric or sulphuric form as described earlier¹⁷. Metal concentrations throughout the experiments were 10^{-5} M.

Apparatus and Distribution Coefficient Measurements

All the experiments were carried out in a thermostatic room at 24° C. Equal volumes (2 ml.) of the aqueous and organic phases were used. Extraction was carried out in polythene vessels and stirring time was 15 minutes. It has been found that in all the systems described the equilibrium is reached after 7–10 minutes of stirring. The phases were separated by centrifugation and the γ -activity of the organic and aqueous phase aliquots (1 ml.) was determined on a γ -scintillation counter. Reproducible results were obtained.

γ -spectra were recorded on a 256 channel analyser using a 3×3 inches NaI(Tl) scintillation crystal. The calibration was performed with standard radiation sources ²²Na, ¹³⁷Cs and ⁶⁰Co.

RESULTS

In all the systems 10^{-5} M aqueous metal solutions and 10^{-2} M ($\sim 0.3\%$) reagent solutions in chloroform were used.

System Nb—Ta — 0.2 M HF — H₂SO₄

Niobium and tantalum extractions from 0.2 M HF solution were studied as a function of the H₂SO₄ concentration. In Tables I—IV the experimental data are collected and separation factors given for DOAE, DOAP, DOAB and DOAA. For all these extractants D_{Ta} is larger than D_{Nb} by about three orders of magnitude and is practically independent of the sulphuric acid

TABLE I
Separation of Niobium and Tantalum with DOAE
 0.2 M HF — H₂SO₄

H ₂ SO ₄ M	Nb		Ta		Separation factor
	D	%	D	%	
0.25	0.11	9.9	48	98	430
0.5	0.078	7.3	46	97.9	590
1.0	0.054	5.1	44	97.8	810
1.5	0.055	5.2	41	97.6	750
2.0	0.047	4.5	40	97.5	850
2.5	0.043	4.1	38	97.5	880
3.0	0.041	3.9	38	97.5	920
3.5	0.041	3.9	36	97.4	880
4.0	0.044	4.2	34	97.2	770
4.5	0.046	4.4	34	97.2	740
5.0	0.050	4.7	33	97.1	660

TABLE II
Separation of Niobium and Tantalum with DOAP
 0.2 M HF — H₂SO₄

H ₂ SO ₄ M	Nb		Ta		Separation factor
	D	%	D	%	
0.25	0.17	9.1	25.6	96.3	150
0.5	0.096	8.8	23.9	96.0	250
1.0	0.064	6.0	21.9	95.6	360
1.5	0.054	5.1	21.7	95.6	400
2.0	0.044	4.2	19.2	95.0	430
2.5	0.044	4.2	16.7	94.3	380
3.0	0.048	4.6	17.1	94.5	350
3.5	0.048	4.6	13.2	93.0	270
4.0	0.063	5.9	12.9	92.8	200
4.5	0.070	6.5	11.8	92.2	170
5.0	0.080	7.4	10.8	91.5	130

TABLE III
Separation of Niobium and Tantalum with DOAB
 0.2 M HF — H₂SO₄

H ₂ SO ₄ M	Nb		Ta		Separation factor
	D	%	D	%	
0.25	0.36	26.4	39	97.5	110
0.5	0.19	16.0	34	97.2	180
1.0	0.10	9.1	33	97.1	330
1.5	0.070	6.5	34	97.2	490
2.0	0.067	6.3	33	97.1	490
2.5	0.042	4.0	33	97.1	790
3.0	0.042	4.0	35	97.3	830
3.5	0.042	4.0	35	97.3	830
4.0	0.042	4.0	35	97.3	830
4.5	0.052	4.9	32	97.0	620
5.0	0.062	5.8	38	97.7	610

TABLE IV
 Separation of Niobium and Tantalum with DOAA
 0.2 M HF—H₂SO₄

H ₂ SO ₄ M	Nb		Ta		Separation factor
	D	%	D	%	
0.25	0.091	8.3	27	96.5	300
0.5	0.061	5.7	24	96.0	400
1.0	0.041	3.9	21	95.5	510
1.5	0.029	2.8	19	95.0	650
2.0	0.025	2.4	17	94.5	680
2.5	0.021	2.0	17	94.5	810
3.0	0.020	1.9	17	94.5	850
3.5	0.020	1.9	17	94.5	850
4.0	0.023	2.2	17	94.5	740
4.5	0.027	2.6	17	94.5	630
5.0	0.030	2.9	18	94.8	600

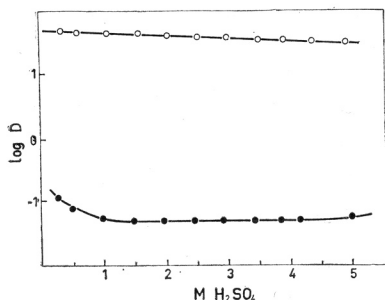


Fig. 1. Extraction of Nb (●) and Ta (○) from 0.2 M HF solutions with DOAE in the presence of H₂SO₄.

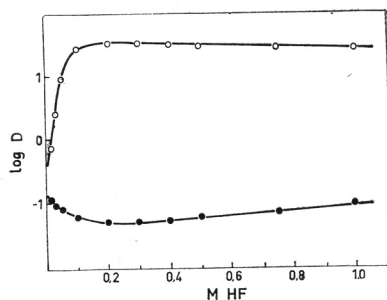


Fig. 2. Extraction of Nb (●) and Ta (○) from 2.5 M H₂SO₄ solutions with DOAE in the presence of HF.

concentration. This typical behaviour is obvious from Fig. 1, where data for DOAE extraction are represented.

System Nb—Ta — 2.5 M H₂SO₄—HF

To determine the optimal hydrofluoric acid concentration for niobium and tantalum separation, the extraction dependence of these metals in 2.5 M H₂SO₄ upon HF concentration was studied. Experimental results for DOAB are shown in Table V, and the separation factors are given. Again typical behaviour was observed, which is represented on Fig. 2 for DOAE.

The results show that D_{Ta} increases rapidly with HF concentration up to 0.2 M HF and then remains practically constant. D_{Ta} is about three orders of magnitude higher than D_{Nb} .

System Nb—Ta — 0.2 M HF—HNO₃ and HCl

In the previous system it was found that 0.2 M HF is a favorable concentration for niobium and tantalum separation. The extraction behaviour of these metals from 0.2 M HF, in presence of other mineral acids, was then examined.

TABLE V
Separation of Niobium and Tantalum with DOAB
 2.5 M H_2SO_4 — HF

HF M	Nb		Ta		Separation factor
	D	%	D	%	
0.03	0.13	13	0.59	37	4
0.05	0.10	9.9	7.5	88	75
0.10	0.060	5.6	26.9	96.5	450
0.2	0.051	4.8	37.5	97.5	740
0.3	0.058	5.5	39.5	97.5	680
0.4	0.058	5.5	35.9	97.5	620
0.5	0.066	6.2	34.5	97	520
0.75	0.082	7.6	31.6	97	380
1.0	0.088	8.1	26.6	96.5	300

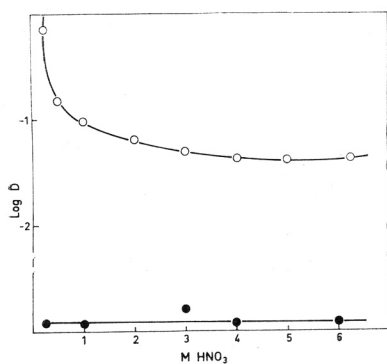


Fig. 3. Extraction of Nb (●) and Ta (○) from 0.2 M HF solutions with DOAE in the presence of HNO_3 .

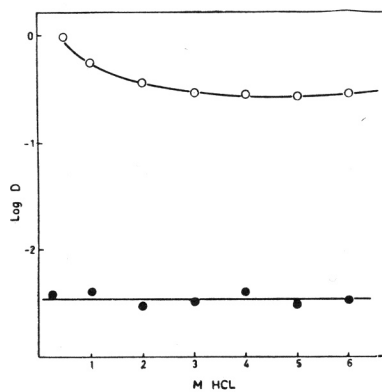


Fig. 4. Extraction of Nb (●) and Ta (○) from 0.2 M HF solutions with DOAP in the presence of HCl.

TABLE VI
Separation of Niobium and Tantalum with DOAP
 0.2 M HF — HNO_3

HNO_3 M	Nb		Ta		Separation factor
	D	%	D	%	
0.5	0.0011	0.11	0.31	23	280
1.0	0.0013	0.13	0.17	15	130
2.0	0.0014	0.14	0.10	9.1	70
3.0	0.0011	0.11	0.094	8.5	85
4.0	0.0016	0.16	0.072	6.7	45
5.0			0.056	4.8	
6.0	0.0018	0.18	0.048	4.5	25

On Fig. 3 the extraction dependence of niobium and tantalum upon the nitric acid concentration is represented for DOAE and in Table VI experimental data are given for DOAP. In this system the extraction of

tantalum decreases with the increase of mineral acid, and D_{Ta} is generally only two orders of magnitude larger than D_{Nb} , which is independent upon the nitric acid concentration. The concentration region where a successful separation could be performed is very narrow (up to 1 M HNO_3).

Extraction dependence of niobium and tantalum in 0.2 M HF upon the hydrochloric acid concentration is represented in Fig. 4 for DOAP. The extraction behaviour is to some extent similar to that of the nitric acid system, D_{Ta} decreasing this time somewhat more steadily with the mineral acid concentration increase, but the separation factors over a wide HCl concentration range are only about 100.

Separation and Stripping of the Tantalum from the Organic Phase

The study of the systems described above has shown that optimal separation conditions are achieved in 0.2 M HF metal solutions in the presence

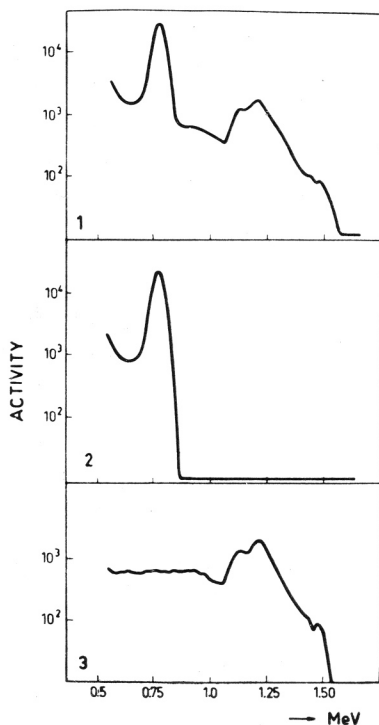


Fig. 5. γ -spectra of: (1) the mixture before the separation — (2) separated Nb in the aqueous phase — (3) separated Ta in the organic phase.

of 1 M H_2SO_4 . DOAE proved to be the most efficient reagent. After the extraction, the organic phase was washed twice with a solution containing 0.2 M HF and 1 M H_2SO_4 and the aqueous phase with 10^{-2} M DOAE solution in chloroform. In this way radiochemically pure solutions of the separated elements were obtained, as shown by γ -spectra of the organic and aqueous phase. On Fig. 5 the spectra of the mixture (1), separated niobium (2) and tantalum (3) are given.

TABLE VII
Stripping of Tantalum with HCl

M HCl	D	Ta in CHCl ₃ (%)	Ta in aqueous phase (%)
0.5	0.026	2.5	97.5
1.0	0.0004	0.04	99.96
2.0	0.0003	0.03	99.97
4.0	0.0002	0.02	99.98
6.0	0.003	0.3	99.70

Stripping of tantalum from the organic phase can be performed with hydrochloric acid, as shown in Table VII, for DOAE. With HCl concentration ranging from 1–6 M, a satisfactory recovery of tantalum can be achieved (~ 99.9%).

Separation with TOA and DOA

To compare the separation efficacy of *N*-substituted long chain amines for niobium and tantalum with the separation ability of simple DOA and TOA, the corresponding experiments were made with these commercial

TABLE VIII
Separation of Niobium and Tantalum with TOA
0.2 M HF — H₂SO₄

H ₂ SO ₄ M	Nb		Ta		Separation factor
	D	%	D	%	
0.25	0.56	35.9	70	98.6	120
0.5	0.21	17.3	66	98.5	310
1.0	0.11	9.9	67	98.5	610
1.5	0.076	7.1	58	98.4	760
2.0	0.070	6.5	56	98.3	800
2.5	0.062	5.8	54	98.2	880
3.0	0.060	5.6	50	98.0	830
3.5	0.068	6.4	47	98.0	690
4.0	0.080	7.4	52	98.2	650
4.5	0.10	9.1	48	98.0	480
5.0	0.13	12.8	44	97.8	340

TABLE IX
Separation of Niobium and Tantalum with DOA
0.2 M HF — H₂SO₄

H ₂ SO ₄ M	Nb		Ta		Separation factor
	D	%	D	%	
0.25	0.36	26.5	14.2	93.5	40
0.5	0.14	12.6	8.5	89.5	60
1.0	0.087	8.0	7.6	88.5	87
1.5	0.051	4.8	7.8	88.6	150
2.0	0.040	3.8	7.6	88.5	190
2.5	0.036	3.5	7.5	88.3	210
3.0	0.035	3.4	7.8	88.6	220
3.5	0.030	2.9	7.9	88.8	260
4.0	0.031	3.0	7.7	88.5	250
4.5	0.035	3.4	8.5	89.5	240
5.0	0.040	3.8	8.8	89.9	220

reagents in chloroform. Systems in which the best separation was achieved, *i. e.*, 0.2 M HF metal solutions in the presence of sulphuric acid were examined. The results are given in Tables VIII and IX.

The results show that commercially available TOA can be successfully employed for niobium and tantalum separation under the described conditions and that DOA is less successful.

DISCUSSION

The results show that *N*-substituted long chain amines in chloroform proved to be suitable extractants for niobium and tantalum separation. It has been found that substitution of the hydrogen atom in secondary amines by 2-hydroxy ethyl, 3-hydroxy propyl, 3-oxo butyl and $-\text{CH}_2\text{COOH}$ group does not essentially change the separation efficacy for niobium and tantalum. This may well not be the case for the other metals, however. The best conditions for niobium and tantalum separation are observed in 0.2 M HF metal solution, containing 1–5 M H_2SO_4 . Under these conditions, a high tantalum extraction occurs, practically independent of the H_2SO_4 concentration. D_{Nb} decreases up to 1 M H_2SO_4 , and then remains practically constant on a further increase of the H_2SO_4 concentration. This wide range of suitable sulphuric acid concentration is important for analytical application of this method. The separation procedure is simple, and radiochemically pure components can be obtained, as shown by the γ -spectra. The stripping of tantalum from the organic phase can be easily performed by hydrochloric acid.

With respect to the separation factors observed under the given conditions, all these *N*-substituted amines display, in a wider sulphuric acid concentration range, larger separation factors than does DOA. The separation factors of TOA are comparable with those of the *N*-substituted amines. The following order of separation efficacy is observed, taking into account the minor differences in 1 M H_2SO_4 and the nearby concentration ranges: $\text{DOAE} > \text{TOA} > \text{DOAA} > > \text{DOAB} > \text{DOAP}$.

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IZVOD

Ekstrakcija niobija i tantala. V. Separacija niobija i tantala sa TOA i nekim *N*-supstituiranim visoko molekularnim aminima

C. Djordjević i D. Sevdic

Opisana je separacija niobija i tantala ekstrakcijom sa di-*n*-oktilamino etanolom (DOAE), di-*n*-oktilamino propanolom (DOAP), di-*n*-oktilamino butanonom (DOAB), di-*n*-oktilamino octenom kiselinom (DOAA), di-*n*-oktilaminom (DOA) i tri-*n*-oktilaminom (TOA) u koncentracionom području metala od 10^{-5} *M* i kloroformom kao organskom fazom. Separacija se postiže u 0.2 *M* HF otopinama, u prisutnosti 1.–5 *M* H₂SO₄. Tantal se ekstrahira u organsku fazu i može se lako reekstrahirati s 1–6 *M* HCl. Separirani metali su radiokemijske čistoće. Provedena je usporedba i diskusija faktora separacije koji se postižu s navedenim ekstrakcionim agensima.

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I

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