Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Huang, Chun-Hui and Bautista, Renato G.(1983) 'The Synergistic Extraction of $Sm(NO_3)_3$ and $Gd(NO_3)_3$ by a Mixture of Tributyl Phosphate and Aliquat 336 in AMSCO and Ammonium Nitrate Medium', Separation Science and Technology, 18: 14, 1667 — 1683

To link to this Article: DOI: 10.1080/01496398308056120

URL: http://dx.doi.org/10.1080/01496398308056120

SEPARATION SCIENCE AND TECHNOLOGY, 18(14&15), pp. 1667-1683, 1983

The Synergistic Extraction of $Sm(NO_3)_3$ and $Gd(NO_3)_3$ by a Mixture of Tributyl Phosphate and Aliquat 336 in AMSCO and Ammonium Nitrate Medium

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ABSTRACT

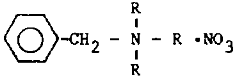
The synergic extraction of Sm and Gd using a mixture of tributyl phosphate and Aliquat 336 is presented. The influence of diluents, salting out agents and acidity on the synergic extractions have been investigated. The separation factor of Sm and Gd was found to be larger than 3. This is one of the best systems for the separation of Sm and Gd. NH_4NO_3 was found to be extracted by pure TBP or pure Aliquat 336, but cannot be extracted by a mixture of TBP and Aliquat 336.

INTRODUCTION

The synergic extraction of rare earths with a mixture of quaternary ammonium base salt and TBP have been reported by several authors (1-3). The reported compositions of the extractable rare earth complexes formed are given in Table 1. The experimental methods used in determining the composition of the extractable complexes in the various studies are the slope and the equimolecu-

0149-6395/84/1814-1667$3.50/0

TABLE 1. The Composition of the Extracted Complexes in the TBP-Quaternary Ammonium Base Salts-Rare Earth Synergic Systems.

Element	Medium	Diluent	Quaternary Ammonium Base Salts	Determination Methods	Composition of Synergic Extracted Complexes	Reference
Ce(III)	3M HNO_3	toluene	trilauryl methyl ammonium nitrate	slope method	$R_3CH_3N)_2Ce(NO_3)_5 \cdot TBP$	[1]
Nd(III)	3M NH_4NO_3	kerosene		EMSM and slope method	$R_3CH_2C_6H_5 \cdot Nd(NO_3)_4 \cdot TBP$	[2]
Pr(III)	1M $NaNO_3$	C_6H_6, CCl_4	Aliquat 336	slope method	$(R_3CH_3N)_2Pr(NO_3)_5 \cdot TBP$	[3]
Sm(II) or Gd(III)	4M NH_4HO_3	AMSCO	Aliquat 336	EMSM and Osmometry	$R_3CH_3N \cdot Gd(NO_3)_4 \cdot 2TBP$ $R_3CH_3N \cdot Sm(NO_3)_4 \cdot 2TBP$	this work

lar series method. The slope method is most appropriate for simple reactions. In complex reaction systems such as the synergic extraction systems, the other equilibrium reactions taking place simultaneously must be taken into account in addition to the main equilibrium reaction. The equimolecular series method can also give the composition of the complexes but the solution is not unique and becomes very complicated with multireaction systems. The different reactions taking place in the TBP-Aliquat 336-$Sm(NO_3)_3$ or $Gd(NO_3)_3$-NH_4NO_3 synergic system are presented in this work.

EXPERIMENTAL

The rare earth oxides used in this work have a purity greater than 99.9% with respect to other lanthanides and were obtained from the Materials Preparation Center of the Ames Laboratory. The rare earth oxides used in the standard samples have a purity of 99.999% by emission spectroscopy.

Aliquat 336 was provided by the Henkel Corporation. Its quaternary salt content is about 90%. The quaternary ammonium chloride is made by the methylation of a straight chain saturated symmetrical tertiary ammine $R_3CH_3N^+Cl^-$, where R is a mixture of 8 to 10 carbon chains with C_8 predominating. The chloride is converted completely into nitrate by contacting with 2.0 M NH_4NO_3 for five or six times until no white precipitate is formed when $AgNO_3$ was added into the stripping solution.

The concentrations of the rare earths were determined by EDTA titration. In the Gd and Sm binary system, the concentration of Gd was determined by atomic absorption and the concentration of Sm was calculated from the difference between the total rare earth concentration obtained by EDTA titration and the concentration of Gd obtained by atomic absorption.

Ammonium ion in organic phase was stripped with 0.2 N H_2SO_4 into the aqueous phase. The ammonium ion was measured with an ammonia electrode Model 95-10 made by Orion Research Inc.

RESULTS AND DISCUSSIONS

Influence of Different Factors on the Synergic Extraction

The extraction conditions have a large influence on the synergic effect in this system. A series of organic solutions containing a total concentration of 0.6 M but with different molar ratios of TBP and Aliquat 336 in AMSCO diluent were contacted with 0.1 M rare earth nitrate and 4.0 M NH_4NO_3 solution at pH 3. The maximum synergic distribution ratio is observed at a mixture concentration containing 0.4 M TBP and 0.2 M Aliquat 336. No synergic effect is observed under the same condition when the diluent used is toluene. The results are given in Table 2 and shown in Fig. 1. It shows that a diluent containing an alkane is much better than an arylated alkane. When chloroform ($CHCl_3$) is used as the diluent, neither the Aliquat 336 or the TBP alone nor their mixture extracted the rare earths.

The effect of the same concentration of different salting out agents on the extraction is shown in Fig. 2. The two curves show the variation of the distribution ratio with the various molar concentration ratio of TBP and Aliquat 336. The maximum synergic distribution ratio is at the same total mixture concentration containing 0.4 M TBP and 0.2 M Aliquat 336. The maximum distribution ratio is equal to 12.4 for 4.0 M $LiNO_3$ and is only 0.525 for 4.0 M NH_4NO_3. $LiNO_3$ is a much better salting out agent than NH_4NO_3 for this extraction system.

The acidity of the aqueous phase also has a large influence on the synergic extraction. A comparison of the first set of data in Table 2 and Table 3 show that various molar ratios of TBP and Aliquat 336 at a total concentration 0.5 M in toluene extract samarium and gadolinium from 4.0 M NH_4NO_3 but not in 1.7 M HNO_3. This is due to the coextraction of HNO_3 in this system. The distribution ratio of HNO_3 with various molar ratios of TBP and Aliquat 336 at a total concentration 0.5 M in toluene is shown in Fig. 3.

The maximum synergic extraction distribution ratio appears at the point where TBP to Aliquat 336 molar ratio is equal to 2.

TABLE 2. Effect of Diluent on the Extraction of Aliquat 336-TBP System.

	Initial Conditions						Equilibrium Conditions				
	pH	NH_4NO_3 M	Diluent	$(RE)_T$ M	TBP M	Aliquat 336 M	pH	$K_{D,RE}$	$K_{D,Sm}$	$K_{D,Gd}$	$\beta_{Sm/Gd}$
1	2.92	4.0	toluene	0.1014	0.00	0.50	3.18	0.404	0.487	0.308	1.58
2	2.92	4.0	toluene	0.1014	0.10	0.40	3.11	0.358	0.418	0.289	1.45
3	2.92	4.0	toluene	0.1014	0.20	0.30	3.04	0.322	0.367	0.267	1.37
4	2.92	4.0	toluene	0.1014	0.25	0.25	3.00	0.302	0.361	0.231	1.56
5	2.92	4.0	toluene	0.1014	0.30	0.20	2.95	0.277	0.314	0.231	1.36
6	2.92	4.0	toluene	0.1014	0.40	0.10	2.85	0.210	0.205	0.217	0.95
7	2.92	4.0	toluene	0.1014	0.50	0.00	2.74	0.027	-	0.095	-
1	2.92	4.0	AMSCO	0.1019	0.00	0.60	3.17	0.415	0.627	0.219	2.86
2	2.92	4.0	AMSCO	0.1019	0.10	0.48	3.29	0.451	0.696	0.232	3.00
3	2.92	4.0	AMSCO	0.1019	0.24	0.36	3.26	0.473	0.727	0.246	2.96
4	2.92	4.0	AMSCO	0.1019	0.30	0.30	3.23	0.496	0.776	0.253	3.07
5	2.92	4.0	AMSCO	0.1019	0.36	0.24	3.21	0.532	0.840	0.270	3.11
6	2.92	4.0	AMSCO	0.1019	0.48	0.12	3.14	0.525	0.793	0.288	2.75
7	2.92	4.0	AMSCO	0.1019	0.60	0.00	3.03	0.174	0.177	0.169	1.05

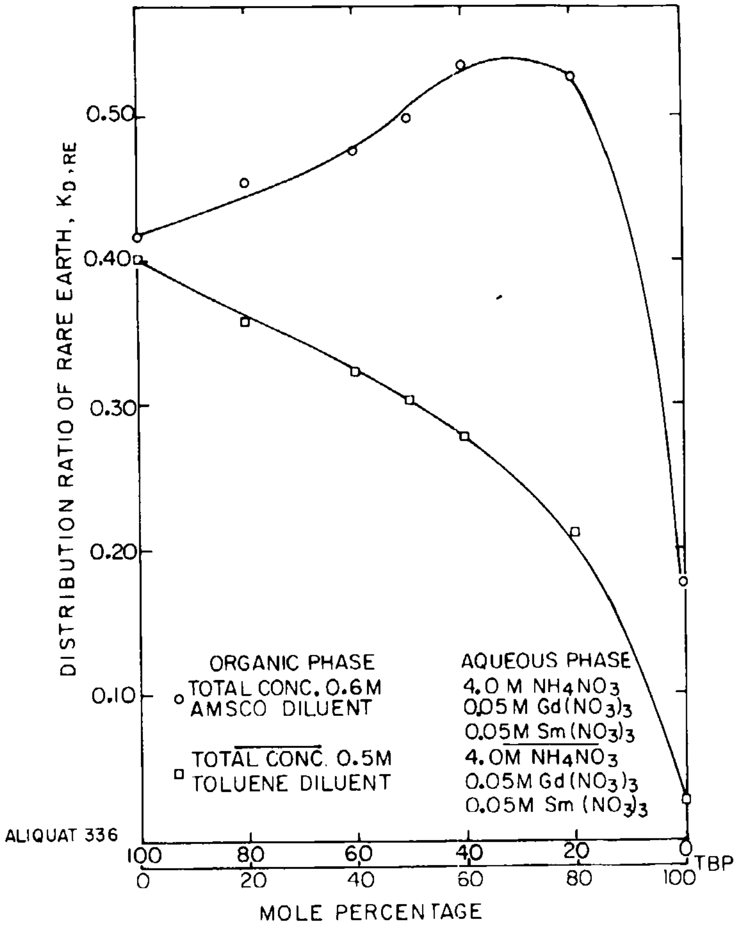


Fig. 1. Effect of diluent on the extraction of TBP-Aliquat 336-$RE(NO_3)_3$-NH_4NO_3 system.

Although the predominant component of the organic phase is TBP, it somehow retains the character and property of amine in extracting rare earths. The distribution ratio of rare earths decrease with increase in the atomic number. For example when a mixture of 0.4 M TBP and 0.2 M Aliquat 336 is used to extract individually $Nd(NO_3)_3$ or $Sm(NO_3)_3$ or $Gd(NO_3)_3$ at pH 3 and 4.0 M NH_4NO_3, the distribution ratios are 1.197, 0.8393, 0.3825, respectively. The calculated

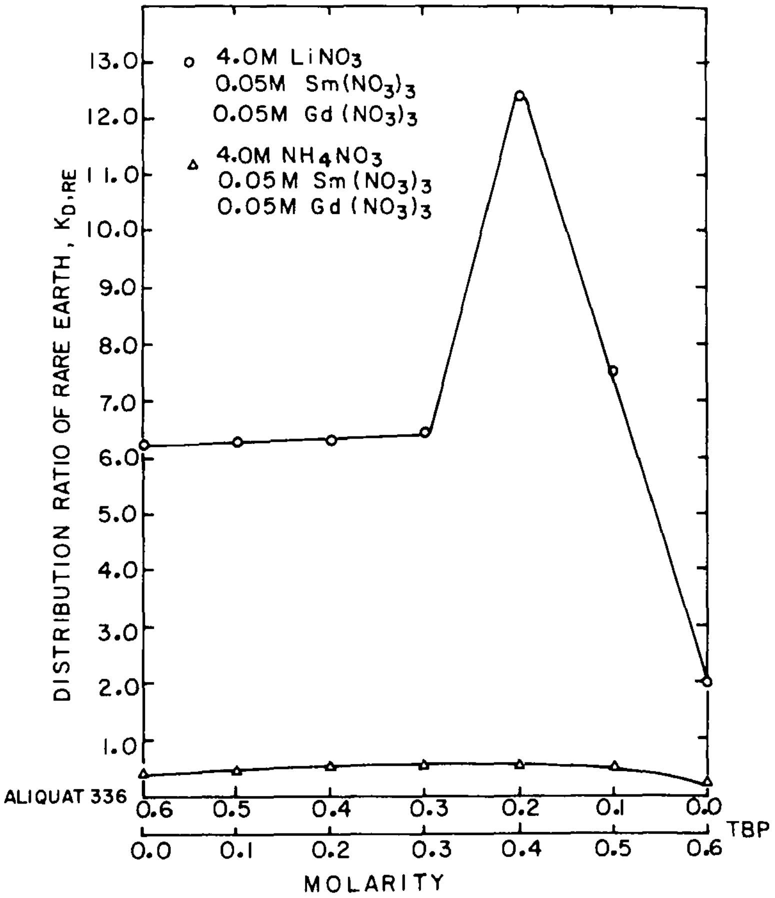


Fig. 2. Effect of salting out agent on the extraction of TBP-Aliquat 336-RE$(NO_3)_3$ system.

separation factor is only 2.19. The separation factor $\beta_{Sm/Gd}$ when extracted from a mixture of Sm and Gd is greater than 3 and this is given in Table 2. The separation factor $\beta_{Sm/Gd}$ becomes smaller when the diluent AMSCO is replaced by toluene. It also decreases when the NH_4NO_3 salting out agent is replaced by $LiNO_3$ regardless of the $LiNO_3$ concentration. This synergic extraction system results in lower viscosity compared with using Aliquat 336

TABLE 3. The Extraction of NH_4NO_3 with TBP.

INITIAL CONDITIONS				EQUILIBRIUM CONDITIONS			
NH_4NO_3	TBP			log [TBP]	K_{D,NH_4^+}	$\log K_{D,NH_4^+}$	$\log K_{eq} = \log \frac{[NH_4NO_3\cdot 2TBP]}{[TBP]^2[NO_3^-[NH_4^+]}$
M	Molarity	[TBP]	$[(TBP)_2]$				
4.00	0.200	0.120	0.040	-0.921	2.57×10^{-5}	-4.59	-3.35
4.00	0.400	0.193	0.104	-0.714	5.83×10^{-5}	-4.23	-3.40
4.00	0.500	0.224	0.138	-0.650	8.12×10^{-5}	-4.09	-3.39
4.00	0.600	0.251	0.175	-0.600	1.01×10^{-4}	-4.00	-3.40

Average $\log K_{eq} = -3.39 \pm 0.02$

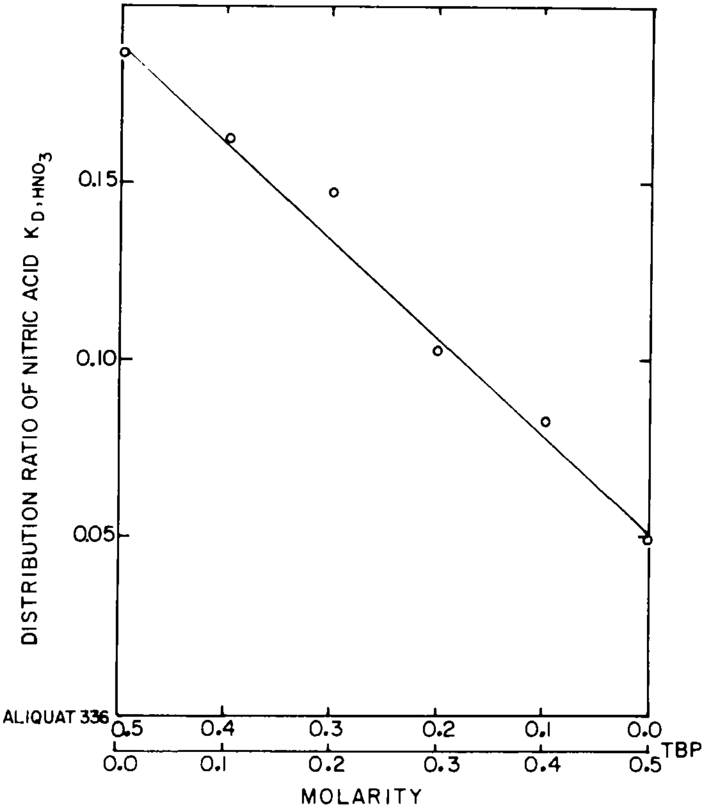


Fig. 3. Extraction of nitric acid with TBP-Aliquat 336 system.

alone and results in a higher separation factor when compared to using TBP alone.

Main Extraction Equilibrium Reactions in the Synergic System

An equilibrium dimerization constant of 2.76 for TBP in hexane has been determined by the authors (4). Aliquat 336 in hexane was found to have a series of aggregation equilibria. The degree of association between TBP and Aliquat 336 was found to be very strong. The reactions in the organic phase can be represented by the following series of reactions:

$$2T \rightleftarrows T_2 \qquad [1]$$

$$An-1 + A \rightleftarrows A_n \qquad [2]$$

where T represents TBP, A represents Aliquat 336 and n is a positive integral which is equal or greater than 2. The interaction reactions can be represented by the equations

$$T + A_n \rightleftarrows TA_n \qquad [3]$$

$$T_2 + A_n \rightleftarrows T_2A_n \qquad [4]$$

where n is a positive integral.

The predominant reaction is assumed to be

$$T_2 + A \rightleftarrows T_2A \qquad [5]$$

on the basis of our experimental data (4). There are a series of species in different states of aggregation on the basis of the calculated aggregation equilibrium constants of Aliquat 336. These are A, A_2, A_3 ••• A_n with A being the prodominant species. TBP is known to dimerize in hexane solution. Within the concentration range of the present work, the TBP monomer is the prodominant species. In a mixture of Aliquat 336 and TBP, the association of Aliquat 336 with dimeric TBP is much stronger than with monomeric TBP, hence the TBP equilibrium will move toward the formation of dimeric TBP species(4). For example, in a solution of 0.4 M TBP in hexane, the total concentration of monomer and dimer species (or apparent molarity) is 0.297 M, where the monomer and dimer concentrations are 0.193 M and 0.104 M, respectively. When 0.2 M Aliquat 336 is introduced into this solution, the total concentration of monomer and dimer species measured by osmometry is reduced to 0.242 M. This is smaller than the 0.4 M TBP and 0.297 M total concentration of both monomer and dimer. In other words, when the new solute is added to the TBP solution, the total number of aggregation in solution is decreased. This may be explained by the association of Aliquat 336 species with TBP species, especially with the TBP dimer. The total number of aggregation in the system is therefore reduced to less than the original number.

The maximum distribution ratio for the extraction of samarium and gadolinium using the mixture with TBP-Aliquat 336 is found when the TBP concentration equals 0.4 M and the Aliquat 336 concentration equals 0.2 M. This is shown in Figure 4. On the basis of the above information it is concluded that the main extraction equilibrium reaction is

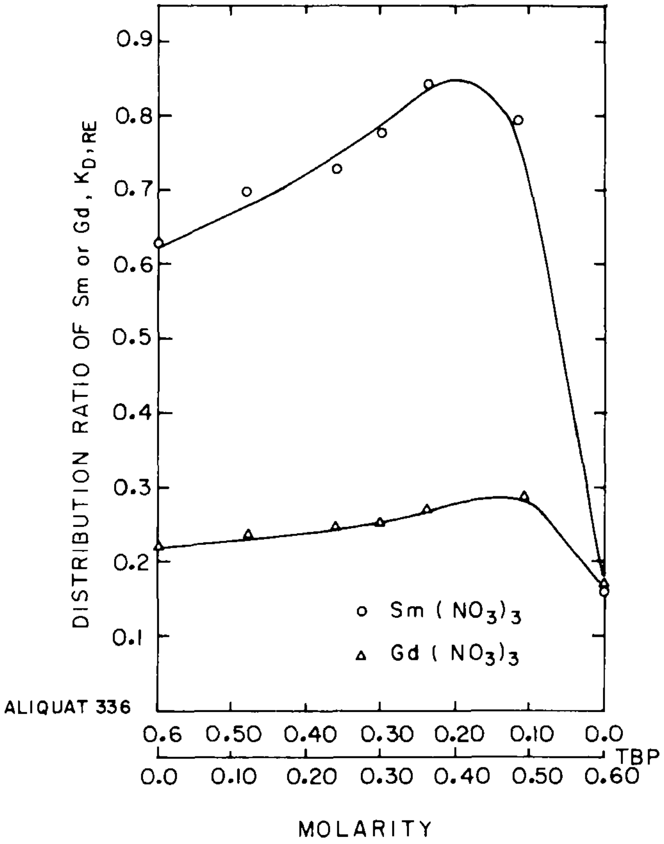


Fig. 4. Synergic extraction of Sm and Gd with TBP-Aliquat 336 system.

$$R_3CH_3NNO_3 \cdot 2TBP + RE^{+++} + 3NO_3^- \rightleftarrows R_3CH\ N^+RE(NO_3)_4^- \cdot 2TBP \qquad [6]$$

where RE = Gd or Sm.

The other extraction reactions previously reported (5,6) are not very significant since very little free extractant is available:

$$3\ TBP + RE^{+++} + 3NO_3^- \rightleftarrows RE(NO_3)_3 \cdot 3TBP \qquad [7]$$

$$3\ R_3CH_3NNO_3 + RE^{+++} + 3NO_3^- \rightleftarrows RE(NO_3)_3 \cdot 3R_3CH_3NNO_3 \qquad [8]$$

Other Significant Extraction Equilibrium Reactions in the Synergic System

a. The extraction of NH_4NO_3 with TBP

In 1968 Chifu (7) reported that $LiNO_3$ was extracted by TBP as the $2TBP \cdot LiNO_3$ complex. The logarithm of the extraction equilibrium constant was reported to be 0.2.

The data shown in Table 3 indicates that TBP also extracts NH_4NO_3, but the equilibrium constant is not as large as that for $LiNO_3$. In Fig. 5 is plotted the logarithm of the distribution ratio of ammonium ion, log K_{D,NH_4^+} versus the logarithm of the concentration of monomeric TBP, log$[TBP]_M$. A straight line with a slope of 1.84 is obtained. This result suggests that the extraction equilibrium reaction is

$$2\ TBP + NH_4^+ + NO_3^- \rightleftarrows NH_4NO_3 \cdot 2TBP \qquad [9]$$

The logarithm of the extraction equilibrium constant as given in Table 3 is equal to -3.39±0.02.

The Extraction of NH_4NO_3 with the Nitrate Form of Aliquat 336

Ammonium thiocyanate can be extracted by trialkylmethylammonium thiocyanate (8). The data shown in Table 4 indicate that $R_3CH_3NNO_3$ can also extract NH_4NO_3. The concentration of ammonium ion in the organic phase increases with increasing concentration of $R_3CH_3NNO_3$. It also increases with increasing concentrations of the NH_4NO_3 salting out agent in the aqueous phase. The logarithm of the extraction equilibrium constant for this reaction

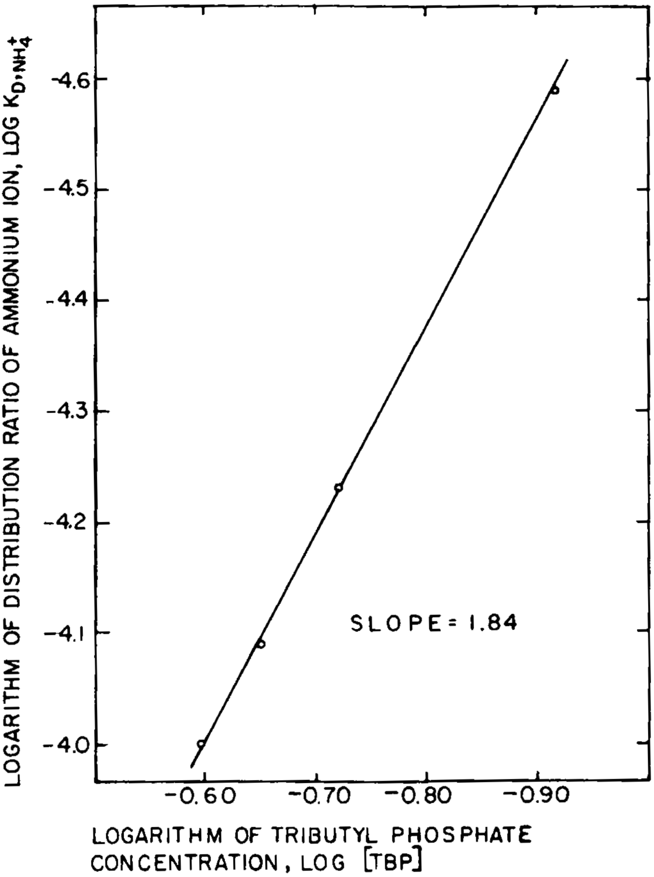


Fig. 5. Extraction of NH_4NO_3 with TBP.

is −2.65±0.08 when the aggregation of quaternary ammine is neglected. This extraction equilibrium constant will become even larger if the aggregation of the quaternary amine is taken into consideration. These results indicate that Aliquat 336 can extract NH_4NO_3 to a much larger extent than TBP.

Non-synergic Extraction of NH_4NO_3 with TBP-Aliquat 336

When NH_4NO_3 is extracted by the mixture with various mole ratios of Aliquat 336 and TBP, the ammonium ion content in the

TABLE 4. Extraction of NH_4NO_3 with Aliquat 336.

Initial Conditions		Equilibrium Conditions					
$R_3CH_3NNO_3$ M	NH_4NO_3 M	$[NH_4^+]_{org}$ M	K_{D,NH_4^+}	$\log K_{D,NH_4^+}$	$R_3CH_3NNO_3$ M	$\log [R_3CH_3NNO_3]$	$\log K_{eq} = \log \frac{[R_3CH_3NNO_3\ NH_4NO_3]}{[R_3CH_3NNO_3][NH_4][NO_3^-]}$
0.30	4.00	1.00×10^{-2}	2.50×10^{-3}	-2.60	0.290	-0.538	-2.66
		1.01×10^{-2}	2.53×10^{-3}	-2.60	0.290	-0.538	-2.66
		1.15×10^{-2}	2.88×10^{-3}	-2.54	0.288	-0.541	-2.60
0.40	4.00	1.29×10^{-2}	3.23×10^{-3}	-2.49	0.387	-0.412	-2.68
		1.40×10^{-2}	3.50×10^{-3}	-2.46	0.386	-0.413	-2.65
		1.30×10^{-2}	3.25×10^{-3}	-2.49	0.387	-0.412	-2.68
0.50	4.00	1.75×10^{-2}	4.38×10^{-3}	-2.36	0.482	-0.317	-2.59
		1.82×10^{-2}	4.55×10^{-3}	-2.34	0.482	-0.317	-2.70
		1.80×10^{-2}	4.50×10^{-3}	-2.35	0.482	-0.317	-2.64
0.60	4.00	2.02×10^{-2}	5.05×10^{-3}	-2.30	0.580	-0.237	-2.67
		1.92×10^{-2}	4.80×10^{-3}	-2.32	0.581	-0.236	-2.69
		1.81×10^{-2}	4.53×10^{-3}	-2.34	0.582	-0.235	-2.71
0.60	2.00	8.70×10^{-3}	4.35×10^{-3}	-2.36	0.591	-0.228	-2.43
	3.00	1.25×10^{-2}	4.17×10^{-3}	-2.38	0.587	-0.231	-2.63
	5.00	2.40×10^{-2}	4.81×10^{-3}	-2.32	0.576	-0.239	-2.77

Average $\log K_{eq} = -2.65 \pm 0.08$

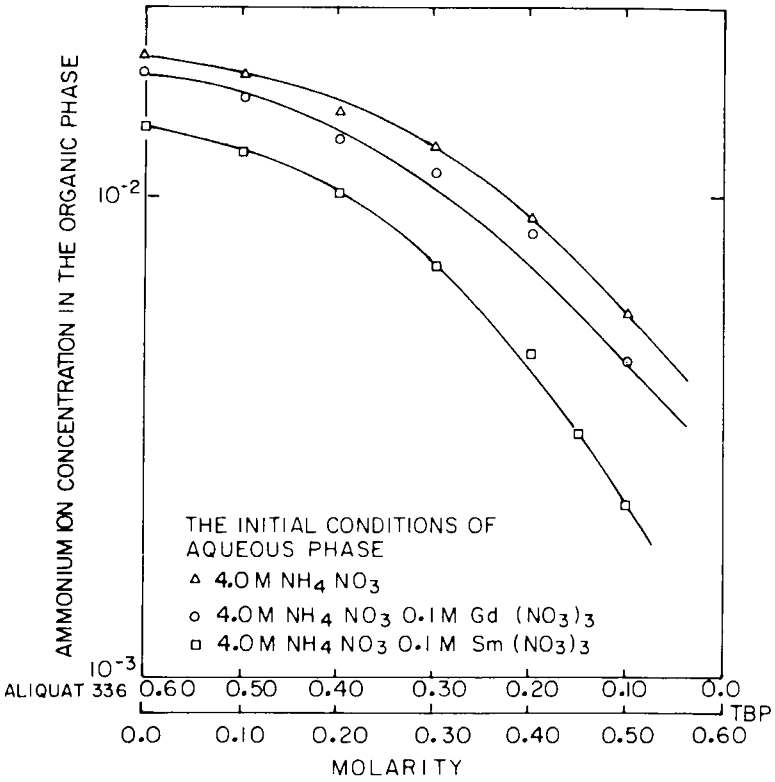


Fig. 6. The extraction of NH_4NO_3 with TBP-Aliquat 336 system under different initial aqueous conditions.

organic phase decreases with decreasing Aliquat 336 concentrations. This is shown in Fig. 6. This indicates that the associated species of the two extractants do not synergically extract NH_4NO_3. When $Gd(NO_3)_3$ or $Sm(NO_3)_3$ is present in the initial aqueous phase, the extraction of NH_4NO_3 is decreased due to the coextraction of $Sm(NO_3)_3$ and/or $Gd(NO_3)_3$. The extractability of $Sm(NO_3)_3$ in this system is greater than $Gd(NO_3)_3$, resulting in a larger decrease of the ammonium ion concentration in the organic phase. These results further support the idea that TBP-Aliquat 336 neither synergically extracts NH_4NO_3 nor coextracts NH_4NO_3 with gadolinium and samarium.

SUMMARY AND CONCLUSIONS

The synergic extraction of samarium and gadolinium in the TBP-Aliquat 336-$Gd(NO_3)_3$ or $Sm(NO_3)_3$-NH_4NO_3 system have been studied. The maximum synergic distribution ratio was obtained at 0.4 M TBP and 0.2 M Aliquat-336. Various molar ratios of TBP and Aliquat 336 at a total concentration of 0.60 M in AMSCO were used to extract $Sm(NO_3)_3$ and $Gd(NO_3)_3$ from 4.0 M NH_4NO_3 solution at pH 3.

This synergic extraction system results in lower viscosity compared to using Aliquat 336 alone. A higher separation factor of 3.11 is obtained compared to 2.86 using Aliquat 336 alone and 1.05 using TBP alone. This is one of the best systems so far reported in the literature for the separation of Sm and Gd.

The composition of the extractable complex was found to be $R_3CH_3N^+RE(NO_3)_4^-\cdot 2TBP$. NH_4NO_3 was found to be extracted by pure TBP or pure Aliquat 336, but cannot be synergically extracted by a mixture of TBP and Aliquat 336. NH_4NO_3 is not a component part of the extractable complex.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy under contract No. W-7405-ENG-82 by the Director for Energy Research, Office of Basic Energy Sciences, Chemical Sciences Program.

C. H. Huang was on sabbatical leave from the Department of Chemistry, Peking University, Beiying, Peoples Republic of China.

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