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Hydrophilic Complexes of the Actinides. I. Carbonates of Trivalent Americium and Europium

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The carbonate complex formation of Am^{3+} and Eu^{3+} has been studied by distribution between 1 M $NaClO_4$ and tributylphosphate (TBP) and by electromigration. The extraction of perchlorate salts as well as the sorption and hydrolysis arising in alkaline solutions have been investigated in some detail.

The distribution data may be explained up to 3 M sodium hydrogencarbonate concentration by assuming the formation of complexes of the type $Me(CO_3)_n^{(3-2n)+}$ with n = 1 and 2. The following constants have been evaluated at 25 °C:

	Eu^{3+}	Am^{3+}
$\log \beta_1$	5.93 ± 0.05	5.81 ± 0.04
$\log \beta_2$	10.72 ± 0.08	9.72 ± 0.10

Evidence was obtained that the hydrolysis of the Eu^{3+} and Am^{3+} ions is negligible for pH $\lesssim 7$.

One of the most important problem areas of nuclear technology is the safe handling and the storage of spent nuclear fuels. Essential information on actinide chemistry in groundwater is lacking. The complexation of the actinide ions in the various oxidation states with hydrophilic ligands in nearly neutral solutions is especially needed because complexation strongly affects their mobility. Among the most important inorganic ligands for which there is insufficient information available is carbonate. We have therefore undertaken a study of its complexation, beginning with the trivalent americium and europium. Ultra micro quantities of the metals were chosen in order to avoid polynuclear complexes. Distribution between an organic and an aqueous phase was employed as the main technique. Also the migration in an electric field was investigated because it gives complementary information about ionic charges, dimensions and mobilities.

EXPERIMENTAL

Procedures. The solvent extraction experiments were performed in a double glass-walled vessel of approximately 50 ml volume, thermostated to 25 °C. 15 ml of aqueous carbonate-perchlorate solution and of preequilibrated pure tributyl phosphate (100 % TBP), plus 10 – 20 μl of ^{241}Am or ^{152}Eu in 0.1 M $HClO_4$ was added. The extraction system was then contacted with CO_2 by bubbling a gas mixture of CO_2 and Ar through the solution. 15 – 20 min stirring periods were found to be sufficient for establishing equilibrium. For some experiments at zero or very low carbonate concentration and near neutral pH, longer stirring times were tested (up to 20 h) in order to follow the kinetics of the loss of activity due to sorption. The sampling, activity and pH measurements were made as described earlier.[1] Total bicarbonate and carbonate concentrations were determined by titration of aqueous samples, to which a known amount of NaOH were added, with $HClO_4$ using a glass electrode and/or methyl red indicator. The TBP was found to not dissolve or extract any appreciable amounts of bicarbonate or carbonate.

The electromigration experiments were carried out, at a field strength of 7.94 V/cm, in aqueous bicarbonate and perchlorate solution, supported by a cellulose filter paper (Whatman 41). In order to be able to account for the increase in viscosity at higher bicarbonate concentrations (up to 3 M $NaHCO_3$) measurements were made with an Ubbelhode viscosimeter. A general description of the method of electromigration has been given earlier.[2]

Chemicals and nuclides. Stock solutions of $NaHCO_3$, $HClO_4$, $NaClO_4$ and NaOH were

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prepared from *p.a.* quality reagents.[1] TBP (obtained from Fluka *puriss p.a.*) was treated by preextractions with NaOH and fresh perchlorate solutions of a composition corresponding to the actual experiment. For the use as a carrier for the trace concentrations of Am and Eu macro concentrations of Eu or La were sometimes used and therefore stock solutions of 1 M $Eu(ClO_4)_3$ and $La(ClO_4)_3$ were prepared from Eu_2O_3 and La_2O_3 (Merck, *p.a.*). Stock solution of the radioactive isotopes ^{241}Am, ^{152}Eu and ^{22}Na obtained from Amersham were prepared as 0.1 M $HClO_4$ solutions containing about 10^5 Bq/ml.

SOLVENT EXTRACTION STUDIES

Extraction mechanisms. Before employing the TBP solvent extraction system, it was neccesary to analyze the extraction mechanisms with respect to the variables like pH, ionic strength and electrolyte composition (with and without carbonate).

From the obtained information about the distribution D of Am^{3+}, Eu^{3+} and Na^+ (see Fig. 1, showing $D=[M(org)]/[M(aq)]$ *versus* log $[NaClO_4]$), it was found that the distribution values of Am^{3+} and Eu^{3+} were suitable in magnitude at 1 molar ionic strength. At this concentration of $NaClO_4$ there will be an appreciable extraction of $NaClO_4$ into the TBP phase which lowers the free TBP concentration and hence affects the extractibility of other metal perchlorates like $Am(ClO_4)_3$. However, if the $NaClO_4$ concentration is kept constant, there will be no need for any correction of the Eu^{3+} and Am^{3+} distribution values.

Furthermore it was found that the distribution of $NaClO_4$ was rather small anyway, *i.e.* less than 20 % reaching its maximum value at about 1−2 M $NaClO_4$. The behaviour of Na^+ agrees well with what has been observed earlier.[3] The extraction of Am and Eu increases sharply with the ionic strength, the log *D* *vs.* the logarithm of the perchlorate concentration gives a slope of about 2.5. There is region of less steep slope, from 0.3 to 4 M $NaClO_4$, which is most likely the result of a reduction in the extraction capacity of TBP due to the simultaneous maximum in the extraction of $NaClO_4$. Based on the above results, one may suggest that the trivalent metals are extracted by solvation according to relation (1). A detailed knowledge on the extraction mechanism is however not necessary for our purpose.

$$M^{3+} + 3\ ClO_4^- + n\ TBP(\text{organic phase}) \rightleftarrows M(ClO_4)_3 \cdot n\ TBP(\text{organic phase}) \quad (1)$$

Hydrolysis. The versatility of the TBP extraction system is apparent from Fig. 2 where the wide pH region of constant D is shown. The distribution of Am^{3+} and Eu^{3+} between 1 molar perchlorate solutions and TBP is constant between pH 2 and up to at least 6.7 (in the case of Am^{3+}) before sorption of the metals on glass surfaces becomes significant. At still higher pH there is a decrease in the distribution values although unexpectedly high values were

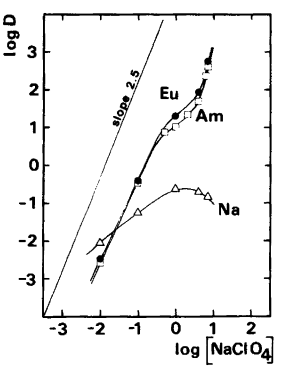

Fig. 1. The effect of the sodium perchlorate concentration on the distribution of Am^{3+}, Eu^{3+} and Na^+ between 100 % TBP and aqueous perchlorates solutions at pH 2 and 25 °C. (□) denotes ^{241}Am, (●) ^{152}Eu and (△) ^{22}Na.

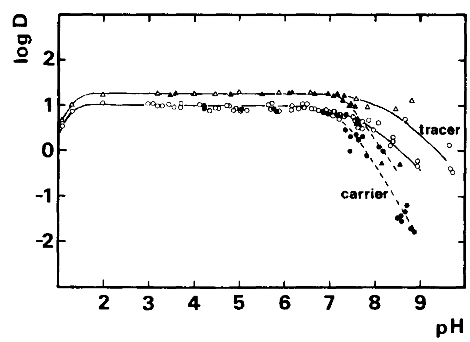

Fig. 2. The effect of pH on the distribution of Am and Eu between 100 % TBP and 1 M $NaClO_4$, at 25 °C. The distribution is shown both in the absence and in the presence of Eu carrier (totally 2×10^{-4} M in both phases). (○) Am tracer, (●) Am tracer + Eu carrier, (△) Eu tracer and (▲) Eu tracer + Eu carrier.

Table 1. Change in the distribution values D of Am and Eu at higher pH in presence and absence of europium carrier. Tentative first hydrolysis constants $*K_1$ ($M^{3+} + H_2O \rightleftarrows MOH^{2+} + H^+$) are derived for 1 M $NaClO_4$, 25 °C.

M(III)	pH (start of decrease in *D*) tracer	Eu-carrier [a]	La-carrier [b]	pH (50 % decrease in *D*) tracer	Eu-carrier [a]	log K_1* tracer
Am	6.7±0.1	6.7±0.1	8.0±0.2	7.5±0.3	7.25±0.08	−7.5±0.3
Eu	7.0±0.1	7.0±0.1		8.1±0.4	7.43±0.08	−8.1±0.4

[a] $0.5-2\times10^{-4}$ M Eu (organic+aqueous phase). [b] $10^{-4}-10^{-3}$ M La (organic+aqueous phase).

occasionally obtained even at a pH as high as 10; in this region the metal sorption was very high (*ca.* 90 %), which made the distribution measurements rather uncertain.

It was also noted that if $Eu(ClO_4)_3$ or $La(ClO_4)_3$ was added as a carrier the *D*-values seemed to become more reproducible and they decreased more sharply. The concentration of the carrier, in the concentration range (organic+aqueous phase) from 0.5 to 2×10^{-4} M Eu and from 10^{-4} to 10^{-3} M La, had no effect. However the influence of La and Eu carrier on the distribution of Am^{3+} were different. Whereas for Eu carrier the decrease in the *D*-values began at lower pH, in comparison with carrier free conditions, the opposite was found for La carrier.

In order to avoid or reduce the possible sorption on suspended (colloidal) impurity particles, we tried

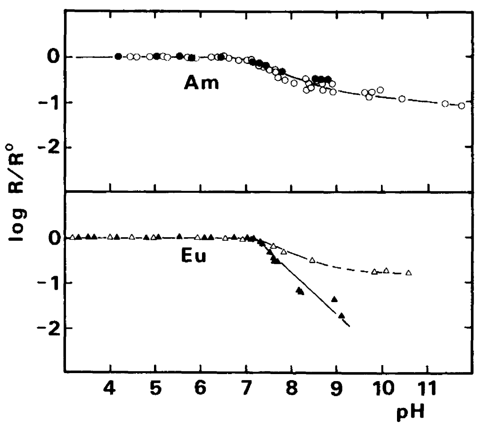

Fig. 3. The effect on the ratio ($R/R°$) due to sorption of Am and Eu in the 100 % TBP-1 M $NaClO_4$ extraction system. Experiments were made both in absence and in presence of Eu carrier (totally 2×10^{-4} M in both phases). R = total soluble activity of both phases (Bq/1) and $R°$ = added total activity of both phases (Bq/l). Same symbols as in Fig. 2.

centrifugation (17000 rpm for one hour) and filtration (pore size 400 nm) of the solutions. However, no remarkable changes compared with the regular solutions were observed. No crucial improvement were obtained either when increasing pH by coulometric electrolysis instead of alkali additions. In Table 1 some data is given on the change in the distribution values at neutral and slightly alkaline conditions. The decreasing extractability is interpreted as due to the onset of hydrolysis of the trivalent metals, and the first hydrolysis constants were estimated from the pH corresponding to a 50 % decrease in the extraction at tracer level (see Table 5). Least-squares regression analysis of the distribution data were also performed giving log $*K_1 = -7.5\pm0.3$ for Am.

Sorption. Strong sorption at higher pH (*i.e.* over pH 6.7 for Am and pH 7.0 for Eu) introduces a source of uncertainty in the experimental determination of the distribution values. It was found that reproducible distribution values with carbonate were only obtained under conditions of no sorption. Negligible sorption could be achieved either at sufficiently low pH or high enough bicarbonate concentration.

The "safe" concentration area of hydrogen and bicarbonate ions was determined by performing a number of experiments at various conditions while checking the extent of sorption by measuring the ratio $R/R°$. This ratio between the equilibrium activity R (Bq/ml) of the combined organic and aqueous phases and the initially added activity $R°$ is a measure of the mass balance and of the extent of loss of activity due to sorption on the glass vessel. From Fig. 3 one concludes that no sorption occurs for pH lower than about 6.7 and that the sorption process, is affected by the presence of macro concentrations of Eu in case of europium tracer but not americium tracer. The sorption characteristics are collected in Table 2. It can be noted that in the absence of carrier the sorption starts at about the

Table 2. Sorption of Am^{3+} and Eu^{3+} during extraction with TBP from 1 M $NaClO_4$, 25 °C. The extent of sorption is obtained from the ratio R/R° where R is the total activity in both phases and R° the initial activity.

M(III)	pH (sorption starts)			pH (50% sorbed)			max ($\delta \log(R/R^\circ)/\delta$ pH)	
	tracer	Eu-carrier[a]	La-carrier[b]	tracer	Eu-carrier[a]	La-carrier[b]	tracer	Eu-carrier[a]
Am	6.7 ± 0.1	6.7 ± 0.1	7.4 ± 0.2	7.7 ± 0.1	7.8 ± 0.1	8.5 ± 0.3	−0.3	−0.3
Eu	7.0 ± 0.1	7.0 ± 0.1		7.9 ± 0.1	7.5 ± 0.1		−0.3	−1

[a] $0.5-2\times10^{-4}$ M Eu (organic + aqueous phase). [b] $10^{-4}-10^{-3}$ M La.

Table 3. Solubility of CO_2 in 1 M $NaClO_4$ at various pH and at 25 °C. 1 atm of CO_2 (g).[a]

pH	$C=[HCO_3^-]$	$\log C$	$\log[CO_2+H_2CO_3]$ ($=pK_1-pH+\log C$)	$[CO_2+H_2CO_3]$ M
5.04	0.0031	−2.51	−1.51	0.031
5.32	0.0054	−2.27	−1.55	0.028
5.61	0.0109	−1.96	−1.53	0.030
6.09	0.0345	−1.46	−1.51	0.031
6.27	0.0501	−1.30	−1.53	0.030
6.57	0.108	−0.97	−1.50	0.032
6.81	0.181	−0.74	−1.51	0.031
7.13	0.436	−0.36	−1.45	0.036
			mean:	0.031 ± 0.002

[a] $K_1=[H^+][HCO_3^-]/[CO_2+H_2CO_3]=10^{-6.04}$.

same pH value as the hydrolysis.

Carbonate complexing. Introduction of carbon dioxide gas into the extraction system produces carbonate and bicarbonate ions, of which HCO_3^- is the predominating species in the pH interval of interest (from pH 6 to pH 9). The resulting formation

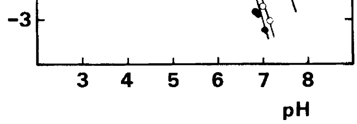

Fig. 4. The distribution D of ^{241}Am and ^{152}Eu between 100% TBP and 1 M $NaClO_4$ saturated with 1 atm. of a gas mixture of CO_2 + Ar as a function of pH at 25 °C. (○) Am, 100% CO_2, (●) Eu, 100% CO_2 and (△) Am, 10% Co_2 + 90% Ar.

of complexes in the aqueous phase can be described by eqn. (2), where M^{3+} is the trivalent metal (Am or Eu), x and y are system parameters. Assuming that the metal carbonates are not extractable, one can derive an expression, eqn. (3) for the distribution D of the metal, where D° denotes the distribution value ($D=[M]$(organic phase)/$[M]$(aqueous phase) in the absence of the complexing ligands L and OH^-. The influence of pH in the presence of 1 atm of CO_2(g) is shown in Fig. 4 in which the sharp decrease in $\log D$ with increased pH above pH 5 is demonstrated. The slope of $\log D$ *versus* pH reaches a value of almost −4 at the highest pH. The decrease in D cannot be a hydrolysis effect, because the acidity of the experiments is high enough to prevent interference from hydrolysis or sorption (*i.e.* pH <7 as derived from Figs. 2 and 3 and Tables 1 and 2). One may therefore interpret the diminishment in the extractibility of Am and Eu as a result of complexing with HCO_3^- and CO_3^{2-} which rapidly increases with increased pH.

$$M^{3+} + xHCO_3^- \rightleftarrows M(HCO_3)_xH_{-y}^{(3-x-y)} + yH^+ \quad x \geq y \qquad (2)$$

$$D/D^\circ = [Me^{3+}]/[Me]_{tot} = 1 + \Sigma\beta_n[L]^n + \Sigma\beta_j[OH]^i \quad (3)$$

Separate analysis was made to determine the solubility of CO_2 in 1 M $NaClO_4$ for the used pH range. The titration data are presented in Table 3, showing a constant solubility of CO_2 of about 0.031 M at 25 °C and 1 atm CO_2. In calculating the concentrations of bicarbonate and carbonate ions from the solubility of CO_2 we used the following acid dissociation constants valid for 1 M $NaClO_4$ at 25 °C; log K_1 ($CO_2 + H_2CO_3 \rightleftarrows H^+ + HCO_3^-$) = −6.04 and log K_2 ($HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$) = −9.57.[4]

Despite the fact that the bicarbonate ion HCO_3^- concentration is dominating over CO_3^{2-} in the entire investigated acidity range, it was found that the bicarbonate ion was not participating in the complexing reactions. The D values did not coincide into one curve, log $D = f([HCO_3])$, for different partial pressures of CO_2, *i.e.* the reaction was pH dependent with $y = 1$ to 2 according to eqn. (2). Hence the complexation instead takes place with CO_3^{2-} according to eqn. (4).

$$M^{3+} + n\ CO_3^{2-} \rightleftarrows M(CO_3)_n^{(3-2n)+} \quad (4)$$

This is confirmed by plotting log D against the CO_3^{2-} concentration, see Fig. 5. The maximum slope of log D/D° against log $[CO_3^{2-}]$ is −2 corresponding to n = 2. It can also be noted that the

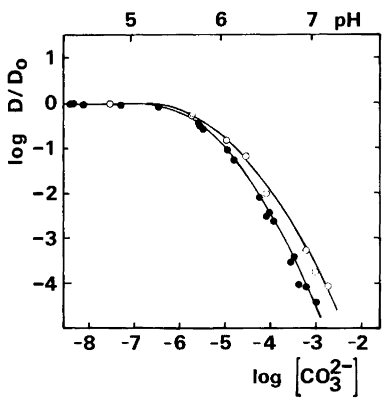

Fig. 5. Normalized distribution (log D/D_o) of Am and Eu between 100 % TBP and 1 M $NaClO_4$ as a function of carbonate ion concentration at 25 °C. The aqueous phase was saturated with 1 atm of CO_2 and the corresponding acidity is indicated. (○) Am.

Eu(III) carbonate is somewhat stronger than the Am(III) carbonate. The stability constants for the metal carbonate complexes were derived by least squares regression analysis of the distribution data in the form of eqn. (2).

The following values ($\pm\sigma$) were obtained for 1 M $NaClO_4$ and 25 °C; $AmCO_3^+$ (log $\beta_1 = 5.81 \pm 0.04$), $Am(CO_3)_2^-$ (log $\beta_2 = 9.72 \pm 0.10$), $EuCO_3^+$ (log $\beta_1 = 5.93 \pm 0.05$) and $Eu(CO_3)_2^-$ (log $\beta_2 = 10.72 \pm 0.08$).

The utilized extraction system behaves very well under the limited conditions employed for deriving the metal carbonate formation constants. However, deviations are found at higher pH or carbonate concentrations. For instance, the aqueous bicarbonate concentration may be limited because $NaHCO_3$ precipitates out at 1 atm of CO_2 at pH about 8. The TBP extraction system was also tested at very high carbonate concentrations and at 1 M $NaHCO_3$ without any $NaClO_4$. It was possible to estimate a maximum extractability of Am and Eu carbonate due to the fact that the D values did not decrease as much as expected at the highest carbonate concentrations, but levelled off at log $D \sim -4$. This indicates that the metal carbonates might be extractable to this very low extent ($D \leq 10^{-4}$) if not some impurities accounted for the small extraction ("background extraction"). Furthermore, it should be mentioned that the ionic strength increased somewhat at pH > 6.5. However, from previous experience of the TBP system it was not considered relevant to make any corrections in D because of the cancelling influence of β_2 and "salting out" effects.

ELECTROMIGRATION STUDIES

The use of the electromigration method, which is based on the transport properties of the ion in an electrolyte solution, offers the possibility of determining the charge of a metal complex.[2] The relation between the charge z_i and the migration velocity v_i of a metal complex i can be formulated as in relation (5), where g_i is a volume ratio factor and m is the charge of the uncomplexed ion M^{m+}. Since g_i for most of the metal complexes investigated varies only little (within ±20 %) one may, as a first approximation, regard the migration velocity as proportional to the charge of the migrating ion.[2]

$$v_i = z_i\ (g_i/m) \quad (5)$$

Table 4. Viscosity of $NaHCO_3 + NaClO_4$ solutions relative to H_2O at 20 °C.

Solution	Viscosity rel. H_2O ($\sigma = \pm 0.03$)	Density g/ml
1 M $NaClO_4$	1.04	1.081
0.1 M $NaHCO_3$ + 0.9 M $NaClO_4$	1.11	1.075
0.2 M $NaHCO_3$ + 0.8 M $NaClO_4$	1.10	1.072
0.4 M $NaHCO_3$ + 0.6 M $NaClO_4$	1.15	1.072
1.0 M $NaHCO_3$	1.31	1.057

The electromigration experiments were carried out in mixtures of $NaHCO_3$ and $NaClO_4$ at 1 M ionic strength and pH about 7.8. In order to improve the accuracy of the migration velocity determinations $^{22}Na^+$ was run simultaneously as a reference ion. Relative migration velocities (v_i/v_{Na^+}) of Am and Eu were calculated and plotted as a function of the total $NaHCO_3$ concentration as shown in Fig. 6. Noticable is the initial increase in migration velocity at low bicarbonate concentrations when sorption and hydrolysis are suppressed by metal carbonate formation. At yet higher bicarbonate concentration (log $[NaHCO_3] > -3.5$ M) there is a continuous decrease in the migration velocities until a plateau value of opposite sign is reached (log $[NaHCO_3] > -0.4$). A possible second plateau corresponding to charge +1 is indicated, but too much emphasis on the shape of the electromigration curve at the lowest $NaHCO_3$ concentrations should not be made because it was difficult to obtain reproducible results for $[NaHCO_3] < 0.01$ M.

The conclusion from the present electromigration study is that the charge of the complexes Am or Eu may become −1, but not more negative (since a plateau of the anionic migration velocities is reached with increasing $NaHCO_3$ concentrations). The "plateau" velocity corresponds to about −32 % of the migration velocity of uncomplexed Am or Eu. It is expected to be −33 % for charge −1 while for charge −2 it would have been −67 %. The absolute migration velocities at the highest bicarbonate concentration is somewhat lower (−27 %) because the ions are moving a little slower due to the increase in viscocity. However, the viscosity of the solutions is nearly constant for carbonate concentrations up to about 0.1 M and increases thereafter somewhat; Table 4.

The conclusion is thus that the highest anionic species formed has a charge −1 which agrees well with the solvent extraction studies where the highest carbonate complex was found to be $Am(CO_3)_2^-$ or $Eu(CO_3)_2^-$. Assuming that a mixture of 50 % MCO_3^+ and 50 % $M(CO_3)_2^-$ moves with zero average speed, which occurs at 0.040 M $NaHCO_3$ and pH about 7.8, one can estimate the formation constant of the second stepwise complex according to eqn. (5); log K_2 becomes 3.2 ± 0.3. This value is

$$AmCO_3^+ + CO_3^{2+} \rightleftarrows Am(CO_3)_2^- \quad (5)$$

somewhat smaller than the log $K_2 = 3.96 \pm 0.09$ derived from the solvent extraction experiments. (The larger uncertainty in the former experiments is due to that the experimental conditions such as pH

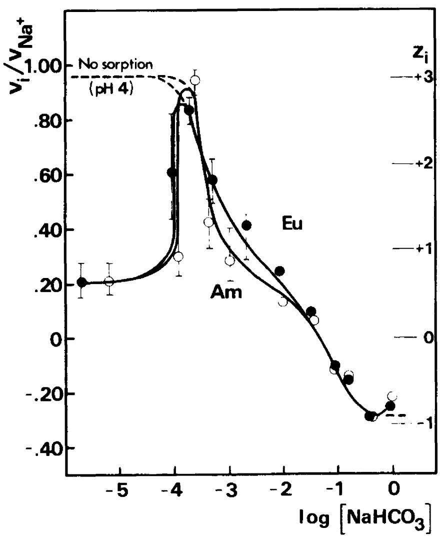

Fig. 6. Electromigration velocities, v_i/v_{Na^+}, relative to Na^+ of Am and Eu in $NaHCO_3 + NaClO_4$ solutions at 1 M ionic strength, pH *ca.* 7.8 and 25 °C. The dashed line shows the migration velosities of the uncomplexed M^{3+} ion obtained in 1 M $NaClO_4$ at pH 4. The charge z_i of the migration complex was estimated by eqn. (5) and is shown for convenience.

and sorption were not controlled as carefully as in the extraction experiments because they were mainly aimed at finding out the maximum anionic charge of the metal carbonates.) A similar deriviation of β_1, although rather uncertain, from the migration curve gives $\log \beta_1 = 5.3 \pm 0.4$ which is not very different from the solvent extraction value ($\log \beta_1 = 5.81 \pm 0.04$).

DISCUSSION

Recently the solubilities of the actinides in neutral or basic solutions were reviewed.[5] Hydrolysis and carbonate complexation were considered to be the two most important systems, in urgent need of reliable data. Our results on hydrolysis and carbonate complexing of Am and Eu will therefore be somewhat extensively discussed and compared with the literature information.

Hydrolysis. The only positively identified hydroxide species of the trivalent actinides or

Table 5. Acid hydrolysis constants K_1^* ($M^{3+} + H_2O \rightleftarrows M(OH)^{2+} + H^+$) of trivalent actinides and lanthanides in $NaClO_4$ solutions at 25 °C. pK_w; 13.80 (1 M $NaClO_4$), 13.79 (0.5 M $NaClO_4$), 13.79 (0.1 M $NaClO_4$), 14.00 (H_2O).

Metal	$\log {}^*K_1$, $\mu=0$	$\log {}^*K_1$, $\mu=0.1$	$\log {}^*K_1$, $\mu=1$ normalized	$\log {}^*K_1$, $\mu=1$	r_c, Å 6-coord [k]	$\log K_s$, $\mu=0$ mol^{-2}
An	-8.0 ± 0.5 [a,b]		-8.7 ± 0.5 [a,b]			-23.5 [a,b]
U	-7 ± 1 [a,c]		-8.0 ± 1 [a,c]		1.03	-24 ± 3 [a,c]
Np	-7.4 ± 0.5 [a,c]		-8.7 ± 0.5 [a,c]		1.01	-24 ± 2 [a,c]
Pu	-6.8 ± 0.5 [a,c]		-7.5 ± 0.5 [a,c]	-5.54 ± 0.04 [l]		-25 ± 2 [a,c]
Pu	-8.0 ± 0.5 [a,d]		-8.7 ± 0.5 [a,d]		1.00	-20 [f,i], -19.7 [j]
Pu	-6.95 [a,f]		-7.7 [a,f]			
Am				-7.03 ± 0.04 [l]		
Am		-5.9 ± 0.1 [g]	-6.2 ± 0.1 [g]	-7.5 ± 0.3 this work	0.99	-24 [e]
Am	(-0.5 to 4.0) [h]		(-1.2 to 4.7 [h])			
Cm		-5.9 ± 0.1 [g]	-6.2 ± 0.1 [g]		0.986	
Bk		-5.7 ± 0.1 [g]	-6.0 ± 0.1 [g]		0.981	
Cf		-5.6 ± 0.1 [g]	-5.9 ± 0.1 [g]		0.976	
La	-8.5 ± 0.2 [a,d]		-9.2 ± 0.2 [a,d]		1.061	-21.7 ± 0.6 [a,d]
Ce	-8.3 ± 0.2 [a,d]		-9.0 ± 0.2 [a,d]		1.034	-22.1 ± 0.6 [a,d]
Pr	-8.1 ± 0.2 [a,d]		-8.8 ± 0.2 [a,d]		1.013	-22.5 ± 0.6 [a,d]
Nd	-8.0 ± 0.2 [a,d]		-8.7 ± 0.2 [a,d]		0.945	-23.4 ± 0.6 [a,d]
Sm				-8.84 ± 0.02 [l]		
Sm	-7.9 ± 0.2 [a,d]		-8.6 ± 0.2 [a,d]		0.964	-25.5 ± 0.6 [a,d]
Eu				-8.12 ± 0.02 [l]		
Eu	-7.8 ± 0.2 [a,d]		-8.5 ± 0.2 [a,d]	-8.1 ± 0.4 this work	0.950	-24.5 ± 0.6 [a,d]
Gd	-8.0 ± 0.2 [a,d]		-8.7 ± 0.2 [a,d]		0.938	-26.4 ± 0.6 [a,d]
Tb	-7.9 ± 0.2 [a,d]		-8.6 ± 0.2 [a,d]		0.923	-25.5 ± 0.6 [a,d]
Dy	-8.0 ± 0.2 [a,d]		-8.7 ± 0.2 [a,d]		0.908	-26.1 ± 0.6 [a,d]
Ho	-8.0 ± 0.2 [a,d]		-8.7 ± 0.2 [a,d]		0.894	-26.6 ± 0.6 [a,d]
Er	-7.9 ± 0.2 [a,d]		-8.6 ± 0.2 [a,d]		0.881	-27.0 ± 0.6 [a,d]
Tm	-7.7 ± 0.2 [a,d]		-8.4 ± 0.2 [a,d]		0.869	-27.0 ± 0.6 [a,d]
Yb	-7.7 ± 0.2 [a,d]		-8.4 ± 0.2 [a,d]		0.858	-27.3 ± 0.6 [a,d]
Lu	-7.6 ± 0.2 [a,d]		-8.3 ± 0.2 [a,d]		0.848	-27.5 ± 0.6 [a,d]

[a] Estimated. [b] Ref. 5. [c] Ref. 13. [d] Ref. 8. [e] Ref. 6. [f] Ref. 14. [g] Ref. 15. [h] Ref. 9 – 12, see text. [i] 0.069 M HCl. [j] Ref. 26. [k] Ref. 16. [l] Ref. 29.

lanthanides are MOH^{2+}, $M(OH)_3(s)$ and $M(OH)_4^-$, assuming similar behaviour as found for Sc, Y and Ln.[5] In evaluating the information on hydrolysis we chose to examine the first hydrolysis reaction only, written in the form of eqn. (6).

$$M^{3+} + H_2O \rightleftarrows MOH^{2+} + H^+ \quad (6)$$

Table 5 summarizes the information from literature. The value of the stability constant log $^*K_1$ of eqn. (6) obtained at different ionic strengths can be related to each other using an empirical relation.[8] It follows that the log $^*K_1$ values decrease with increasing ionic strength; by 0.37 units for 0.1 M $NaClO_4$, 0.60 units for 0.5 M $NaClO_4$ and 0.7 units for 1 M $NaClO_4$ at 25 °C in comparison with pure water. Similtaneously the pK_w values decreases from 14.00 in pure water to 13.80±0.02 for any of the above ionic strengths.

It can be seen from Table 5 that the information at large consists of estimates which are based on very few measurements. It is predicted that the value for Am and Eu lies around log $^*K_1 = -8.7 \pm 0.5$ and -8.5 ± 0.5, respectively, in 1 M $NaClO_4$.[5,8] This means roughly that 50% hydrolysis would be expected at pH between 8.7 and 8.5. However, our experiments indicate that the hydrolysis values are somewhat higher, the log $^*K_1$ being -7.5 ± 0.3 for Am and -8.1 ± 0.4 for Eu. This difference is not surprising, considering that hydrolysis studies generally are complicated by simultaneous occurring disturbing processes like sorption, precipitation and/or formation of polynuclear and colloid species. In the present work the measured distribution values are not affected by the two first processes. (In principle, the distribution values should be independent of loss of material due to sorption or precipitation.) Further, polynuclear or colloid species should be avoided by applying the tracer technique. Precipitation should be no problem because the aqueous phase was undersaturated even when Eu carrier was added, resulting in an aqueous concentration of $0.2 \times 10^{-5} - 4 \times 10^{-4}$ M. The solubility of Am hydroxide would be much higher, around 0.01 – 0.025 M at pH 6.7, where the decrease in the distribution values are observed to begin, as estimated from the solubility product (log $K_s = -24$ and log $K_s = -23.5$ at zero ionic strength).[6,5] It has also been reported that there was no loss of material from a 10^{-5} M Am solution, of about 0.1 M ionic strength, from pH 5 up to about 7.5.[7]

Table 6. Carbonate complexes of trivalent actinides and lanthanides. Stability constants β_n refers to the reaction $M^{3+} + n\,CO_3^{2-} \rightleftarrows M(CO_3)_n^{3-2n}$.

Metal(III)	log β_1	log β_2	log β_3	log β_4	Remarks (solid complexes, ionic media *etc.*)
Pu	9.6 ?	12.8 ?	16.1 ?	–	$\mu=0$, estimated[18]
Am	5.81±0.04	9.72±0.10	–	–	1 M $NaClO_4$, 25 °C, no higher complexes than 1:2 at pH ≤10. This work.
Am					Only Am^{3+}, $Am(CO_3)^+$ and $Am(CO_3)_2^-$ species in in 1 M($NaClO_4 + NaHCO_3$) at pH 3–9.[19]
Am					Precipitation of $NaAm(CO_3) \cdot 4H_2O(s)$ from 0.5 M $NaHCO_3$ and $Na_3Am(CO_3) \cdot 3H_2O(s)$ from 1.5 M Na_2CO_3. No evidence for formation of $Am(CO_3)_4^{5-}$.[20]
An	6.5	11.0	14.5	–	$\mu=0$, estimate.[5]
La	<6.6				$\mu=0$, 1 M $NaClO_4$. Recalculated from Ref. 21.
La	5.7				3 M $NaClO_4$[27]
Ce	6.5	10.95	14.5		3 M $NaClO_4$[27]
Nd				1.08 ?	5.35 M KCl[23]
Eu	5.93±0.05	10.72±0.08	–	–	1 M $NaClO_4$, 25 °C. This work.
Eu					Only Eu^{3+}, $Eu(CO_3)^+$ and $Eu(CO_3)_2^-$ in 1 M ($NaClO_4 + NaHCO_3$) at pH 3–9.[19]
Eu	–	–	–	15.55±0.09	$\mu=2.5$, 0.5 M $NaHCO_3$ + 0.5 M Na_2CO_3, pH 10.3. Relative stability to the EDTA complex.[24]
La–Lu	–	–	–	14.4–17.1	$\mu=2.5$, 0.5 M $NaHCO_3$ + 0.5 M Na_2CO_3, pH 10.3. Relative stability to the EDTA complex.[24]

Due to the unknown influence of the sorption and colloid formation on the distribution values the estimated hydrolysis constants for Am and Eu may be more uncertain than indicated from the numeric analysis only (Table 5). Differences in the interpretation of the sorption processes seem to be the reason for the large discrepancies between different investigators. Hence, some authors on the hydrolysis of Am and other actinides have concluded that the hydrolysis starts already in much more acid media. Using an electrophoretic technique Marin and Kikindai found that $\log {}^*K_1 = -2.7$ at $\mu = 0.005$.[9] Shalinets and Stepanov found $\log {}^*K_1 = -3.1$ for Am and $\log {}^*K_1 = -3.2$ for Cm.[10] From various sorption studies Samartseva found that $\log {}^*K_1 \leq -3.5$ to 4.0.[11] Using paper chromatography and cation exchange Korotkin arrives at $\log {}^*K_1 \sim -0.5$, *i.e.* the hydrolysis "starts" already at pH 0.5, which indicates a many orders of magnitude stronger hydrolysis than concluded in the present work.

Recently, the formation and properties of americium colloids in aqueous systems were studied with sorption/centrifugation techniques and with electromigration. True hydroxide colloid were indicated at pH above 12 whereas small fractions of pseudocolloid, *i.e.* Am sorbed on colloidal impurities, could be found even at pH down to 3.[28] Due to these problems, the present technique (and other methods as well) for obtaining hydrolysis constants should be used with caution. Without doubt the soprtion and colloidal properties are very important and deserve more studies.

Finally, two independent corraborative investigations of the hydrolysis of Am have appeared during the completion of this work. Using potentiometric titration Nair and coworkers obtain $\log {}^*K_1 = -7.03 \pm 0.04$ in 1 M $NaClO_4$ and by solvent extraction Choppin and coworkers arrive at $\log {}^*K_1 = -6.93 \pm 0.03$ in 0.7 M NaCl.

Carbonate complexing. Literature about the complexation of trivalent actinides with carbonate is very meager. Comparison can be made with the lanthanides, even here however the material available is small, see Table 6. The complexation with carbonate ions may be considered to occur according to eqn. (4), *i.e.* by consequtive addition of CO_3^{2-} ligands to the metal. No bicarbonate complexes seem to be formed, even in $NaHCO_3$ solutions, where no higher carbonate complexes than the 1:2 metal to ligand have been observed. In Na_2CO_3 solution the activity of the carbonate ion may become high enough to produce a tricarbonate complex.[20] Tetracarbonates have not been observed for the trivalent actinides in contrast to the lanthanides.[24] The stability constant for the 1:1 carbonates was estimated to be $\log \beta_1 = 9.6$ for Pu^{3+} but this value has been regarded to be largely overestimated.[18,5,19,22] The present value for Am, $\log \beta_1 = 5.81 \pm 0.04$, seems more reasonable and agrees well with the expected behaviour for trivalent actinides, which is around $\log \beta_1 = 6$.[5] However the uncertainty ($\pm \sigma$) in the $\log \beta$ values seems to be somewhat small due to that the ratio K_1/K_2 is too different for the two metals. The ratio K_1/K_2 should be rather similar but is around 80 for Am and around 14 for Eu. Hence an additional systematic uncertainty of about the same size as the given error limits is indicated.

The stability of the lanthanide tetracarbonate complexes was derived from measurements of the relative complexing ability of carbonate in comparison with EDTA.[24] However, it seems likely that the reported $\log \beta_4$ values are perhaps 3 orders of magnitude too large because the values (*e.g.* $\log \beta_4 = 15.55 \pm 0.09$ for Eu) imply that the tri- and tetracarbonates would dominate already for carbonate concentrations over 10^{-4} M while this work does not give any indication of these higher complexes at least up to $10^{-2.5}$ M.

Although the stability of the Am carbonate complex is now found to be weaker than expected earlier, it should be realized that the stability is quite sufficient to suppress hydrolysis and sorption. It

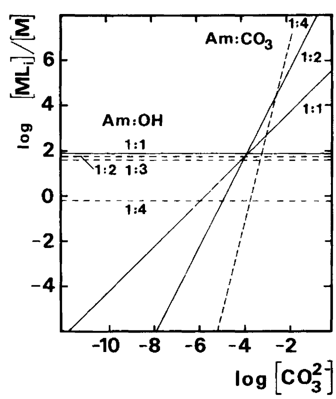

Fig. 7. The ratio log $[ML_i]/[M]$ for Am(III) as a function of the carbonate concentration in 1 M $NaClO_4$ at pH 9 and 25 °C. Stability constants are from this work (solid lines) and estimated (see Tables 5 and 6, broken lines).

follows that the carbonate ion is a stronger complexing agent, by one order of magnitude, than the hydroxide ion OH^-. This is illustrated in Fig. 7 where $\log[ML_i]/[M]$ is shown as a function of $\log[CO_3^{2-}]$ at pH 9. It follows that the hydrolysis (and sorption) could easily be completely suppressed even at such a high pH.

In this connection one might also comment on the state of Am and Eu in groundwater. Most groundwaters contain 60 – 400 mg HCO_3^- per liter and have a pH in the range from 7.2 to 8.5.[25] As a result of these conditions the carbonates will contribute significantly or even dominate the metal speciation.

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