

THE COMPOSITION OF COMPLEXES IN THE ORGANIC PHASE
DURING THE EXTRACTION OF Eu(III) AND Am(III)
BY BENZYL-DIBUTYLAMINE AND BENZYL-TRIALKYLAMMONIUM
NITRATES

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The extraction of americium and europium from acid nitrate solutions by benzene solutions of benzyl-dibutylamine nitrate (*I*) and quaternary ammonium salts benzyl-lauryldimethylammonium nitrate (*II*) and benzyl-trioctylammonium nitrate (*III*) has been studied. During extraction with *I*, $\{(R_3NH^+)_2, Me(NO_3)_2^-\}$ is formed in the organic phase, extraction with *II* yields $\{(R_4N^+), Me(NO_3)_4^-\}$ and $\{(R_4N^+)_2, Me(NO_3)_2^-\}$ is formed during extraction with *III*. The concentration of nitrate ions does not have an unambiguous effect on the stoichiometry of the extraction. In addition to favouring the formation of the nitrate complexes of Am^{3+} and Eu^{3+} , which are extracted by amines, nitrate ions also have a nonspecific salting out effect. The changes in the water content in the organic phase in dependence on the concentration of the metal complex suggests that the complex of Eu with *II* is not hydrated in the organic phase.

Benzyl-dialkylamines and quaternary benzyl-trialkylammonium salts are suitable agents for the extraction of lanthanoids and trivalent actinoids from nitrate solutions of low acidity and high concentration of the salts of the alkalies and alkaline earths¹⁻³. They exhibit higher separation factor for separation from various fission and corrosion products⁴ than trialkylamines and tetraalkylammonium salts. The suitable properties of benzyl-substituted amines are based primarily on their low basicity, leading to low competitive extraction of nitric acid.

So far little data is available on the stoichiometry of extractions in these systems; only the work of Michlin and coworkers⁵ deals with the extraction of Nd by benzyl-substituted quaternary ammonium nitrate. Systems containing only alkyl-substituted amines⁶, primarily in chloride⁷⁻⁹, but also in nitrate medium^{10,11}, have been studied far more extensively. It can be assumed that, while the stoichiometry of the extraction will not change much on substitution of the alkyl in the amine by benzyl, the change in the basicity of the amine can affect not only the degree of extraction of the individual elements, but also the composition of the complexes that are formed during the extraction.

This work was carried out in order to obtain information on the stoichiometry of these complexes to complement information obtained from the infrared spectra of the organic phase.

EXPERIMENTAL

Reagents. The amines used and their salts were prepared by methods that have been described previously: benzyldibutylamine (*I*) by alkylation of benzylamine by *n*-butylbromide¹², benzyl-lauryldimethylammonium nitrate (*II*) by conversion of the bromide¹ and benzyltrioctylammonium nitrate (*III*) by the reaction of trioctylamine and benzylbromide and subsequent conversion to the nitrate¹³. $\text{Eu}(\text{NO}_3)_3$ was prepared by dissolving Eu_2O_3 in HNO_3 and was doubly recrystallized. The remaining reagents were of *p.a.* purity (Lachema). The isotope ^{241}Am (Amersham, England) was used in trace concentrations ($\sim 10^{-9} \text{ mol l}^{-1}$).

Procedure. The extraction was carried out by shaking identical volumes of both phases in test tubes with ground-glass stoppers for ten minutes at room temperature (22–25°C). The distribution of $^{152,154}\text{Eu}$ and ^{241}Am was determined by measuring the γ -activity of both phases in the NaI(Tl) well-type scintillation detector combined with the NZQ 615 (Tesla). The concentration of the $\text{Eu}(\text{NO}_3)_3$ stock solution was found by titration with EDTA using xylenol orange indicator. The concentration of the LiNO_3 stock solution was found from its density determined by the differential float method. The concentration of Li in the equilibrium organic phase was found by atomic emission spectrometry using an AAS-1 instrument (Zeiss, Jena) and the concentration of water in the organic phase by dead-stop titration by the K. Fischer method using the DST-1 instrument (Znak, Brno). The equilibrium concentration of HNO_3 in the organic phase was found by titration with a 0.1M solution of NaOH in ethanol with bromothymol blue indicator.

RESULTS AND DISCUSSION

The extraction of Am and Eu by the nitrate of tertiary amine *I* and quaternary ammonium nitrates *II* and *III* was studied in dependence on the concentration of the extractant and, in systems containing *I* and *II*, also in dependence on the LiNO_3 concentration in the aqueous phase and on the europium concentration. The water and nitric acid contents in the equilibrium organic phase were also determined for these systems.

The initial aqueous phase for extraction systems with *II* and *III* contained 0.11 mol \cdot l^{-1} HNO_3 . Systems containing tertiary amine *I* exhibited a tendency to form a third, transparent, phase; consequently, cetyl alcohol was added as a solubilizer in an amount of 1 g/100 ml organic phase, yielding a concentration of 0.04 mol l^{-1} .

The Dependence of the Extraction on the Concentration of the Extractant

These dependences were determined for two concentrations of LiNO_3 in the initial aqueous phase (4.04 and 5.88 mol l^{-1}) and are depicted in Fig. 1. Table I lists the values of the slopes of the straight lines drawn through the experimental points.

TABLE I
The slopes of straight lines drawn through the $\log D = f(\log c_B)$ dependences in Fig. 1

B	Aqueous phase			
	Eu		Am	
	4.04M-LiNO ₃	5.88M-LiNO ₃	4.04M-LiNO ₃	5.88M-LiNO ₃
Benzyltributylammonium nitrate	2.5	2.5	2.5	2.4
Benzylhexyldimethylammonium nitrate	1.0	1.1	1.0	1.0
Benzyltrioctylammonium nitrate	2.2	2.3	2.1	1.8

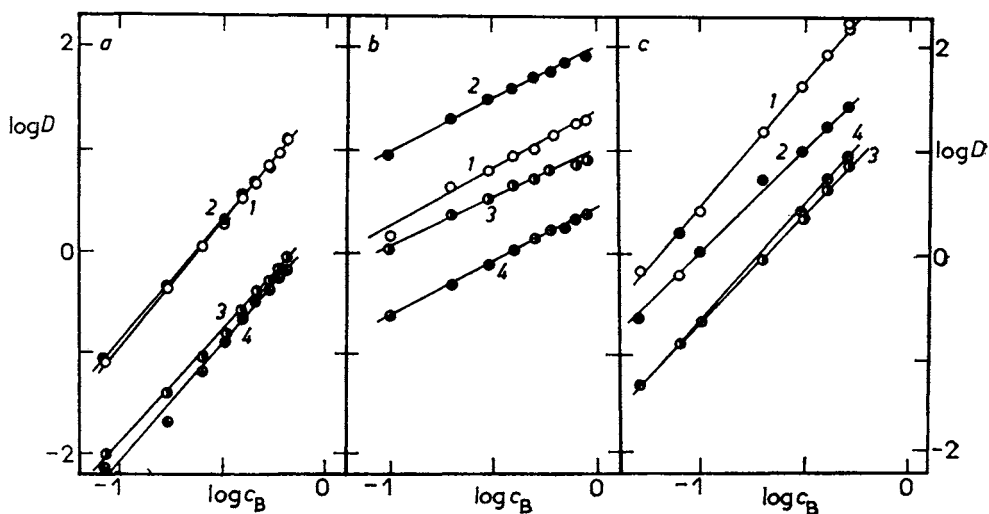


FIG. 1

The dependence of the distribution ratio (D) for Eu and Am on the concentration (c_B) of benzyltributylammonium *a*, benzylhexyldimethylammonium *b* and benzyltrioctylammonium *c* nitrate in benzene. *a* — aqueous phase: 4.04 mol l⁻¹ LiNO₃ (⊕, ⊙) or 5.88 mol l⁻¹ LiNO₃ (○, ●). The systems with Eu (⊕, ○) contain 1.46 · 10⁻³ mol l⁻¹ Eu, the systems with Am (⊙, ●) contain trace amounts of Am (≈ 10⁻⁹ mol l⁻¹). The organic phases contain 10 g/l cetyl alcohol. *b* and *c* — aqueous phase: 0.11 mol l⁻¹ HNO₃ and 4.04 mol l⁻¹ LiNO₃ (⊕, ⊙) or 5.88 mol l⁻¹ LiNO₃ (○, ●). The systems with Eu contain 1.73 · 10⁻³ mol l⁻¹ Eu (⊕, ○), the systems with Am contain trace amounts of Am (≈ 10⁻⁹ mol l⁻¹) (●, ⊙)

During extraction using *I* and *II*, the organic phase was found to contain complexes with similar composition as those formed in systems with purely alkyl-substituted amines⁹⁻¹¹, *i.e.* with a metal: amine ratio of 1 : 2 for tertiary amines and 1 : 1 for quaternary ammonium salts.

From this point of view, the behaviour of quaternary ammonium salt *III* is unusual, as it forms a 1 : 2 complex, similar to that of tertiary amines. This is apparently a result of the steric and polar properties of molecule *III*. All the data for the 1 : 1 complexes (ref.^{9,10}) were determined for amine salts of the $\{R_3CH_3N^+, NO_3^-\}$ type, where R is an octyl to decyl group. Michlin and coworkers⁵ employed an ammonium salt structurally similar to *III* $\{BzR_3N^+, NO_3^-\}$, where Bz is benzyl and R is heptyl to nonyl, in a study of the extraction of Nd. The aqueous phase was $\frac{5}{3}M$ $Al(NO_3)_3$ with pH 3. The slope of the logarithmic dependence of D_{Nd} on the concentration of reagent (c_B) was equal to 2 for lower c_B values (0.01 to 0.1 mol l⁻¹) and 1 for $c_B = 0.1$ to 0.6 mol l⁻¹. The authors explain this change in the slope value by suggesting that the ammonium salt is monomeric at lower concentrations and primarily dimeric in the concentration region $c_B = 0.1 - 0.6$ mol l⁻¹. No study has been carried out of the formation of oligomers of *III* or of the amine employed by Michlin and coworkers⁵; however, data on the aggregation of tetraheptylammonium nitrate¹⁴ suggest that these ammonium salts will be aggregated to a large extent in the region $c_B = 0.01 - 0.1$ mol l⁻¹ and that the change of slope at higher c_B will probably be the result of other factors than aggregation of the extractant.

The relationship between aggregation of alkylammonium extraction reagents and the stoichiometry of their metal complexes is not yet clear. This problem has been studied by a number of authors, but the conclusions drawn in the literature differ considerably. Suggestions have been made of association of the metal salt with the monomer of the alkylammonium salt, formed by depolymerization of the oligomer⁵ (*e.g.* $(R_4N^+)_2\{[Nd(NO_3)_5]^{2-}\}$), and, on the other hand, association of the metal salt with the partly dissociated alkylammonium salt with no change in its degree of aggregation, $q^{7,15}$, (*e.g.* $\{[(R_3NH^+Cl^-)_{q-1}R_3NH^+]_pMCl_{3+p}^-\}$), and even the formation of aggregated complexes^{14,16} (*e.g.* $(R_3NHCl)_{10}(FeCl_3)_3$) has been proposed.

The ammonium salts employed here form oligomers in benzene solutions. Cryoscopic and osmometric measurements have indicated that salt *I* exists primarily as the tetramer¹⁷ (with an association constant value of $\beta_4 = [(B.HNO_3)_4]/[B.HNO_3]^4$ at 25°C of $\log \beta_4 = 5.58 \pm 0.02$) and salt *III* primarily as the pentamer¹⁸ ($\log \beta_5 = 8.97$). The monomer content in solutions of *I* decreases from 20% to 5% in the concentration range employed (0.085 - 0.65 mol l⁻¹) and, in solutions of *III*, from 9% to 2% (0.1 - 0.9 mol l⁻¹); the mean degree of aggregation of *I* increases from 2.0 to 7.2 and of *II* from 3.7 to 5.4.

However, the dependence of $\log D$ on $\log c_B$ is linear over the whole range without any observable tendency for the slope to change at the extremes. As the aggregation

of metal complexes has not been studied in these systems, the simplest stoichiometric composition of the complexes will be assumed, *i.e.* $\{(R_3NH^+)_2, Me(NO_3)_5^{2-}\}$ for *I*, $\{(R_4N^+), Me(NO_3)_4^-\}$ for *II* and $\{(R_4N^+)_2, Me(NO_3)_5^{2-}\}$ for *III*.

While the values of the slopes of the $\log D = f(\log c_B)$ dependence are close to whole numbers for the quaternary ammonium salts *II* and *III*, that for *I* approaches a value of 2.5. This deviation is a result of the presence of cetyl alcohol, added to the organic phase as a solubilizer. Jain and Duyckaerts⁸ observed a similar phenomenon, connected with a decrease in the *D* value, in the extraction of Am from a chloride medium using a trilaurylamine hydrochloride solution. It is well known that higher alcohols combine with amine salts to form compounds, *e.g.* $TOA.HNO_3 \cdot 2 ROH$ ¹⁹, decreasing the effective amine concentration. The concentration of cetyl alcohol is constant in the studied system containing *I* and thus the relative decrease in the concentration of the free trialkylamine salt is greatest at low amine concentrations and produces an increase in the slope of the $\log D = f(\log c_B)$ dependence.

The Dependence of the Extraction on the Concentration of Nitrate Ions

The concentration of nitrate ions in the aqueous phase was adjusted by addition of $LiNO_3$ at a constant HNO_3 concentration. As the ionic strength was not maintained constant in the aqueous phase, the dependence of $\log D$ on the logarithm of the activity of $LiNO_3$ is given for the systems with *I* and *II* (Fig. 2). This dependence was not studied for *III*.

The slope of this dependence in the extraction using *I* is equal to 3.2 for Eu and 3.8 for Am. In the system with the quaternary salt *II*, the slope increases with increasing concentration of $LiNO_3$. The $\log D = f(\log a_{LiNO_3})$ curves have two branches, with a slope of 1.6 for Eu and 1.8 for Am at lower c_{LiNO_3} and with a slope of 2.8 for both metals at higher c_{LiNO_3} .

It is apparent from the high slope values that, similarly to the extraction from $LiCl$ solutions^{7,9,20}, in extraction from nitrate medium the slope values cannot be employed to determine the number of nitrate groups required for conversion of the nitrate complex of Eu^{3+} or Am^{3+} in the aqueous phase into an extractable electro-neutral complex, such as $Eu(NO_3)_3$.

The stability constants of the first two nitrate complexes of Eu are known for aqueous solutions with high ionic strength (at $c_{LiNO_3} = 4.0 \text{ mol l}^{-1}$, $\log K_1 = 0.20$ and $\log K_2 = -0.6$), and for $AmNO_3^{2+}$ ($\log K_1 = 0.26$ for $c_{LiNO_3} = 1.0 \text{ mol l}^{-1}$; *ref.*²¹). As the K_1 values are similar for Am^{3+} and Eu^{3+} , it can be assumed that the K_2 values will also be similar (Marcus and Gievon²² demonstrated the existence of higher complexes than $AmNO_3^{2+}$).

At the lowest $LiNO_3$ concentrations employed in the dependences in Fig. 2, the Eu^{3+} form predominates in aqueous solution; at $c_{LiNO_3} = 1.5 \text{ mol l}^{-1}$, the $EuNO_3^{2+}$ form is present, and at higher $LiNO_3$ concentrations, the $Eu(NO_3)_2^+$ form. The degree

of complex formation $\bar{n} = \sum n\beta_n[\text{NO}_3]_n / \sum \beta_n[\text{NO}_3]_n$ increases from 0.07 at $\log a_{\text{LiNO}_3} = -0.433$ to 0.98 at $\log a_{\text{LiNO}_3} = 0.102$ and 1.58 at $\log a_{\text{LiNO}_3} = 1.302$. Thus, from 2.93 to 1.42 NO_3^- groups are required to complete the coordination sphere of Eu^{3+} to $\text{Eu}(\text{NO}_3)_3$ in the studied range of LiNO_3 concentrations. In systems containing *II*, the slope is less than $3 - \bar{n}$ at $c_{\text{LiNO}_3} < 1 \text{ mol l}^{-1}$ and greater than $3 - \bar{n}$ at $c_{\text{LiNO}_3} > 3 \text{ mol l}^{-1}$; the slope value is much greater than $3 - \bar{n}$ in systems containing *I*.

Marcus⁷ observed a similar phenomenon (slope 3) in the extraction of Am from a chloride medium and explained it in terms of coextraction of a stoichiometric amount of LiCl , assuming a single ionic form of the chloro complex, AmCl_2^+ , over the whole concentration range of LiCl studied. To determine whether this explanation could also be valid for nitrate medium, the concentration of lithium in the organic

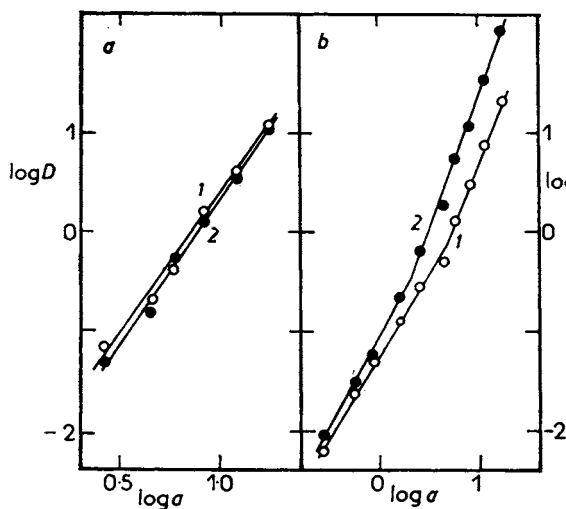


FIG. 2

The dependence of the distribution ratio (D) for Eu and Am in the extraction with a 0.53M solution of benzyltributylammonium nitrate *a* and with a 0.5M solution of benzyltriethylammonium nitrate *b* in benzene on the activity, a , of LiNO_3 in the aqueous phase. *a* — initial aqueous phase: $\circ 1.46 \cdot 10^{-3} \text{ mol l}^{-1}$ Eu; $\bullet \approx 10^{-9} \text{ mol l}^{-1}$ Am, the organic phase contains 10 g/l cetyl alcohol. *b* — initial aqueous phase: $\circ 1.73 \cdot 10^{-3} \text{ mol l}^{-1}$ Eu, $0.11 \text{ mol l}^{-1} \text{ HNO}_3$; $\bullet \approx 10^{-9} \text{ mol l}^{-1}$ Am, $0.11 \text{ mol l}^{-1} \text{ HNO}_3$

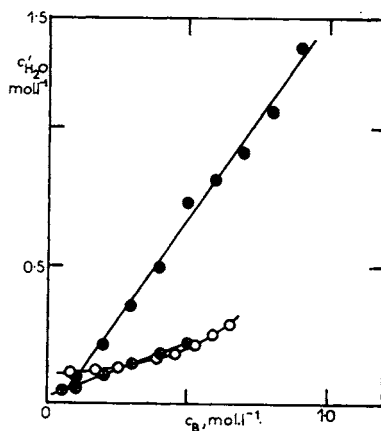


FIG. 3

The dependence of the concentration of water in the organic phase ($c'_{\text{H}_2\text{O}}$) on the concentration of extraction reagent (c_{B}) in the extraction of Eu. Initial aqueous phase: $0.11 \text{ mol l}^{-1} \text{ HNO}_3$, $4.04 \text{ mol l}^{-1} \text{ LiNO}_3$, $1.73 \cdot 10^{-3} \text{ mol l}^{-1}$ Eu. Organic phase: \circ benzyltributylammonium nitrate, 10 g. l^{-1} cetyl alcohol in benzene, \bullet benzyltriethylammonium nitrate in benzene, \oplus benzyltrioctylammonium nitrate in benzene

phase was determined (Tab. II). The tertiary amine, *I*, extracts far less lithium than *II*. In both systems, the concentration of lithium in the organic phase decreases with increasing Eu concentration in this phase, indicating that LiNO_3 is extracted independently and is forced out of the organic phase by increasing Eu concentrations.

Thus the course of the $\log D = f(\log a_{\text{LiNO}_3})$ dependence is not determined solely by the stoichiometry of the nitrate complex formation during the extraction, but also by nonspecific effects of the electrolyte on the extraction process, especially by the dehydration effect on the Eu^{3+} ions and nitrate complexes, *i.e.* salting out²³; thus the predominant nitrate complex in the aqueous phase cannot be found from this slope. These two factors, *i.e.* formation of the saturated complex and salting out, have opposite effects on the slope. In extraction with *I*, these two effects are apparently complementary, so that the dependence is more or less linear; however, this is not true of extractions using *II* and the dependence is thus not linear (Fig. 2).

Extraction of Water and HNO_3

In the extraction of europium, the coextraction of water and HNO_3 was measured in dependence on varying concentration of *I*, *II* or *III* (Fig. 3), LiNO_3 (Fig. 4) and Eu (Fig. 5).

The concentration of water in the organic phase increases with increasing concentration of amine nitrate (Fig. 3). The equilibrium concentrations of water and amine are in a ratio of roughly 1 : 1 in the system containing *II* and 1 : 2 in systems containing *I* and *III*. In view of the low concentration of Eu compared to the concentration of amine, possible hydration of the metal complex can be neglected. Thus each

TABLE II

The equilibrium concentration of Eu and Li in the organic phase (c') in extraction with benzylidibutylammonium nitrate (*I*) or benzyl-lauryldimethylammonium nitrate (*II*) from $6M\text{-LiNO}_3$

B	c'_{Eu} mol l^{-1}	c'_{Li} mol l^{-1}
<i>I</i> ^a	$8.44 \cdot 10^{-2}$	$7.9 \cdot 10^{-4}$
	$8.8 \cdot 10^{-3}$	$8.1 \cdot 10^{-4}$
	$8.8 \cdot 10^{-4}$	$8.9 \cdot 10^{-4}$
<i>II</i> ^b	$8.6 \cdot 10^{-2}$	0.21
	$4.3 \cdot 10^{-2}$	0.34
	$8.9 \cdot 10^{-3}$	0.57
	$9.0 \cdot 10^{-4}$	0.57

^a $c_{\text{B}} = 0.52 \text{ mol l}^{-1}$; ^b $c_{\text{B}} = 0.50 \text{ mol l}^{-1}$.

monomeric unit of amine nitrate salt is hydrated by one water molecule in the equilibrium organic phase containing *II* (at least $c_{\text{LiNO}_3} = 4 \text{ mol l}^{-1}$), while oligomers are hydrated in solutions containing *I* and *III*, i.e. for *I*, the tetramer is hydrated by two water molecules.

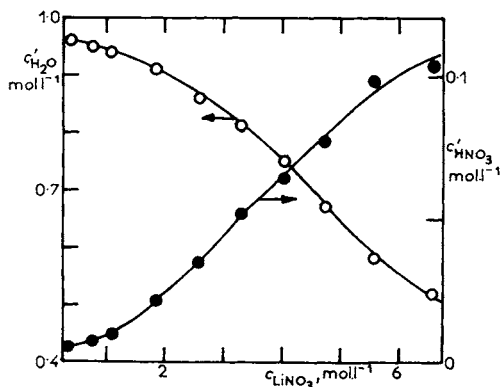


FIG. 4

The dependence of the concentration of water (○) and HNO_3 (●) in the equilibrium organic phase (c') on the initial concentration of LiNO_3 (c) during extraction with a solution of benzylauryldimethylammonium nitrate in benzene ($c_{\text{B}} = 0.5 \text{ mol l}^{-1}$). The initial phase contains $0.11 \text{ mol l}^{-1} \text{ HNO}_3$ and $1.73 \cdot 10^{-3} \text{ mol l}^{-1} \text{ Eu}$

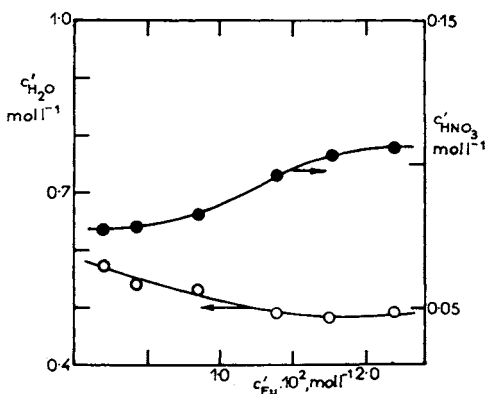


FIG. 5

The dependence of the concentration of water (○) and HNO_3 (●) in the equilibrium organic phase (c') on the equilibrium concentration of Eu in the organic phase (c') during extraction with a solution of benzylauryldimethylammonium nitrate in benzene ($c_{\text{B}} = 0.5 \text{ mol l}^{-1}$). The initial aqueous phase contains $6.0 \text{ mol l}^{-1} \text{ LiNO}_3$ and $0.11 \text{ mol l}^{-1} \text{ HNO}_3$

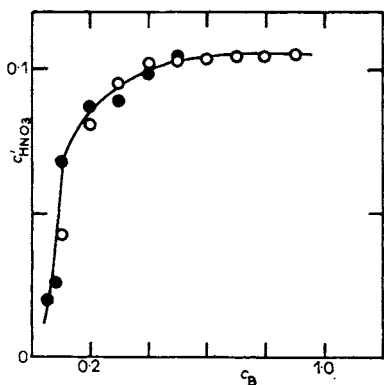


FIG. 6

The dependence of the concentration of HNO_3 in the equilibrium organic phase (c') on the initial concentration of benzylammonium nitrate (○) and benzyltrioctylammonium nitrate (●) in benzene (c_{B}) in the extraction of Eu. The initial aqueous phase contains $0.11 \text{ mol l}^{-1} \text{ HNO}_3$, $5.88 \text{ mol l}^{-1} \text{ LiNO}_3$ and $1.73 \cdot 10^{-3} \text{ mol l}^{-1} \text{ Eu}$

The hydration of the organic phase is strongly dependent on the concentration of LiNO_3 in the aqueous phase (Fig. 4). At the lowest LiNO_3 concentrations, *i.e.* highest H_2O activity in the aqueous phase, there are two water molecules for one monomeric unit of *II*. Thus this extraction system can be assumed to contain both the mono- and the dihydrate of *II*.

The slight decrease in the water concentration in the organic phase (Fig. 5) with increasing Eu concentration is the result of dehydration of *II* during complexation with Eu. Thus, an increase in the concentration of Eu from $4 \cdot 10^{-3}$ to $2 \cdot 19 \cdot 10^{-2}$ mol \cdot l^{-1} is accompanied by a decrease in $c'_{\text{H}_2\text{O}}$ from 0.56 to 0.49 mol l^{-1} , *i.e.* an increase in the Eu concentration by 0.02 mol l^{-1} is accompanied by a decrease in $c'_{\text{H}_2\text{O}}$ by 0.07 mol l^{-1} . The decrease in the H_2O concentration is greater than would correspond to the composition of the complex derived above and apparently indicates that this complex is not hydrated. These conclusions contradict those drawn by Leuze and Baybarz²⁴, who assumed the presence of $\{\text{R}_4\text{N}^+, \text{Me}(\text{NO}_3)_4^-, \text{H}_2\text{O}\}$ ($\text{Me} = \text{Am}, \text{Eu}$) on the basis of analysis of the organic phase, although the amines employed in their work did not contain a benzyl group.

The coextraction of HNO_3 increases rapidly with both increasing concentration of quaternary ammonium nitrate (Fig. 6) and with increasing concentration of LiNO_3 (Fig. 4) and of Eu (Fig. 5). The $c'_{\text{HNO}_3} = f(c_{\text{B}})$ dependence for *II* (Fig. 6) indicates that *II* bonds more than the stoichiometric amount of HNO_3 , as has also been demonstrated on the basis of the infrared spectra¹. However, the study of this dependence is limited by the relatively low initial concentration of HNO_3 in the aqueous phase, so that the equilibrium concentration of HNO_3 in the organic phase soon attains a value equal to the initial HNO_3 concentration. It follows from the ascending part of the curve in Fig. 4 that the molar ratio $c'_{\text{HNO}_3} : c_{\text{B}} < 0.5$. Lithium nitrate increases the transfer of HNO_3 to the organic phase through a salting-out effect, while the reasons for the dependence between the increase in the concentration of HNO_3 in the organic phase and the concentration of Eu in the aqueous phase (Fig. 5) are not apparent.

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