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Report

REPROCESSING WITH AMINE-ETHER SYSTEMS

Part 2. Distribution coefficients.

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AERE R 4440 (Part II)

Reprocessing with Amine-Ether Systems

Part II. Distribution Coefficients

by

I. L. Jenkins, H. A. C. McKay, C. G. C. Shorthill
and A. G. Wain

ABSTRACT

Results have been obtained for the extraction of uranium, plutonium, nitric acid and fission products into tertiary amines in ether diluents, and for the backwashing of plutonium from the organic phase. Most of the work has been with a solution of Alamine 336 in dibutyl cellosolve (DBC). The results show that the preferential extraction of plutonium from a mixture of plutonium, uranium and fission products is feasible, and that acetic acid-nitric acid mixtures can be used for backwashing.

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May 1965

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DIAGRAMS

1. Introduction

The choice of an amine-ether combination (Alamine 336 and DBC) and the choice of solvent extraction systems for examination have been discussed in Part I.(1) Various amines and ethers were examined before a final choice was made and the results given here therefore cover several amine-ether combinations. In general the results are closely parallel to those obtained by other authors for amine-hydrocarbon systems;(2)(3) the main difference is that the ether diluents themselves extract appreciable amounts of nitric acid.

2. Experimental

Dibutyl cellosolve was purified as described in Part I. Ether 710 (from I.C.I.) was washed with acid ferrous sulphate to remove peroxides. Alamine 336 (from General Mills Chemicals, U.S.A.) was used as received.

Amine-ether mixtures were prepared by taking a known volume of amine in a measuring flask, and making up to the mark with ether. References in the text to, say, 10% v/v amine in ether imply that the starting material was made up in this way; during the experiments, the amine concentration is of course reduced below the initial value by nitric acid and other substances entering the organic phase.

Plutonium(IV) nitrate was purified by adsorbing the plutonium on to Deacidite FF from about 8M HNO_3, and eluting it again with 1M HNO_3; americium was not adsorbed, and was therefore removed from the plutonium. The fission products were obtained from R.C.C. Amersham and were first fumed down several times with concentrated nitric acid to ensure that they were in the nitrate form. This was unnecessary with ruthenium which was supplied in the form of nitrosylruthenium nitrato complexes in nitric acid.

Distribution measurements were usually made by stirring together equal volumes of the organic and aqueous phases for three minutes, centrifuging, separating the phases and determining the concentration of the species concerned in each phase. The distribution coefficients for ^{91}Y, $^{95}Zr/^{95}Nb$, ^{144}Ce and ^{147}Pm in the presence of 1.4M aluminium nitrate were obtained by adding a known amount of the tracer to the initial aqueous phase, measuring that found in the organic phase after equilibration, and calculating that in the aqueous phase at equilibrium by difference.

3. Results and Discussion

3.1 Uranium(VI) extraction

The times needed to reach equilibrium during extraction were checked by stirring equal volumes of 10% v/v TLA in DBC or 10% v/v Alamine 336 in DBC with an aqueous phase whose initial composition was 1M HNO_3 + 0.126M $UO_2(NO_3)_2$ and measuring D_U for different times of stirring at 25°C. The results show that equilibrium is established within 20 sec:

Stirring time (sec)	20	40	120	300	600
D_U for 10% TLA in DBC	0.190	0.190	0.190	0.191	0.194
D_U for 10% Alamine 336 in DBC	0.24	0.24	0.24	0.24	0.24

The dependence of D_U on the concentration of amine at low uranium concentration (0.0126M) and constant acidity (2M HNO_3) was determined for 10% v/v TLA in Ether 710, and for 10% v/v Alamine 336 in DBC. Both systems give the usual slope of about unity(2) for the plot of log D_U against log C_{amine} (Fig. 1). The extraction of uranium into the organic phase, at any given equilibrium concentration of uranium in the aqueous phase, increases with the acidity of the aqueous phase as shown in Table I. Table I also shows the additional extraction of uranium found with DBC as diluent.

The distribution of uranium between aqueous nitric acid and 5, 10 and 15% Alamine 336 in DBC is given in Table II.

3.2 Plutonium(IV) extraction

A plot of log D_{Pu} against log C_{amine} (Fig. 4) yields, as expected,(2) a line of slope about 2 for the Alamine 336 in DBC system. The change in D_{Pu} with plutonium concentration at a fixed acidity and amine concentration is shown in Fig. 2.

TABLE I

The extraction of uranium from aqueous nitric acid by 10% v/v (0.156M) TLA in Ether 710 and in DBC

Equilibrium Concentrations				D_U	
Aqueous phase		Amine phase			
HNO_3	U	U		Ether 710	DBC
		Ether 710	DBC		
1M	0.0063M	0.00122M	0.0023M	0.19	0.36
	0.126	0.017	0.0228	0.133	0.18
	0.315	0.031	0.048	0.099	0.15
	0.630	0.051	0.099	0.081	0.15
	1.260	0.082	-	0.065	-
2M	0.0063	0.002	-	0.33	-
	0.126	0.023	-	0.184	-
	0.315	0.041	-	0.130	-
	0.630	0.059	-	0.094	-
	1.260	0.091	-	0.072	-
4M	0.0063	0.004	-	0.61	-
	0.126	0.037	-	0.296	-
	0.315	0.053	-	0.169	-
	0.630	0.070	-	0.112	-
	1.260	0.123	-	0.098	-
6M	0.0063	0.005	-	0.73	-
	0.315	0.066	-	0.21	-
	0.630	0.083	-	0.131	-
	1.260	0.127	-	0.101	-

TABLE II

The extraction of uranium from aqueous nitric acid by Alamine 336 in DBC

Equilibrium Concentrations				D_U	Density of organic phase	
Aqueous Phase		Amine Phase 5% v/v (0.099M) Alamine 336/DBC				
HNO_3	U	HNO_3	U			
0.5M	0.0126M	0.08M	0.000925M	0.073	0.840 g/cc	
	0.126	0.11	0.00976	0.077	0.842	
	0.315	0.13	0.0232	0.074	0.845	
	0.630	0.16	0.0466	0.074	0.854	
1.0M	0.0126M	-	-	-	-	
	0.126	0.15	0.0134	0.11	0.845	
	0.315	0.175	0.0290	0.092	0.851	
	0.630	0.215	0.0623	0.099	0.862	
		10% v/v (0.198M) Alamine 336/DBC				
0.5M	0.0126M	0.152	0.00227	0.180	0.842	
	0.126	0.175	0.0224	0.177	0.847	
	0.315	0.205	0.0500	0.158	0.858	
	0.630	0.225	0.0955	0.151	0.872	
1.0M	0.0126M	0.24	0.00466	0.37	0.840	(a)
	0.126	0.265	0.0301	0.27	0.850	(b)
	0.315	0.29	0.0592	0.188	0.862	
	0.630	0.325	0.118	0.186	0.880	(c)
		15% v/v (0.297M) Alamine 336/DBC				
1.0M	0.0126M	-	0.00597M	0.48	-	
	0.126	0.355	0.0445	0.35	0.864	
	0.315	0.375	0.0840	0.27	0.876	
	0.630	0.385	0.150	0.24	0.897	

(a), (b) and (c). See section 3.2.

The extraction of plutonium by amine is in most cases reduced by the presence of uranium,(3) as the following results for 10% v/v Alamine 336 in DBC and 1M HNO_3 (aqueous) show:

$C_{U(aq)}$	0.0126M	0.126M	0.630M
$D_{Pu(IV)}$	61	27.5	10.5

(The conditions correspond to (a), (b) and (c) respectively of Table II.) Such values are still sufficiently high to enable virtually complete extraction of plutonium in presence of uranium to be achieved in a counter-current system.

3.3 Fission product extraction

It is well-known that most fission products are but weakly extracted into amine/diluent systems. A few confirmatory results for 10% v/v Alamine 336 with DBC as diluent have been obtained under strong salting-out conditions (aqueous phase, 1.8M nitric acid and 1.4M aluminium nitrate):

D_Y	3.0×10^{-5}	D_{Ce}	8.7×10^{-3}
$D_{Zr/Nb}$	4.8×10^{-3}	D_{Pm}	1.5×10^{-3}

Even lower figures would be expected in the absence of a salting-out agent.

Extraction of ruthenium, however, is not negligible.(4) Tertiary amines extract the tri- and tetranitrato nitrosylruthenium complexes from nitric acid solutions,(5) and the use of DBC as diluent enhances the extraction especially of the trinitrato complex. Typical partition coefficients at 20°C with a hydrocarbon diluent are (for 0.25M TLA in toluene):(6)

	1M	2M	3M	6M HNO_3
Trinitrato complex	0.35	0.09	0.016	-
Tetranitrato complex	75	25	8	0.3

The following results at 20°C show the effect of the DBC diluent; the starting solution (aqueous) contained 48% of the ruthenium as the tri- and 10% as the tetranitrato complex; stirring times of 30 sec were used. The distribution coefficients were:

	Extraction ($1M\ HNO_3$)	Backwash ($6M\ HNO_3$)
0.25M TLA in toluene	0.3	0.3
0.25M TLA in DBC	0.8	2.2
0.25M Alamine 336 in toluene	0.45	0.35
0.25M Alamine 336 in DBC	1.0	2.2
Pure DBC	0.05	0.5

These results indicate a relatively high partition coefficient (> 2) for the trinitrato complex between 0.25M amine and 1M nitric acid, when DBC is used as the diluent. Both the tri- and the tetra- complexes must therefore be taken into account in considering ruthenium decontamination; about 2-7% of the ruthenium is in these forms at 1-2M nitrate ion concentration. Furthermore, under the conditions of interest the trinitrato complex nitrates to the tetranitrato with a half-time of only about 5 min;(6) so that even with a hydrocarbon diluent, when the trinitrato complex is not itself appreciably extracted, it contributes indirectly to poor decontamination from ruthenium under low acid conditions.

3.4 The extraction of nitric acid

The results in Fig. 3 for the extraction of nitric acid by 0.1M TNA in xylene are typical of amine behaviour when diluted with solvents which do not extract nitric acid to any great extent. Over the aqueous acidity range from 0.1 to 1.0M HNO_3 the amount of acid extracted corresponds to the formation of a 1:1 $TNA{:}HNO_3$ complex. At higher acidities more nitric acid is extracted.

With DBC as diluent the position is more complicated as DBC itself extracts some nitric acid (see Part I). The extraction of nitric acid by 15% v/v (0.297M) Alamine 336 in DBC is shown in Fig. 3. For equilibrium aqueous acidities less than the initial concentration of amine, D_{HNO_3} is greatly in favour of the organic phase owing to the formation of the amine nitrate complex. At higher acidities up to about 1M HNO_3 the excess acid in the organic phase (over and above that needed for the 1:1 complex) is mainly due to extraction by the DBC.

When 10% v/v (0.198M) Alamine 336 in DBC was stirred with aqueous nitric acid of initial concentration less than 0.2M, emulsions were formed, but none were formed at acidities greater than 0.2M. No emulsions were observed with 15% v/v Alamine 336 in DBC.

It is important to note that when uranium is extracted into 10% Alamine 336 in DBC the amount of nitric acid extracted increases as shown in Fig. 4; this affects flowsheet calculations.

3.5 The backwashing of plutonium from the amine phase

Simple backwashing of plutonium(IV) from the organic phase with dilute nitric acid is impractical as $D_{Pu(IV)}$ is still as high as 7 even at 0.2M HNO_3 with 15% v/v Alamine 336 in DBC. Both reducing and complexing backwashes have therefore been considered, especially ferrous sulphamate in the former category, and acetic acid(7) in the latter.

Champion and Chesne(8) have reported a time-dependence in the backwashing of plutonium(IV) by 0.05M ferrous sulphamate from 20% TLA in dodecane, the reaction being still incomplete after 30 min with a 0.5M nitric acid aqueous phase. We have obtained similar results in our own system (2 g/l plutonium(IV) in 15% v/v Alamine 336 in DBC, backwashed into 0.1M ferrous sulphamate, 0.5M nitric acid):

Time	1	3	10	30	60 min
D_{Pu}	11.0	2.4	0.33	0.06	0.05

We have also observed a time-dependence in backwashing plutonium(IV) with acetic acid (organic phase as before, backwashed into 0.5M acetic acid):

Time	1	3	10	30	60 min
D_{Pu}	1.85	1.23	0.93	0.86	0.81

and Streeton has found a similar effect with uranium(IV).

We believe that these time effects arise from the high partition coefficients of plutonium(IV) (and uranium(IV)) in amine systems. Whether we depend on reduction or complexing, the reaction concerned presumably occurs in the aqueous phase; but most of the unreacted material at any instant is in the organic phase, and only a small fraction is available in the aqueous phase to participate in the reaction. If this explanation of the kinetics is correct, then the time effects must be regarded as a rather general phenomenon, and we can only hope to eliminate them by using a reagent that enters the organic phase, if any suitable one can be found. The shorter time required to reach equilibrium with acetic acid, as compared with ferrous sulphamate, may indeed be due to acetic acid entering the organic phase.

The use of ferrous sulphamate for backwashing at room temperature would necessitate the use of contactors of rather long residence time, and attention has therefore been directed principally to acetic acid. Acetic acid alone is not satisfactory, because on successive backwashing either a white precipitate (amine acetate?) or a second organic phase is formed. Mixtures of acetic and nitric acids can, however, be used, just enough nitric acid being added to prevent formation of two organic phases; higher concentrations of nitric acid tend to favour extraction of plutonium by the amine. Our results, with a standardised stirring time of 3 min, are given in Tables III and IV. The rapid fall in D_{Pu} as backwashing proceeds, demonstrated by the results in Table IV, is a fortunate feature, and can be ascribed to progressive displacement of nitrate by acetate ion in the amine phase.

Small amounts of acetic acid can be tolerated in recycling amine. Measurements for 5% v/v 336 in DBC in contact with 2M HNO_3 (aqueous) showed that $D_{Pu(IV)}$ did not change significantly on addition of acetic acid up to 0.05M in the organic phase.

TABLE III

Plutonium backwashing with acetic acid

Conditions: Equal volumes
3 min stirring
Pu(IV) extracted into 15% v/v Alamine 336 in DBC from 2M HNO_3

Acetic acid (initial aqueous)	Initial $C_{Pu(org)}$ = 0.084M			Initial $C_{Pu(org)}$ = 0.0125M		
	Final $C_{Pu(org)}$	Final $C_{Pu(aq)}$	D_{Pu}	Final $C_{Pu(org)}$	Final $C_{Pu(aq)}$	D_{Pu}
0.5M	0.048M	0.036M	1.36	0.0040M	0.0044M	0.91
1.0	0.035	0.049	0.72	0.0029	0.0055	0.52
2.0	0.026	0.056	0.46	0.0013	0.0071	0.18
3.0	0.018	0.065	0.28	-	-	-

TABLE IV

Plutonium backwashing with acetic-nitric acid mixtures

Conditions: Equal volumes
3 min stirring
Pu(IV) extracted into 15% v/v Alamine 336 in DBC from 2M HNO_3

Initial $C_{Pu(org)}$	Initial aqueous phase	D_{Pu}		
		1st backwash	2nd backwash	3rd backwash
0.0925M	1.0M HAc + 0.1M HNO_3	1.77	1.16	0.19
0.0735	" + 0.05M HNO_3	0.76	0.20	0.06
0.0735	0.5M HAc + "	1.77	0.42	0.03

4. Conclusions

The results presented in section 3 indicate that a flowsheet of the type shown in Part I is feasible for the extraction of plutonium from a mixture of plutonium, uranium and fission products.

Plutonium can be conveniently backwashed from the organic phase by a mixture of acetic acid and nitric acid.

5. Acknowledgements

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References

(1) E. S. Lane, A. Pilbeam and J. M. Fletcher, Part I of this report (1965).

(2) W. E. Keder, J. C. Sheppard and A. S. Wilson, J. Inorg. Nucl. Chem. 12, 327 (1960).

(3) F. Baroncelli, G. Scibona and M. Zifferero, Radiochimica Acta 1, 75 (1963).

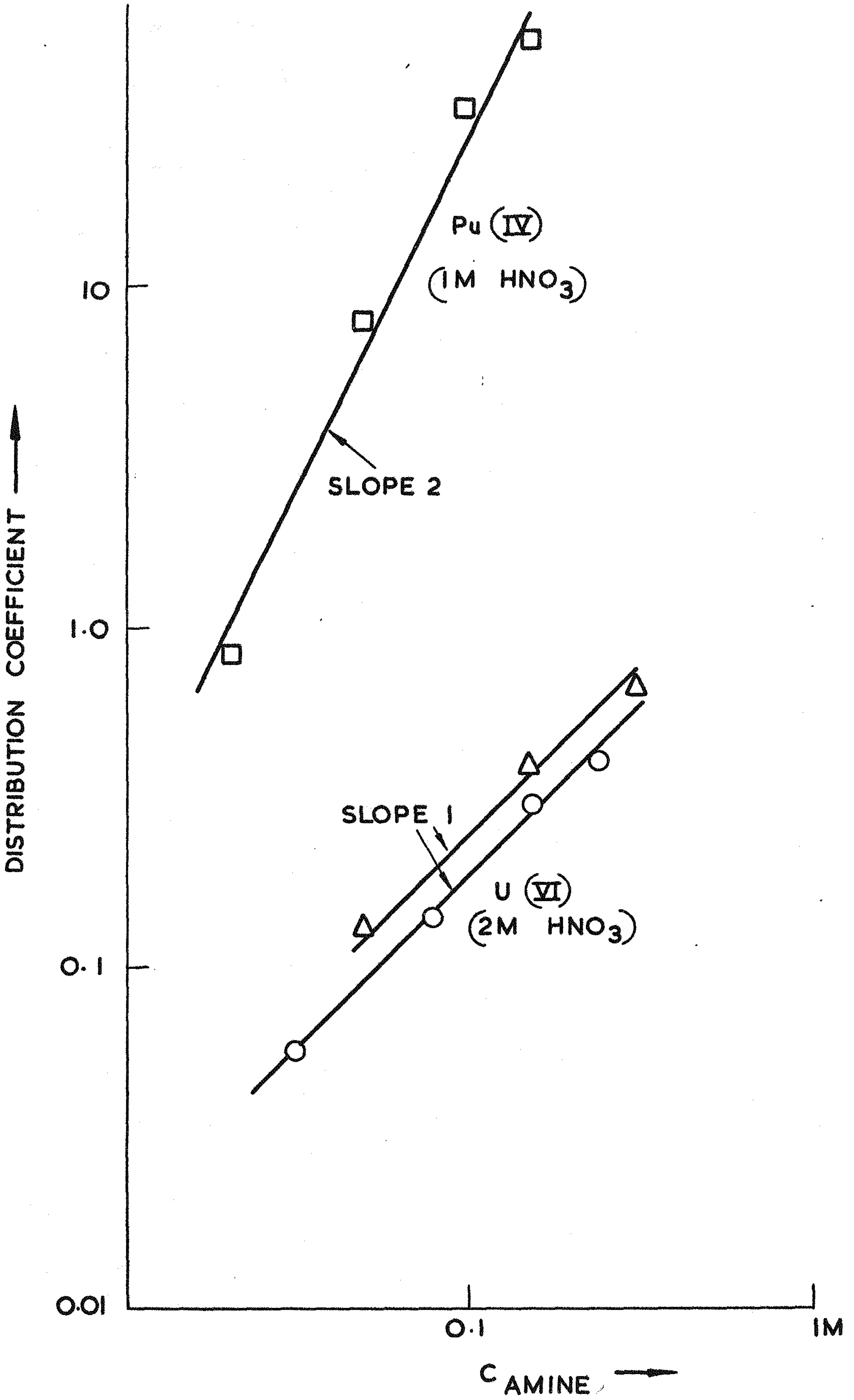
(4) The information in this paragraph is due to D. Scargill.

(5) R. E. Skavdahl and E. A. Mason, M.I.T.N.E.-20 (1962); D. Scargill, C. E. Lyon, N. R. Large and J. M. Fletcher, J. Inorg. Nucl. Chem. 27, 161 (1965).

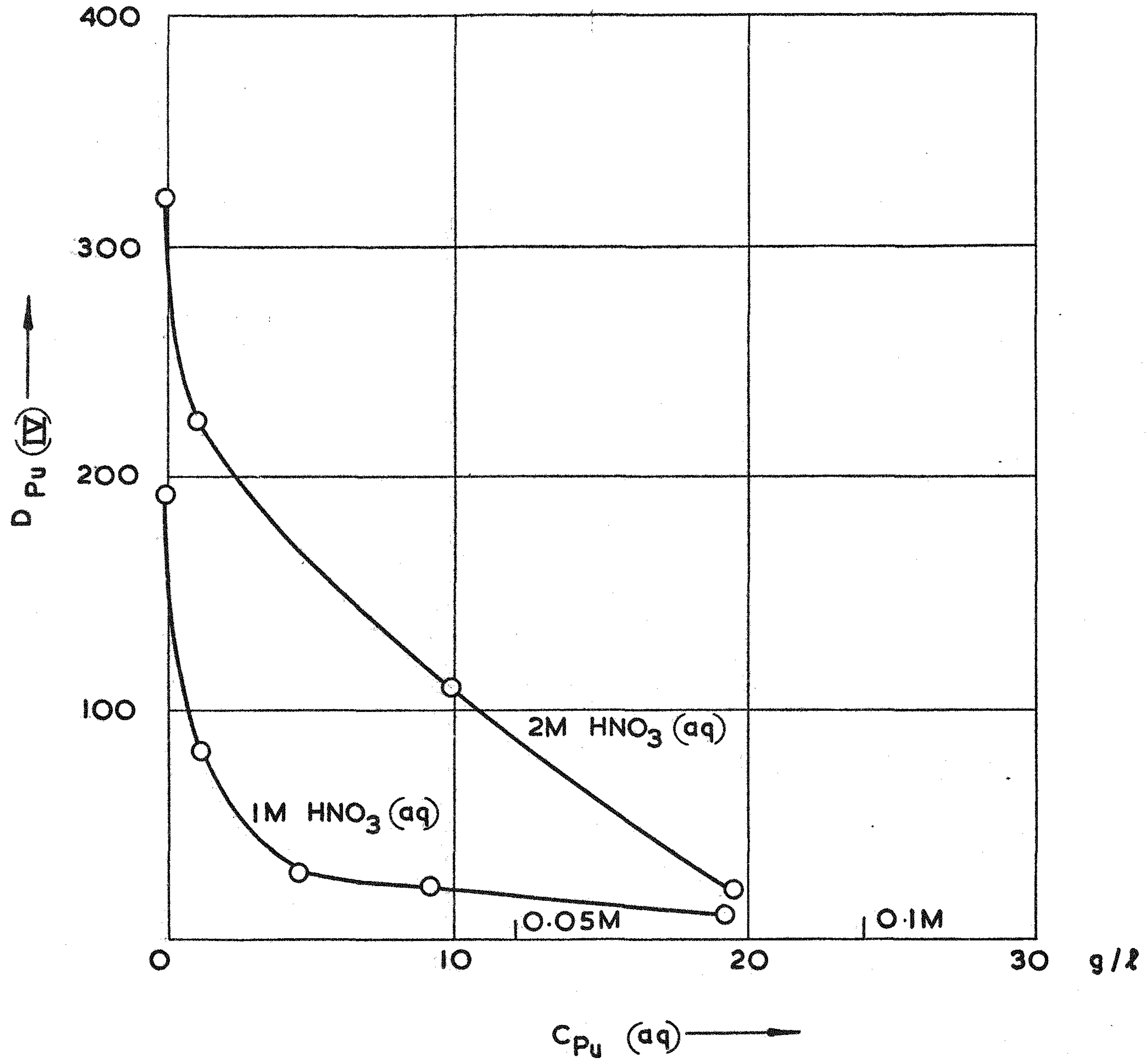
(6) D. Scargill, AERE - R 4922 (1965).

(7) C. F. Coleman, ORNL-CF-61-5-74 (1961).

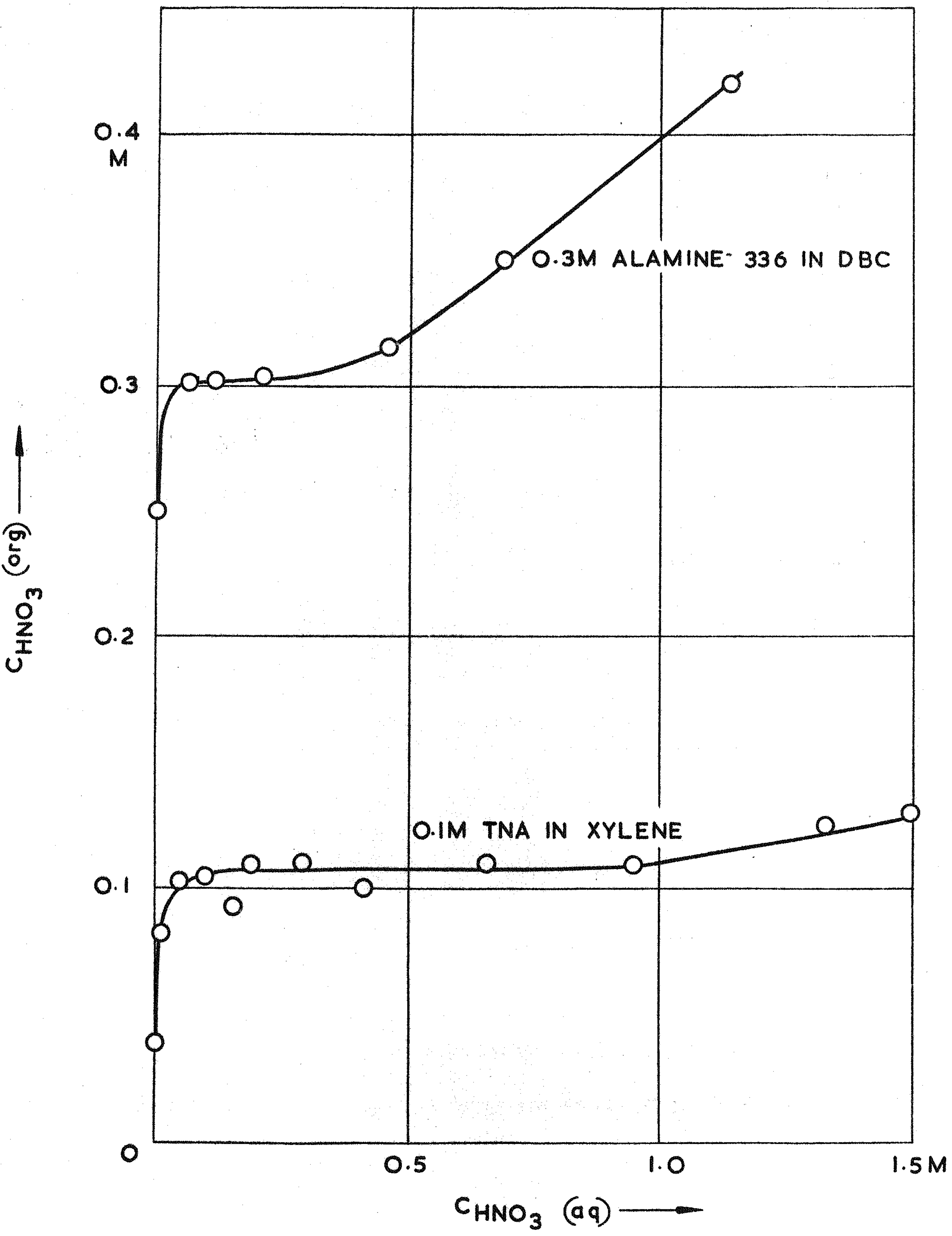
(8) J. Champion and A. Chesne, CEA R-2607 (1964).



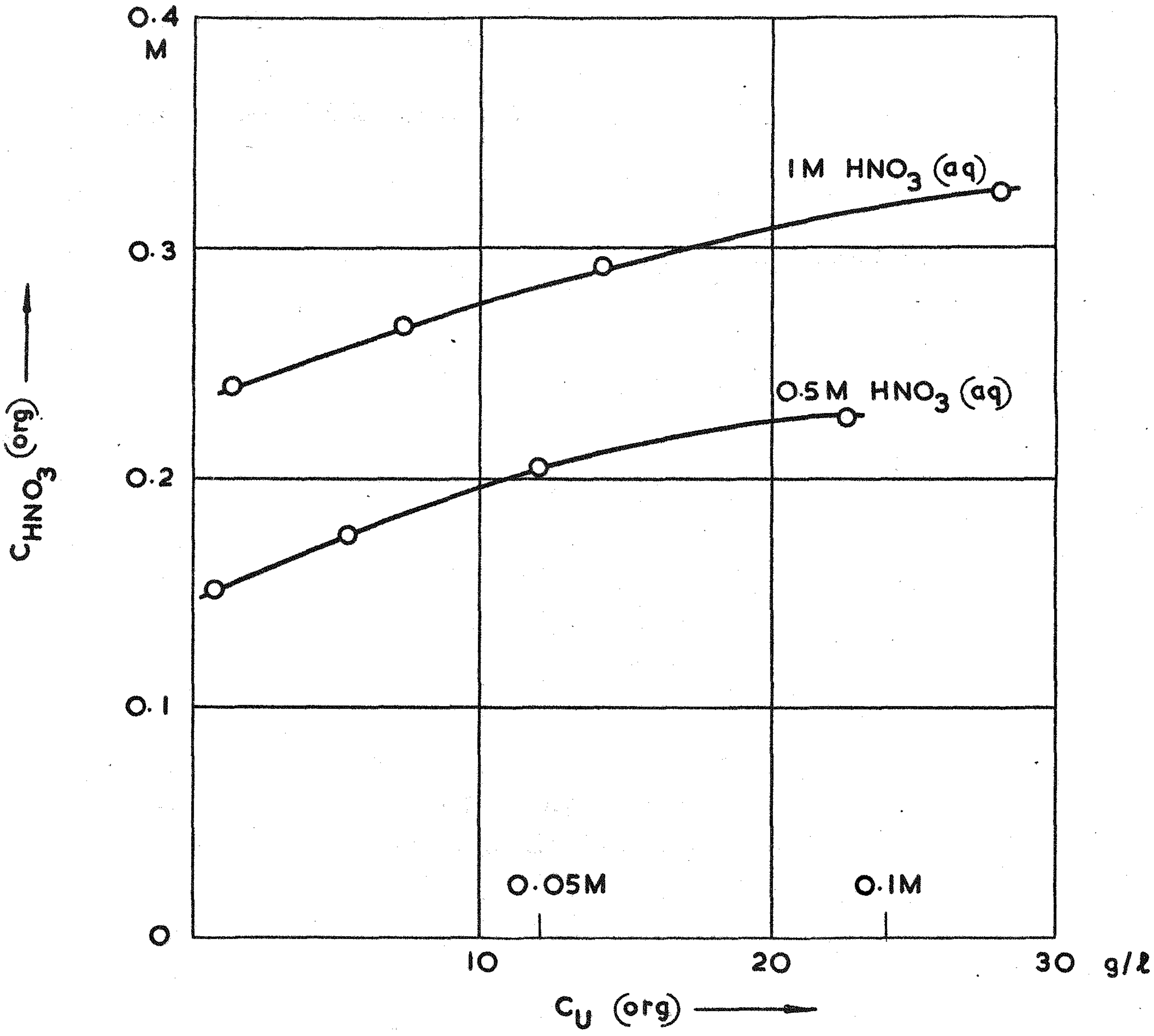
A.E.R.E. R4440 (PART 2) FIG.1 THE VARIATION OF LOG D_U AND LOG D_{Pu} (IV) WITH LOG C_{AMINE}



A. E. R. E. R 4440 (PART 2) FIG 2 THE VARIATION OF $D_{Pu(IV)}$ WITH PLUTONIUM CONCENTRATION



A.E.R.E. R.4440 (PART 2) FIG. 3 NITRIC ACID DISTRIBUTION DATA



A.E.R.E. R4440 (PART 2) FIG.4 THE VARIATION OF C_{HNO_3} (org) WITH C_U (org) FOR 10% ALAMINE 336 IN DBC

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