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SOME ANALYTICAL APPLICATIONS OF SOLVENT
EXTRACTION FROM SULPHATE SOLUTION WITH
LONG CHAIN ALKYL AMINES

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by

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ABSTRACT

A study has been made of the extraction of a number of ions from sulphate solution, using the tertiary alkyl amine tri-isooctyl amine, and the secondary alkyl amines, amine 9D-178 and di(tridecyl P) amine, in various diluents. The purpose of this work was to investigate the use of these amines as an analytical tool in the separation and determination of thorium and the rare earths.

Extraction coefficients have been determined for uranium, thorium and a number of other ions, using amine 9D-178 in Varsol, and a comparison has been made of the effect of various diluents on uranium and thorium extraction. Extraction coefficients were also determined for uranium, thorium, zirconium and the rare earths with tri-isooctyl amine in Varsol, and for thorium, titanium and the rare earths with di(tridecyl P) amine in Varsol and carbon tetrachloride. The effect of pH and high sulphate content on extraction of various ions with tri-isooctyl amine and di(tridecyl P) amine was determined.

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QUELQUES APPLICATIONS ANALYTIQUES DE L'EXTRACTION
PAR SOLVANT À PARTIR DE SOLUTION SULFATÉE,
À L'AIDE D'ALKYLAMINES À LONGUE CHAÎNE

par

R.J. Guest* et J.-A.-F. Bouvier**

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RÉSUMÉ

On a fait l'étude de l'extraction d'un certain nombre d'ions à partir de solution sulfatée, à l'aide d'une alkylamine tertiaire (tri-isooctyle) et d'alkylamines secondaires (9D-178 et di(tridécyle P)) dans divers diluants. Il s'agissait de déterminer si l'on pourrait, à l'aide de ces amines, faire la séparation et le dosage analytiques du thorium et des terres rares.

On a déterminé les coefficients d'extraction dans le cas de l'uranium, du thorium et d'un certain nombre d'autres ions, à l'aide de l'amine 9D-178 dissoute dans du Varsol, et l'on a comparé les effets de divers diluants sur l'extraction de l'uranium et du thorium. On a aussi déterminé les coefficients d'extraction dans le cas de l'uranium, du thorium, du zirconium et des terres rares, à l'aide de tri-isooctylamine dissoute dans du Varsol, ainsi que dans le cas du thorium, du titane et des terres rares, à l'aide d'amine di(tridécyle P) dissoute dans du Varsol et du tetrachlorure de carbone. On a également déterminé l'effet du pH et d'une forte teneur en sulfate sur l'extraction de divers ions à l'aide d'amines tri-isooctyle et di(tridécyle P).

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CONTENTS

	<u>Page</u>
Abstract	i
Introduction	1
Reagents and Apparatus	3
Procedure	6
Determination of Extraction Coefficient	6
Equilibration of the Amine	7
Experimental	7
Extraction of Various Ions by Amine 9D-178	8
(Uranium; Thorium; Zirconium and Molybdenum; Lanthanum, Cerium and Mixed Rare Earths; Titanium; Cobalt, Nickel, Manganese, Vanadium and Iron)	
Extraction of Various Ions with Tri-isooctylamine	16
(Uranium; Thorium; Zirconium)	
Extraction of Various Ions with Di(tridecyl P) amine	20
(Thorium; Titanium; Lanthanum and Mixed Rare Earths)	
Results and Discussion	26
Conclusions	28
References	30
Figures 1 to 8	32-39

INTRODUCTION

Recently, a great deal of attention has been directed towards liquid-liquid extraction of uranium from sulphate solution by means of long chain alkyl amines in a suitable diluent. Thorium, zirconium and molybdenum have also been found to extract with certain amines under suitable conditions. Much of the work reported has been carried out in the United States, and a large amount of literature is available on the subject (1, 2, 3, 4). Most of this literature is concerned primarily with large-scale operations as a means of obtaining a high purity uranium or thorium product. Some work along these lines has also been carried out at the Mines Branch, in Ottawa, by Simard (5, 6, 7).

Considerably less information is available, however, on analytical applications of solvent extraction using long chain alkyl amines. This report, then, deals with the solvent extraction of various ions, primarily from the viewpoint of possible application to analytical problems.

As a considerable amount of information can be found in the references previously given on process applications of amine solvent extraction, it would be redundant to give more than a brief summary of factors that should be considered in choosing suitable amines with which to work. Primary amines are strong extractants for thorium, but selectivity for this ion is not good since uranium, ferric iron, and most tetravalent metals also tend to extract. Better selectivity for thorium extraction is found with the straight chain amines or the moderately-branched secondary amines (branching distant from the nitrogen atom). Although uranium

is extracted to a substantial extent, less of the tetravalent metals and ferric iron is extracted. Extraction of uranium increases, and that of thorium decreases, with highly branched secondary amines (branching close to the nitrogen), while selectivity is much better with respect to tetravalent metals and ferric iron. With the tertiary amines, selectivity is best of all, extraction of uranium being high and that of most other metals, including thorium, negligible. With all of these various types of amines, zirconium and molybdenum (VI) will extract strongly but molybdenum can be partially removed in the stripping operation. Vanadium (V) will extract at a pH of 2 or greater, but vanadium (IV) will not extract. Stripping of uranium and thorium from the organic phase may be carried out by means of sodium carbonate, hydrochloric acid, nitric acid, magnesia, or other compounds. It can generally be expected that extraction coefficients will increase with increasing pH values and will decrease with increasing sulphate content of the liquor. Further information of this type may be found in references (1 to 7).

A number of analytical applications of amines have been reported in the literature. These include separation of niobium from tantalum (8, 9), of protoactinium from niobium (10), and of cobalt from zinc (11). A separation of titanium from thorium, using amine extraction, has been carried out in this laboratory (12). Tri-isooctylamine has been used in hydrochloric acid medium to separate a number of contaminants from thorium (13).

In the study reported here, three amines were used in various diluents. These amines were: a) amine 9D-178, a secondary amine with branching close to the nitrogen atom; b) tri-isooctylamine, a tertiary amine with a moderately-branched alkyl chain; and c) di(tridecyl P) amine, a moderately-branched secondary amine with branching distant from the nitrogen atom. These amines were chosen because they were available and had shown promise as thorium and/or uranium extractants in process work. In most of the early tests, amine 9D-178 was used, as this amine was the first of the three amines available in plentiful quantities. A number of diluents were tested as to their efficiency in extraction power, as well as their sink/float qualities. The value of the long chain alcohol, decyl alcohol, as an aid in phase separation, was tested.

REAGENTS AND APPARATUS

Reagents

5% Amine 9D-178 in Varsol

Mix 50 ml of amine 9D-178 (Rohm and Haas) with 940 ml of Varsol and 10 ml of decyl alcohol.

10% Amine 9D-178 in Varsol

Mix 100 ml of amine 9D-178 with 880 ml of Varsol and 20 ml of decyl alcohol.

5% Amine 9D-178 in Carbon Tetrachloride

Mix 50 ml of amine 9D-178 with 950 ml of carbon tetrachloride.

10% Amine 9D-178 in Carbon Tetrachloride

Mix 100 ml of amine 9D-178 with 900 ml of carbon tetrachloride.

15% Amine 9D-178 in Carbon Tetrachloride

Mix 150 ml of amine 9D-178 with 850 ml of carbon tetrachloride.

10% Amine 9D-178 in Chloroform

Mix 100 ml of amine 9D-178 with 900 ml of chloroform.

5% Tri-isooctylamine in Varsol

Mix 50 ml of tri-isooctylamine (Carbide and Carbon Chemicals Co.) with 950 ml of Varsol and 10 ml of decyl alcohol.

15% Tri-isooctylamine in Carbon Tetrachloride

Mix 150 ml of tri-isooctylamine with 850 ml of carbon tetrachloride.

5% Di(tridecyl P) Amine in Varsol

Mix 50 ml of di(tridecyl P) amine (Carbide and Carbon Chemicals Co.) with 940 ml of Varsol and 10 ml of decyl alcohol.

5% Di(tridecyl P) Amine in Carbon Tetrachloride

Mix 50 ml of di(tridecyl P) amine with 950 ml of carbon tetrachloride.

15% Di(tridecyl P) Amine in Carbon Tetrachloride

Mix 150 ml of di(tridecyl P) amine with 850 ml of carbon tetrachloride.

Uranium Solution

Dissolve an appropriate amount of uranium trioxide (UO_3) in dilute sulphuric acid and make up to volume in a volumetric flask.

Thorium Solution

Dissolve an appropriate amount of thorium sulphate (Lindsay Chemical Co. $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$) in cold distilled water, using gradual stirring to achieve solution.

Zirconium Solution

Dissolve zirconium sulphate ($\text{Zr}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$) in distilled water and add 5 ml of 18N sulphuric acid before diluting to volume.

Molybdenum Solution

Take molybdic acid ($\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$) to fumes with sulphuric acid, cool and dilute with distilled water to an appropriate volume.

Titanium Solution

Dissolve the desired quantity of titanium sulphate (IV) by evaporating to fumes of sulphuric acid and then adding distilled water, warming until complete solution. Dilute to an appropriate volume with distilled water.

Alternatively, dissolve titanium sulphate (IV) with dilute sulphuric acid, adding hydrogen peroxide to aid solution.

Cobalt, Manganese, Nickel and Vanadium Solutions

Dissolve sulphate salts of cobalt ($\text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$), nickel ($\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$), manganese ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) and vanadium ($\text{VOSO}_4 \cdot 2 \text{H}_2\text{O}$) in distilled water and make up to the desired volumes in volumetric flasks.

Iron Solution

Dissolve ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 6 \text{H}_2\text{O}$) in 0.1% sulphuric acid solution.

Cerium Solution

Dissolve ceric sulphate ($\text{Ce}(\text{HSO}_4)_4$) in water, adding hydrogen peroxide to aid solution.

Lanthanum Solution

Add lanthanum oxide to a dilute sulphuric acid solution, take to sulphuric acid fumes, and dilute with distilled water to a desired volume.

Mixed Rare Earths Solution

Add mixed rare earths (Lindsay Chemical Co. Code 330) to a dilute sulphuric acid solution, take to sulphuric acid fumes and dilute with distilled water to a desired volume. If necessary, add a little hydrogen peroxide to aid solution.

Apparatus

Beckman pH meter, model "G"

Beckman "B" or "DU" spectrophotometer

PROCEDURE

Determination of Extraction Coefficient

An appropriate aliquot of a solution of the ion to be tested was placed in a 100 ml beaker, and the pH of the solution was adjusted by means of a dilute sulphuric acid solution, using a Beckman pH meter, model "G", for pH measurements. The measured volume of solution was then transferred to a 60 or 125 ml separatory funnel and shaken for 2 minutes with a measured volume of organic reagent. After separation of layers, the organic layer was stripped twice with a 10% hydrochloric acid solution. Each time, the volume of strip solution was equal to the aqueous portion of the sample solution. The aqueous and organic phases were then assayed. Alternatively, if the amount of ion taken was accurately known, only one of the phases (the one expected to contain the smallest portion of material being tested) was assayed. The extraction coefficient was then calculated from:

$$\frac{\text{Concentration of ion in organic}}{\text{Concentration of ion in aqueous}} = E_a^{\circ}$$

If the tests were carried out at such high acidity levels that their pH could not be measured with a pH meter, the acid requirements were calculated and the acidity adjusted by adding a measured amount of strong acid to an aliquot of the test solution. The extraction procedure already described was then followed.

Equilibration of the Amine

Shake the amine-diluent mixture with a solution of 2.5% sulphuric acid. Draw off and discard the aqueous fraction, and wash the organic fraction with portions of 0.5% sulphuric acid solution until the aqueous fraction maintains a constant level of about pH 1. In practice, 200 ml of 5% amine 9D-178 in Varsol - 1% decyl alcohol requires about 25 ml of 2.5% sulphuric acid, followed by two washes of 25 ml each of 0.5% sulphuric acid.

EXPERIMENTAL

The general plan followed in this work was to obtain the extraction coefficients, in sulphate solution, of uranium, thorium, and zirconium and of a number of other ions which were expected to be found in typical sample material. Conditions were varied with respect to pH, selection of diluent, and presence of neutral salts. It was hoped that sufficient information would be obtained to provide the basis of analytical methods for thorium and/or the rare earths. In any case, separation of thorium and the rare earths from a number of contaminants might be achieved. Particular attention was given to ions which caused interference with the thorium-Thorin colorimetric method. These ions included small amounts of zirconium and titanium, as well as gross amounts of uranium and the rare earths. Further work on analytical applications of results found here will be the subject of later reports.

Many of the early tests were carried out using non-equilibrated amine. While these results served to indicate possible separations, it was noted that free acidity values were affected considerably by the basicity of the hydroxyl form of the amine. pH values of solutions of low acidity, therefore, were affected quite markedly during the extraction. It was found that the pH of 25 ml of aqueous solution increased from 1.0 to 1.4 after contact with 25 ml of 5% 9D-178 in Varsol - 1% decyl alcohol. This resulted in higher apparent extraction, using non-equilibrated amine, than with equilibrated amine, but in reality this effect was caused by pH change. In all later tests, therefore, the solution of amine in diluent was equilibrated with sulphuric acid solution before use. Except where noted, then, all solutions of amine in diluent were equilibrated as described under PROCEDURE (page 6).

The procedure used in determining extraction coefficients is that described on page 6, except where deviations are noted. In tests where pH values of 0.5 and lower were used, these pH values are considered to be approximate when based on pH meter readings. Where measured amounts of acid were added the acidity figures are quoted in terms of molarity.

Extraction of Various Ions by Amine 9D-178

Uranium

Extraction coefficients were determined for uranium in sulphuric acid solution, using amine 9D-178 in various diluents. Details of these tests are given in Table 1, and a comparison of the different

TABLE I

Extraction of Uranium with Amine 9D-178 in Various Diluents

Test	g/l Uranium (as U ₃ O ₈)			Acidity in H ₂ SO ₄		Phase Ratio, org/aq	Remarks	Extraction Coefficient, E _a	Organic Phase
	Present	Organic phase	Aqueous phase	pH	Molarity				
1	1.70	1.75	0.002	1.1	0.06	1:1	Non-equilibrated amine	875	5% amine-85% Varsol -10% hexane
2	"	1.60	0.055	-	0.54	"	"	29	"
3	"	1.58	0.25	-	1.0	"	"	6.3	"
4	"	1.23	0.30	-	1.2	"	"	4.1	"
5	"	1.00	0.70	-	1.5	"	"	1.4	"
6	"	0.75	1.00	"	1.8	"	"	0.75	"
7	8.00	-	0.014	1.5	0.02	2:1	Equilibrated amine	285	5% amine-94% Varsol -1% decyl alcohol
8	"	-	0.031	1.0	0.08	"	"	128	"
9	"	-	0.72	-	0.6	"	"	5.1	"
10	"	-	2.28	-	1.4	"	"	1.2	"
11	8.00	-	0.072	1.0	0.08	1:1	"	111	10% amine - 88% Varsol -2% decyl alcohol
12	"	-	0.260	0.6	0.20	"	"	30	"
13	"	-	2.80	-	1.4	"	"	1.9	"
14	6.67	-	0.006	1.45	0.03	1.7:1	"	654	5% amine in carbon tetrachloride
15	8.00	-	0.012	0.90	0.10	2:1	"	332	"
16	"	-	0.40	-	0.60	"	"	9.5	"
17	"	-	1.32	-	1.0	"	"	2.5	"
18	4.00	7.84	0.003	2.0	-	1:2	"	2613	10% amine in carbon tetrachloride
19	"	7.84	0.016	0.95	0.09	"	"	490	"
20	"	7.74	0.073	0.6	0.2	"	"	106	"
21	"	6.93	0.45	-	1.0	"	"	15	"
22	"	5.82	1.00	-	1.5	"	"	5.8	"
23	6.67	-	0.002	1.0	-	1:1	H ₂ O ₂ present	>3300	15% amine in carbon tetrachloride
24	"	-	0.002	1.0	-	"	Ascorbic acid	>3300	"
25	6.67	-	0.043	1.45	-	1:1	Equilibrated amine	154	10% amine in chloroform
26	8.00	-	0.17	0.90	-	-	"	46	"
27	"	-	3.24	-	1.0	-	"	1.5	"

solvent mixtures is shown graphically in Figure 1. Results of these tests indicated that uranium extracted readily with amine 9D-178 at low acidities but extraction fell off sharply at higher acidities. Carbon tetrachloride was the most satisfactory of the three diluents tried, whereas chloroform was least efficient, from the standpoints both of extraction efficiency and of spraying loss during the shaking procedure. Phase separation in all cases was satisfactory, although 5% solutions of amine in diluent generally separated more quickly than stronger solutions of amine. It was not considered that the use of amine solutions stronger than 5% would be justified except where gross amounts of uranium were concerned and convenience assumed greater importance.

Thorium

Extraction coefficients determined for thorium, under conditions shown in Table 2, followed the same general pattern as for uranium. These results, also shown in Figure 2, indicated that thorium was extracted more readily by amine 9D-178 in carbon tetrachloride than in Varsol diluent. The extraction of thorium generally tended to fall off more sharply at stronger acidities than was the case with uranium.

The use of decyl alcohol to obtain better phase separation was found to be very helpful for both uranium and thorium when using Varsol diluent. It was found that the extraction coefficients for thorium were lowered as the amount of decyl alcohol increased (Figure 3). Use of a 2% decyl alcohol solution showed no appreciable improvement in phase separation over a 1% solution. It was decided that for future tests using Varsol as the diluent, a diluent mixture of 1% decyl alcohol per 5% unit of amine concentration would be used.

TABLE 2

Extraction of Thorium with Amine 9D-178 in Various Diluents

Test	g/l Thorium (as ThO ₂)			Acidity in H ₂ SO ₄		Phase Ratio, org/aq	Remarks	Extraction Coefficient E _a ^o	Organic Phase
	Present	Organic phase	Aqueous phase	pH	Molarity				
1	1.28	1.19	0.020	0.6	0.20	1:1	Non-equilibrated amine	60	5% amine - 94% Varsol - 1% decyl alcohol
2	"	0.26	0.97	-	1.0	"	"	0.27	"
3	"	0.063	1.24	-	1.5	"	"	0.05	"
4	2.50	-	0.022	1.4	-	1:1	Equilibrated amine	113	5% amine - 94% Varsol - 1% decyl alcohol
5	"	-	0.14	1.0	-	"	"	17	"
6	"	-	0.91	0.6	-	"	"	1.8	"
7	1.28	-	0.009	1.5	-	"	"	142	"
8	"	-	0.038	1.0	-	"	"	33	"
9	"	-	0.83	0.65	-	"	"	0.54	"
10	1.28	-	0.069	0.95	-	1:1	Equilibrated amine	18	10% amine - 88% Varsol - 2% decyl alcohol
11	1.28	-	0.002	1.5	-	1:1	Equilibrated amine	639	5% amine in carbon tetrachloride
12	"	-	0.017	1.0	-	"	"	74	"
13	"	-	0.54	0.65	-	"	"	1.4	"
14	1.28	-	0.0035	1.5	-	1:1	Equilibrated amine	366	15% amine in carbon tetrachloride
15	"	-	0.009	0.95	-	"	"	137	"

Zirconium and Molybdenum

As other workers (4) had indicated that zirconium and molybdenum extracted from sulphate solutions with long chain alkyl amines, extraction coefficients were determined for these ions at various sulphuric acid concentrations. Tests on zirconium were carried out using non-equilibrated amine, while molybdenum tests utilised both equilibrated and non-equilibrated amine. Details of these tests are given in Table 3.

It was evident, from these results, that zirconium and molybdenum extracted strongly with amine 9D-178 in Varsol over a fairly wide range of acidities. A comparison of extraction coefficients of uranium, thorium, zirconium and molybdenum, using non-equilibrated amine 9D-178, indicated that a partial separation of thorium from the other three ions could be obtained by extracting at higher acidities (Figure 4). Possibility of a considerable separation of molybdenum from these other ions was indicated by the inefficient stripping of molybdenum from the organic phase with 10% hydrochloric acid. Thorium, uranium and zirconium stripped very well under the same conditions.

Lanthanum, Cerium and Mixed Rare Earths

A number of tests were carried out to evaluate the extraction of lanthanum, cerium, and mixed rare earths with amine 9D-178 in various diluents. These results are shown in Table 4. In the case of lanthanum, it was found that 15% solutions of the amine in carbon tetrachloride tended to form emulsions at pH values of 1 and greater. Extraction

TABLE 3

Extraction of Zirconium and Molybdenum with Amine 9D-178 in Various Diluents

Test	g/l zirconium (as ZrO ₂)			Molarity in H ₂ SO ₄	Phase Ratio, org/aq	Remarks	Extraction Coefficient, E _a	Organic Phase
	Present	Organic phase	Aqueous phase					
1	1.38	1.30	<0.025	0.09	1:1	Non-equilib- rated amine	>50	5% amine-85%Varsol -10% hexane
2	"	1.32	0.065	0.54	"	"	20	"
3	"	1.14	0.21	1.04	"	"	5.4	"
4	"	1.04	0.37	1.20	"	"	2.8	"
5	"	0.87	0.61	1.50	"	"	1.4	"
6	"	0.66	0.77	1.80	"	"	0.86	"
<u>g/l* molybdenum (as Mo)</u>								
7	1.50	0.58	0.007	0.10	1:1	Some H ₂ O ₂ present -Also 0.6 g/l ascorbic acid	213	Non-equilibrated 5% amine -94% Varsol-1% decyl alcohol
8	"	0.24	0.07	1.0	"	"	20	"
9	"	0.23	0.11	1.35	"	"	13	"
10	2.76	0.38	0.020	0.20	"	Some H ₂ O ₂ present	137	Equilibrated 5% amine -94% Varsol-1% decyl alcohol
11	"	0.63	0.095	1.0	"	-	28	"
12	"	0.64	0.17	1.5	"	-	15	"

* Molybdenum was incompletely stripped from the organic phase with hydrochloric acid, so the E_a value was calculated from the Mo present and the Mo found in the aqueous barren.

TABLE 4

Extraction of Lanthanum, Cerium and Mixed Rare Earths with Amine 9D-178 and Tri-isooctyl Amine in Various Diluents

Test	Element	g/l Constituent			Acidity in H ₂ SO ₄		Phase Ratio, org/aq	Remarks	E _a	Organic Phase
		Present	Organic	Aqueous	pH	Molarity				
1	La	1.25	0.011	-	1.0	-	1:1	-	0.009	15% TIOA in CCl ₄
2	"	1.25	0.017	-	1.5	-	"	-	0.014	"
3	"	1.25	0.24	-	1.0	-	0.75:1	light emulsion	0.17	15% 9D-178 in CCl ₄
4	"	1.25	0.38	-	1.5	-	1:1	heavy emulsion	0.44	"
5	"	2.00	0.12	-	1.0	-	1:1	-	0.064	5% 9D-178 in CCl ₄
6	"	2.00	0.35	-	1.1	-	"	-	0.21	"
7	"	1.14	0.11	-	1.1	-	"	-	0.11	"
8	"	1.00	0.070	-	1.1	-	"	6g/l ascorbic	0.075	"
9	"	1.33	0.069	-	1.0	-	1:1	-	0.054	5% 9D-178 in Varsol
10	Mixed Rare Earths Oxides	1.67	0.096	1.56	1.0	-	1:1	An excess of H ₂ O ₂ present	0.062	5% 9D-178 in CCl ₄
11	"	1.82	0.019	1.79	1.0	-	1:1	"	0.011	15% TIOA in CCl ₄
12	"	5.1	0.23	4.67	-	0.10	1:1	"	0.049	Non-equilibrated 5% 9D-178 -94% Varsol-1% decyl alcohol
13	"	"	0.10	4.92	-	0.25	"	"	0.020	"
14	"	"	0.12	4.95	-	0.50	"	"	0.024	"
15	"	"	0.11	4.95	-	1.0	"	"	0.022	"
16	CeO ₂	2.4	0.17	2.17	-	0.20	1:1	12.5 g/l ascorbic acid	0.078	"
17	"	"	1.9	0.36	-	0.20	"	-	5.3	"

coefficients were high in this case but lower values were obtained with 5% amine solutions.

The results of tests where Varsol was used as a diluent indicated that lower coefficients might be expected with this diluent. Cerium was extracted to a considerably smaller degree in the presence of ascorbic acid than was the case in the absence of a reducing agent. In the case of mixed rare earths, extraction coefficients were generally satisfactory in the presence of hydrogen peroxide. The general trend of higher extraction coefficients at lower acidities was found to apply here. Three tests using tri-isooctylamine are included in Table 4, for convenience. Low extraction of lanthanum and mixed rare earths was found with this amine.

Titanium

A series of tests was carried out to evaluate the selectivity of amine 9D-178 with respect to titanium. As seen from Table 5, there is some pickup of titanium in all tests, especially at higher pH values. Hydrogen peroxide and/or ascorbic acid were present in all cases. Results appeared to vary and were seldom reproducible. Titanium extraction was generally higher with carbon tetrachloride than with Varsol as diluent. It apparently would be necessary to work at a pH of about 0.6, or lower, to get satisfactorily low coefficients, or else several scrubs would be required. The presence of titanium interferes in the colorimetric determination of thorium with thorin and could not be tolerated in more than trace amounts. This would make the use of

TABLE 5

Extraction of Titanium with Amine 9D-178 in Varsol and Carbon Tetrachloride

Test	g/l Titanium (as Ti)			Acidity in H ₂ SO ₄		Phase Ratio, org/aq	Remarks	E _a	Organic Phase
	Present	Organic phase	Aqueous phase	pH	Molarity				
1	0.96	0.62	0.34	0.6	0.20	1:1	H ₂ O ₂ present	1.8	Non-equilibrated 5% amine-94% Varsol - 1% decyl alcohol
2	2.39	0.11	2.27	-	1.0	"	"	0.049	"
3	"	0.075	2.32	-	1.5	"	"	0.032	"
4	0.71	0.22	0.50	0.6	0.20	"	"	0.44	"
5	0.34	-	0.32	0.6	0.20	"	12.5 g/l ascorbic acid present	0.063	"
6	0.71	0.080	0.60	0.6	-	"	25 g/l ascorbic acid	0.13	Equilibrated 5% amine-94% Varsol -1% decyl alcohol
7	"	0.043	-	0.6	-	"	"	0.065	"
8	"	0.045	0.57	0.6	-	"	"	0.079	"
9	"	0.17	0.52	0.80	-	"	"	0.33	"
10	"	0.35	0.33	1.0	-	"	"	1.1	"
11	"	0.24	0.45	1.0	-	"	"	0.53	"
12	1.50	0.46	0.95	0.6	0.20	"	25 g/l ascorbic acid + a little H ₂ O ₂	0.48	"
13	"	0.10	1.29	-	1.0	"	"	0.078	"
14	"	0.12	1.26	-	1.5	"	"	0.095	"
15	0.71	0.23	-	1.0	-	"	25 g/l ascorbic acid	0.48	5% amine in carbon tetrachloride
16	1.41	0.71	0.69	1.0	-	"	"	1.0	"
17	"	0.18	1.21	0.6	-	"	"	0.15	"

amine 9D-178 of questionable value as a way of separating thorium and titanium before thorium determination.

Cobalt, Nickel, Manganese, Vanadium and Iron

The extraction characteristics of a number of common ions with amine 9D-178 were determined, with the results shown in Table 6. The ions tested were cobalt, nickel, manganese, vanadium and iron. None of the ions tested extracted to any large extent, although some iron pickup was noted at low acidities. Due to the fact that non-equilibrated amine was used in these tests, the acidity values shown, at low acidity levels, were not reliable. The acidity value shown in Test 16 in Table 6 was considerably higher, therefore, than the actual acidity of the aqueous solution during shake out and does not indicate the true iron pickup at 0.1M. In spite of this, however, the tests indicated that a separation of the five ions shown here from thorium, uranium, zirconium and molybdenum, could be obtained readily, using amine 9D-178.

Extraction of Various Ions with Tri-isooctylamine

Uranium

Extraction coefficients for uranium with tri-isooctylamine were determined. Results, as shown in Table 7 and Figure 5, indicate that uranium readily extracts over a fairly wide pH range, with reasonable extraction being obtained at pH values as low as 0.3. The effect of different amounts of sodium sulphate on uranium extraction with TIOA was found to be considerable, with extraction falling off as the amount of sodium sulphate increased (Figure 6). In all cases, uranium extraction increased at higher pH values.

TABLE 6

Extraction of Various Ions with Amine 9D-178 in Various Diluents

Test	g/l Constituent		Aqueous phase	Molarity in H ₂ SO ₄	Phase Ratio, org/aq	Remarks	E _a [*]	Organic Phase
	Present	Organic phase						
1	1.04 g/l cobalt (as Co)	0.069	0.91	0.20	1:1	12.5 g/l ascorbic acid	0.076	Non-equilibrated 5% 9D-178 -94% Varsol-1% decyl alcohol
2	"	0.071	0.91	1.0	"	"	0.078	"
3	"	0.070	0.90	1.5	"	"	0.077	"
4	1.03 g/l nickel (as Ni)	0.011	0.97	0.20	"	"	0.011	"
5	"	0.017	0.97	1.5	"	"	0.018	"
6	1.65 g/l manganese (as Mn)	0.009	1.57	0.20	"	"	0.006	"
7	"	0.006	1.57	1.0	"	"	0.004	"
8	"	0.007	1.61	1.5	"	"	0.004	"
9	2.51 g/l vanadium (as V)	0.20	2.49	0.20	"	Excess of H ₂ O ₂	0.080	"
10	"	0.045	2.56	1.5	"	"	0.018	"
11	0.63 g/l V	0.056	0.53	0.10	"	12.5 g/l ascorbic acid	0.11	"
12	"	0.028	0.57	1.0	"	"	0.049	"
13	"	<0.02	0.53	1.35	"	"	<0.04	"
14	0.57 g/l iron (as Fe)	<0.005	0.53	1.0	"	"	<0.01	"
15	"	0.005	0.53	1.35	"	"	0.009	"
16	0.22 g/l Fe	0.050	0.11	0.10	"	"	0.45	Non-equilibrated 5% 9D-178 in hexane
17	2.32 g/l Fe	0.076	2.20	0.50	"	"	0.035	Non-equilibrated 5% 9D-178 -85% Varsol-10% hexane
18	"	0.034	2.27	1.0	"	"	0.015	"
19	"	0.072	2.25	1.5	"	"	0.032	"

TABLE 7

Extraction of Uranium with 5% TIOA in Varsol

Test	g/l Uranium (as U ₃ O ₈)		pH	Phase Ratio, org/aq	Sodium Sulphate Added, g/l Na ₂ SO ₄	Extraction Coefficient, E _a [*]	Organic Phase
	Present	Found in aqueous phase					
1	2.55	0.014	1.0	1:2	-	362	5% TIOA-94% Varsol-1% decyl alcohol
2	2.55	0.049	1.0	1:2	25	102	"
3	2.04	0.003	1.0	1:1	-	679	"
4	"	0.011	1.0	"	20	184	"
5	"	0.026	1.0	"	100	77	"
6	"	0.014	0.5	"	-	145	"
7	"	0.029	0.5	"	20	69	"
8	"	0.066	0.5	"	100	30	"
9	"	0.055	0.3	"	-	36	"

Thorium

The extraction coefficients of thorium with tri-isooctylamine were determined at various pH values, both in the absence and in the presence of sodium sulphate. Extraction of thorium was very low as compared with uranium, but as the pH was increased extraction of thorium also increased. In order to get a satisfactory separation of uranium and thorium, it would probably be necessary to work at a pH of about 0.6. As the presence of sodium sulphate cuts down thorium extraction, a satisfactory separation of uranium and thorium could probably be obtained at a higher pH by adding sodium sulphate. These results are given in Table 8, and are shown graphically in Figures 5 and 6. The presence of large amounts of sulphate caused erratic thorium assays, so a preliminary ammonium precipitation step for removal of sulphate was required before final colorimetric determination of thorium by the Thorin method. A few discrepancies still exist at the 0.5 pH level, however, as can be seen from tests 12-16, in Table 8.

Zirconium

Extraction coefficients for zirconium with 5% TIOA in Varsol were determined with and without the presence of sulphate. As shown in Table 9 and Figure 5, zirconium extracted to a considerable extent at a pH of 0.5 and higher, provided sodium sulphate was absent. The presence of sodium sulphate reduced extraction coefficients for zirconium at all acidities tried, and particularly at a pH about 0.5 (Figure 7). Assays tended to be erratic, especially at low levels of zirconium, and

TABLE 8

Extraction of Thorium with 5% TIOA in Varsol

Test	g/l Thorium (as ThO ₂)			pH	Phase Ratio, org/aq	Sodium Sulphate added, g/l Na ₂ SO ₄	Extraction Coefficient E _a **	Organic Phase
	Present	Organic phase	Aqueous phase					
1	0.85	0.55	-	1.5	1:1	-	1.8	5% TIOA-94% Varsol-1% decyl alcohol
2	"	0.20	0.52	1.5	"	83	0.31	"
3	"	0.27	-	1.0	"	-	0.47	"
4	"	0.23	-	1.0	"	8.3	0.37	"
5	"	0.15	-	1.0	"	25	0.21	"
6	"	0.061	0.61	1.0	"	83	0.078	"
7	"	0.27	0.55	1.0	"	-	0.47	"
8	"	0.15	-	0.70	"	-	0.21	"
9	"	0.025	-	0.70	"	20	0.030	"
10	"	0.026	0.68	0.70	"	33	0.031	"
11	"	0.018	0.63	0.70	"	83	0.022	"
12	"	0.003	-	0.5	"	-	0.004	"
13	1.02	0.045	0.86	0.5	"	-	0.05	"
14	0.93	0.004	0.80	0.5	"	20	0.004	"
15	1.02	0.007	0.73	0.5	"	100	0.007	"
16	1.02	0.049	0.88	0.3	"	-	0.05	"

* 10 g/l ascorbic acid present.

** E_a calculated from total thorium taken and thorium extracted into the organic phase. Because of the high sulphate content of the solution, thorium assays on the aqueous fraction were often low.

TABLE 9

Extraction of Zirconium with 5% TIOA in Varsol

Test	g/l Zirconium			pH	Phase Ratio, org/aq	Sodium Sulphate added, g/l Na ₂ SO ₄	Extraction Coefficient, E _a *	Organic Phase
	Present	Organic phase	Aqueous phase					
1	0.40	0.68	0.009	1.0	1:2	-	76	5% TIOA-94% Varsol-1% decyl alcohol
2	0.16	0.30	0.008	1.0	1:2	20	38	"
3	0.32	0.30	0.004	0.90	1:1	-	75	"
4	0.32	0.18	0.12	0.90	1:1	20	1.5	"
5	0.32	0.25	0.008	0.90	1:1	130	31	"
6	0.32	-	0.016	0.70	1:1	-	19*	"
7	0.40	0.82	0.009	0.70	1:2	-	91	"
8	0.32	0.40	0.062	0.70	1:2	20	6.5	"
9	0.32	-	0.004	0.70	1:1	27	79	"
10	0.32	0.32	0.008	0.70	1:1	40	40	"
11	0.32	0.27	0.027	0.70	1:1	170	10	"
12	0.32	0.32	0.006	0.5	1:1	-	53	"
13	0.64	0.65	0.010	0.5	1:1	-	65	"
14	0.32	0.23	0.19	0.5	1:1	20	1.2	"
15	0.64	0.29	-	0.5	1:1	100	0.83	"
16	0.32	0.092	0.27	0.3	1:1	-	0.34	"
17	0.32	0.090	0.20	0.3	1:1	-	0.45	"
18	0.26	-	0.13	0.5	1:1	50	1.0	"
19	0.26	-	0.18	0.5	1:1	100	0.44	"

* Hydrolysis noted in aqueous fraction.

several assays included in Table 9 (i.e. Tests 4 to 9) illustrate the extent of variance of results in some cases. It was felt that the cause of this was mainly the difficulty of determining low amounts of zirconium, although some trouble was encountered from hydrolysis of the zirconium test solution. In any event, it was felt that much of the zirconium could be separated from thorium by TIOA extraction, with the efficiency of the separation dependent on the conditions used.

Extraction of Various Ions with Di(tridecyl P) Amine

Thorium

Extraction coefficients for thorium with di(tridecyl P) amine (DTDA) in Varsol and carbon tetrachloride were determined at various pH levels. The effect of sodium sulphate on extraction coefficients was also determined. Results of these tests, as shown in Table 10, indicated that this amine is considerably better than amine 9D-178 as a thorium extractant over the pH range 0.6-1.0. A comparison of the thorium extraction of these amines is shown in Figure 8. The presence of sodium sulphate decreased the extraction coefficient, but this effect was less at pH 0.6 than at pH 1.0. Whereas Varsol and carbon tetrachloride were equally suitable as diluents at pH 1.0, carbon tetrachloride proved to be the superior diluent at pH 0.6.

Titanium

Extraction coefficients were determined for titanium with di(tridecyl P) amine in Varsol and carbon tetrachloride at pH values of 1.0 and 0.6. The effect of sodium sulphate on titanium extraction was

TABLE 10

Extraction of Thorium with Di(tridecyl P) Amine in Varsol and Carbon Tetrachloride

Test	g/l Thorium (as ThO ₂)		pH	Phase Ratio, org/aq	Sodium Sulphate added, g/1Na ₂ SO ₄	Extraction Coefficient, E _a	Organic Phase
	Present	Found in aqueous					
1	1.02	0.0016	1.0	1:2	-	1275	5% DTDA-94% Varsol-1% decyl alcohol
2	"	0.0028	1.0	"	20	728	"
3	"	0.0048	1.0	"	50	422	"
4	"	0.0018	0.8	"	-	1134	"
5	"	0.0068	0.6	"	-	298	"
6	"	0.0080	0.6	"	20	252	"
7	"	0.0078	0.6	"	50	260	"
8	"	0.0018	1.0	"	-	1134	5% DTDA in carbon tetrachloride
9	"	0.0034	1.0	"	20	600	"
10	"	0.0030	1.0	"	50	680	"
11	"	0.0016	0.8	"	-	1275	"
12	"	0.0038	0.6	"	-	534	"
13	"	0.0040	0.6	"	20	508	"
14	"	0.0036	0.6	"	50	564	"

also studied. The results obtained appeared at first to give low titanium pickup at pH 0.6, in the presence of ascorbic acid. Subsequent work (Table 11), however, showed that the titanium complex formed was extracted quite strongly by DTDA, even at pH 0.5, and was inefficiently stripped from the organic phase with 1 M hydrochloric acid. The amount and freshness of the ascorbic acid added appeared to affect results. The fresher the ascorbic acid solution and the larger the amount added, the greater the titanium pickup. This phase of the work will receive further investigation.

By using hydrogen peroxide instead of ascorbic acid, lower extraction coefficients were obtained for titanium (Table 11). No difficulty was found in stripping the titanium complex from the organic fraction in this case. The titanium pickup was too high, however, to show much promise of a separation of thorium and titanium unless several scrubs were used. It was further noted that, as might be expected from previous tests, titanium pickup was enhanced by using carbon tetrachloride as a diluent, and lessened in the presence of sodium sulphate salts.

TABLE 11

Extraction of Titanium with Di(tridecyl P) Amine in Varsol and Carbon Tetrachloride

Test	g/l Titanium (as Ti)			pH	Phase ratio org/aq	Special reagents added	Extraction coefficient E_2	Organic Phase	
	Present	Found in aqueous phase	Found in stripped organic phase						
1	1.09	0.18	-	-	1.0	1:1	25 g/l ascorbic acid	5.1	5% DTDA -94% Varsol-1% decyl alcohol
2	1.09	0.48	-	-	0.5	1:1	6.3 g/l ascorbic acid	1.3	"
3	1.21	0.45	0.51	0.26	0.5	1:1	25 g/l ascorbic acid	1.7	"
4	1.09	0.63	-	-	0.5	1:1	25 g/l ascorbic acid +25 g/l sodium sulphate	0.73	"
5	1.09	0.44	-	-	1.0	1:1	an excess of hydrogen peroxide	1.5	"
6	1.09	0.81	-	-	0.5	1:1	"	0.35	"
7	1.21	0.91	0.002	0.29	0.5	1:1	"	0.33	"
8	1.09	0.85	-	-	0.5	1:1	excess hydrogen peroxide +25g/l sodium sulphate	0.28	"
9	1.09	0.19	-	1.59	1.0	1:2	25 g/l ascorbic acid	9.5	5% DTDA in carbon tetrachloride

Lanthanum and Mixed Rare Earths

As knowledge of extractability of lanthanum and mixed rare earths with di(tridecyl P) amine was of value in a possible separation of these ions from thorium, particularly in a procedure for the isolation of the rare earths, extraction coefficients for lanthanum and mixed rare earths were determined for di(tridecyl P) amine in Varsol and carbon tetrachloride. These results, as shown in Table 12, indicated that rare earth pickup was low enough to permit separation from thorium. The mixed rare earth solution was prepared from Lindsay rare earth mixture No. 330. Rare earth pickup with di(tridecyl P) amine was greater when using carbon tetrachloride as diluent.

TABLE 12

Extraction of Lanthanum and Mixed Rare Earths with Di(tridecyl P) Amine
in Varsol and Carbon Tetrachloride

* Test	g/l mixed rare earths (as RE ₂ O ₃)		pH	Phase Ratio, org/aq	Sodium Sulphate added, g/l Na ₂ SO ₄	Extraction Coefficient, E _a [*]	Organic Phase
	Present	Found in organic phase					
1	2.00	0.46	1.0	1:1	-	0.30	5% DTDA -94% Varsol- 1% decyl alcohol
2	"	0.053	0.6	"	-	0.027	"
3	"	0.054	0.6	"	40	0.028	"
4	"	1.01	1.0	"	-	1.0	5% DTDA in carbon tetrachloride
5	"	0.092	0.6	"	-	0.048	"
6	"	0.040	0.6	"	40	0.020	"
<u>g/l lanthanum(as La)</u>							
**							
7	1.25	0.81	1.5	1:1	-	1.8	15% DTDA in carbon tetrachloride
8	"	0.70	1.0	"	-	1.3	"
9	2.00	1.31	1.5	"	-	1.9	5% DTDA in carbon tetrachloride
10	1.14	0.69	1.1	"	-	1.5	"
11	1.00	0.51	1.1	"	-	1.0	"
12	2.00	0.98	1.0	"	-	0.96	"
13	1.60	0.41	1.0	"	-	0.35	5% DTDA in Varsol

* 10 g/l ascorbic acid present in Tests 1-6, and 6 g/l ascorbic acid in Test 11.

** Some tendency towards emulsions appeared in Tests 7-13.
This was more pronounced with stronger DTDA solutions.

RESULTS AND DISCUSSION

Thorium was found to be extracted efficiently by both amine 9D-178 and di(tridecyl P) amine (DTDA) at a pH of 1.0 or higher. Extraction coefficients at pH values as low as 0.6 were satisfactorily high in the case of DTDA, but not with 9D-178. Tri-isooctyl amine (TIOA) did not extract appreciable amounts of thorium, especially at pH levels approaching 0.5. Pickup of thorium by TIOA was lessened by the presence of salts, such as sodium sulphate. In the case of DTDA, the effect of sodium sulphate was negligible at pH levels around 0.6.

Uranium was readily extracted by TIOA and 9D-178. It could be separated from thorium by extraction with TIOA at pH levels below 1.0, and preferably close to 0.5. The presence of large quantities of sodium sulphate inhibited the extraction of uranium to some extent.

Zirconium and molybdenum extracted readily with 9D-178 and TIOA. The same extraction characteristics have been noted with DTDA (4). These amines would be expected to follow the general tendency of decreasing extraction coefficients with rising acidity and rising salt content. Thorium could be separated, at least partially, from zirconium, molybdenum and uranium by working at acidity levels of about 1.2-1.5 M in sulphuric acid, and extracting with 9D-178. In such a case, virtually all of the thorium would remain in the aqueous fraction, while the major portion of the zirconium, molybdenum and uranium would be taken into the organic fraction. A further separation of molybdenum could be obtained as a result of the difficulty of extracting this ion from 9D-178 with the 10% hydrochloric acid stripping agent.

It was found that 9D-178 gave low extraction coefficients for titanium at a pH level of about 0.6. Because of the low thorium extraction with 9D-178 at this pH, a good separation of titanium from thorium, using this amine, would be unlikely. The results obtained using DTDA at pH 0.5, in the presence of hydrogen peroxide, indicated that most of the titanium could be separated from thorium, particularly in the presence of sodium sulphate and/or with the use of several scrubs of the organic fraction.

Extraction coefficients for lanthanum and the rare earths were reasonably low for amine 9D-178 and TIOA at a pH of about 1.0. DTDA showed a fairly high extraction coefficient for these elements at this pH, however, and it was found advisable to lower the pH to about 0.6 with this amine if a satisfactory separation of the rare earths from thorium were to be obtained.

Ions such as manganese, nickel, cobalt and vanadium showed little tendency to be extracted by non-equilibrated amine 9D-178 over a wide acidity range, although there was some pickup of iron indicated at low pH levels.

The use of carbon tetrachloride as a diluent generally resulted in higher extraction coefficients than was the case with a Varsol diluent. At the same time, pickup of undesirable ions was also greater. The choice of diluent, then, would be largely a matter of convenience, after considering a number of factors.

CONCLUSIONS

From the viewpoint of analytical considerations several conclusions can be drawn from this work:

1. Thorium can be separated from uranium and zirconium by extraction from sulphate solutions of the latter ions with TIOA in Varsol. It would be necessary to adjust the pH of the solution mixture to about 0.7 or lower, and preferably use a scrub of the organic fraction to ensure recovery of thorium. The presence of a high concentration of sodium salts is desirable, except where zirconium is high, in which case complete extraction of zirconium might be difficult, especially if the pH of the solution is approaching pH 0.5. This general technique, then, is of value in possible procedures for thorium, and/or the rare earths, on sample material where uranium and zirconium are present.

2. Thorium may be separated from the bulk of the uranium, zirconium and molybdenum by extracting the latter ions with 9D-178 from a solution 1.3-1.5 molar in sulphuric acid thereby leaving thorium in the aqueous fraction. Alternatively, thorium, uranium, zirconium and molybdenum may be separated from many other contaminants by first extracting with amine 9D-178 at a pH of about 1.0 and then removing thorium from the organic fraction by stripping with 1.3-1.5 molar sulphuric acid solution. These techniques are applicable to thorium determination on material containing zirconium and considerable amounts of uranium and molybdenum.

3. Titanium may be partially separated from thorium by the extraction technique described in 2, using 9D-178 at pH 1.0. Sufficient titanium would be extracted, however, to cause interference in the Thorin colorimetric method for thorium. It would be necessary to lower the pH to below 0.6 before the titanium extraction coefficient would be sufficiently low, and at this pH thorium extraction is not efficient.

4. Efficient separation of thorium and titanium would not be expected with DTDA at pH values as low as 0.5, in the presence of ascorbic acid. By using several scrubs, reasonable separation of thorium and titanium might be obtained at pH 0.5 if hydrogen peroxide is present, and ascorbic acid is absent.

5. The rare earths may be freed of uranium, zirconium, thorium and molybdenum by the techniques described in 1, 2 and 3. A particular application which shows promise is for rare earth determination on high grade uranium or thorium precipitates. No solvent extraction technique was found which would adequately separate titanium and the rare earths.

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(Figures 1 to 8 follow,
on pages 32 to 39.)

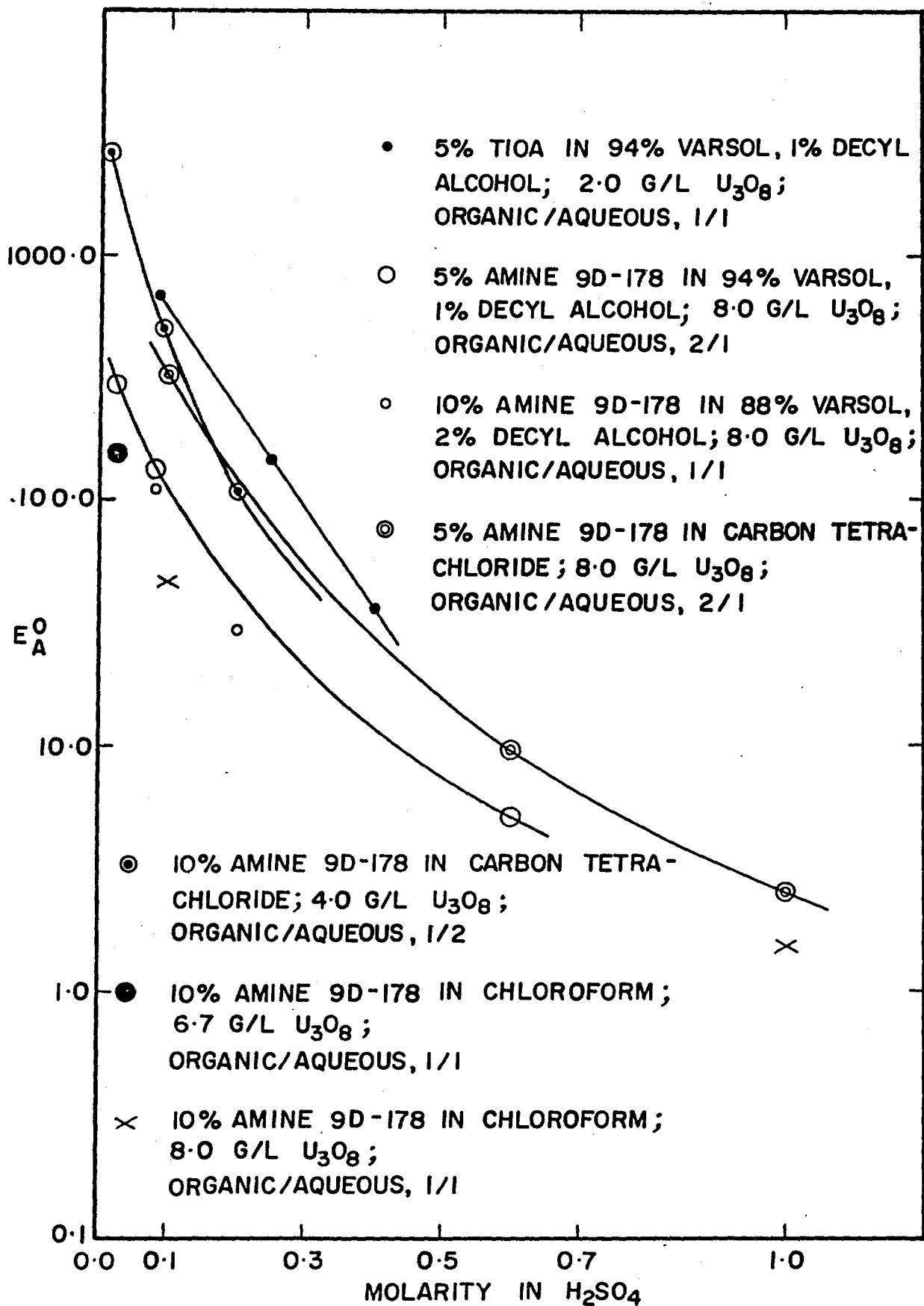


FIGURE 1

EXTRACTION OF URANIUM WITH TRI-ISOOCTYLAMINE
AND AMINE 9D-178 IN VARIOUS DILUENTS

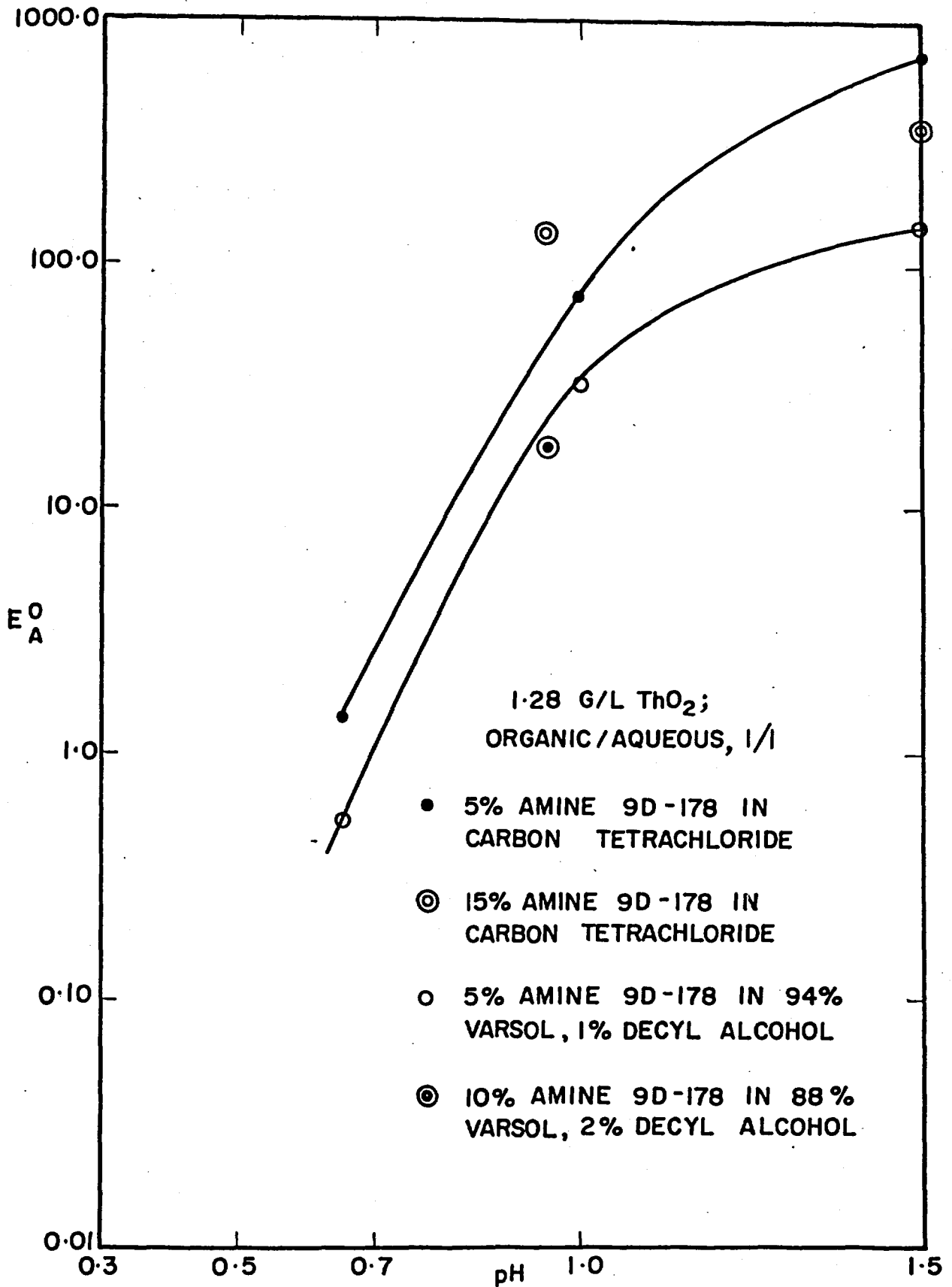


FIGURE 2

EXTRACTION OF THORIUM WITH AMINE
9D-178 IN VARSOL AND CARBON TETRACHLORIDE

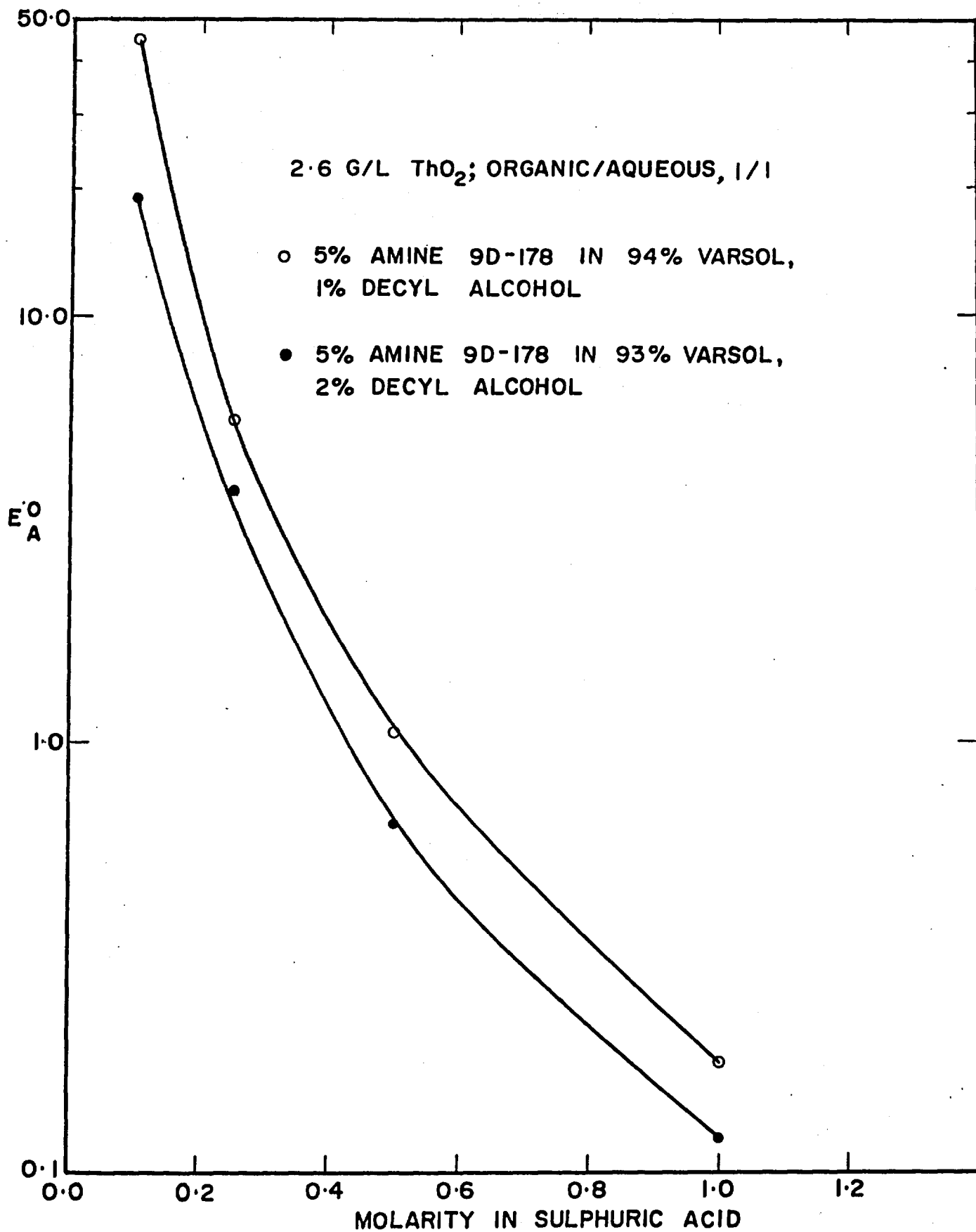


FIGURE 3

EFFECT OF DECYL ALCOHOL ON EXTRACTION OF THORIUM WITH AMINE 9D-178 IN VARSOL

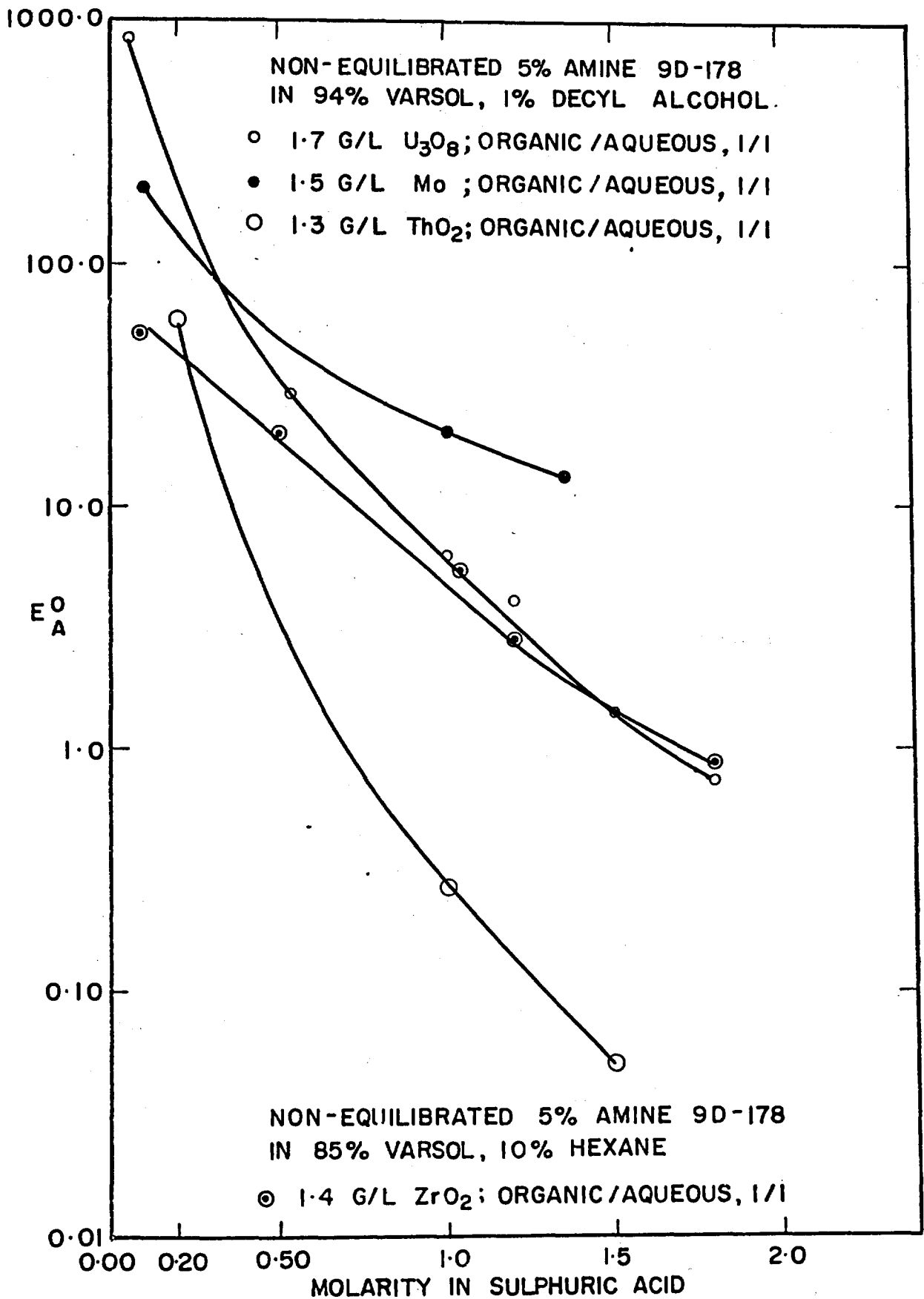


FIGURE 4

EXTRACTION COEFFICIENTS OF URANIUM, ZIRCONIUM, THORIUM AND MOLYBDENUM WITH NON-EQUILIBRATED AMINE 9D-178 IN VARSOL

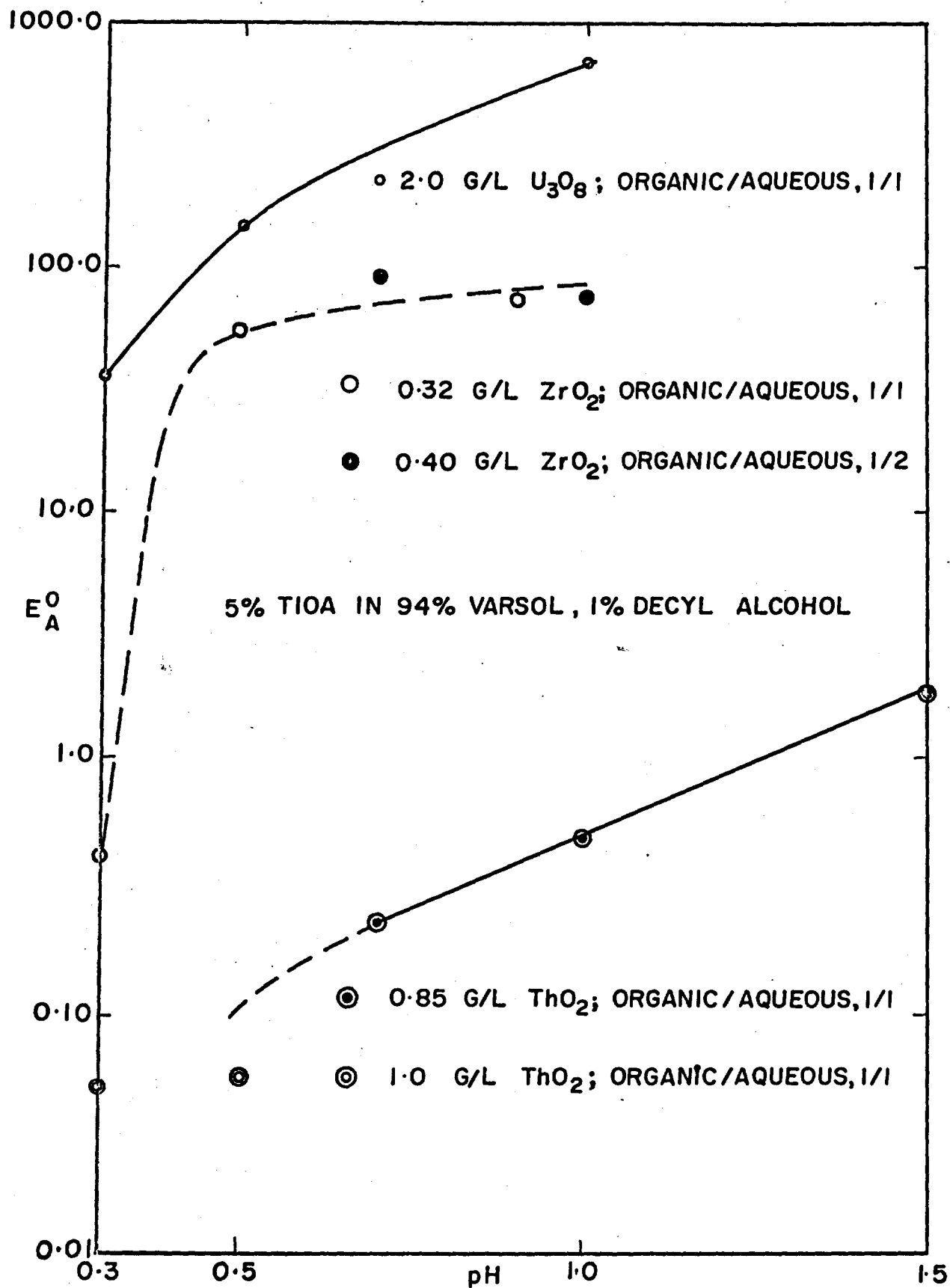


FIGURE 5

EXTRACTION COEFFICIENTS OF URANIUM, THORIUM AND ZIRCONIUM
WITH TRI-ISOOCTYLAMINE IN VARSOL

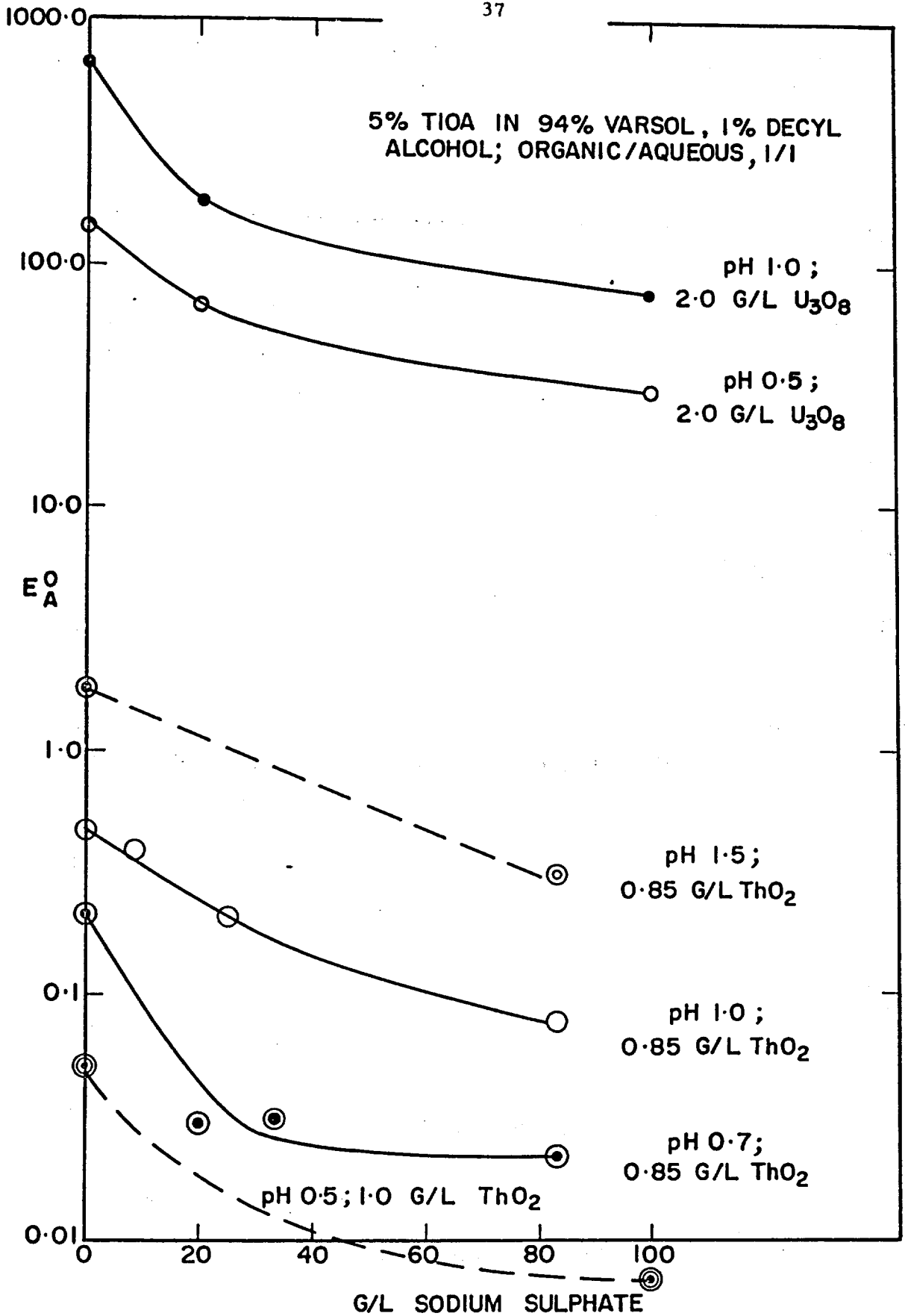


FIGURE 6

EFFECT OF SODIUM SULPHATE ON EXTRACTION OF URANIUM AND THORIUM WITH TRI-ISOOCTYLAMINE IN VARSOL

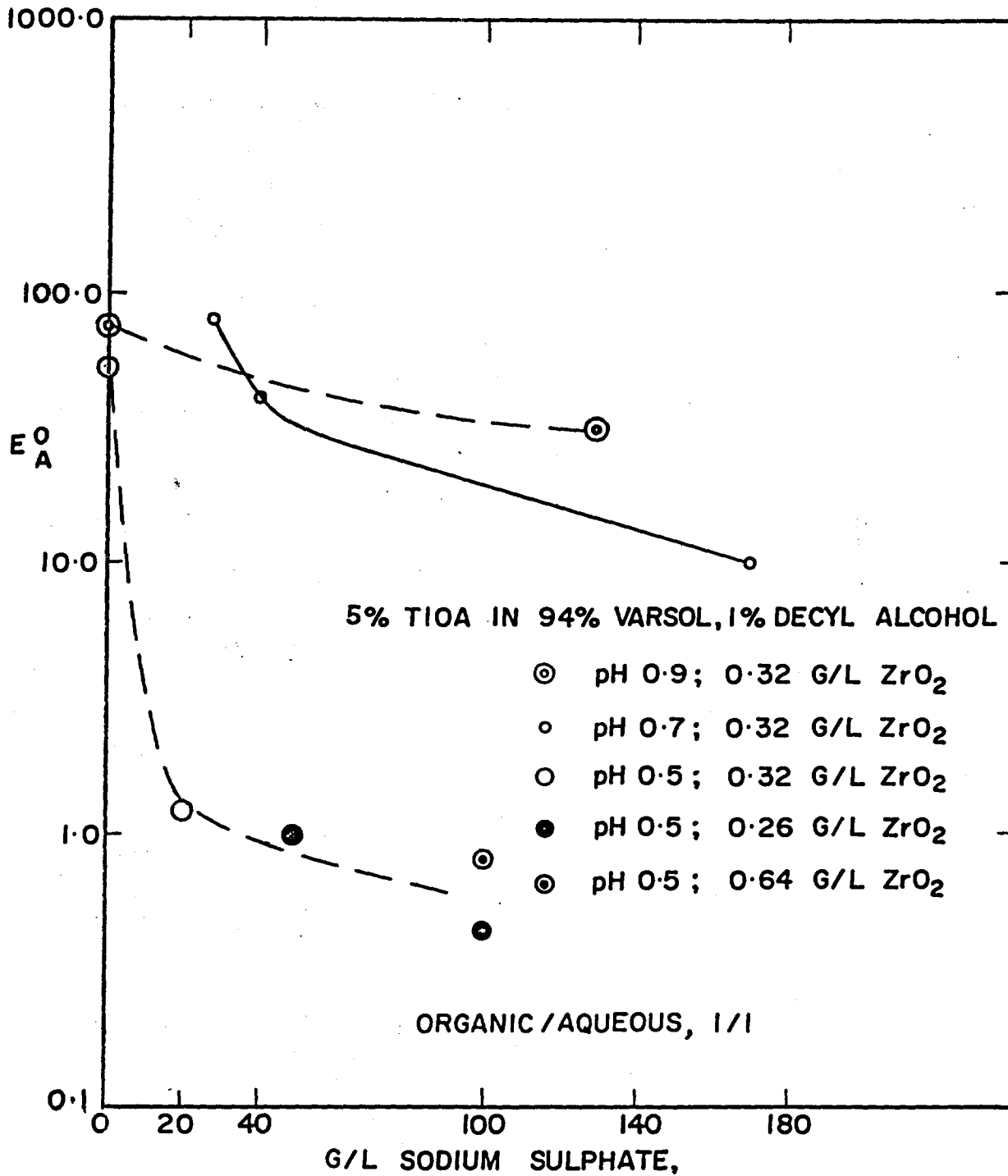


FIGURE 7

EFFECT OF SODIUM SULPHATE ON EXTRACTION OF ZIRCONIUM WITH TRI-1SOOCTYLAMINE IN VARSOL

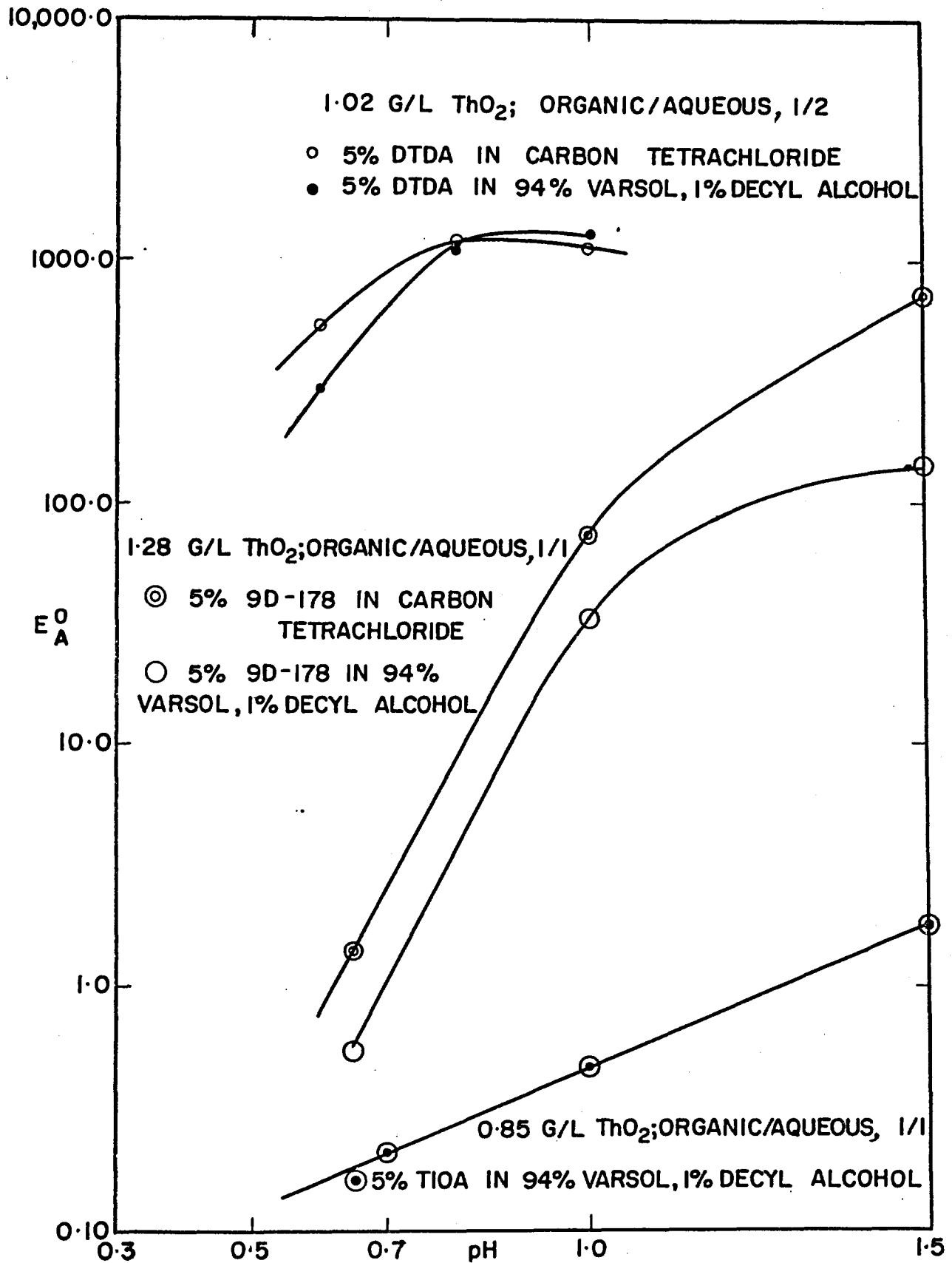


FIGURE 8

EXTRACTION OF THORIUM WITH DI(TRIDECYL P) AMINE,
AMINE 9D-178 AND TRI-ISOOCTYLAMINE IN VARIOUS DILUENTS

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