EQUILIBRIUM EXTRACTION CHARACTERISTICS
OF
ALKYL AMINES AND NUCLEAR FUELS METALS
IN
NITRATE SYSTEMS

PROGRESS REPORT XII

January 1, – September 31, 1963

BY

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Progress Report for the Period

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1.0 Summary

1.1 Niobium

During this period, January 1 to September 31, 1963, the work on niobium extraction by alkyl amines has been completed. A final report has been prepared ($\underline{1}$) and should be issued shortly.
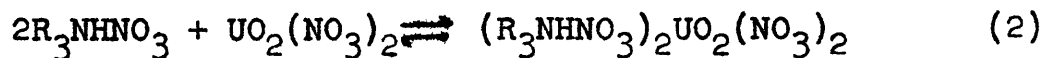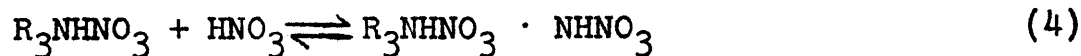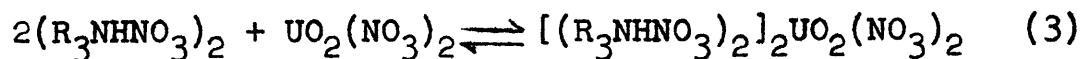
1.2 Extraction of Mercury, Antimony and Selenium

Using radiotracers, the distribution of these metals between nitric acid and trilaurylamine in toluene was studied as a function of nitric acid and amine concentration. There was no significant effect of time of contact in the range 2 to 24 hours. Mercury showed a maximum extraction coefficient of ~1, selenium of ~0.1, and antimony of ~0.005, all at 0.1$\underline{N}$ nitric acid concentration, and 0.32$\underline{M}$ amine in toluene. The effect of nitric acid concentration was similar in each case, minima being observed at ~5$\underline{M}$ nitric acid.

1.3 Extraction of Uranium

In an attempt to elucidate the chemistry of uranium extraction, a careful study was made of the system $UO_2(NO_3)_2$ - NH_4NO_3 - HNO_3 - H_2O - TLA - $C_6H_5CH_3$ at varying uranium, amine and nitric acid concentrations and constant nitrate concentration. It was found that 1) for every uranyl ion transferred to the organic phase, two nitrate ions were also transferred; 2) that the number of amine nitrate molecules associated with each extracted uranyl ion varied between 2 and 4, depending on the amine and acid concentrations and 3) the only available hydrogen ions in the organic phase were those due to hydrolysis of the amine nitrate and those of the "unbound" nitric acid.

Based on these results and on the observation that in xylene, trilaurylamine nitrate exists in both monomeric and polymeric forms, where the polymers are almost entirely dimers, a model of extraction was proposed in which the uranyl nitrate was solvated by both amine nitrate monomers and dimers, and in which the free amine nitrate concentration available for taking part in the monomer-dimer equilibrium and subsequent extractions, was reduced by the extraction of "unbound" nitric acid. The equilibria considered were:

$$2R_3NHNO_3 \rightleftharpoons (R_3NHNO_3)_2 \tag{1}$$

$$2R_3NHNO_3 + UO_2(NO_3)_2 \rightleftharpoons (R_3NHNO_3)_2UO_2(NO_3)_2 \tag{2}$$

$$2(R_3NHNO_3)_2 + UO_2(NO_3)_2 \rightleftharpoons [(R_3NHNO_3)_2]_2UO_2(NO_3)_2 \quad (3)$$

$$R_3NHNO_3 + HNO_3 \rightleftharpoons R_3NHNO_3 \cdot NHNO_3 \quad (4)$$

Values of the equilibrium constants for the first three equilibria could be obtained from some of the experimental data, and it was shown that this model was capable of explaining all of the experimental data quantitatively.

1.4 Identification of the Extractable Complexes of Ruthenium

A study of the extractable complexes of ruthenium was begun. Earlier work (2) has shown that there are two definite species of ruthenium which are extractable. An attempt has been made to identify these by titration of the organic phase (2). Instead, it is proposed to study the variation in nitrate content of the organic phase under conditions where the mole fraction of each of the extractable species in the organic phase can be calculated.

It was found impossible to determine the unbound nitric acid in the organic phase by titration due to reaction of the alkali titrant with the extracted ruthenium. However, it was found that the conductivity of the organic phase was a function only of the unbound nitric acid content of that phase. Using this, it is supposed that it will be possible to calculate the number of nitrate ions associated with the ruthenium, and thus determine the number associated with each ruthenium species.

1.5 Multicomponent Metal Extraction Using Radiotracers

A study was commenced of the extraction of several metals simultaneously from a nitrate solution by trilaurylamine nitrate in toluene. It is hoped that by determining distribution of the metals by radiotracer techniques, it will be possible to determine the extraction behavior of many elements throughout the periodic table more rapidly than previously. Initially, studies are being made of the extraction of copper, silver and gold.

2.0 Extraction of Niobium

During this period, experimental work centered about the effect of contact time on the distribution of niobium between nitrate solutions and Primene JM-T in toluene, in an attempt to elucidate the behavior of the extractable complexes. This work has been completed and written up. A final report will be published shortly (1).

3.0 Extraction of Mercury, Selenium and Antimony

3.1 Introduction

A short study was made of the solvent extraction behavior of mercury (II), selenium (IV) and antimony (III) in nitric acid solution as a function of acid and amine concentrations, as part of a general study of the extraction of metals by the tri-laurylamine nitrate-toluene system.

The metal concentrations in the aqueous and organic phases were determined by using radiotracers. Aliquots of each phase were counted in a well-type scintillation counter. Hg^{203} in nitric acid was purchased from Isotopes Division, ORNL. Se^{75}, Sb^{122} and Sb^{124} were produced by irradiation of the oxides in the MITR. After irradiation and cooling to allow unwanted activities to decay, these were each dissolved in minimum hydrochloric acid, evaporated close to dryness, and dissolved in nitric acid of the requisite strength. As the nitrate concentration was always at least 100 times that of the chloride, in the final solution, it was felt that any interference from the chloride anion would be negligible.

The amine, dissolved in toluene, was precontacted with nitric acid of the required strength. Aliquots of the amine nitrate in toluene and the metal in nitric acid were then equilibrated by shaking in screw top tubes in a constant temperature bath. Agitation times ranged from two hours to one day. Little effect of time of contact on the extraction was noted.

3.2 Extraction of Mercury

The results on the extraction of mercury are summarized in Figures 1 and 2. Good extraction is noted from dilute nitric acid solutions, but after passing through a minimum at approximately $5\underline{M}$, the extraction rises again at high acid concentrations.

It is possible that two different species are extracted at the low and high nitric acid concentrations. Figure 2 shows that, if the usual mass action expressions hold, the ratio of mercury to amine is 1:1 at low nitric acid concentrations, and 2:1 at high. Choi and Tuck (3) carried out studies using a different amine and diluent to that used here, and noted a similar 1:1 mercury to amine ratio at low nitric acid concentrations, which they ascribed to the extraction of $Hg(NO_3)_3$ via

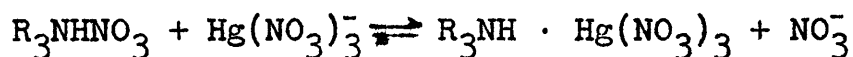$$R_3NHNO_3 + Hg(NO_3)_3^- \rightleftharpoons R_3NH \cdot Hg(NO_3)_3 + NO_3^-$$

Figure 1, Variation of Mercury Distribution Coefficient with Total Amine Concentration
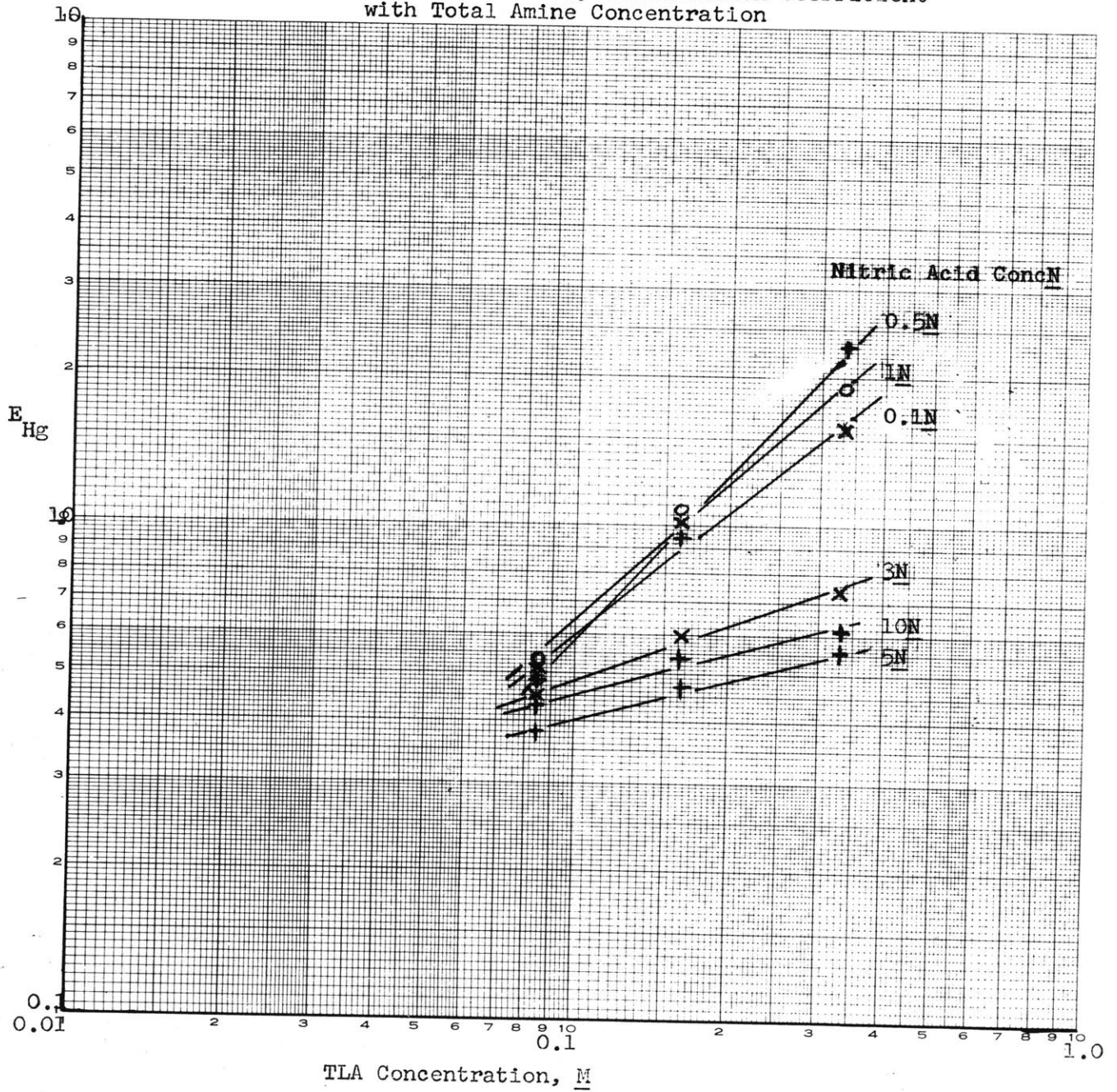
Figure 2, Variation of Mercury Distribution Coefficient
with Initial Nitric Acid Concentration

Initial HNO$_3$ Concentration, $\underline{M}$
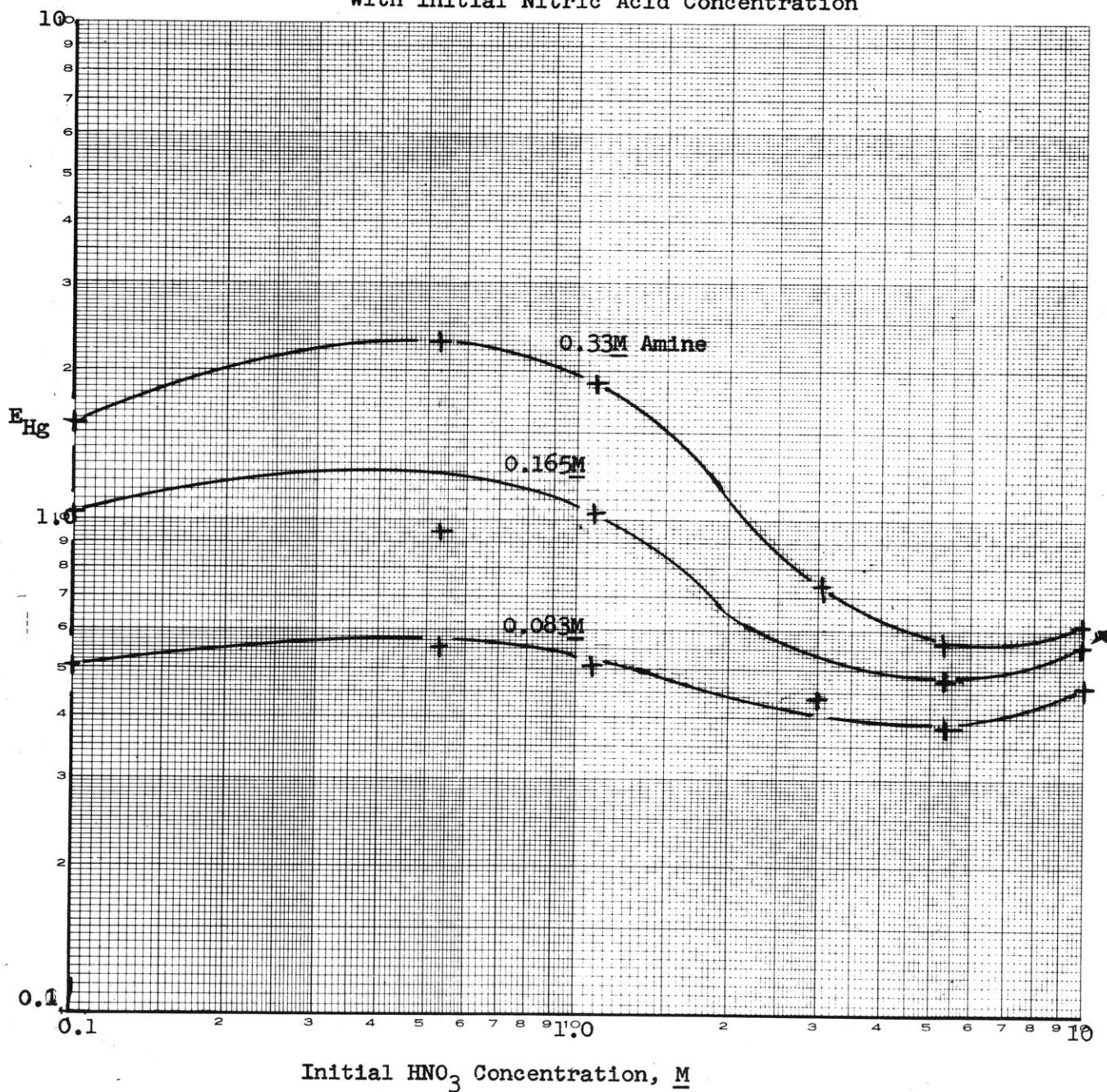
However, in the present study it was noted that, particularly at low nitric acid concentrations, a mercury species was present which tended to adsorb onto the walls of the contacting tube. This effect was noted both from the difficulty of decontaminating contacting tubes and from the poor "mass balance" for the liquid phases.

The minimum in extraction in the region of $5\underline{M}$ nitric acid is remarkable, as some elements show maxima in this region. These maxima have been ascribed to the effect of reduction of the free amine nitrate concentration by extraction of excess nitric acid, above $5\underline{M}$, leading to a decrease in the extraction of the metal ion (4). The increase in the extraction of these metal ions below $5\underline{M}$ is supposed to be due to the salting-out effect of the nitrate ions. In the case of mercury, no such mechanism can operate. Possibly a hydrolyzed mercury species is extracted at low acid concentrations. Increasing the acid concentration would then lead to a decrease in concentration of this species, until at the higher acid concentrations a different extractable species becomes dominant.

3.3 Extraction of Selenium

The data on the extraction of selenium are summarized in Figures 3 and 4. The behavior is very similar to that of mercury, though the magnitude of the extraction coefficients are lower by a factor of roughly 10^2. However, at both high and low nitric acid concentrations, the slopes of the logarithmic plots of distribution coefficient versus amine concentration are close to 1, possibly indicating a 1:1 amine-selenium ratio in the extracted complexes. The anomalous point at the highest amine and lowest acid concentration may possibly be due to incomplete precontacting of the organic phase. If this were so, then the equilibrium acid concentration for the metal extraction would be lower than the reported value, which is the initial acid concentration. This decrease in the acid concentration could lead to a more extractable species of selenium, or could give high values of the extraction coefficient due to entrainment of the aqueous phase in the organic, since the interfacial tension between the two phases decreases as the pH increases.

3.4 Extraction of Antimony

These results are not reported in detail since there was considerable scatter in the results. This was due both to the very low extraction coefficients observed, of the order of a factor of 10 less than those for selenium, and to the low activity of the initial antimony sample. Both of these effects resulted in very low activity in the organic phase on extraction, so that the statistical error of counting was of the same order as that of the background. Again, however, a relatively high extraction

Figure 3, Variation of Selenium Distribution Coefficient
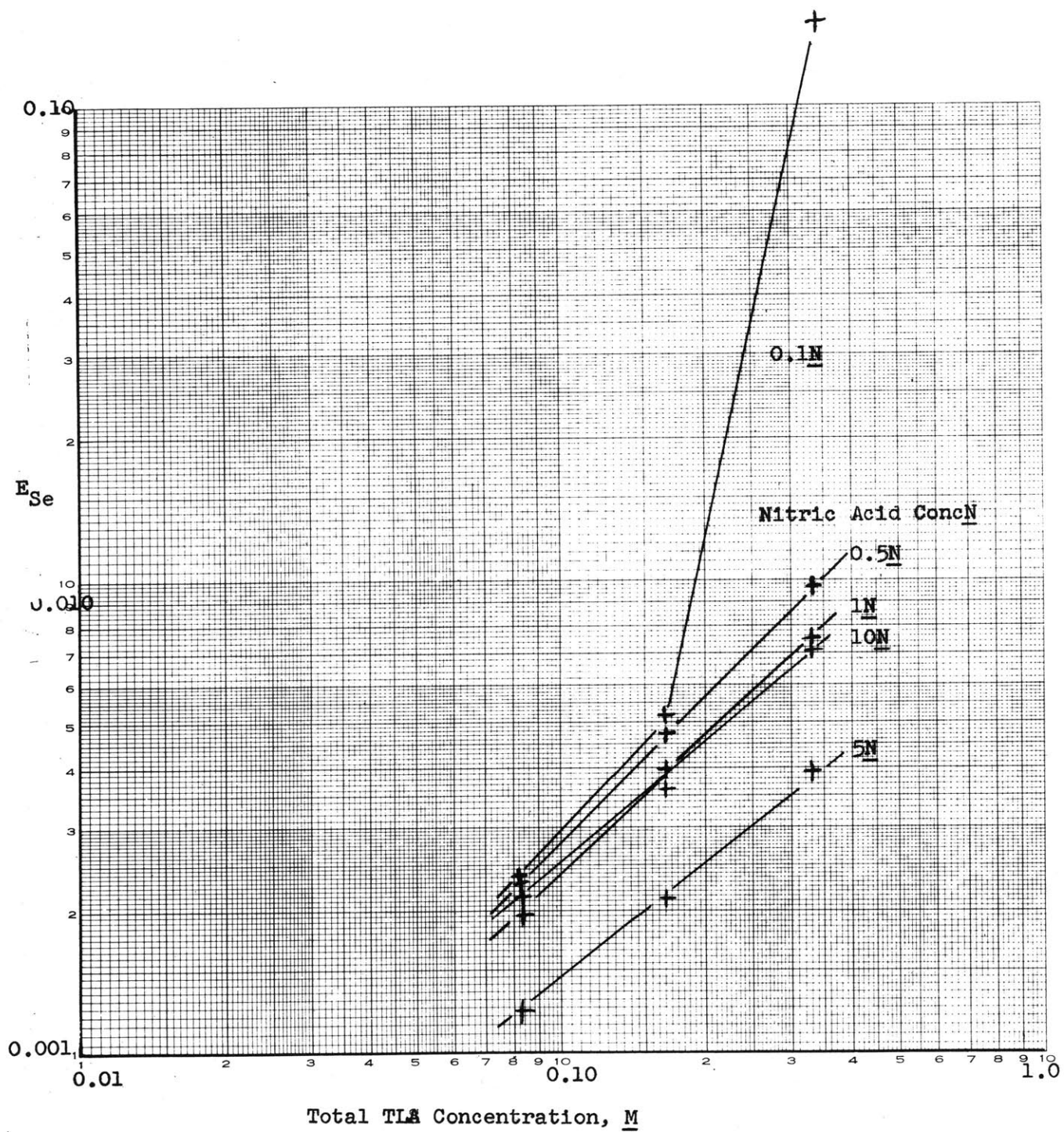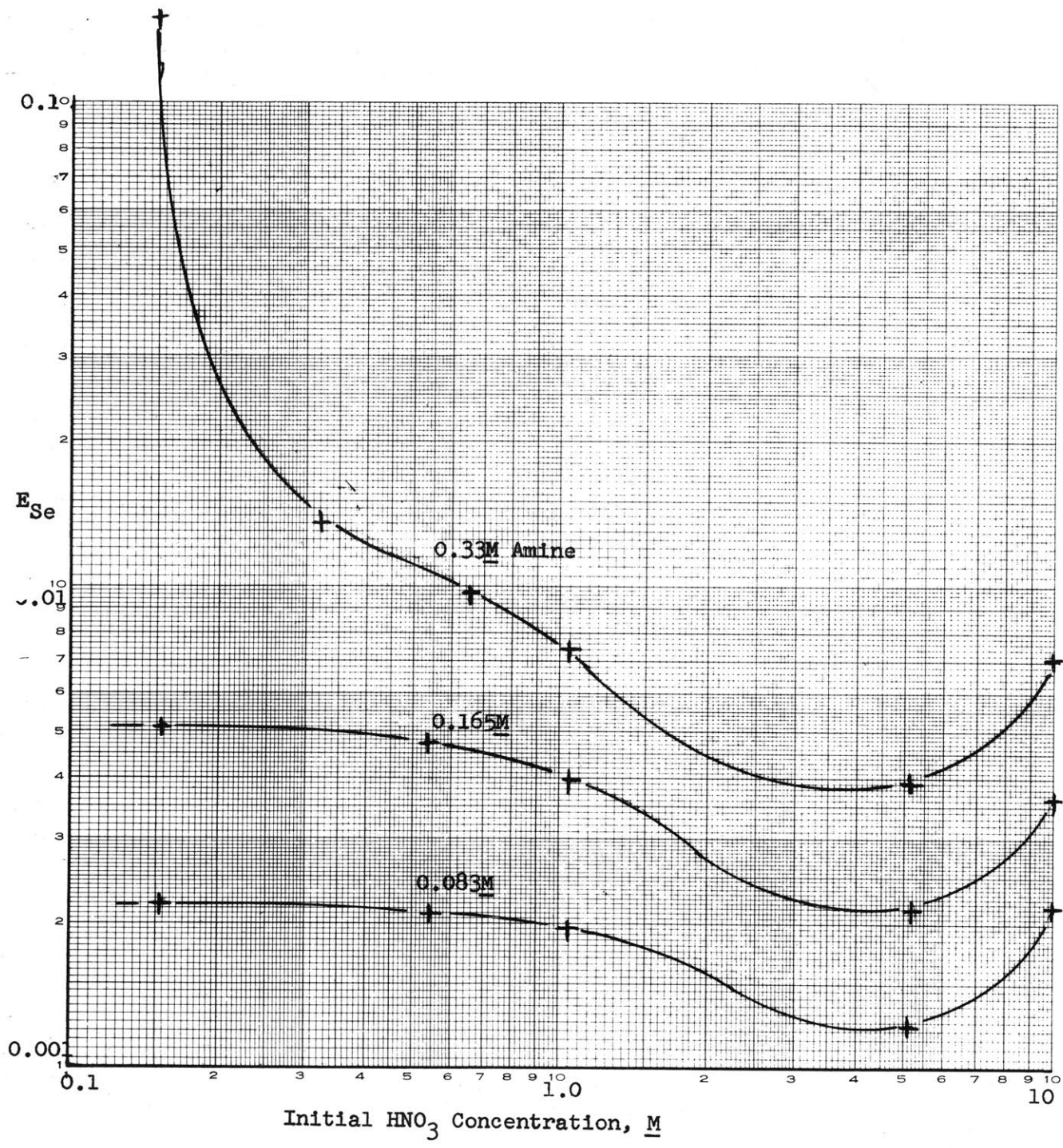with Total Amine Concentration

Figure 4, Variation of Selenium Distribution Coefficient
with Initial Nitric Acid Concentration

coefficient was observed at the lowest acid and highest amine concentration, and a third phase formed at the interface. The organic phase was observed in a Tyndal beam, but failed to show any evidence of aggregation. Moreover, on standing, a white precipitate was observed to form in the most dilute acid solutions. It seems likely that a hydrolyzed species may be extracted to some small extent at low acid concentrations.

4.0 The Extraction of Uranium by Trilaurylamine

4.1 Objectives

Earlier studies at this laboratory (4) had shown that uranium extraction data could be correlated by assuming that approximately 1.85 amines were associated with each extracted uranium, for several tertiary amine nitrates in toluene. Other workers (5) have found a range of amine to uranium ratios between 1:1 and 2:1, for different amines in various diluents. It has been postulated that these variations in amine to uranium ratio in the extracted complex may be due either to the extraction of different uranium species (6) or to the aggregation of the amine nitrates (6). A careful study of the system uranyl nitrate - nitric acid - tri-dodecylamine - toluene was therefore undertaken in an attampt to decide between these alternatives. It was also felt that the techniques developed in this study might be useful in a study of the extractable complexes of nitrosyl ruthenium (see Section 5).

4.2 Experimental Procedure

The variation of uranium distribution coefficient with amine and uranium concentration was followed at constant total nitrate concentration ($\sim 3M$) and hydrogen ion concentrations between 0.005 and 1M, additional nitrate being added as ammonium nitrate. In 1-5M ammonium nitrate solution, the activity coefficient of uranyl nitrate is practically constant (7), so that in the interpretation of the results uranium concentrations could be used in place of activities, without introducing serious error.
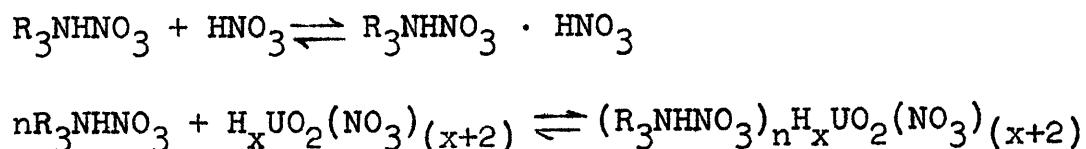
The amine was pre-equilibrated with the desired aqueous solution containing no uranium. Preliminary experiments showed that at the highest acidities and amine concentrations, four contacts of the organic phase with fresh aqueous phase at 1:1 phase volume ratio were necessary for equilibrium of the organic phase with nitrate and hydrogen ions. The amine nitrate solution was used almost immediately.

Aliquots of the aqueous and organic phases were shaken vigorously in a screw-top centrifuge tube, then equilibrated at 25.0°C by gentle shaking for 1 hour in a constant temperature bath. The phases were centrifuged and separated. A portion of the organic phase was titrated potentiometrically in acetone with aqueous NaOH, and a further portion was stripped with 1M Na_2CO_3 for determination of total nitrate and uranium.
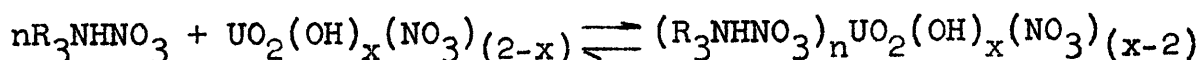
4.3 Results and Discussion

The results are summarized in Tables 1 and 2. Figure 5 shows the curves of the titration of the organic phase. Three breaks in this curve were noted, all of which were evident when "unbound" nitric acid, in the form $R_3NHNO_3 \cdot HNO_3$, and uranium were present in the organic phase. It was found possible to determine the unbound nitric acid concentration, $C_{unbound\ H^+}$, in the presence of uranium, by extrapolation of the curve to the halfwave potential of the reaction. Moreover, it was noted that in all cases the difference between the unbound acid end point was given by 3 equivalents of NaOH per U, as required by the precipitation of sodium di-uranate, which is evidence for the extraction of a uranyl nitrato species, rather than an acid uranyl nitrato species.

Nitrate in the organic phase is due to the amine nitrate, unbound nitric acid, and the nitrate associated with the uranium, according to the equilibria

$$R_3NHNO_3 + HNO_3 \rightleftharpoons R_3NHNO_3 \cdot HNO_3$$

$$nR_3NHNO_3 + H_xUO_2(NO_3)_{(x+2)} \rightleftharpoons (R_3NHNO_3)_n H_xUO_2(NO_3)_{(x+2)}$$

or possibly at very low acid concentrations

$$nR_3NHNO_3 + UO_2(OH)_x(NO_3)_{(2-x)} \rightleftharpoons (R_3NHNO_3)_n UO_2(OH)_x(NO_3)_{(x-2)}$$

Thus $C_{\underline{NO_3}} = C_{R_3N} + C_{unbound\ H^+} + XC_{\underline{U}}$

where X is the number of nitrate ions transferred with each uranium to the organic phase, and organic phase concentrations of species which may be present in both phases are indicated by underlining. Thus a plot of $C_{\underline{NO_3}}$ - $(C_{R_3N} + C_{unbound\ H^+})$ versus $C_{\underline{U}}$ should be of slope X. Such a plot is shown in Figure 6. The straight line through the points is of slope 2.0. This indicates that two nitrate ions are associated with each uranyl ion during the extraction, which is evidence that no acidic or hydrolyzed uranium species are extracted.

Attempts to determine the amine to uranium ratio by conventional means failed. Log-log plots of distribution coefficient versus free amine nitrate concentration gave a slope close to 2.0, which would indicate two amines per uranium. The free amine nitrate concentration was determined by subtracting the unbound nitric acid concentration and twice the uranium concentration. However, points at higher uranium concentration deviated seriously, as shown

Table 1
Effect of Amine Concentration on Uranium Distribution Coefficient

	Aqueous						Organic						
Amine Concen.	Initial Uranium	Initial Nitrate	Initial H^+	Equil. Uranium	Equil. Nitrate	Equil. H^+	Equil. Uran.	Equil. Nitrate	Equil. Total H^+	Equil. Unbound H^+	Phase Ratio	Mass Bal.	D_U
$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{M}$	$\underline{M}$	A/O	%	
.346[a]	.0170	2.72	.010	.00537	2.72	.010	.0158	.372	.393	Nil	4/3	101	2.91
.210[a]	"	"	"	.00941	2.72	.010	.00983	.229	.239	Nil	4/3	99	1.04
.109[a]	"	"	"	.0141	—	—	.00357	.116	—	—	4/3	99	.254
.0501[a]	"	"	"	.0162	—	—	.00102	—	—	—	4/3	100	.0624
.0201[a]	"	"	"	.0168	—	—	.00024	—	—	—	4/3	100	.0141
.0101[a]	"	"	"	.0169	—	—	.00005	—	—	—	1/1	100	.0030

									Initial Unbound H^+	Final Unbound H^+			
.339[b]	.0152	2.94	.945	.00609	2.90	.929	.0089	.446	.0984	.0933	1/1	98	1.45
.204[b]	"	"	"	.0083	2.93	.947	.0059	.269	.0531	.0512	1/1	94	.706
.103[b]	"	"	"	.0128	2.95	.945	.00210	.129	.0240	.0239	1/1	96	.169
.0515[b]	"	"	"	.0140	—	—	.00084	.0661	.0118	.0118	1/1	98	.060
.0208[b]	"	"	"	.0150	—	—	.000126	—	.0049	.0049	1/1	100	.0084
.0105[b]	"	"	"	.0152	—	—	.000084	—	.0025	.0024	1/1	100	.0006

a) Amine in equilibrium with 2.75 $\underline{M}$ NO_3^-, 0.010 $\underline{M}$ H^+

b) Amine in equilibrium with 2.95 $\underline{M}$ NO_3^-, 0.93 $\underline{M}$ H^+

Table 2

Effect of Uranium Concentration on Distribution Coefficient

		Aqueous					Organic						
Amine Concen.	Initial Uranium	Initial Nitrate	Initial H^+	Equil. Uranium	Equil. Nitrate	Equil. H^+	Equil. Uranium	Equil. Nitrate	Initial Unbound H^+	Final Unbound H^+	Phase Ratio	Mass Bal.	D_U
M	M	M	M	M	M	M	M	M	M	M	A/O	%	
.346[a]	.0153	2.72	.0048	.00350	2.71	.0048	.0114	.363	Nil	Nil	1/1	98	3.27
"	.0374	2.74	.0048	.0108	2.76	.0045	.0256	.387	–	–	1/1	97	2.37
"	.0910	2.80	.0046	.0415	2.82	.0046	.0486	.428	–	–	1/1	99	1.18
"	.187	2.86	.0042	.115	2.86	.0041	.0687	.474	–	–	1/1	99	.597
"	.384	2.80	.0043	.287	2.80	.0041	.0921	.511	Nil	Nil	1/1	98	.321
.339[b]	.0383	2.90	.945	.0172	2.91	.946	.0203	.468	.105	.093	1/1	98	1.18
"	.0936	2.92	.938	.0530	2.84	.940	.0410	.490	.105	.072	1/1	100	.775
"	.189	2.92	.940	.123	2.85	.950	.0616	.518	"	.058	1/1	98	.503
"	.405	3.22	.941	.312	3.16	.956	.0950	.578	"	.046	1/1	101	.305
"	.405	3.22	.941	.355	3.07	.962	.0996	.582	"	.042	2/1	100	.281

a) In equilibrium with 2.72 $\underline{M}$ NO_3, .0047 $\underline{M}$ H^+

b) In equilibrium with 2.90 $\underline{M}$ NO_3, .940 $\underline{M}$ H^+

Figure 5, Potentiometric Titration of Organic Phase

A Amine Nitrate, Nitric Acid
B Amine Nitrate, Uranyl Nitrate
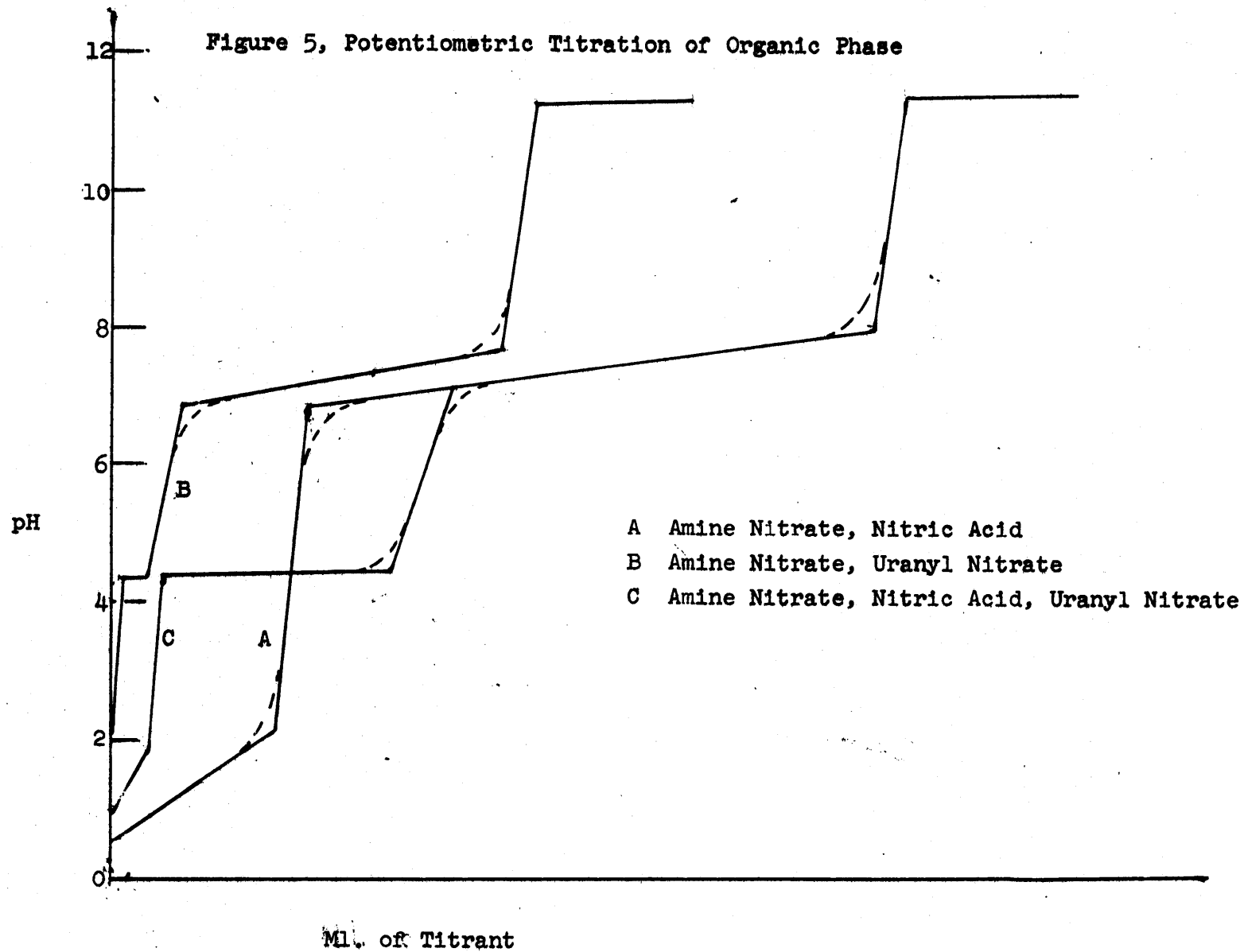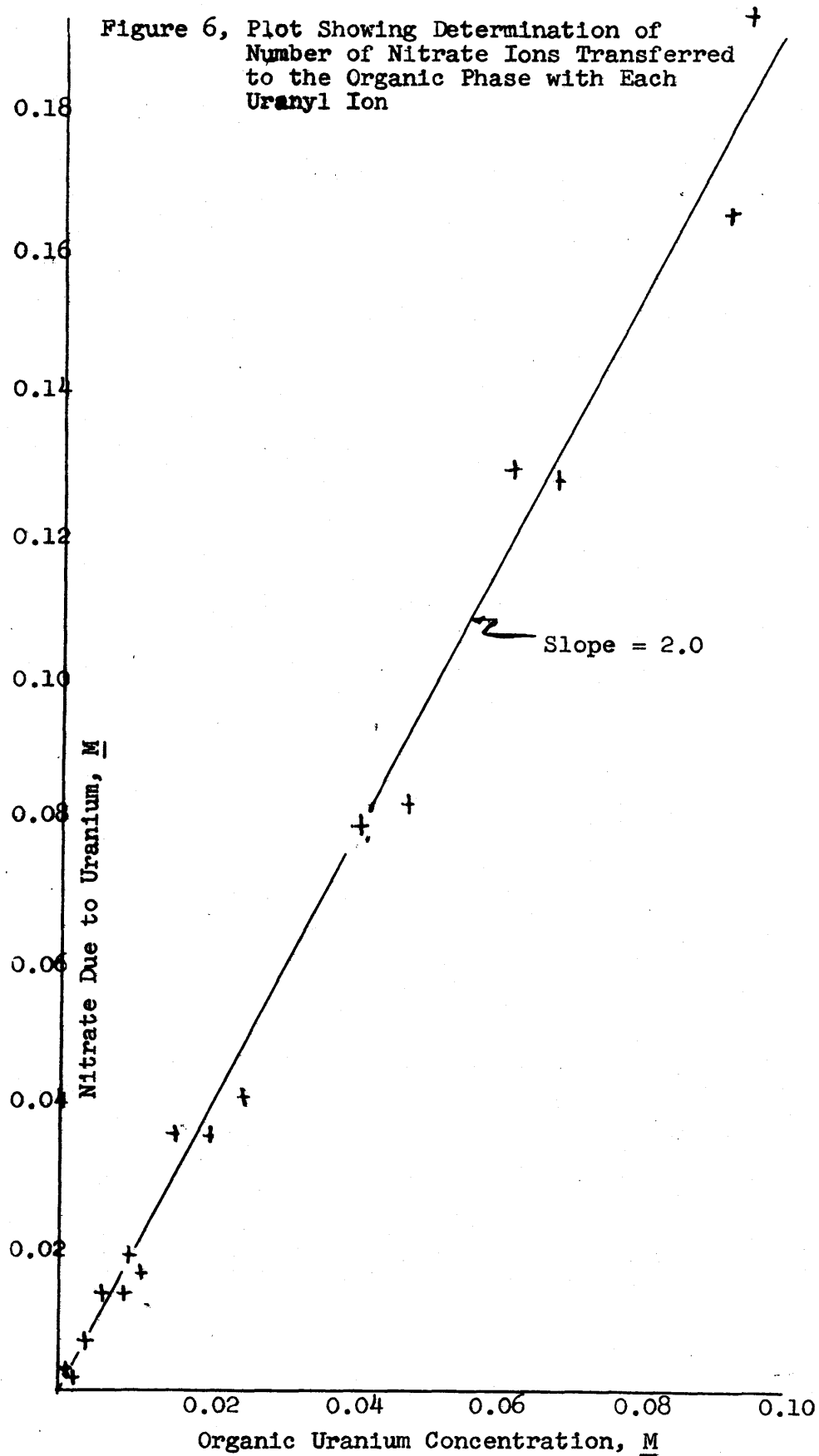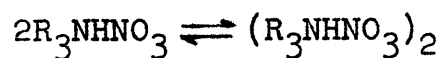C Amine Nitrate, Nitric Acid, Uranyl Nitrate

Figure 6, Plot Showing Determination of Number of Nitrate Ions Transferred to the Organic Phase with Each Uranyl Ion

in Figures 7 and 8. This is further illustrated by comparison of the experimental extraction isotherm with theoretical isotherms calculated assuming amine to uranium ratios between 1:1 and 4:1 as shown in Figure 9. It is evident that at low uranium concentrations there are between 3 and 4 amines per uranium, and at high uranium concentrations between 2 and 3.
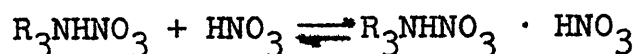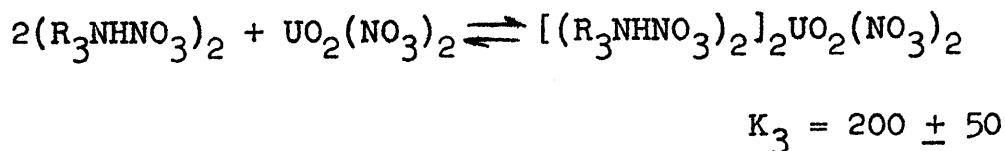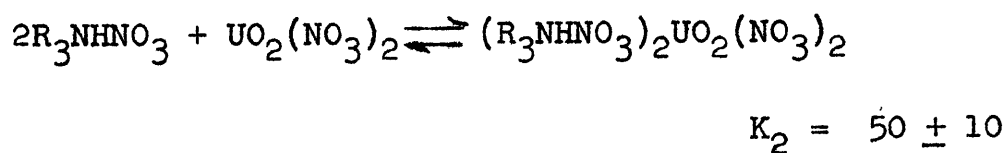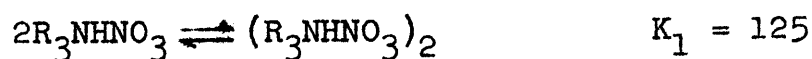
This is similar to the phenomenon noted in uranium extraction by di-2 ethylhexyl phosphoric acid, which was ascribed to polymerization of the complex at high uranium concentrations ($\underline{8}$). However, studies on the viscosity of the amine phase as a function of uranium concentration showed a decrease rather than the required increase in viscosity with increasing uranium loading (see Figure 10). Thus it seemed unlikely that this polymerization was responsible for the variation in amine to uranium ratio.

Attention was drawn to the results of Hogfeldt on dimerization of trilaurylamine nitrate in o-xylene ($\underline{9}$). The equilibrium constant for the equilibrium:

$$2R_3NHNO_3 \rightleftharpoons (R_3NHNO_3)_2$$

was found to be 125 + 25. Then our results might be explained by assuming that the amine dimer is able to extract uranium, as well as the monomer. Further, it was assumed that the amine nitrate - nitric acid complex was monomeric.

Using this model, it was found that the data could be calculated using

$$2R_3NHNO_3 \rightleftharpoons (R_3NHNO_3)_2 \qquad K_1 = 125$$

$$2R_3NHNO_3 + UO_2(NO_3)_2 \rightleftharpoons (R_3NHNO_3)_2UO_2(NO_3)_2$$

$$K_2 = 50 \pm 10$$

$$2(R_3NHNO_3)_2 + UO_2(NO_3)_2 \rightleftharpoons [(R_3NHNO_3)_2]_2UO_2(NO_3)_2$$

$$K_3 = 200 \pm 50$$

$$R_3NHNO_3 + HNO_3 \rightleftharpoons R_3NHNO_3 \cdot HNO_3$$

where, based on Hogfeldt's work, values of K_1 = 100, 125 and 150 were assumed, and least square values for K_2 and K_3 were determined by simultaneous solution of the mass action expressions for these equilibria.
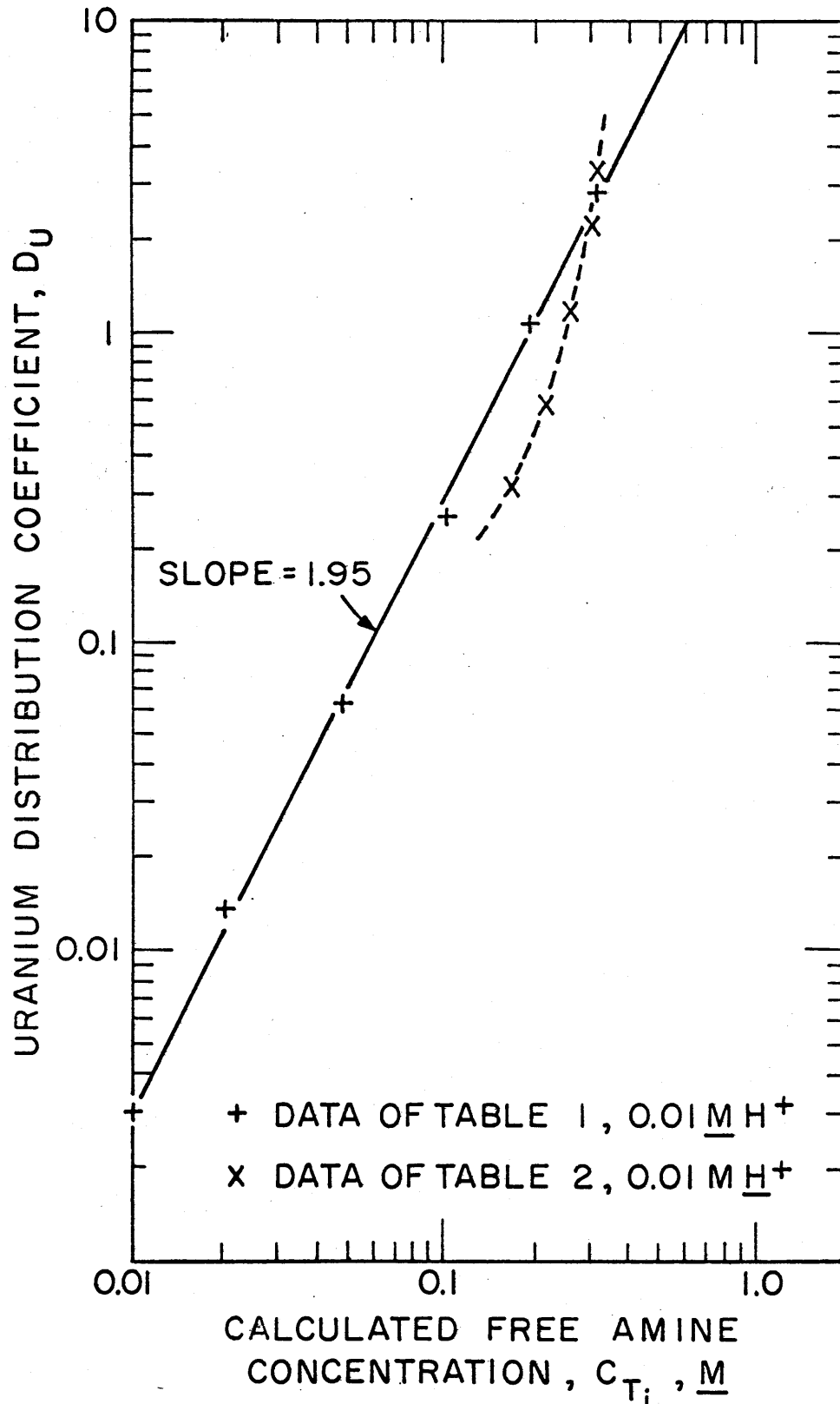
Figure 7, Variation of Uranium Distribution
Coefficient With Apparent Amine
Concentration, 0.01$\underline{N}$ H$^+$
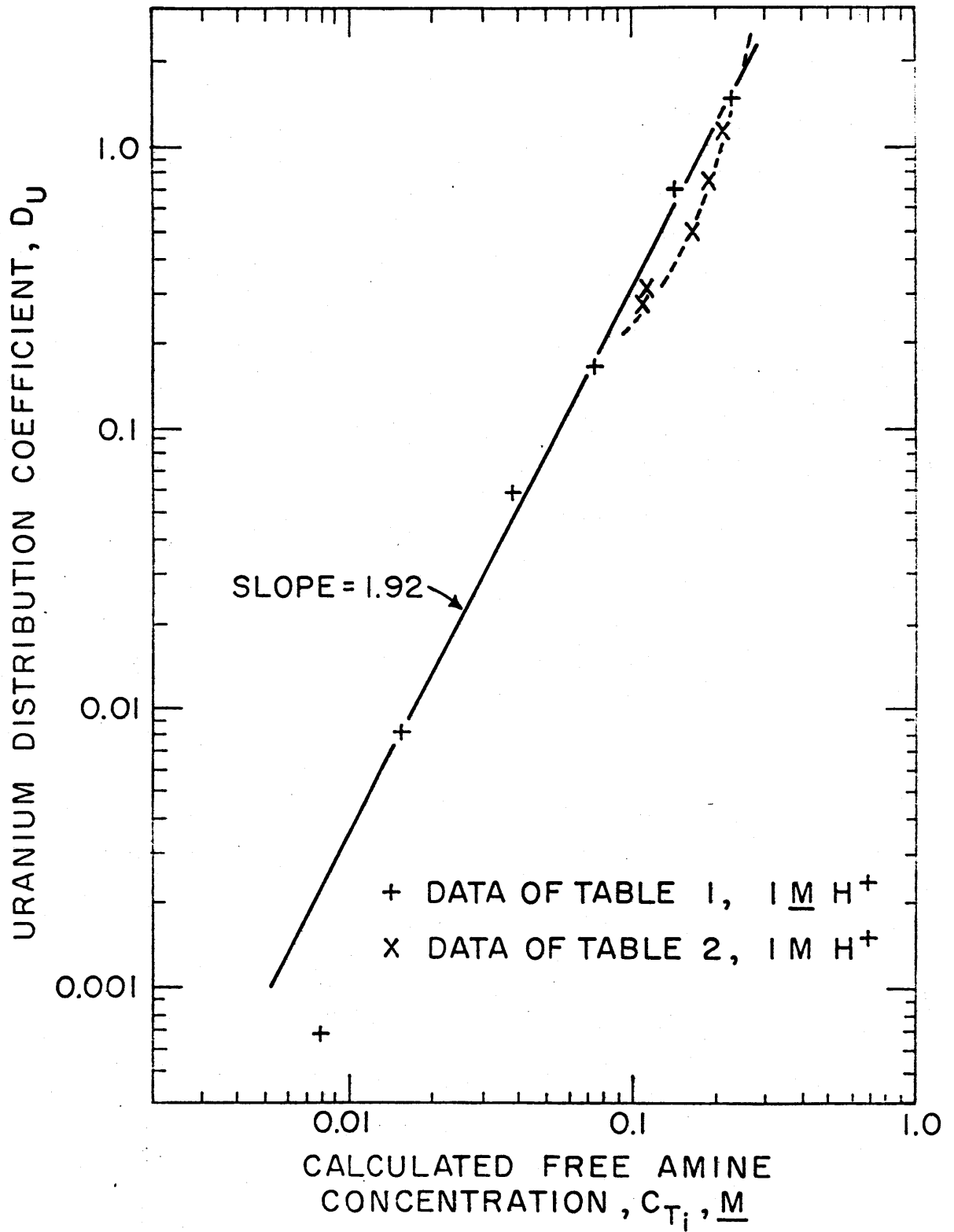
Figure 8, Variation of Uranium Distribution Coefficient With Apparent Amine Concentration, 1.0$\underline{N}$ H$^+$

Figure 9, Comparison of Experimental and Theoretical Isotherms, for 0.346M Total Amine
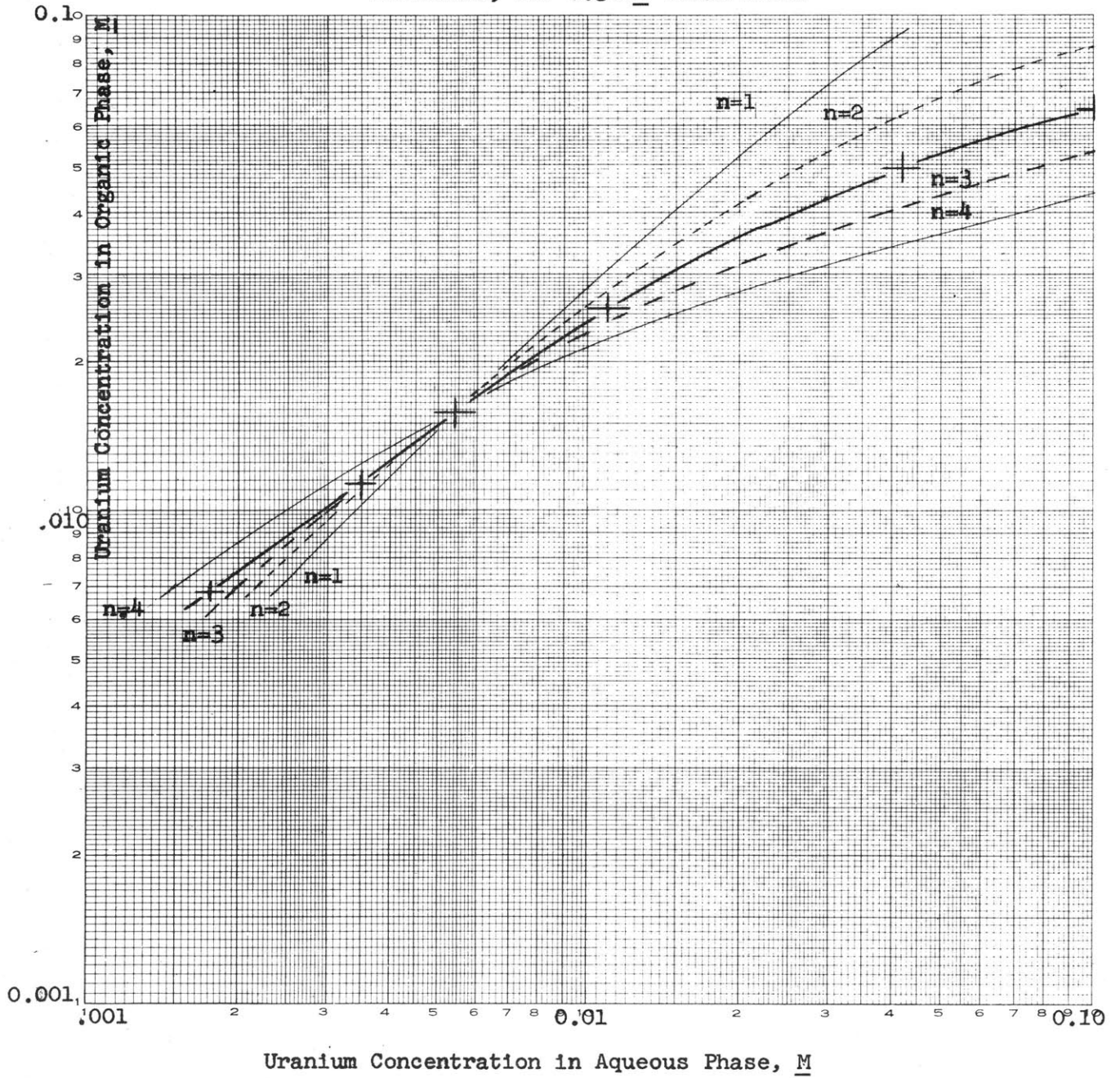
Figure 10, Variation of Viscosity with Uranium Concentration, Organic Phase, 0.346M Total Amine
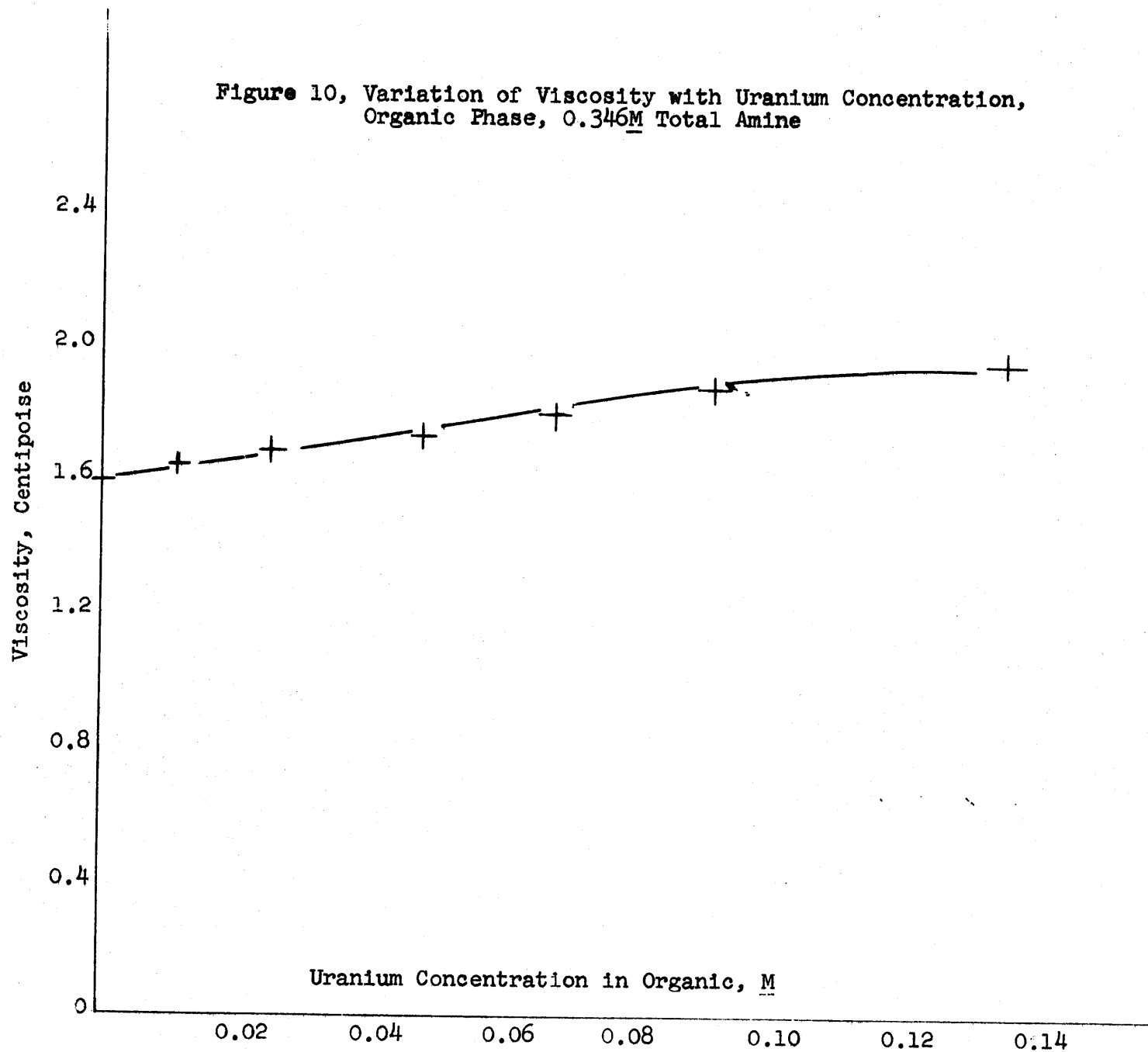
Figure 11 shows a correlation of the distribution data versus the free amine concentration, where the free amine concentration is calculated using the above equilibrium constants. The data fall very close to the line calculated directly for the above equilibria, and it is interesting to note that this line is approximately linear and of apparently non-integral slope.

The model which has been developed assuming extraction of the uranyl nitrate by both amine monomers and dimers explains quantitatively the variation in uranium distribution with total uranium, amine and hydrogen ion concentrations for the system trilaurylamine nitrate - toluene. In other systems it seems probable that higher aggregates are formed - in benzene there is evidently slight aggregation of trilaurylamine (6) and in n-octane, as many as 40 amine nitrates are evidently present in a micelle (9). In order to take this into account, it would be necessary to determine equilibrium constants for equilibria such as $(R_3NHNO_3)_x \rightleftharpoons xR_3NHNO_3$.
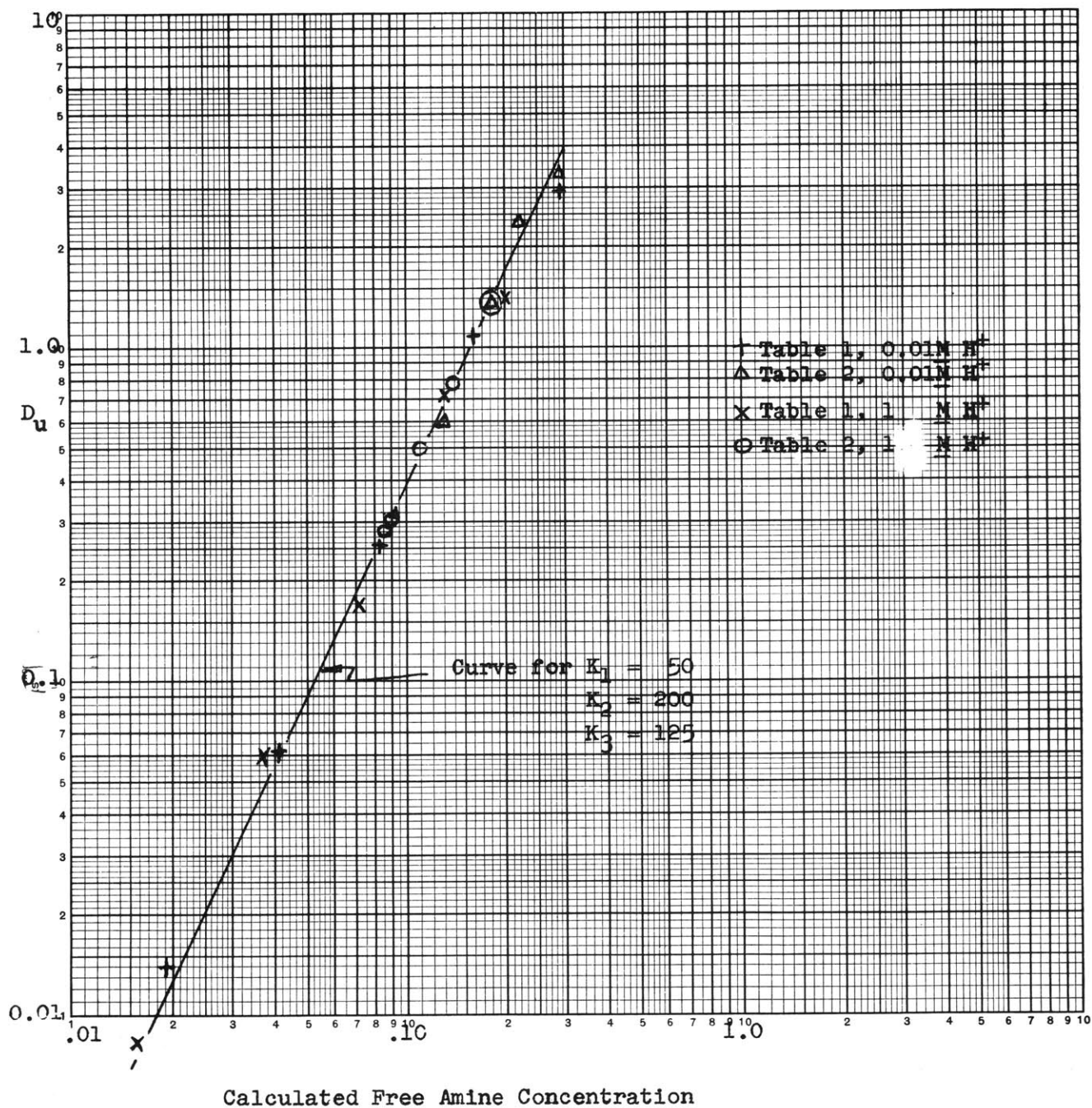
It is of interest that various amine nitrates in benzene have shown apparent amine - uranium ratios between 1.1:1 and 2:1 (6), while in kerosene the ratio for a wide variety of amines is apparently 1:1 (10).

Keder (11) has noted a spectrum corresponding to $UO_2(NO_3)_3^-$ in the organic phase. This suggests that one amine nitrate is bonded strongly to the uranyl ion. A second amine nitrate monomer might then be bonded to this amine - such a bond obviously exists if amine dimers are to be formed. Thus the structure of the extracted complex, involving amine nitrate monomers, is probably

$$(R_3NHNO_3) \rightarrow R_3NH^+UO_2(NO_3)_3^-.$$
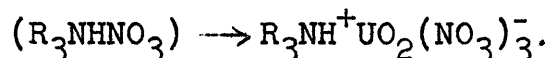
In this case it is possible that at very high uranium concentrations the amine nitrate - amine bond may be broken to give a 1:1 amine-uranium ratio.

Figure 11, Correlation of Extraction Data Allowing for
Amine Dimerisation

Curve for $K_1 = 50$
$K_2 = 200$
$K_3 = 125$

Table 1, 0.01N H$^+$
Table 2, 0.01N H$^+$
Table 1, 1 N H$^+$
Table 2, 1 N H$^+$

D_u

Calculated Free Amine Concentration

5.0 Extraction of Ruthenium

5.1 Objective of Study

Earlier work (2, 12) has shown that there are two definite species of nitrosyl-ruthenium which are extractable by TLA nitrate in toluene. Skavdahl (2) attempted to identify the species by potentiometric titration of the organic phase, but the curves he obtained showed a variety of inflections capable of several interpretations. More detailed knowledge of the nature of these complexes is required in order to understand conditions under which they might form.

5.2 Outline of Experiment

The mole fractions and partition coefficients of the extractable species are known to a fair degree of accuracy, as a function of nitric acid concentration in the aqueous phase (2, 12). "Rapid dilution" experiments are capable of giving significant quantities of ruthenium in the organic phase, and the fraction of ruthenium present as each species can be calculated from the partition coefficient data.

Then the nitrate ions associated with each ruthenium species can be calculated for a given experiment from an equation analogous to that in Section 4.3.

$$C_{NO_3} = C_{R_3N} + C_{unbound\ H^+} + xC_{Ru_1} + yC_{Ru_2}$$
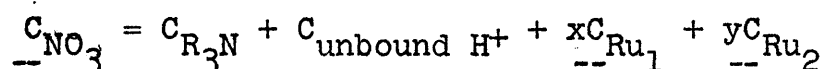
where x and y are the number of nitrate ions associated with the two extractable ruthenium species Ru_1 and Ru_2. Presumably all the unknowns in this equation except x and y can be determined, and by performing rapid dilution experiments under various conditions, it should be possible to determine reasonable values of x and y.

5.3 Results

Experiments on the lines of those described above have been carried out, and data has been obtained on the total nitrate concentration, the total amine concentration, and the ruthenium concentration in the organic phase. However, attempts to determine the unbound nitric acid concentration by potentiometric titration, similar to that shown in Figure 5, have failed due to the interference of ruthenium. The results of Skavdahl could not be reproduced, and, in acetone, the end points obtained appeared to be largely a function of the time of titration. Methanol and dioxane were also used, with similar results.

However, it was found (13) that the conductivity of
the organic phase varies markedly with the unbound nitric
acid concentration. Investigation showed that for a given
total amine concentration, the conductivity of the organic
phase was almost as good a measure of the unbound nitric
acid concentration as titration, in the absence of ruth-
enium.

One hundred ml of 0.26M trilaurylamine in toluene
were equilibrated with 2M nitric acid at 25.0°C. After
separating the phases, the conductivity of the organic
phase was measured using an Industrial Instruments, Inc.
conductivity bridge, Model RC-1682, at 1000 cycles with
a cell of 0.100 cm^{-1} constant. Five ml of the organic
phase were removed for determination of the unbound nitric
acid concentration by titration against standard NaOH.
The remaining organic phase was washed with roughly 1 ml
of distilled water to remove a fraction of the unbound
nitric acid, and the experiment repeated. The results
are shown on Figure 12.

In order to see whether the extracted nitrosyl-
ruthenium complexes increased the conductivity to any
marked extent, a single volume of amine was contacted
three times with twice its volume of rapidly-diluted
ruthenium in 0.5N nitric acid. The organic phase, con-
taining approximately 25 gm Ru/lit, was washed three
times with one quarter its own volume of distilled water,
a procedure shown in preliminary experiments to be suf-
ficient to remove completely any unbound nitric acid.
Approximately 5 gm Ru/lit remained in the organic phase,
and this did not appear to result in any increase in the
conductivity of the organic phase - both for the amine
nitrate and the amine nitrate-ruthenium mixture no con-
ductance could be measured.

It is, of course, possible that some conducting
species of ruthenium may have been washed out of the
organic phase with the unbound nitric acid; this will,
however, show in the final experiments if the conductivity
of the organic phase containing ruthenium is above that of
the organic phase containing excess nitric acid alone.

Figure 12, Variation of Conductivity with Unbound Nitric Acid, Organic Phase, 0.26M Amine
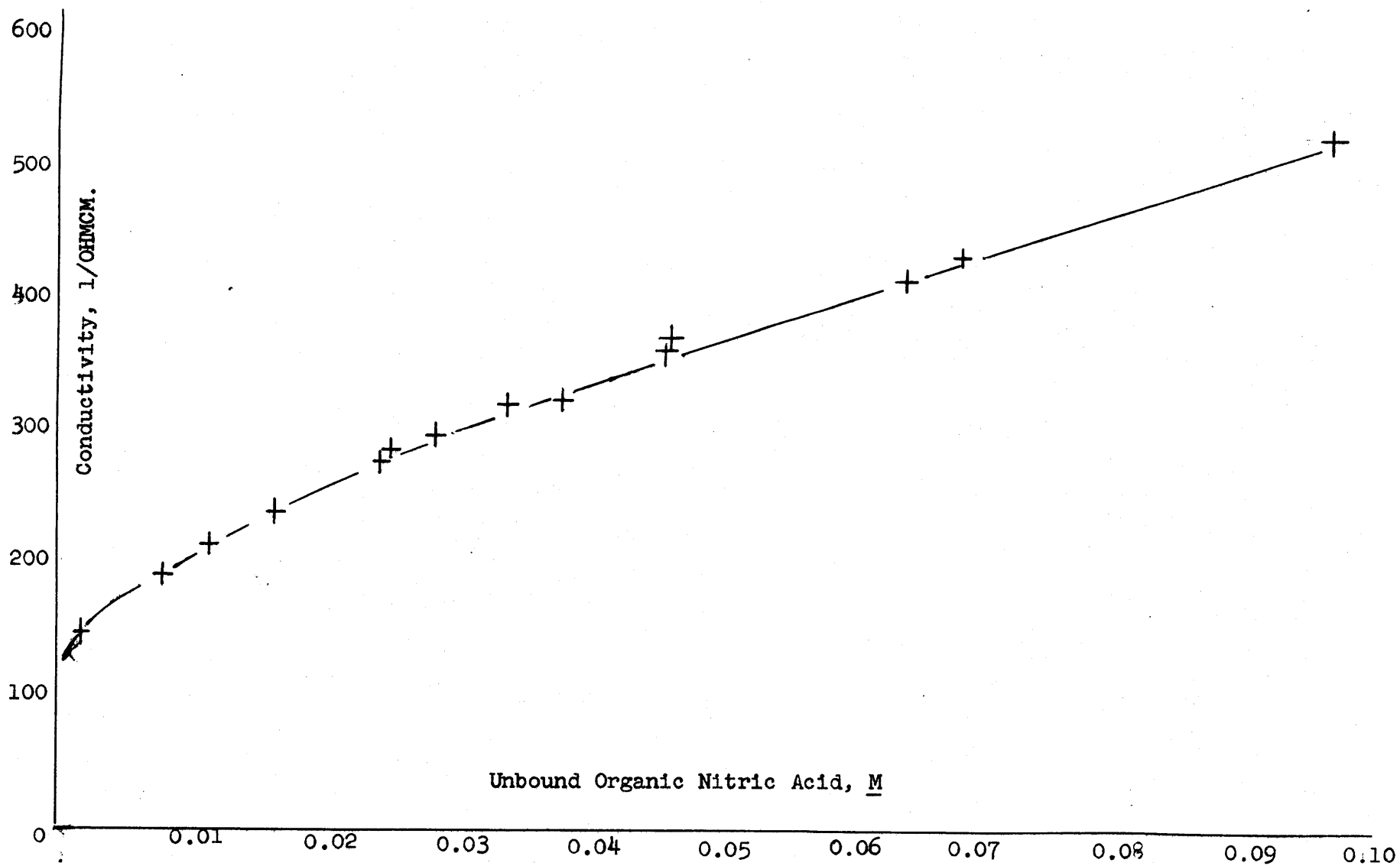
6.0 Multicomponent Metal Extraction Using Radiotracers

6.1 Concepts

In solvent extraction studies, particularly for fuels reprocessing, it is useful to know details of the extraction behavior of many elements throughout the periodic table. In fuels reprocessing, not only are the fission products present, but other elements may possibly enter the system as corrosion products or be added to assist in processing. Their solvent extraction behavior is required in order to be able to predict how good a separation from the fuels metals may be expected.

Studies of this sort can normally be carried out on only one metal at a time and are therefore extremely tedious. However, as the only information really required is an estimate of the magnitude of the distribution coefficient at varying nitric acid concentrations, it is necessary to perform many extractions under virtually identical conditions. If, however, the study is made of trace levels of metal concentration, there seems no difficulty in extracting several metals simultaneously, as long as a method of analysis for each of the metals in the presence of the others is available.

Optical emission spectroscopy is one such method that would seem feasible. It suffers from the drawbacks of being time consuming, of relatively low quantitative accuracy, and of presenting difficulties where the metals are not present at similar concentrations due to masking of the fainter spectral lines.

It is possible that the use of radiotracers may overcome these difficulties. The accuracy is probably better than that of optical spectroscopy, and the absolute concentration need not be a factor since it is possible to employ relatively high activity solutions. Moreover, many problems such as interference from short-lived activities, normally encountered in multicomponent radiometric determinations should be simplified as it is possible to select the isotopes employed.

Two methods are available for determining the concentrations of the active species. The first involves determination of the complete spectrum of the sample, using a multichannel analyzer. Spectra of the components known to be present are subtracted from the complete spectrum to leave zero residue. This procedure has been investigated by Breen and co-workers (14), who noted the difficulties of a) having to set up a complete library of the standard spectra for the individual components and

b) standardizing the equipment so that the channel corresponding to a given energy did not vary.

The alternative procedure is to obtain the decay curve of the mixture. Knowing the half lives of the individual species, it is possible to calculate their initial activities. A computer program (15) developed at MIT is available for doing this, and it has been shown that it is possible to obtain accurate results provided the half lives of the individual species differ by a factor of more than two. Although this procedure is more time consuming than the first, it seems to offer greater accuracy, and is therefore the method which it is intended to employ first.

6.2   State of Investigation

In order to test the above concept, it is proposed to investigate the extraction behavior of copper, silver and gold simultaneously from nitric acid solutions. Employed will be 12.8 hr Cu^{64}, 270 d Ag^{110} and 64.8 hr Au^{198}, the first of which will be produced by irradiation of copper in the MITR.

These three elements have been chosen as they have similar chemical properties, yet widely different extractabilities, the order of extraction being Cu $\ll$ Ag $\ll$ Au (16). They also possess easily obtainable radioactive isotopes of suitable half lives.

Tests using inactive species have been started to demonstrate the feasibility of the chemistry involved. The Au^{198} is available as a solution in aqua regia; and to prevent precipitation of silver chloride on mixing the species, it is necessary to separate the gold and chloride ions. An investigation into the use of ion exchange resins for accomplishing this is in progress.

Finally, hypothetical data calculated using distribution data of Ishimori (16) is being generated for use in testing the FRANTIC computer program.

6.0 References

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