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LOS ALAMOS SCIENTIFIC LABORATORY
of the
UNIVERSITY OF CALIFORNIA

Report written:
January 4, 1955

LA-1861
CHEMISTRY—GENERAL

EXTRACTION OF AMERICIUM NITRATE WITH TRIBUTYL PHOSPHATE

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CLASSIFICATION CANCELLED
DATE APR 1 1957
For The Atomic Energy Commission
H. F. Carroll
Chief, Declassification Branch

Price $ 0.35

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

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ABSTRACT

The extraction of americium nitrate with tributyl phosphate has been investigated for aqueous solutions containing sodium nitrate and nitric acid. Americium nitrate is found in the organic phase as free molecules or ions and as the complex $Am(NO_3)_3 \cdot 3TBP$. Aqueous solutions containing nitric acid introduce a competitive factor through the formation of a $TBP \cdot HNO_3$ complex in the solvent layer. In addition, americium nitrate is complexed in the aqueous phase by nitric acid as $HAm(NO_3)_4$.

Three reactions prevail in the extraction process; they may be written as:

$$Am^{+++}, aq + 3\ NO_3^-, aq \rightarrow Am(NO_3)_3, org \qquad K_d = 0.0109$$

$$Am^{+++}, aq + 3\ NO_3^-, aq + 3\ TBP \rightarrow Am(NO_3)_3 \cdot 3TBP, org \qquad K_c = 0.00653$$

$$Am^{+++}, aq + 4\ NO_3^-, aq + H^+, aq \rightarrow HAm(NO_3)_4, aq \qquad K_a = 0.038$$

These equilibrium constants were evaluated for systems containing 1M to 5M sodium nitrate and/or 2M to 5M nitric acid, a range in which the activity coefficient of americium nitrate is nearly constant.

The equilibrium expressions for the three principal reactions can be combined in terms of the extraction coefficient, E_a^o, which is the ratio of the americium concentration in the organic phase to that in the aqueous.

$$E_a^o = \frac{0.0109\ (NO_3^-)^3 + 0.00653\ (NO_3^-)^3\ (TBP)^3}{1 + 0.038\ (H^+)\ (NO_3^-)^4}$$

The degree of ionization of nitric acid in aqueous sodium nitrate solutions is not available. Measuring the extraction coefficient for one salt and acid mixture gives a means of calculating the hydrogen ion concentration. A reasonable approximation of E_a^o can then be made by assuming that the degree of ionization of nitric acid is constant at that salt concentration. This assumption is more valid for solutions of higher salt content, such as those most generally encountered during recovery operations.

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INTRODUCTION

The extraction of plutonium nitrate from aqueous solutions with tributyl phosphate is generally used for the recovery and purification of plutonium from waste solutions. Although the recovery process usually employs tetravalent plutonium nitrate, the trivalent ion can also be extracted from aqueous solutions with solvent systems containing tributyl phosphate. The similarity between trivalent plutonium and trivalent americium nitrates is the basis for the solvent extraction process for the concentration and recovery of americium at Los Alamos.(1) Extraction of waste solutions for americium recovery is made at a different acidity following the extraction of most of the tetravalent plutonium. However, the nature of the extraction reaction and the optimum conditions for americium extraction have not been definitely established.

By analogy with other extraction reactions involving tributyl phosphate, the recovery of americium should involve the formation of a complex between americium nitrate and tributyl phosphate. To determine the composition of this complex, the distribution of americium nitrate between aqueous systems containing sodium nitrate and nitric acid and tributyl phosphate systems was measured. The extraction behavior of americium can probably be extended to the extraction of trivalent plutonium nitrate from solutions containing sulfate, fluoride, or other anions which interfere with the recovery of tetravalent plutonium nitrate by solvent extraction.

EXPERIMENTAL PROCEDURE

Waste solutions from plutonium recovery contain anions which may have adverse effects on the extraction of americium nitrate. To avoid this unknown factor, aqueous solutions containing the desired concentrations of sodium nitrate and nitric acid were employed for the distribution measurements. Tracer quantities of purified americium nitrate were added during the preparation of the aqueous feed solutions.

Tributyl phosphate (TBP) contains small quantities of the dibutyl- and monobutyl- acid phosphates. Dibutyl acid phosphate forms a strong complex with tetravalent plutonium nitrate, which tends to give high values for the plutonium content of the organic phase; its effect on trivalent metal nitrates has not been ascertained. These impurities are removed by scrubbing the solvent with ten per cent sodium hydroxide solution. However, Kennedy and Grimley(2) have detected an additional impurity, tentatively identified as tetrabutyl pyrophosphate, which is not removed by the alkali scrubbing. This component is slowly hydrolyzed to dibutyl acid phosphate under the conditions of extraction processes. It can be eliminated by hydrolysis and transfer to the aqueous alkaline solution as the sodium salt of dibutyl acid phosphate by means of a steam distillation in contact with two per cent sodium hydroxide. During this treatment, butanol and butyraldehyde impurities are also removed. Tributyl phosphate purified by steam stripping in this manner was shown by Kennedy and Grimley to undergo no further hydrolysis in contact with 5M nitric acid.

The method of Kennedy and Grimley was used to purify the tributyl phosphate employed for americium extraction. Commercial TBP in 500-ml quantities was steam sparged in contact with two per cent sodium hydroxide until 800 ml of condensate had been collected. This condensate included about 25 ml (5 per cent of the original TBP) of a water-insoluble material with a characteristic ester odor not generally associated with TBP. The product was separated and scrubbed with water.

Specific gravity measurements of the water-saturated tributyl phosphate gave a value of 0.9790 at 20°C. The temperature coefficient of the specific gravity of tributyl phosphate was 0.000656 per degree in the region of room temperature. In calculating TBP concentrations in moles per liter an average room temperature of 25°C was assumed, for which the specific gravity is 0.9757.

A stock solution of solvent was prepared by mixing 35 volumes of water-saturated purified tributyl phosphate with 65 volumes of Gulf BT, giving a so-called 35 per cent TBP solution. This mixture was analyzed for TBP content by determining the uranium content after saturating a weighed sample with uranyl nitrate. The solvent was found to be 1.2139M in tributyl phosphate.

In the distribution measurements five ml of the desired aqueous feed solution was shaken with five ml of the solvent in a separatory funnel. The equilibrated mixture was transferred to a centrifuge tube to complete the separation of the two phases.

Samples of the organic phase were evaporated on tantalum plates; the americium content was obtained by alpha-counting. Evaporation of aqueous samples would give an excessive absorption error in alpha-counting with the high salt content. Consequently, the americium in aqueous samples was first separated from the sodium nitrate by carrying with lanthanum in a double precipitation of the hydroxide with ammonia. The precipitate was dissolved and diluted to a 10 ml volume, from which aliquots were removed for alpha counting to give the americium content of the aqueous phase.

The simultaneous distribution of nitric acid was measured by direct titration of samples of each phase with standard sodium hydroxide to the phenolphthalein end point. The concentration of nitric acid in the organic phase is useful in evaluating the final TBP concentration, since some of the TBP is combined as a complex with nitric acid.

The dependency of the extraction reaction on nitrate ion concentration was determined by a series of measurements using aqueous systems of variable sodium nitrate content. A condition of essentially constant final TBP concentration was maintained by minimizing the nitric acid content. The aqueous feed solution was initially at a pH of approximately 3, which would avoid hydrolysis of americium nitrate.

The TBP content of the organic complex with americium nitrate was determined by measuring the extraction with organic systems of variable TBP content. The equilibrations were made with an equal volume of an aqueous feed solution, containing 5.00M sodium nitrate and 0.116M nitric acid with tracer amounts of americium nitrate.

EXPERIMENTAL RESULTS

The measurement of the extraction of americium nitrate with tributyl phosphate from aqueous solutions containing 0M, 0.5M, 1.0M, 2.0M, 3.0M, 4.0M and 5.0M sodium nitrate with variable nitric acid concentrations was completed. These extractions were made with 35 per cent TBP in Gulf BT diluent using equal volumes of the solvent and the aqueous feed solution.

The extraction coefficient for aqueous nitric acid solutions was obtained for the entire range of acidity. The extraction coefficient, E_a^o, is the ratio of the americium concentration in the organic phase to that in the aqueous layer. The results of these measurements are given in Table I and the data have been plotted in Figure 1 as log E_a^o against the stoichiometric HNO_3 concentration of the feed solution. Since the extraction behavior of americium nitrate is quite different from that for tetravalent plutonium nitrate, the results of McKay and Woodgate(3) for the extraction of plutonium with 20 per cent TBP have been added in Figure 1 for comparison.

The results of extraction measurements with systems containing sodium nitrate and nitric acid are combined in Table II. To avoid confusion from the intersection of many curves, only the data for 0.5M, 2.0M, and 4.0M sodium nitrate have been included in Figure 2 to illustrate the trends resulting from increases in salt and acid content of the feed solution.

Those extractions from aqueous systems having no free nitric acid give the condition of constant final TBP concentration. From these data

TABLE I

Americium Extraction with 35% TBP from Aqueous HNO_3

Distribution of Nitric Acid		E_a^o for Americium
Aqueous, M	Organic, M	
14.984	1.901	0.1229
13.925	1.784	0.09216
12.271	1.516	0.02612
11.294	1.334	0.01691
9.734	1.241	0.01091
8.380	1.245	0.01028
7.431	1.251	0.01245
6.661	1.189	0.01301
5.663	1.121	0.01503
4.652	0.9902	0.01771
3.792	0.8654	0.02768
3.225	0.7782	0.02742
2.387	0.6045	0.03036
1.626	0.4140	0.02425
0.8448	0.1898	0.01324
0.1286	0.0076	0.00088

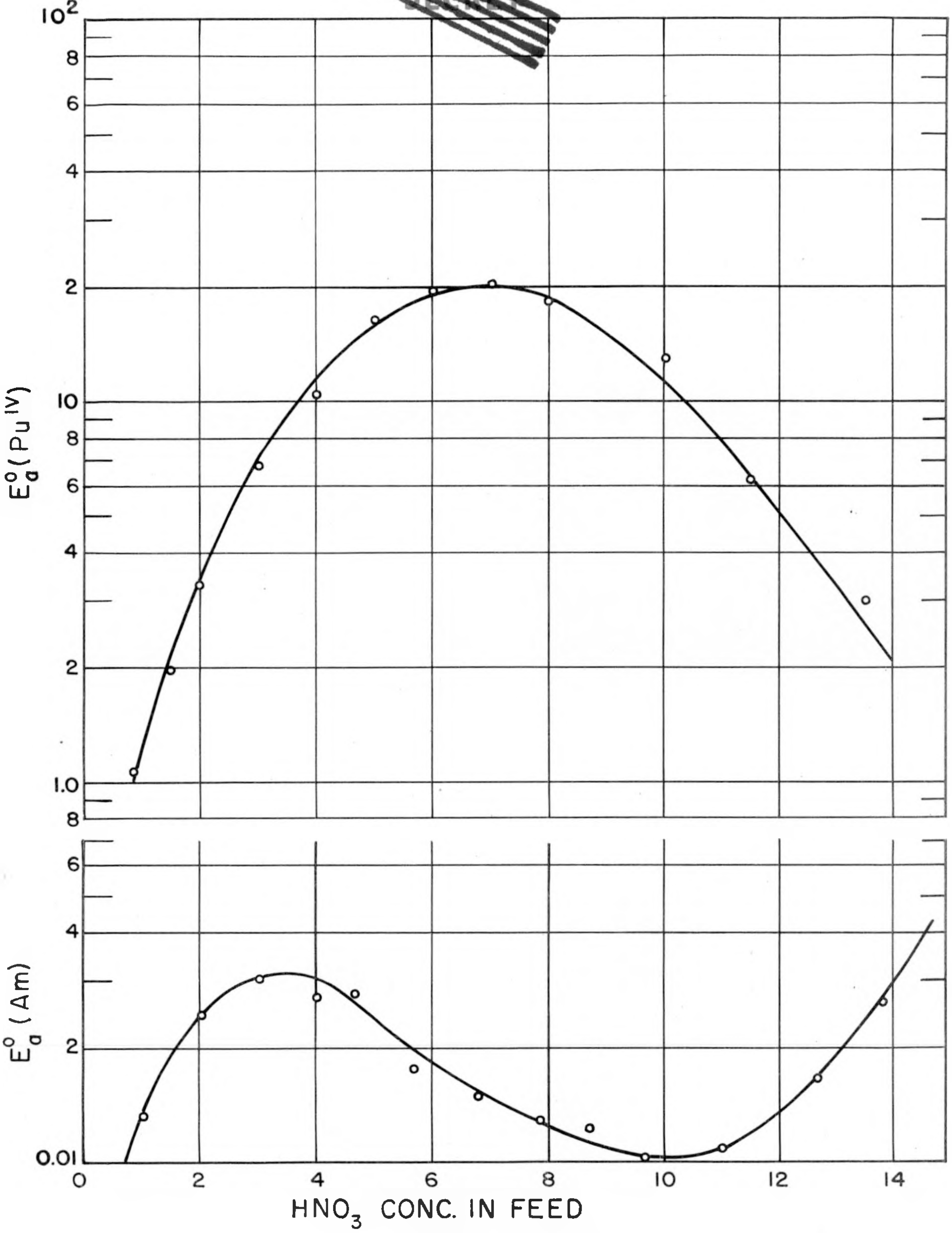

Figure 1
Pu IV Extraction with 20% TBP - Am Extraction with 35% TBP

TABLE II

Americium Extraction with 35% TBP from Aqueous $NaNO_3$-HNO_3

Aqueous Feed Solution		HNO_3 Distribution		E_a^o for Am
Conc. of $NaNO_3$, M	Conc. of HNO_3, M	M in Aqueous	M in Organic	
0.50	0	---	---	0.00812
0.50	1.00	0.816	0.235	0.0276
0.50	2.00	1.607	0.469	0.0415
0.50	3.00	2.461	0.559	0.0479
0.50	4.73	3.876	0.849	0.0377
0.50	4.81	3.899	0.907	0.0371
0.50	5.83	4.803	1.023	0.0284
0.50	7.21	6.061	1.150	0.0177
0.50	7.88	6.708	1.173	0.0115
1.00	0	---	---	0.0268
1.00	1.00	0.710	0.257	0.0547
1.00	2.00	1.488	0.471	0.0500
1.00	3.00	2.266	0.674	0.0483
1.00	4.00	3.118	0.832	0.0341
1.00	5.00	4.005	0.988	0.0275
1.00	6.00	4.958	1.014	0.0203
1.00	7.00	5.980	1.066	0.0162
2.00	0	---	---	0.175
2.00	1.00	0.624	0.300	0.111
2.00	2.00	1.388	0.556	0.0714
2.00	3.00	2.141	0.758	0.0590
2.00	4.00	3.000	0.898	0.0361
2.00	5.00	3.941	0.953	0.0240
2.00	6.00	4.962	1.078	0.0187
3.00	0	---	---	0.552
3.00	1.00	0.587	0.395	0.152
3.00	2.00	1.344	0.633	0.0951
3.00	3.00	2.128	0.855	0.0700
3.00	4.00	3.024	0.995	0.0312
3.00	5.00	3.965	1.080	0.0235
4.00	0	---	---	1.262
4.00	0.50	0.214	0.266	0.370
4.00	1.00	0.517	0.450	0.212
4.00	1.50	0.887	0.597	0.124
4.00	2.00	1.255	0.718	0.104
4.00	2.50	1.706	0.823	0.0651
4.00	3.00	2.085	0.900	0.0574
4.00	3.50	2.563	0.963	0.0423
5.00	0	---	---	2.989
5.00	0.50	0.193	0.314	0.623
5.00	1.00	0.486	0.507	0.336
5.00	1.50	0.837	0.654	0.175
5.00	2.00	1.230	0.781	0.121

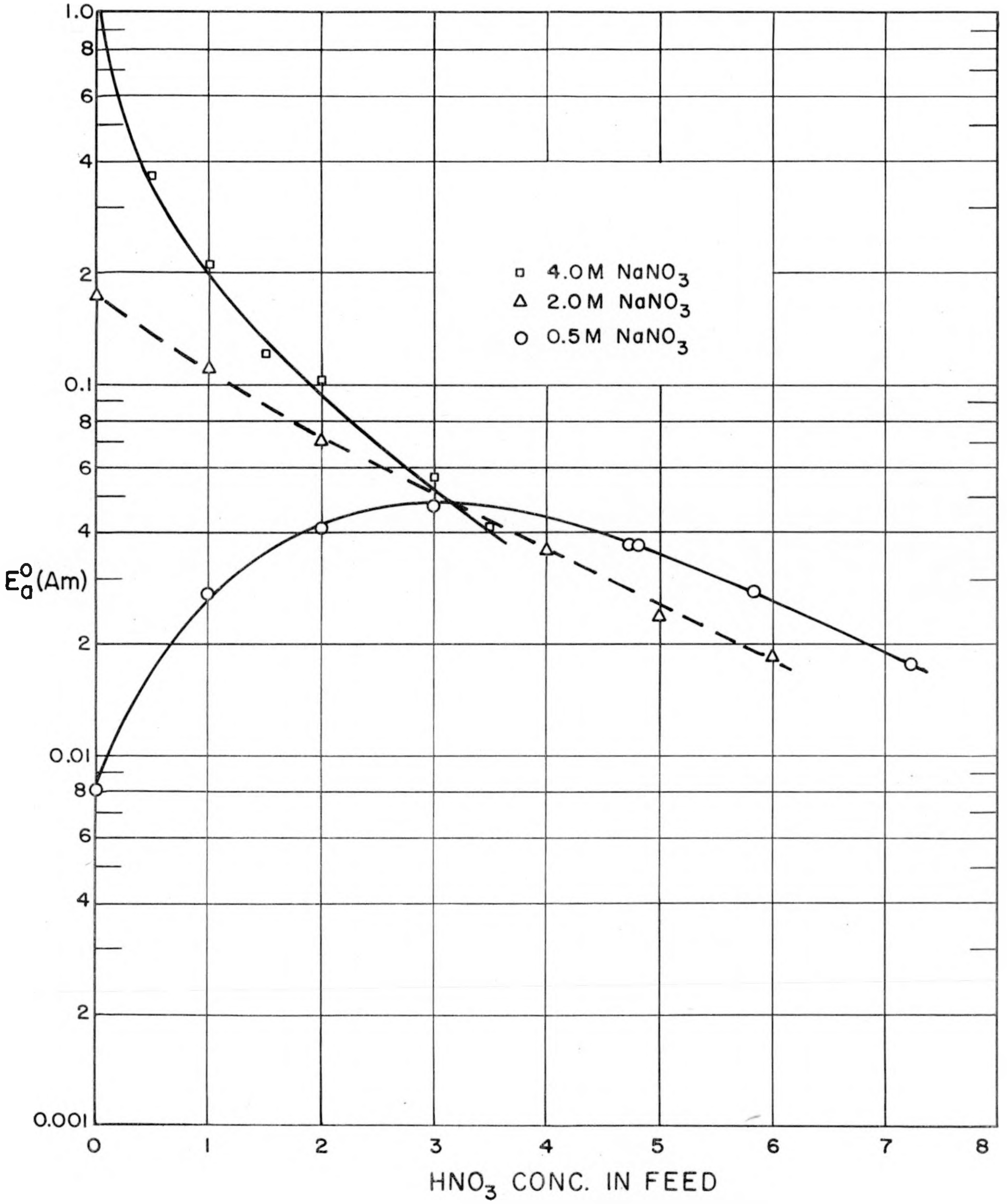

Figure 2
TBP Extraction of Am from $NaNO_3$-HNO_3 Systems

the nitrate ion dependency of the extraction reaction will be ascertained. For this reason, the measurements in the absence of free nitric acid have been isolated in Table III.

In another series of extraction measurements, organic solutions of variable TBP content were equilibrated with an aqueous feed solution, containing 5.00M sodium nitrate and 0.116M nitric acid with tracer americium. The results of these measurements are listed in Table IV. Since the TBP solutions were prepared by diluting the desired volume of water-saturated TBP with Gulf BT to 100 ml, corrections for the volume of water separating were made. Corrections were also made for the nitric acid in the organic phase with the assumption it was present as the complex, $TBP \cdot HNO_3$. These adjusted concentrations of TBP were plotted with the extraction coefficients for americium nitrate in Figure 3.

TABLE III

Americium Extraction with 35% TBP from Aqueous $NaNO_3$

M of $NaNO_3$	0.50	1.00	2.00	3.00	4.00	5.00
E_a^o for Am	0.00812	0.0268	0.175	0.552	1.262	2.989

TABLE IV

Americium Extraction with Variable TBP from 5.00M $NaNO_3$

Volume % TBP	E_a^o for Am	Final (TBP), M
10	0.0526	0.328
20	0.446	0.659
30	1.40	0.993
40	2.44	1.328
50	5.18	1.663
60	6.62	1.999
70	9.31	2.334
80	17.0	2.666
90	21.9	2.994
100	30.2	3.320

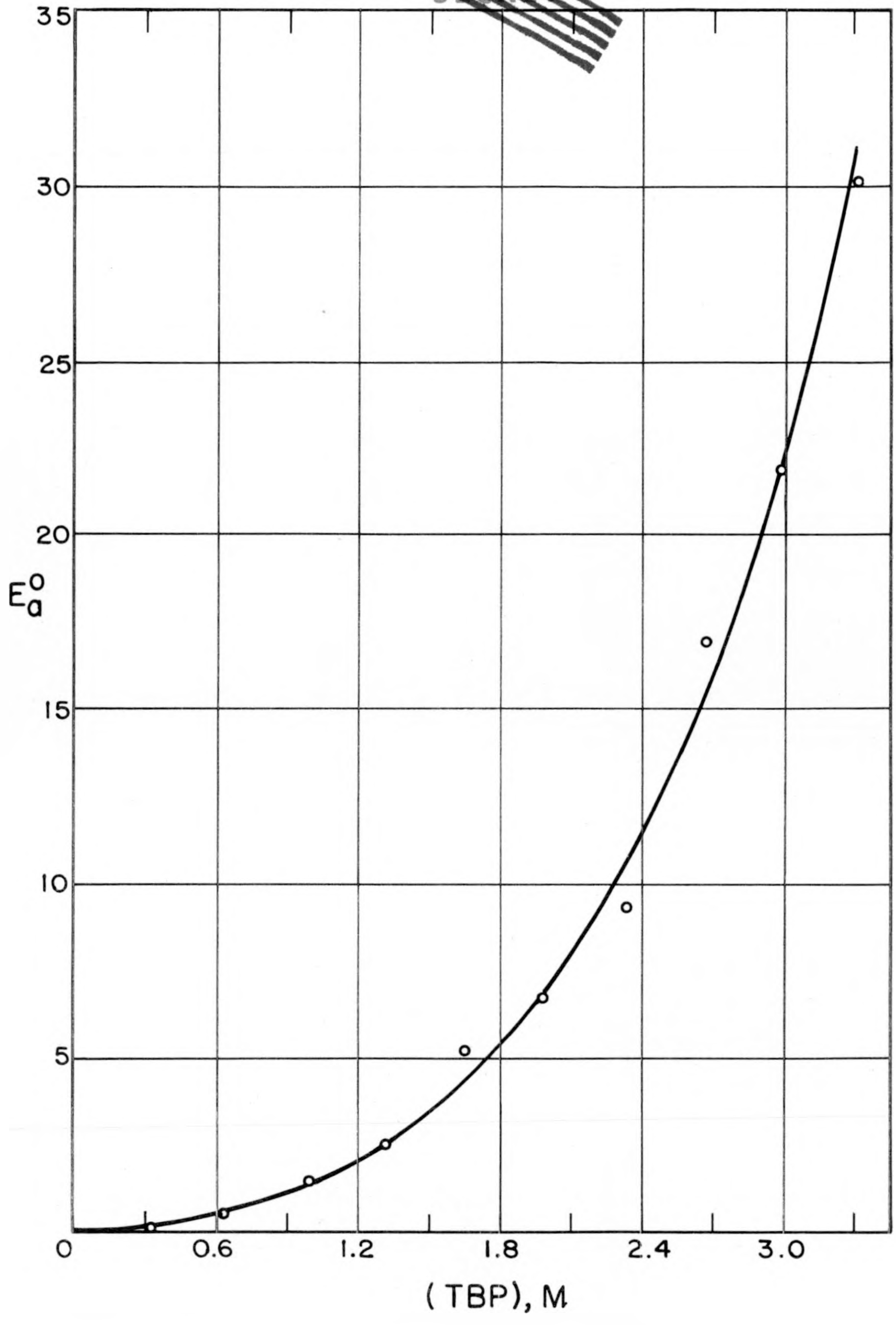

Figure 3
E_a^o for Variable TBP

DISCUSSION

An initial understanding of the variables in the extraction behavior of americium nitrate requires the establishment of the reaction with tributyl phosphate. Although water-saturated tributyl phosphate in the diluent is considered to be a mixture(4) of free TBP and the complex TBP•H_2O, the variable water content does not seem to alter the course of the extraction process.

In the experimental measurements, the americium distribution in the absence of free nitric acid provides a condition of constant TBP concentration. Under these conditions, a plot of log E_a^o against log NO_3^- activity should be linear. Activity coefficient data for sodium nitrate show that the nitrate ion activity is nearly proportional to its molar concentration above 1M. Since the tracer concentrations of americium nitrate do not appreciably alter the ionic strength of the solution, the activity coefficient for americium nitrate should also remain nearly constant in solutions containing more than 1M sodium nitrate. On this basis, the data of Table III were employed in the plot of log E_a^o against log NO_3^- concentration in Figure 4. This gives a linear curve for which the average slope was calculated to be 2.90. This result corresponds with the expected ratio of three nitrate groups with each americium in the organic phase. It is probably more important that the assumption of a constant activity coefficient for americium nitrate is valid.

Americium nitrate in the organic phase is present as free molecules and as a complex with TBP. If the contribution of free americium nitrate

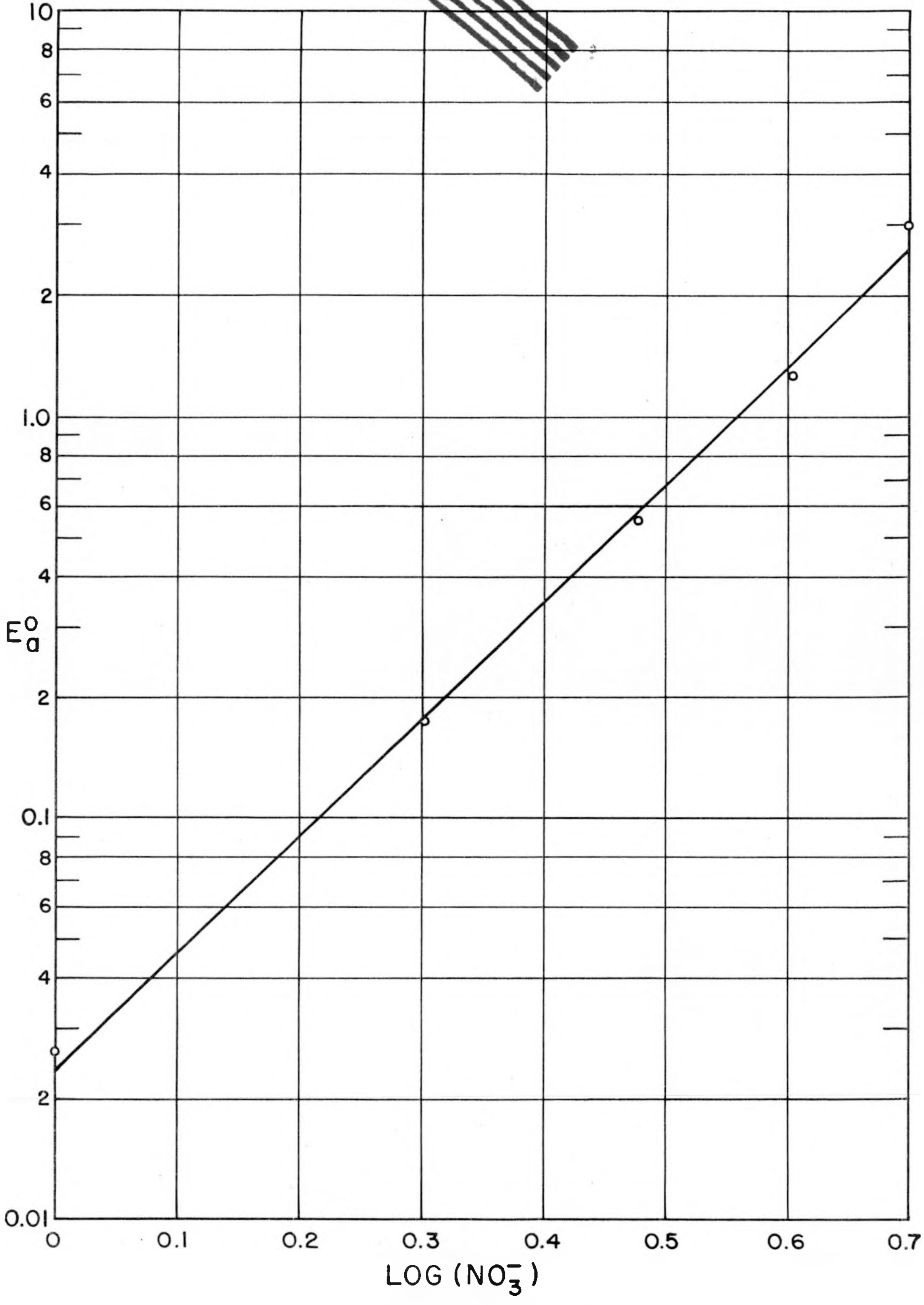

Figure 4
Log E_a^o vs Log (NO_3^-)

is small, it becomes relatively less important for the higher values of E_a^o, the extraction coefficient. The experimental measurements in Table IV were made with a nearly constant aqueous system and a variable TBP concentration in the solvent. Plotting these data in Figure 5 as $\log E_a^o$ against log (TBP) gives the TBP dependency for complex formation. Using TBP concentrations greater than 30 per cent, a slope of 2.87 is obtained for the line through the points. Therefore, americium nitrate is also present in the organic phase as the complex $Am(NO_3)_3 \cdot 3TBP$.

In Figure 5 the values of E_a^o at the lower TBP concentrations are larger than expected for the formation of the organic complex alone. The contribution of free americium nitrate is significant in this range. The extraction process can be represented as the normal distribution between two immiscible phases and as the formation of a new molecular species through a reaction with TBP in the solvent:

$$Am^{+++}, aq + 3\ NO_3^-, aq \rightarrow Am(NO_3)_3, org \qquad (1)$$

$$Am^{+++}, aq + 3\ NO_3^-, aq + 3\ TBP, org \rightarrow Am(NO_3)_3 \cdot 3TBP, org \qquad (2)$$

The reaction with the aqueous ions in Reaction (2) is employed, since Hahn(5) has found that the rate-determining step in the analogous uranium extraction is the diffusion of the TBP complex from the interface of the two phases through the bulk of the solvent.

The expression for the distribution coefficient in the first reaction can be arranged to give

$$[Am(NO_3)_3] = K_d\ (Am^{+++})\ (NO_3^-)^3\ \gamma_\pm^4 \qquad (3)$$

and the equilibrium expression for the complexing reaction leads to

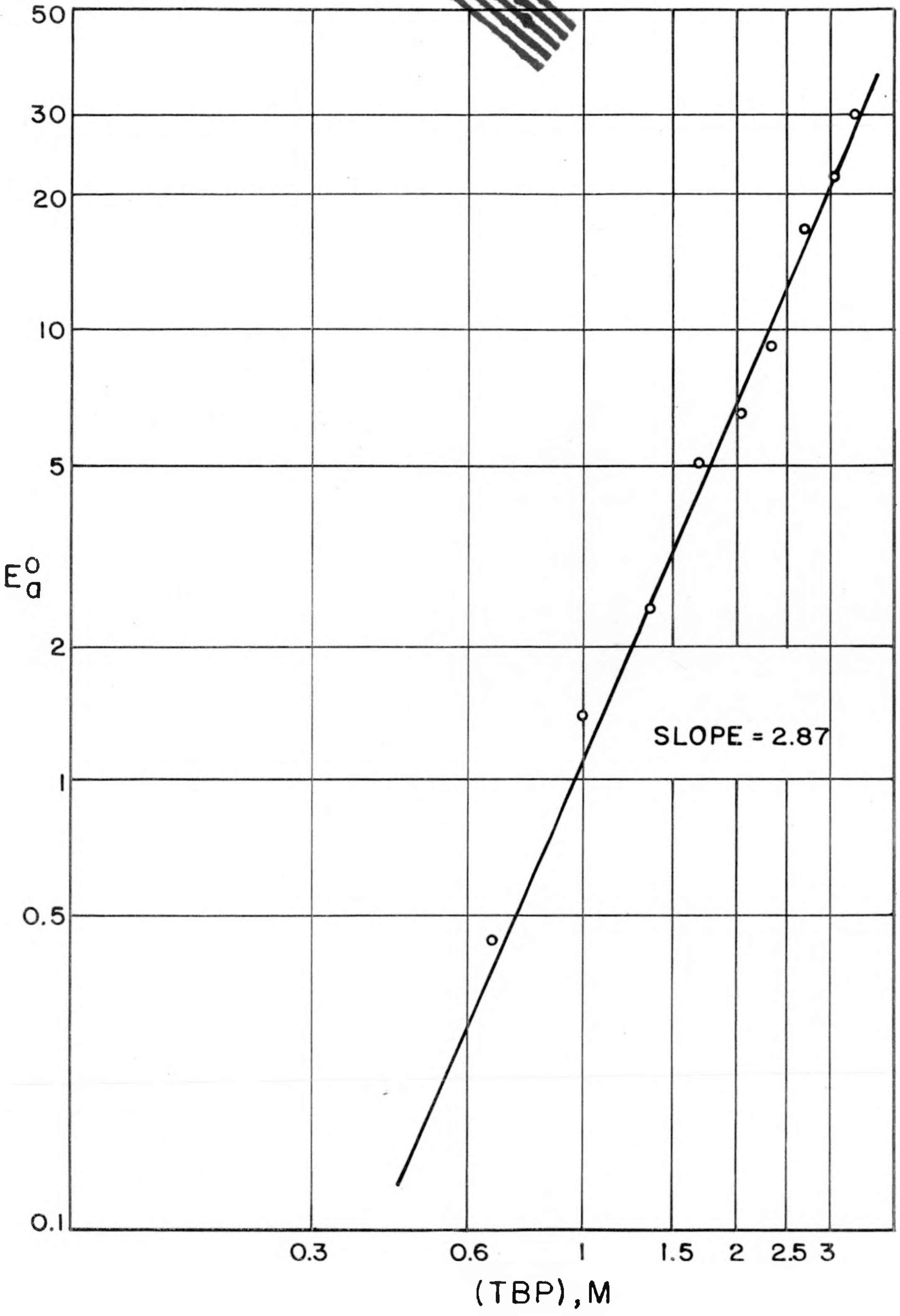

Figure 5
TBP Dependency of E_a^o for Am

$$[Am(NO_3)_3 \cdot 3TBP] = K_c \ (Am^{+++}) \ (NO_3^-)^3 \quad \gamma_{\pm}^4 \ (TBP)^3 \qquad (4)$$

The mean molar ionic activity coefficient of americium nitrate, $\gamma_{\pm}$, was shown to remain nearly constant in Figure 4 for aqueous systems containing 1M to 5M sodium nitrate. With tracer quantities, the activity of the americium in the organic phase should remain proportional to its concentration.

Combining Equations (3) and (4) for the total americium concentration of the organic layer yields

$$\Sigma Am, org = K_d \ (Am^{+++})(NO_3^-)^3 + K_c \ (Am^{+++})(NO_3^-)^3 \ (TBP)^3$$

which can be rearranged to

$$\frac{\Sigma Am, org}{(Am^{+++})} = K_d \ (NO_3^-)^3 + K_c \ (NO_3^-)^3 \ (TBP)^3 \qquad (5)$$

For the series of extractions with 5.00M sodium nitrate using variable TBP concentrations, irregularities in the experimental data were reduced by using smoothed values of E_a^o taken from Figure 3. These values of E_a^o were plotted against $(TBP)^3$ in Figure 6. From the slope of the line obtained for points above 30 per cent TBP, a value of 0.00653 was obtained for K_c.

The evaluation of K_d was made from the measurements of americium extraction with 35 per cent TBP in the absence of free acid. These data gave an average value of 0.0109 for K_d.

Equation (5) becomes

$$\frac{\Sigma Am, org}{(Am^{+++})} = 0.0109 \ (NO_3^-)^3 + 0.00653 \ (NO_3^-)^3 \ (TBP)^3 \qquad (6)$$

for systems employing 35 per cent TBP and aqueous solutions containing

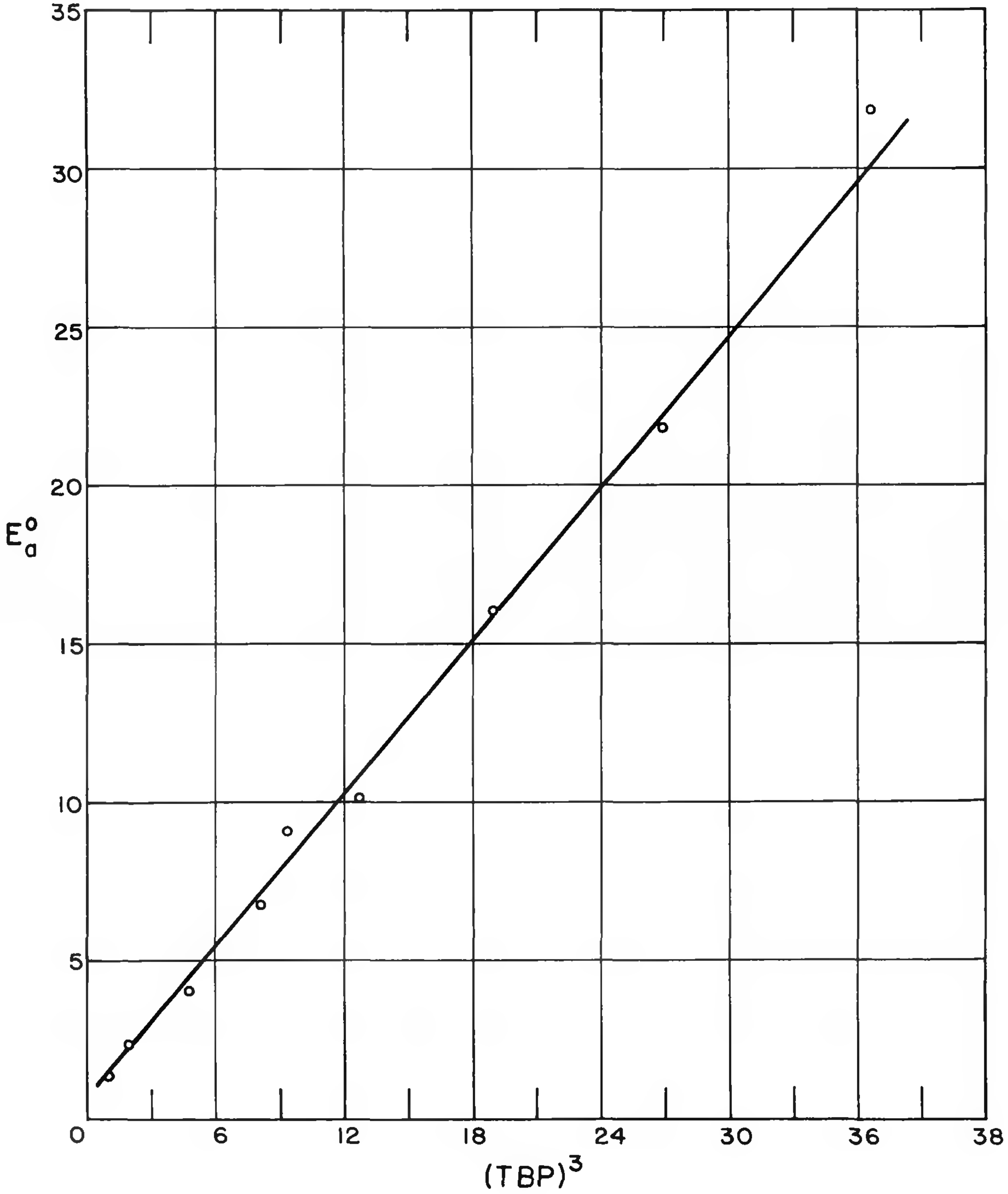

Figure 6
E_a^o vs $(TBP)^3$

1M to 5M sodium nitrate. K_d is a function of the TBP concentration, and both constants include a term $\gamma_{\pm}^{4}$ for the activity coefficient of americium nitrate.

Applying Equation (6) to systems containing sodium nitrate and free nitric acid gives values which are much higher than the observed extraction coefficients. This observation was made only when acid was present, so the addition of nitric acid must reduce the trivalent ionic americium concentration so that

$$(Am^{+++}) = \alpha(\Sigma Am,\ aq)$$

Making this addition to Equation (6) gives

$$E_a^o = \frac{\Sigma Am,\ org}{\Sigma Am,\ aq} = \alpha\left[0.0109\ (NO_3^-)^3 + 0.00653\ (NO_3^-)^3(TBP)^3\right] \qquad (7)$$

Further evidence for this complexing of americium in aqueous nitric acid is offered by Cunningham and Asprey,$^{(6)}$ who reported considerable change in the absorption spectrum of americium in concentrated nitric acid from that in 1.0M perchloric acid, although little difference was noted for 1.0M nitric acid solutions.

In the evaluation of K_c and K_d, the ability to use E_a^o in Equation (6) indicates that all of the americium was present as Am^{+++} in aqueous solutions containing no free acid. The dependency of α on the acid content of the aqueous system can be expressed in the general equation

$$Am^{+++} + (3+x)\ NO_3^- + x\ H^+ \rightarrow H_xAm(NO_3)_{3+x}$$

The equilibrium expression for this reaction can be rearranged to

$$K_u(H^+)^x(NO_3^-)^{3+x} = \frac{\Sigma Am,\ aq - (Am^{+++})}{(Am^{+++})} = (1/\alpha) - 1 \qquad (8)$$

The degree of ionization of nitric acid in solutions containing sodium nitrate is not available. This information has been obtained for aqueous nitric acid by Maranville and Young(7). Using smoothed values of E_a^o from Figure 1, α was computed for extractions from nitric acid. The TBP concentration was taken as the difference between the initial TBP concentration, corrected for volume changes which accompany HNO_3 extraction, and the stoichiometric concentration of HNO_3 in the organic phase. The results of these calculations are included in Table V. From these data, a plot of $\log\left[(1/\alpha)-1\right]$ against $\log\ (H^+)$ was made in Figure 7. The slope of the best line through these points was 5.0. Since hydrogen and nitrate ion concentrations are equal, this slope corresponds with the value (3+2x). Trivalent americium ion is complexed by nitric acid in aqueous solutions in accordance with the reaction

$$Am^{+++} + 4\ NO_3^- + H^+ \rightarrow HAm(NO_3)_4 \qquad (9)$$

The activity coefficient of americium nitrate is not as stable in aqueous nitric acid solutions as in sodium nitrate systems. However, an average value of 0.038 was obtained for K_a for acidities greater than 2.0f nitric acid.

TABLE V

Complexing of Americium Nitrate in Nitric Acid

Aqueous HNO_3 f	E_a^o (Am)	(H^+) M	α
1.0	0.0152	0.972	0.981
1.5	0.0229	1.442	0.526
2.0	0.0284	1.892	0.322
2.5	0.0306	2.326	0.201
3.0	0.0304	2.743	0.128
3.5	0.0290	3.141	0.0834
4.0	0.0263	3.517	0.0547
4.5	0.0210	3.869	0.0331
5.0	0.0144	4.194	0.0179

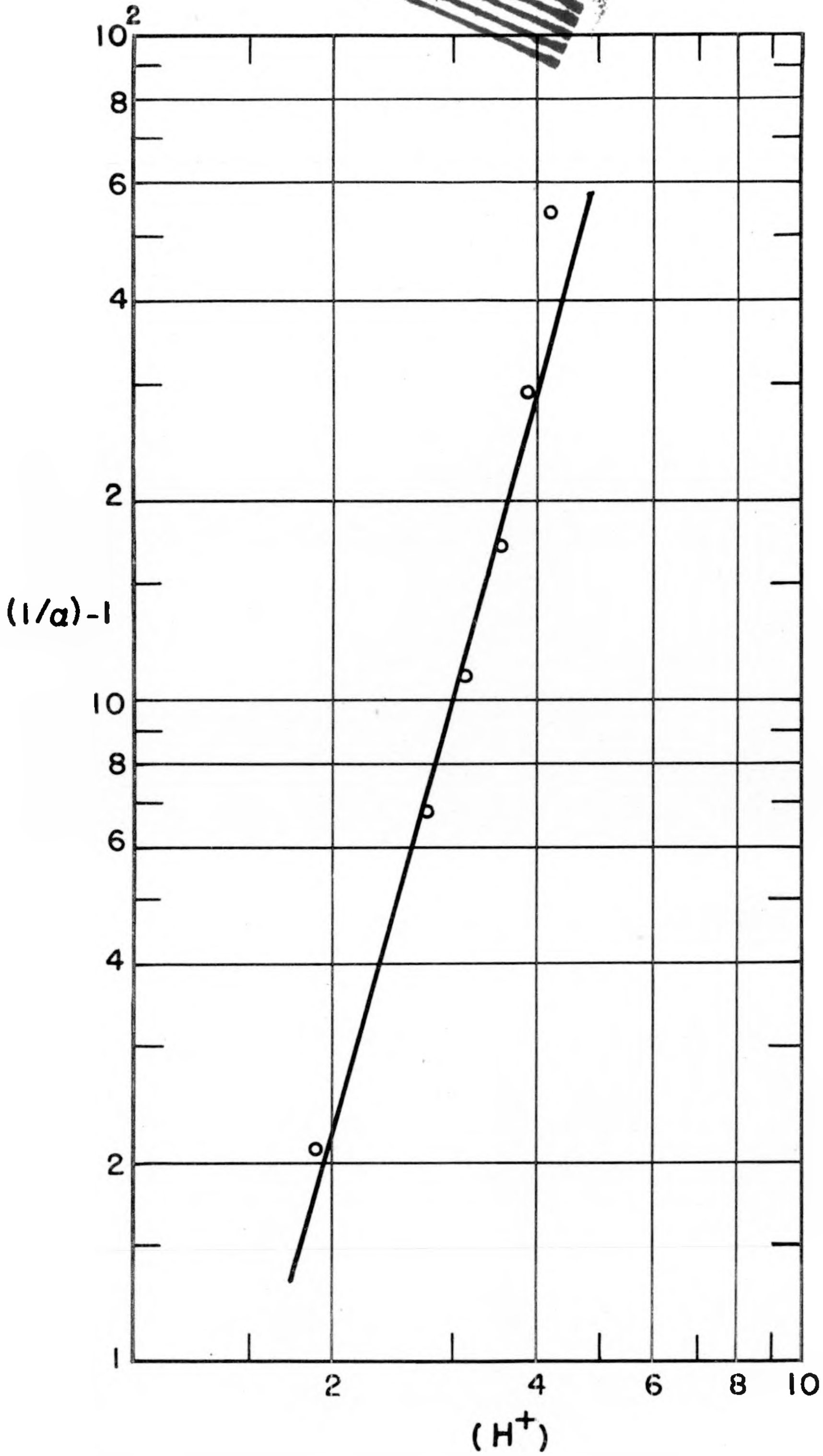

Figure 7
Am Complexing by HNO_3

The prevailing extraction reactions in Equation (6) can be combined with the reaction for complex formation in acidic aqueous solutions as the general equation

$$E_a^o = \frac{0.0109(NO_3^-)^3 + 0.00653(NO_3^-)^3\ (TBP)^3}{1 + 0.038\ (H^+)\ (NO_3^-)^4} \qquad (10)$$

The utility of this equation is limited by lack of knowledge of the degree of ionization of nitric acid in sodium nitrate solutions. Reasonable approximations can be made by determining the degree of ionization from the extraction coefficient for a given system containing sodium nitrate and nitric acid. If the degree of ionization of nitric acid is assumed to be constant for solutions of that sodium nitrate content, extraction coefficients for americium within 10 per cent of the measured values can be computed for different acidities.

SUMMARY

The extraction of americium nitrate with TBP results from the normal distribution between two immiscible phases as a relative solubility effect and through the formation of the complex $Am(NO_3)_3 \cdot 3TBP$. The presence of nitric acid in the aqueous system is detrimental to the extraction. In addition to the completion for TBP in the solvent, nitric acid complexes americium in the aqueous phase as $HAm(NO_3)_4$.

The equilibrium expressions for the three prevailing reactions in the solvent extraction process have been combined to give the extraction coefficient, E_a^o,

$$E_a^o = \frac{\Sigma Am,\ org}{\Sigma Am,\ aq} = \frac{0.0109(NO_3^-)^3 + 0.00653(NO_3^-)^3\ (TBP)^3}{1 + 0.038\ (H^+)\ (NO_3^-)^4} \qquad (10)$$

The constants were evaluated for systems containing 1M to 5M sodium nitrate and 2M to 5M nitric acid, so that the activity coefficient of americium nitrate remained nearly constant.

The degree of ionization of nitric acid in aqueous sodium nitrate imposes a limitation on the utility of Equation (10). From a measurement of the americium extraction coefficient at one acidity in a given sodium nitrate solution, the hydrogen ion concentration can be calculated. Reasonable approximations of E_a^o at other acidities can be obtained by assuming that the degree of ionization of nitric acid is constant for that particular salt concentration. These approximations are more valid for higher salt contents, where the common nitrate ion effect is dominant.

Solutions of this type are most frequently encountered in recovery operations.

The simultaneous distribution of nitric acid between the aqueous and solvent phases should be the key for estimating hydrogen ion concentrations. The acid content of the organic phase should be a function of the properties of the aqueous phase, which determine the extraction behavior of americium nitrate.

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