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The Extraction of Am(III) and Eu(III) from Aqueous Ammonium Thiocyanate by Dihexyl-*N,N*-diethylcarbamoylmethylphosphonate and Related Compounds

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Abstract

The extraction behavior and separation factors of Am(III) and Eu(III) from low acid ammonium thiocyanate solutions were studied using dihexyl-*N,N*-diethylcarbamoylmethylphosphonate (DHDECMP) and related compounds. It was found that very dilute (<0.1 *M*) solutions of ammonium thiocyanate were sufficient to allow quantitative extraction of Am(III) with DHDECMP. Significant differences between DHDECMP and dibutylbutylphosphonate (DB[BP]) in the extraction of Am(III) and Eu(III) from thiocyanate were found and indicate chelation is occurring with DHDECMP, unlike the situation in the low acid lithium nitrate system. Infrared spectroscopy of the extracted complexes of La(III) and extraction studies with dihexyl-*N,N*-diethylcarbamoylethylphosphonate (DHDECEP), dihexyl-*N,N*-diisobutylcarbamoylmethylphosphonate (DHDIBCMP), and di-(2-ethylbutyl)-*N,N*-diethylcarbamoylmethylphosphonate (DEBDECMP) confirm that chelation occurs with thiocyanate complexes of Am(III) and Eu(III). Separation factors, α, for Am(III) and Eu(III) were the lowest with DB[BP] ($\alpha = 5.84$) and the highest with DHDIBCMP ($\alpha = 10.8$).

INTRODUCTION

A previous study by the authors (*1*) examined the extraction of trivalent actinides and lanthanides by dihexyl-*N,N*-diethylcarbamoylmethylphosphonate, DHDECMP, from nitric acid and lithium nitrate solutions. In these studies the trivalent actinides were found to extract along with the light lanthanides. In an effort to effect a group separation of trivalent actinides from lanthanides, further studies have been made using a different aqueous medium. Ammonium thiocyanate, NH_4SCN, was chosen since previous studies have shown extraction of thiocyanate complexes to be effective in the separation of Am(III) from Ln(III) using quaternary ammonium salts (*2, 3*). In addition, there have been a few studies on the extraction of trivalent actinides from thiocyanate solutions with neutral organophosphorus compounds (*4–6*). Khopkar and Narayanankutty (*4*) and Sekine (*6*) compared Am(III) with lanthanides in their extraction with TOPO, TBPO, and TBP but found only a small separation factor; for example, $\alpha < 3$ between Am(III) and Eu(III).

Preliminary experiments on the extraction of ^{241}Am(III) with DHDECMP showed only very low concentrations of thiocyanate were necessary to obtain high K_d's. It is possible that such low concentrations of thiocyanate (<0.1 *M*) could be tolerated by the stainless steel used in centrifugal contactors (*7*) to be used in large-scale processing of high level liquid waste (HLLW).

In our lithium nitrate study at low acidity (*1*), the differences in K_d between DHDECMP, DHDECEP (dihexyl-*N,N*-diethylcarbamoylethylphosphonate), and DB[BP] (dibutylbutylphosphonate) were small, indicating chelation does not occur in the bifunctional extractants. However, significant differences between DHDECMP and DB[BP] were observed in the extraction of Am(III) and Eu(III) from thiocyanate solution. These studies suggested chelation does occur between the metal ion and DHDECMP in the thiocyanate system. The purpose of this study was to further investigate the extraction properties of DHDECMP and related compounds from aqueous ammonium thiocyanate.

EXPERIMENTAL

Materials

The source and purification of the dihexyl-*N,N*-diethylcarbamoylmethylphosphonate, DHDECMP, the dibutylbutylphosphonate, DB[BP], and the dihexyl-*N,N*-diethylcarbamoylethylphosphonate, DHDECEP, were described earlier (*8*) with the exception that the DHDECEP was purified by vacuum distillation at 0.01 mmHg instead of by third-phase formation with 8 *M* HNO_3. In all cases *p*-diisopropylbenzene, DIPB (99% purity, Aldrich Chemical Co.), was used as the organic phase diluent.

Dihexyl-*N,N*-diisobutylcarbamoylmethylphosphonate, DHDIBCMP, was prepared by the Arbuzov reaction between trihexylphosphite, prepared by transesterification of trimethylphosphite with *n*-hexanol, and N,N-diisobutylchloroacetamide, prepared by a modification of the procedure of

Neeman (*9*). The reaction was carried out under nitrogen at a pressure of 90 torr, distilling off hexylchloride as the bath temperature was raised slowly from 160 to 215°. Purification (*10*) via mercury salt precipitation, recrystallization, and regeneration with KCN/Na_2CO_3 gave a product of >99% purity (g.c.) in 93% overall yield. Di(2-ethylbutyl)-*N,N*-diethylcarbamoylmethylphosphonate, DEBDECMP, was prepared similarly (99% purity, 87% overall yield) from tri(2-ethylbutyl) phosphite, prepared by transesterification of trimethylphosphite with 2-ethylbutanol, and *N,N*-diethylchloroacetamide also prepared by a modification of the procedure of Neeman (*9*).

The spectral properties of DEBDECMP and DHDIBCMP are quite similar to those of DHDECMP. Listed in the order DHDECMP, DEBDECMP, DHDIBCMP, they include M.S.: small parent peaks at m/e 363, 363, 419. UV in hexane: λ_{max} 204, 204, 206 nm; ε_{max} 8100, 8200, 8100 $L \cdot mol^{-1}\ cm^{-1}$. NMR ($\delta$ in CCl_4 relative to TMS): 3.96, 3.91, 3.98 ppm (OCH_2); 2.81, 2.82, 2.85 ($OPCH_2CO$); 3.30 and 3.42, 3.31 and 3.43, 3.09 and 3.18 (NCH_2). IR: 2860–2960 cm^{-1} (all), C—H str; 1640, 1637, 1645, C=O str; 1430–1468 (all), C—H bend; 1255, 1260, 1260, P=O str; 995, 1010, 1002, POC str.

Fresh stock solutions of ammonium thiocyanate were prepared every 2–3 weeks using ultrapure water obtained from a Milli-Q2 system water purifier (Millipore Corporation) and reagent grade ammonium thiocyanate (J. T. Baker Co.) dried at 110°C for 20 min to remove surface water. The stock solution (~0.25 *M*) was standardized by titrating an aliquot of 0.1 *N* primary standard silver nitrate solution ($AgNO_3$ from J. T. Baker Co.) plus dilute nitric acid (Ultrex grade, J. T. Baker Co.) and ferric ammonium sulfate indicator. Additional ammonium thiocyanate solutions were prepared by dilution and adjustment of the pH with hydrochloric acid (Ultrex grade, J. T. Baker Co.).

The source and purity of the radioisotopes used as tracers, ^{241}Am and $^{152,154}Eu$ were described earlier (*1*), as was the stable lutetium nitrate solution.

Measurement of Distribution Ratios, K_d's

Distribution ratios (K_d's) were determined by equilibration of the aqueous and organic phases in 13 × 100 mm Pyrex culture tubes wtih Teflon-lined screw caps. Prior to the K_d measurement the organic phase was preconditioned three successive times with fresh ammonium thiocyanate solution of the concentration used in the measurement. An aliquot of the tracer containing both ^{241}Am and $^{152,154}Eu$ in an approximately 5:1 activity ratio was evaporated to dryness in the culture tube and redissolved in the ammonium thiocyanate solution. An equal volume of the preconditioned organic phase was added to the resulting aqueous phase. The tubes were thermostated in a water bath at 25 ± 0.01°C. Chemical equilibrium was attained by vigorous mixing of the two phases for 1 min with a vortex mixer.

Radiometric assays were performed immediately after centrifugation and phase separation using a Beckman Biogamma 3-channel analyzer (NaI detector) to simultaneously count ^{241}Am and ^{152,154}Eu γ-radiation. Correction was made for the overlap of ^{152,154}Eu on ^{241}Am.

K_d measurements for DHDECEP were performed in the presence of 10^{-4} to 10^{-3} *M* Lu(III) to offset the effect of an acidic contaminant in the DHDECEP that a preliminary study showed caused elevated K_d's at very low acidities.

Thermodynamic values were obtained in the range 0–50°C as described previously (*11*).

The pH of the equilibrated aqueous phase was determined with a Sargent combination electrode and a Beckman Model 4500 digital pH meter calibrated with a pH = 3.00 buffer.

Infrared Studies

Infrared studies were carried out as described previously (*8*) except that the complexes were studied both neat and in *p*-diisopropylbenzene solution.

NMR Studies

^{13}C-NMR Spectra were recorded with a Nicolet NT-200 wide bore spectrophotometer. DHDECMP and its complexes with $La(NO_3)_3$ and $La(SCN)_3$ were dissolved in benzene-d_6 and placed in 12 mm tubes.

RESULTS AND DISCUSSION

The K_d's of Am(III) and Eu(III) as a function of the concentration of each of the five extractants studied are shown in Figs. 1–4. The data for DHDECMP are repeated in each of the figures for easy comparison. The straight lines in the log K_d vs log (extractant concentration) plots are determined from linear least squares fits and their slopes are listed in Table 1. It can be seen that the dependencies range from less than third up to fourth power depending on the extractant. The aqueous phase composition in all cases was 0.02 *M* NH_4SCN, 0.001 *M* HCl.

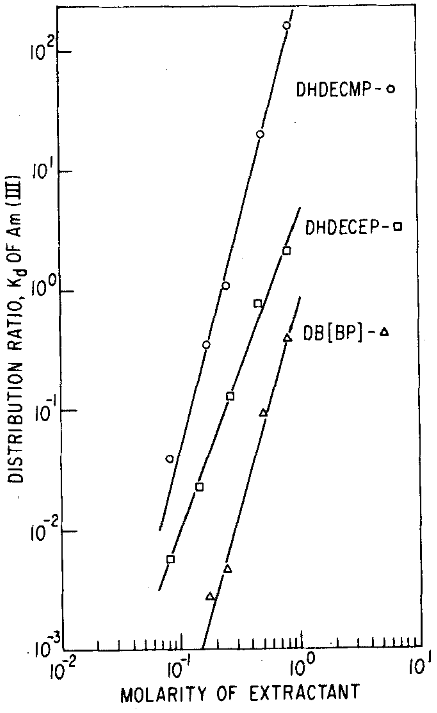


FIG. 1. Distribution ratio of Am(III) vs molarity of extractant in DIPB. Aqueous phase = 0.02 M NH_4SCN, 0.001 M HCl, $T = 25°C$.

Figures 5–8 show the dependence of the extaction of Am(III) and Eu(III) on ammonium thiocyanate concentration at a constant extractant concentration of 0.244 M. Again DHDECMP is included in all figures for comparison purposes. The slopes of the straight lines are all close to 2. On first analysis, the data indicate that the extractants are behaving in an acidic manner. However, this possibility can be ruled out for two reasons. First, our previous study of the extraction of trivalent actinides and lanthanides from lithium nitrate solution (*1*) with DHDECMP, DHDECEP, and DB[BP] showed these compounds behave as neutral extractants. Consequently, acidic behavior with the bifunctional extractants seems unlikely in the thiocyanate system and, in the case of DB[BP], it is impossible. Second, confirmation that DHDECMP, DHDECEP, and DB[BP] behave as neutral extractants is shown in Fig. 9 where the absence of a first power dependence of the K_d of Am(III) and Eu(III) on hydrogen ion activity confirms that these compounds are not ionizing and exchanging protons for metal ions. The small pH dependence observed at the higher acidities can be explained by the

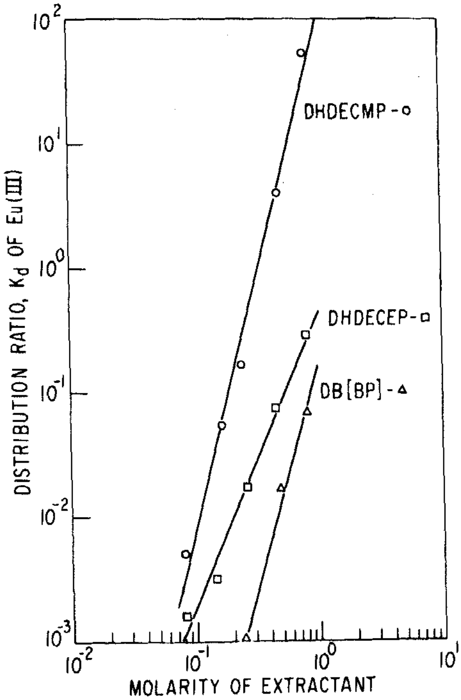


FIG. 2. Distribution ratio of Eu(III) vs molarity of extractant in DIPB. Aqueous phase = 0.02 M NH_4SCN, 0.001 M HCl, $T = 25°C$.

extraction of HCl or HSCN and the accompanying loss in effective extractant concentration.

Obviously, corrections similar to those done previously (*1*) for complexation of the metal ion by aqueous anions and for variations in the metal ion's activity coefficient with ionic strength are required to obtain a third power dependence on thiocyanate concentration. Unfortunately, the stability constants of Am(III) and Eu(III) with thiocyanate at low ionic strength (<0.1 M) are not available and are difficult to measure.

Consequently, the equation for the extraction of Am(III) and Eu(III) from ammonium thiocyanate may be written

$$M^{3+} + 3SCN^- + x\bar{E} \rightleftharpoons \overline{M(SCN)_3E_x} \qquad (1)$$

where $x = 3–4$, E represents DP[BP], DHDECMP, DHDECEP, DEBDECMP, and DHDIBCMP, and a bar denotes a species in the organic phase.

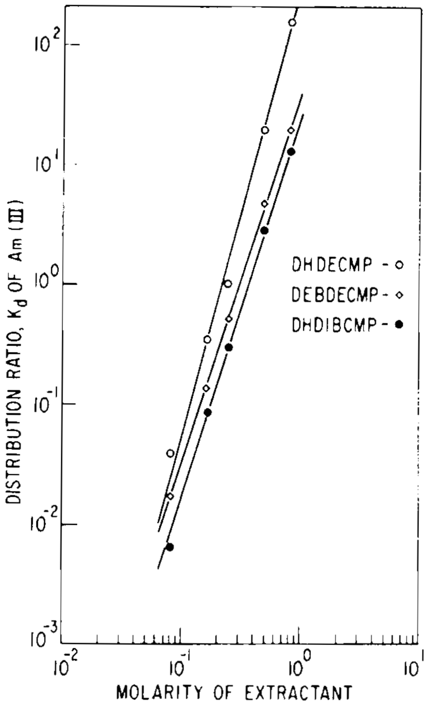


FIG. 3. Distribution ratio of Am(III) vs molarity of extractant in DIPB. Aqueous phase = 0.02 *M* NH_4SCN, 0.001 *M* HCl, T = 25°C.

Since the series of extractants have similar mechanisms of extraction, *i.e.*, they behave as neutral extractants, several interesting comparisons can be made. Most importantly, the K_d of Am(III) and of Eu(III) from ammonium thiocyanate for DHDECMP is over two orders of magnitude greater than that for DB[BP], in marked contrast to the small difference in K_d's for the two extractants in the lithium nitrate system (K_d ratio ≤ 5). In the lithium nitrate system, this small difference in K_d's between DB[BP] and DHDECMP and other evidence (*1*, *8*) was attributed to the hypothesis that DHDECMP was not chelating the metal ion. In the thiocyanate system, it is reasonable to state the converse. That is, the large increase in extraction with DHDECMP over DB[BP] is due to enhanced stability of DHDECMP-metal-thiocyanate complexes due to the formation of chelate rings between the Am(III) or Eu(III) and the phosphoryl and carbonyl oxygens of the DHDECMP.

The assertion that chelation occurs with DHDECMP is completely supported by the data for the other extractants studied. First, K_d values with DHDECEP are intermediate between those for DHDECMP and DB[BP]

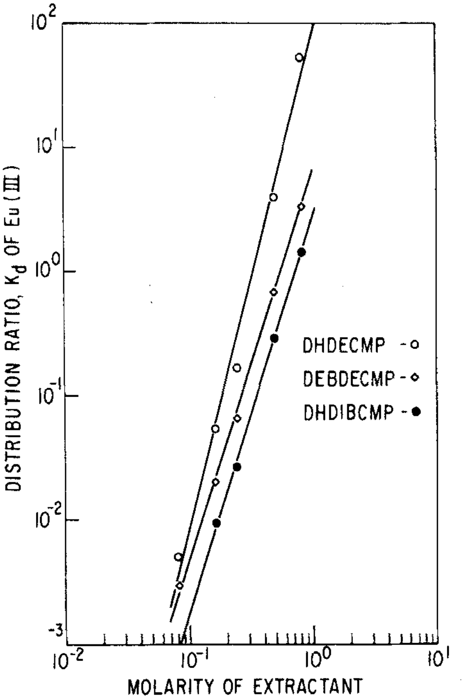


FIG. 4. Distribution ratio of Eu(III) vs molarity of extractant in DIPB. Aqueous phase = 0.02 M NH_4SCN, 0.001 M HCl, $T = 25°C$.

TABLE 1

Extractant Dependencies[a]

Extractant	Am(III)	Eu(III)
DHDECMP	3.65 ± 0.17[b]	4.02 ± 0.25
DB[BP]	3.62 ± 0.28	3.55 ± 0.18
DHDECEP	2.69 ± 0.12	2.34 ± 0.16
DEBDECMP	3.11 ± 0.04	3.11 ± 0.08
DHDIBCMP	3.30 ± 0.09	3.18 ± 0.10

[a] Aqueous phase = 0.02 M NH_4SCN, 0.001 M HCl; organic phase = 0.0815–0.815 M extractant.

[b] Error limits are one standard deviation.

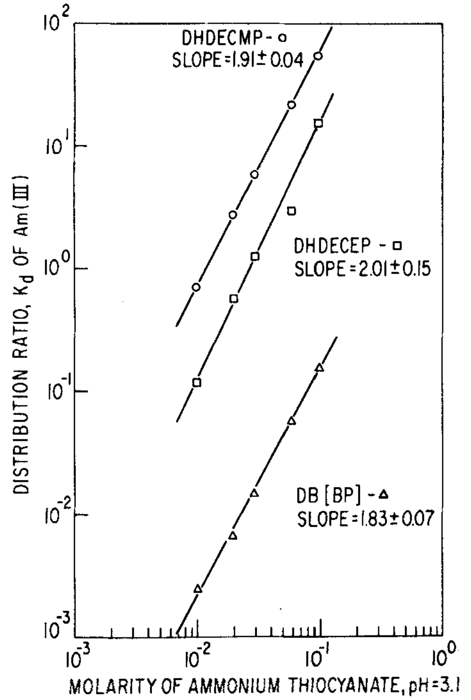


FIG. 5. Distribution ratio of Am(III) vs molarity of ammonium thiocyanate (0.001 *M* HCl). Organic phase = 0.244 *M* extractant in DIPB, $T = 25°C$.

(Figs. 1, 2, 5, and 6). Since the structure of DHDECEP includes an ethylene bridge between the phosphoryl and the carbonyl groups, DHDECEP would form a seven-membered chelate ring, which is much less stable than the six-membered ring formed by DHDECMP. However, DHDECEP apparently does form a chelate, which leads to greater stability than monodentate DB[BP].

Second, the data for the branched analogs of DHDECMP also support the chelation hypothesis. Figures 3, 4, 7, and 8 show that, under all conditions studied, the K_d's of Am(III) and Eu(III) are lower with DEBDECMP and DHDIBCMP than with DHDECMP, which may be explained by steric crowding of the phosphoryl and carbonyl groups by the branched alkyl groups. This evidence supports the chelation hypothesis since branching on either end of the molecule, near the phosphoryl group in DEBDECMP and near the carbonyl group in DHDIBCMP, leads to depression of the stability of the extracted complex. The branching of the extractants should have negligible effects on the basicities of the coordinated oxygen atoms (*12*).

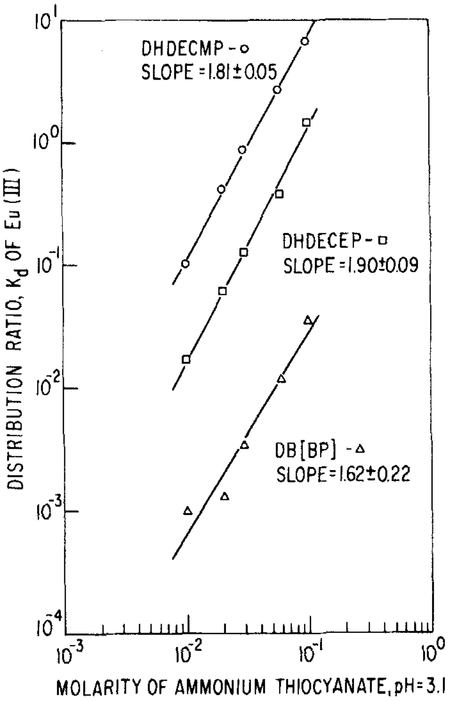


FIG. 6. Distribution ratio of Eu(III) vs molarity of ammonium thiocyanate (0.001 *M* HCl). Organic phase = 0.244 *M* extractant in DIPB, $T = 25°C$.

Table 2 summarizes the relative extraction power of the five extractants at constant extractant concentration of 0.489 *M* and a constant ammonium thiocyanate concentration of 0.02 *M* (0.001 *M* HCl).

The most likely explanation for the difference in the behavior of DHDECMP, and DHDECEP, and DB[BP] between the lithium nitrate system and the ammonium thiocyanate system lies in the properties of the aqueous anions. Nitrate is a bidentate ligand (*13*) whereas thiocyanate is strictly monodentate. Consequently, the presence of nitrate in the extracted metal complex encourages the bifunctional extractants to be monodentate while the presence of thiocyanate allows the extractant to be bidentate and thus fulfill the coordination number of the metal ion.

It is possible that the extractant concentration dependencies also reflect the bidentate behavior of DHDECMP, DHDECEP, DHDIBCMP, and DEBDECMP. As can be seen in Table 1, the dependencies of Am(III) and Eu(III) with DHDECMP and DB[BP] are the same (3.6) within the error

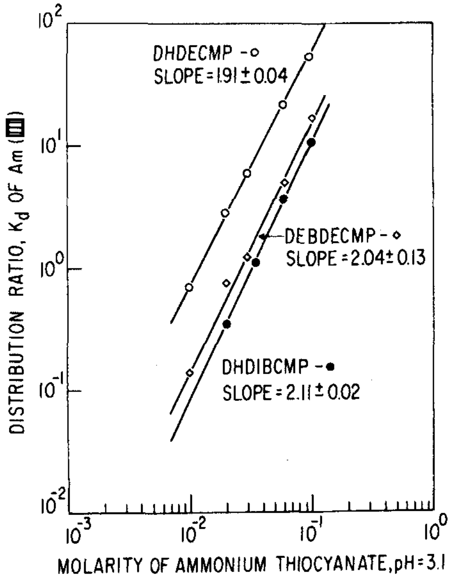


FIG. 7. Distribution ratio of Am(III) vs molarity of ammonium thiocyanate (0.001 *M* HCl). Organic phase = 0.244 *M* extractant in DIPB, $T = 25°C$.

limits and serve as a standard for comparison. The DHDECEP dependency is significantly less (2.7), reflecting difficulty in packing four of these longer, bulkier, bidentate molecules around a metal ion. In contrast, the dependencies for these three extractants were all third power in the lithium nitrate system (*1*). The dependencies for DHDIBCMP (3.3) and DEBDECMP

TABLE 2

Relative Extractability (*R*) of Am(III) and Eu(III)[a]

Extractant	*R*, Am(III)[b]	*R*, Eu(III)
DHDECMP	1000	1000
DHDECEP	38.6	18.4
DB[BP]	4.48	4.15
DEBDECMP	240	168
DHDIBCMP	143	70.9

[a] [Extractant] = 0.489 *M*, 0.02 *M* NH_4SCN (pH = 3.1).

[b] $R = 1000\ (K_d^X \div K_d^{\mathrm{DHDECMP}})$; $K_d^{\mathrm{Am}} = 20.2$, $K_d^{\mathrm{Eu}} = 4.01$ with DHDECMP.

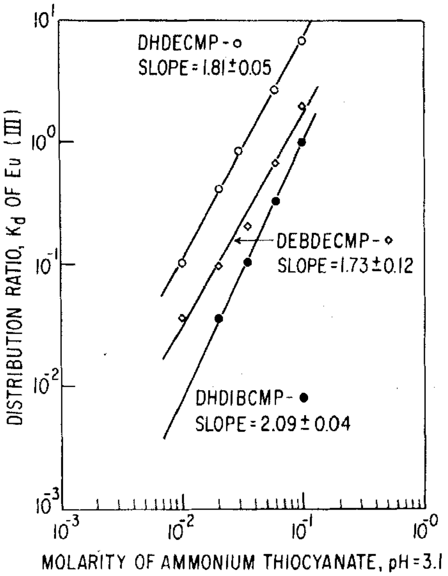


FIG. 8. Distribution ratio of Eu(III) vs molarity of ammonium thiocyanate (0.001 *M* HCl). Organic phase = 0.244 *M* extractant in DIPB, $T = 25°C$.

(3.1) are also somewhat less than those for DHDECMP and DB[BP], again reflecting a tendency to favor fewer bulky bidentate molecules around the metal ion.

Infrared and NMR Studies

The large differences in the extraction data for DHDECMP and DB[BP] from ammonium thiocyanate solution led to a reexamination of the infrared studies performed previously with $La(NO_3)_3$ complexes with DHDECMP (*1*). The original results were inconsistent with the extraction data since they showed a significant shift in the carbonyl stretching frequency ($\nu_{C=O}$), indicating bonding of this group to the lanthanum ion. On the other hand, experiments with ^{13}C NMR of these complexes showed (Table 3) the carbonyl carbon (#1) to be shifted more in the $La(SCN)_3$ complex than in the $La(NO_3)_3$ complex. Initial infrared spectra of neat solutions of $La(NO_3)_3(DHDECMP)_3$ and $La(SCN)_3(DHDECMP)_4$ showed no appreciable difference in $\nu_{C=O}$ between the two complexes (Table 4). However, dilution of the neat solutions with DIPB had a dramatic effect: $\nu_{C=O}$ in the nitrate complex became the same as in uncomplexed DHDECMP while $\nu_{C=O}$ in the thiocyanate complex remained substantially shifted.

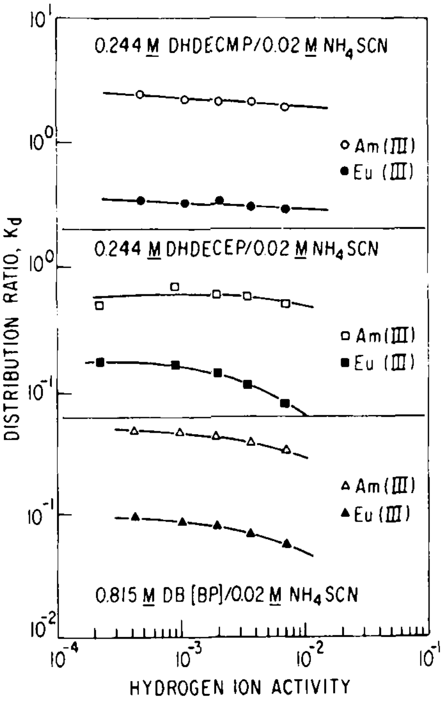


FIG. 9. Distribution ratios of Am(III) and Eu(III) vs aqueous hydrogen ion activity. Extractant concentrations: DHDECMP and DHDECEP = 0.244 *M*, DB[BP] = 0.815 *M* in DIPB. Aqueous phase = 0.02 *M* NH_4SCN, pH adjusted with hydrochloric acid.

The evidence appears unequivocal: DHDECMP is monodentate in its complex with $La(NO_3)_3$ and bidentate in its complex with $La(SCN)_3$ when either is in dilute solution.

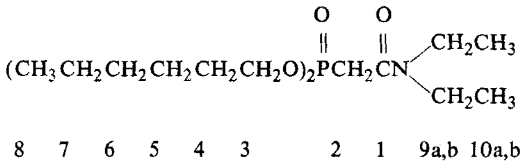
Thermodynamic Studies

It was hoped that chelation should show some effects on the thermodynamic constants of the extraction system when compared to the constants for the monodentate lithium nitrate system. Consequently, the values of ΔG, ΔH, and ΔS for the extraction of Am(III) and Eu(III) from ammonium thiocyanate with DHDECMP and DB[BP] were determined and are shown in Table 5 along with the data for the lithium nitrate system (*1*) in SI units.

Unfortunately, the thermodynamic values are not so clear-cut as the extraction data and the infrared spectra. The obvious features of the data

TABLE 3

^{13}C NMR of DHDECMP in C_6D_6 (0.5 *M*)
Carbon Numbering System


$(CH_3CH_2CH_2CH_2CH_2CH_2O)_2P(=O)CH_2C(=O)N(CH_2CH_3)_2$

Carbon	δ, ppm (δ C_6D_6 = 128.70)	Δ δ(downfield = +) of complexes HNO_3[a]	 $La(NO_3)_3[HNO_3]$[b]	 $La(NO_3)_3$[c]	 $La(SCN)_3$
1	164.51	+0.28	+1.58	+1.98	+2.28
2	34.80	−0.94	−2.25	−2.75	−2.25
3	67.05	+0.91	+1.76	+1.70	+1.97
4	32.40	−0.11	−0.04	−0.08	+0.09
5	31.59	−0.19	−0.21	−0.15	+0.13
6	26.25	−0.14	−0.14	−0.15	+0.11
7	23.49	−0.01	0.0	+0.01	+0.06
8	14.76	−0.05	−0.06	−0.04	−0.07
9a	43.67	+0.21	+0.55	+0.54	+0.62
9b	41.13	+0.28	+1.10	+1.33	+1.30
10a	14.76	−0.18	−0.06	−0.04	+0.07
10b	13.81	−0.27	−0.34	−0.22	+0.01

[a] DHDECMP equilibrated with 3 *M* HNO_3.
[b] DHDECMP equilibrated with $La(NO_3)_3$ in 3 *M* HNO_3.
[c] DHDECMP equilibrated with $La(NO_3)_3$ in 3 *M* $LiNO_3$.

TABLE 4

Phosphoryl and Carbonyl Frequencies for DHDECMP Extractant and Complexes (cm^{-1})

	$\nu_{P=O}$	Shift[a]	$\nu_{C=O}$	Shift[a]
DHDECMP	1255		1648	
$La(NO_3)_3$/DHDECMP (neat)	1209	−46	1608	−40
$La(NO_3)_3$/DHDECMP (dilute)	1213	−42	1648	0
$La(SCN)_3$/DHDECMP (neat)	1211	−44	1606	−42
$La(SCN)_3$/DHDECMP (dilute)	1211	−44	1604	−44

[a] Defined as the $\nu_{P=O}$ or $\nu_{C=O}$ in the complex minus the corresponding band in the unbound extractant.

TABLE 5

Thermodynamic Values and Equations for the Variable Temperature Extraction of Am(III) and Eu(III) from 2.0 *M* $LiNO_3$/0.01 *M* HNO_3 by 0.25 *M* Extractant and from 0.02 *M* NH_4SCN/0.001 *M* HCl by 0.489 *M* Extractant

System	Equation for ln K_d	Equation for ln K_{eq}	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol°K)
Am/DB[BP]/NO_3^-	$= \frac{4765}{T} - 17.90$	$= \frac{4765}{T} - 14.40$	−3.94	−39.6	−120
Am/DHDECMP/NO_3^-	$= \frac{5092}{T} - 17.89$	$= \frac{5092}{T} - 14.39$	−6.67	−42.3	−120
Eu/DB[BP]/NO_3^-	$= \frac{4969}{T} - 18.09$	$= \frac{4969}{T} - 14.49$	−5.39	−41.3	−120
Eu/DHDECMP/NO_3^-	$= \frac{4495}{T} - 15.98$	$= \frac{4495}{T} - 12.38$	−6.68	−37.4	−103
Am/DB[BP]/SCN^-	$= \frac{9731.1}{T} - 35.3$	$= \frac{9731.1}{T} - 20.9$	−29.0	−80.8	−174
Am/DHDECMP/SCN^-	$= \frac{10523}{T} - 32.0$	$= \frac{10523}{T} - 17.4$	−44.4	−87.4	−144
Eu/DB[BP]SCN^-	$= \frac{7970.8}{T} - 31.2$	$= \frac{7970.8}{T} - 16.6$	−25.2	−66.1	−138
Eu/DHDECMP/SCN^-	$= \frac{11304}{T} - 36.2$	$= \frac{11304}{T} - 21.6$	−40.5	−94.1	−179

include much more negative ΔG's and ΔH's for the thiocyanate system as well as more negative ΔS values. These results probably arise from more metal–ligand bonds being formed in the thiocyanate system since one more extractant molecule is coordinated in the thiocyanate system than in the nitrate system.

A comparison of the thermodynamic data between DB[BP] and DHDECMP for the extraction of Eu(III) from thiocyanate solutions shows the effects of chelation on ΔH and ΔS, assuming the species extracted by DHDECMP and DB[BP] are dehydrated to the same extent and translational entropy effects cancel out. Specifically, ΔH for DHDECMP is 28 kJ/mol more negative and ΔS is 41 J/mol°K more negative than for DB[BP]. However, the corresponding data for Am(III) show only a small difference between DHDECMP and DP[BP] in ΔH, 6.6 kJ/mol, and a less negative

ΔS, 30 J/mol°K, for DHDECMP. Apparently the assumptions mentioned above are not met in the thiocyanate system and further speculations are unwarranted without much more information about the structures of the extracted species.

Separation Factors

The initial reason for investigating the thiocyanate system was to determine the ability of DHDECMP to separate trivalent actinides from light lanthanides. Since Am(III) and Eu(III) are one of the most difficult pairs to separate, only they were investigated. Table 6 lists the maximum separation factors obtained with the five extractants studied along with the experimental conditions. The constraints of K_d of Am(III) > 1 and K_d of Eu(III) < 1 were imposed since these conditions must be met in a countercourrent liquid–liquid extraction system in order to completely separate the two metal ions. The greatest selectivity was found with DHDIBCMP ($\alpha_{\mathrm{Eu}}^{\mathrm{Am}} = 10.8$) at 0.244 *M* extractant concentration and 0.06 *M* NH_4SCN (0.001 *M* HCl). Unfortunately, none of the extractants was found to give a separation factor of about 20, a level necessary to obtain a good separation in a reasonable number of stages in a countercurrent system.

SUMMARY

DHDECMP and related compounds act as neutral extractants toward Am(III) and Eu(III) ions from thiocyanate solutions. The extractant dependencies range from less than third power for DHDECEP to fourth power for DHDECMP. The uncorrected thiocyanate dependencies are all close to second power. The pH dependencies are much less than first power.

In contrast to the extraction of Am(III) and Eu(III) from low acid lithium nitrate solutions, large differences in extration power are found among DHDECMP, DHDECEP, and DB[BP] in the thiocyanate system. Since DHDECMP is a stronger extractant than DHDECEP which is a much stronger extractant than DB[BP], chelation of the metal ion is probably occurring. Infrared spectra of solutions of DHDECMP complexes with $La(NO_3)_3$ and $La(SCN)_3$ confirm that the carbonyl group is bonded to the metal ion in the thiocyanate complex but is not bonded in the nitrate complex. ^{13}C-NMR and thermodynamic data are inconclusive.

Studies with branched analogs of DHDECMP, namely DHDIBCMP and DEBDECMP, confirm that chelation occurs in the thiocynate system since branching on either end of the molecule reduces both the K_d and the extractant dependency.

TABLE 6

Maximum Separation Factors[a]

Extractant	$\alpha_{\mathrm{Eu}}^{\mathrm{Am}}$	[Extractant], M	[NH_4SCN], M
DHDECMP	6.76	0.244	0.02
DHDECEP	8.40	0.815	0.02
DB[BP]	5.84[b]	0.815	0.02
DEBDECMP	7.08	0.244	0.06
DHDIBCMP	10.8	0.244	0.06

[a] $K_d^{\mathrm{Am}} > 1$, $K_d^{\mathrm{Eu}} < 1$.
[b] $K_d^{\mathrm{Am}} < 1$, $K_d^{\mathrm{Eu}} \ll 1$.

The maximum Am(III)-Eu(III) separation factor was found to be 10.8 with DHDIBCMP.

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