Hydrolysis and Carboxylate Complexation of Trivalent Americium

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(Received October 1, 1986)

Abstract

Hydrolysis and complexation of trivalent americium in the presence of acetic acid and tartaric acid have been studied by solvent extraction. It has been found that in basic solutions (pH 8.0), while hydrolysis of the metal ion predominates in the presence of acetic acid, complexation by the chelating ligand suppresses hydrolysis to some extent. The stability constants for the formation of AmL^{2+} (acetate) and AmL^{1+} and AmL_2^{1-} (tartarate) have been determined and the data used for computing the first hydrolysis constant (K_1^*) of Am(III). Using experimentally determined β_1 and K_1^* values, the speciation diagrams for Am(III) in acidic (pH 4.0) and neutral solutions have been deduced.

Introduction

The behaviour of actinide ions in natural and waste water systems is influenced to a great extent by hydrolysis and complexation reactions. This paper describes our studies on the hydrolysis and complexing behaviour of trivalent americium in aqueous solutions containing acetic acid and tartaric acid by solvent extraction with dinonylnaphthalene sulphonic acid (HD). The data reported [1] in literature on the complexation of Am(III) with acetate and tartarate are limited to acidic conditions with practically no contribution from hydrolysis reactions. The present investigation has been carried out at acidic and alkaline pH with a view to understanding the extent of hydrolysis, complexation and the nature of the species under such conditions. An interesting observation in our study is that the hydrolysis of Am(III) is suppressed by the presence of tartarate and not by acetate in basic solutions.

Experimental

All the reagents used were of A.R. grade. ^{241}Am-(III), which was used in the present study, was

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purified by ion exchange and checked for radio-chemical purity by alpha spectrometry. The tracer was taken in perchloric acid medium (by evaporation with $HClO_4$) and used in the experiments.

Details of the experimental procedure for the determination of the distribution coefficient (K_d), concentration of the complexing anion, etc. have been described elsewhere [2]. HD was standardised and converted to NH_4D by a procedure previously reported [2]. A stock solution of ^{241}Am(III) in 0.0023 F NH_4D in benzene was prepared by extracting an appropriate amount of the tracer ($\approx 10^{-8}$ M) and used as such.

The aqueous phase consisted of the required concentration of the ligand at the desired pH and ionic strength (H^+, NH_4^+, ClO_4^-). 3 ml of the aqueous phase was equilibrated with an equal volume of 0.0023 F NH_4D in benzene containing ^{241}Am(III) tracer for one hour, which was found sufficient for the attainment of equilibrium. The pK value of 4.76 for acetic acid [3] and the reported [4] value of 2.9 ($H_2L \rightleftharpoons HL^- + L^+$) and 3.94 ($HL^- \rightleftharpoons H^+ + L^{2-}$) for tartaric acid were used for the calculation of the concentration of the complexing anions. Under the experimental conditions (pH 4 and 8), L^{2-} is the main complexing anion in the case of tartaric acid.

K_d values were determined in duplicate experiments and the agreement was within ±5%. Material balance was also found to be in agreement within these limits in experiments. In the case of experiments at pH 8.0, the activity in the aqueous phase for the computation of K_d was taken as the difference in the activities of the organic phase before and after equilibration. This was to eliminate errors due to adsorption of the activity in the aqueous phase.

Data Treatment

The distribution coefficient (K_d) for Am^{3+} in the aqueous and organic phases as a function of the ligand concentration [L] is given by [5]

$$\frac{1}{K_d} = \frac{1}{K_d^0} + \frac{\beta_1^L[L]}{K_d^0} + \frac{\beta_2^L[L]^2}{K_d^0} + \dots + \frac{\beta_n^L[L]^n}{K_d^0}$$

$$(1)$$

where $\beta_1{}^L$, $\beta_2{}^L$, etc. represent the overall stability constants defined by

$$\beta_n{}^L = \frac{[ML_n]}{[M][L_n]} \qquad (2)$$

where $[ML_n]$ represents the concentration of the nth complex of the metal ion M^{n+} and K_{d^o} is the distribution coefficient in the absence of the ligand.

In cases where the metal ion is partially hydrolysed and partially complexed (at neutral or basic pH), K_d is given by [6]

$$\frac{1}{K_d} = \frac{1}{K_{d^o}} + \frac{\beta_1{}^{L'}[L]}{K_{d^o}} + \frac{\beta_2{}^{L'}[L]^2}{K_{d^o}} + \ldots + \frac{\beta_n{}^{L'}[L]^n}{K_{d^o}} \qquad (3)$$

where

$$\beta_n{}^{L'} = \frac{\beta_n{}^L}{1 + \beta_n{}^{OH}(OH)^n} \qquad (4)$$

$\beta_n{}^{OH}$ in the above equation represents the formation constant for the hydrolysed species. In the present work (pH = 8.0), no hydrolysed species higher than the monohydroxy species are reported [7] to be present for trivalent americium. Hence in eqn. (4), n becomes equal to 1.

From the above discussion it is evident that by independently determining K_d values as a function of [L] at two different pH values — one at an acidic pH, where the hydrolysis of the metal ion is negligible because of complexation and the other at neutral or basic pH, where hydrolysis of the metal ion is significant besides complexation — it is possible to obtain $\beta_n{}^L$ and $\beta_n{}^{L'}$ and hence the formation constant $\beta_1{}^{OH}$ for the hydrolysed species.

Results and Discussion

Complexation

The results of distribution coefficient measurements at pH 4.0 are summarised in Table I. Regression analysis of the data indicates the formation of

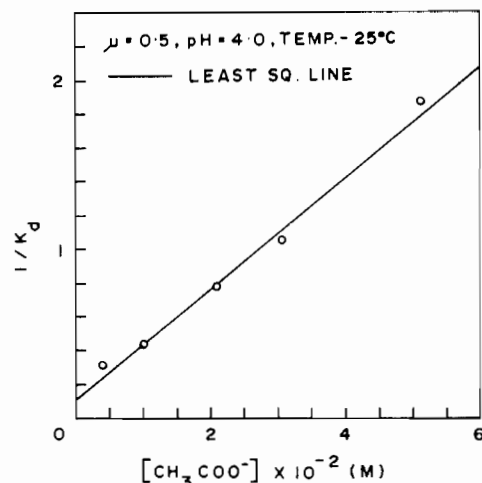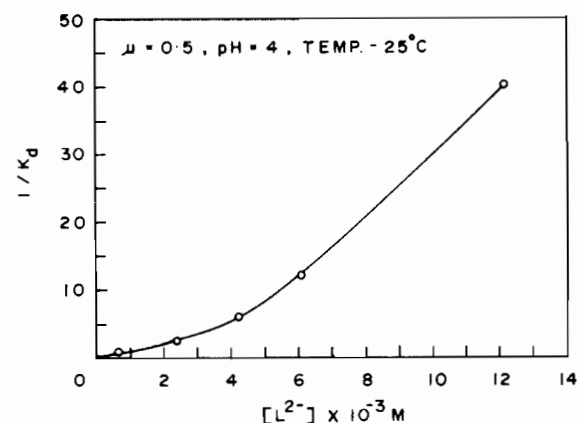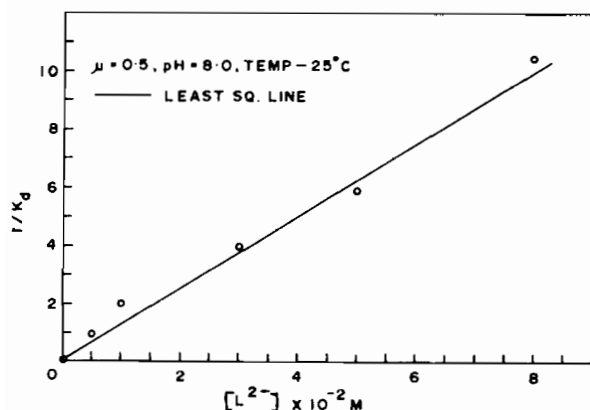

Fig. 1. Plot of $1/K_d$ vs. acetate.

Fig. 2. Plot of $1/K_d$ vs. tartarate.

AmL^{2+} in the case of acetic acid, while AmL^{1+} and $AmL_2{}^{1-}$ are formed in the case of tartaric acid (Figs. 1 and 2) for the concentrations of the ligand used.

At basic pH, K_d has been found to be independent of the acetate concentration (Table II), indicating the

TABLE I. Distribution Coefficients of Am^{3+} as a Function of the Tartarate and Acetate Concentration. $\mu = 0.5$ M, pH = 4, temperature = 25 ± 0.5 °C

Total tartarate concentration (M)	Distribution coefficients (K_d)	Total acetate concentration (M)	Distribution coefficients (K_d)
2×10^{-2}	0.025	2.5×10^{-1}	0.54
1×10^{-2}	0.08	1.5×10^{-1}	0.95
7×10^{-3}	0.17	1×10^{-1}	1.32
4×10^{-3}	0.40	5×10^{-2}	2.26
1×10^{-3}	2.40	2×10^{-2}	3.04

TABLE II. Distribution Coefficients of Am^{3+} as a Function of the Tartarate and Acetate Concentration. $\mu = 0.5$ M, pH = 8, Temperature = 25 ± 0.5 °C.

Total tartarate concentration (M)	Distribution coefficient (K_d)	Total acetate concentration (M)	Distribution coefficient (K_d)
8×10^{-2}	0.08	6×10^{-2}	16.6
5×10^{-2}	0.14	5×10^{-2}	18.9
3×10^{-2}	0.35	3×10^{-2}	16.8
1×10^{-2}	0.60	1×10^{-2}	18.2
5×10^{-3}	1.04	5×10^{-3}	18.9

Fig. 3. Plot of $1/K_d$ vs. tartarate.

TABLE III. Stability Constants Determined for: Am^{3+} + $nL^- \rightleftharpoons [AmL_n]^{3-n}$ (acetate system) and Am^{3+} + $nL^{2-} \rightleftharpoons [AmL_n]^{3-2n}$ (tartarate system)

Ligand	Ionic strength (M)	T (°C)	log β_1	log β_2	Reference
Acetate	2.0	25	1.95		10
Acetate	1.0	20	2.08		9
Acetate	0.5	20	2.30		
Acetate	0.5	25	2.39 ± 0.05		present study
Tartarate	0.1	25	3.90	6.78	8
Tartarate	0.5	25	4.20 ± 0.06	6.84 ± 0.07	present study

absence of complexation of Am^{3+} by this ion. A complex of the type AmL^{1+} is, however, formed at basic pH (Fig. 3) in the case of tartarate as the ligand. The formation of mixed complexes of the type Am(OH)L or Am(OH)L$_2^{2-}$ is precluded since such a possibility was ruled out in the complexing of trivalent americium by oxalate under identical conditions [7].

The stability constants are summarised in Table III along with those reported in the literature for the acetate and tartarate systems. An interesting observation in our study is that while Am^{3+} is hydrolysed in the presence of a monocarboxylic acid (acetic) at basic pH, the hydrolysis is suppressed to an extent in the presence of a chelating ligand (tartaric acid). β_1 and β_2 values obtained by us are in close agreement with the only values reported, i.e. those by Stary [8] for the tartarate complexes. The β_1 value for the acetate complex obtained in the present study is in agreement with that reported [9] at $\mu = 0.5$. Other values [9, 10] are lower than our β_1 value and this may be attributed to the higher ionic strengths employed in these studies.

The possibility of carbonate or bicarbonate complexing of Am^{3+} during our experiments at pH 8.0

has been looked into, although utmost care was taken in preparing the solution (carbonate free) with least exposure (15 min) to the atmosphere. The equilibrium concentration of the carbonate at pH 8.0 has been calculated to be of the order of ~10^{-6} M. Making use of the β_1 values [11, 12] for Am–CO$_3^{1+}$ and Am–HCO$_3^{2+}$, the estimated error in our β_1 values has been found to be within the experimental uncertainty quoted.

Hydrolysis

Using β_1^L and $\beta_1^{L'}$ values of the tartarate system, the first hydrolysis constant for the reaction

$$Am^{3+} + H_2O \rightleftharpoons AmOH^{2+} + H^+$$
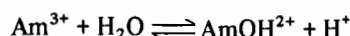
is calculated using the relation

$$K_1^* = \beta_1^{OH} K_W$$

The information on K_1^* values available in the literature for Am^{3+}, along with the one obtained in the present study, is summarised in Table IV. The values reported at different ionic strengths can be correlated with each other by an empirical relation [13] which states that the log K_1^* values decrease with increasing ionic strength by 0.37 units for 0.1 M NaClO$_4$, 0.6 units for 0.5 M NaClO$_4$ and 0.7 units for 1 M NaClO$_4$ at 25 °C. Simultaneously, the pK_w values decrease from 14.0 to 13.80 ± 0.02 for any of the above ionic strengths. In accordance with this relation, our K_1^* value appears to be in agreement with the recently reported values [7, 12, 14]. However, there is a large spread in some of the values reported in older literature [15–19] (see Table IV).

TABLE IV. First Hydrolysis Constant K_1^* for Am^{3+} + H$_2$O $\rightleftharpoons$ AmOH^{2+} + H$^+$

Ionic strength (M)	T (°C)	$-\log K_1^*$	Reference
1.0	25	7.50 ± 0.30	12
1.0	25	7.03 ± 0.04	14
0.7	21	7.54 ± 0.20	7
0.5	25	6.80 ± 0.30	present study
0.1	25	5.90 ± 0.10	15
0	25	0.5 to 4.0	16–19
0	25	8.0 ± 0.5	13

Speciation

From our hydrolysis constant and beta values, it is possible to obtain the relative concentrations of the probable species of Am(III) in water at neutral and acidic pH as a function of the ligand concentration. This is represented by a set of curves (Figs. 4 and 5). At pH 7.0 and for ligand concentrations in
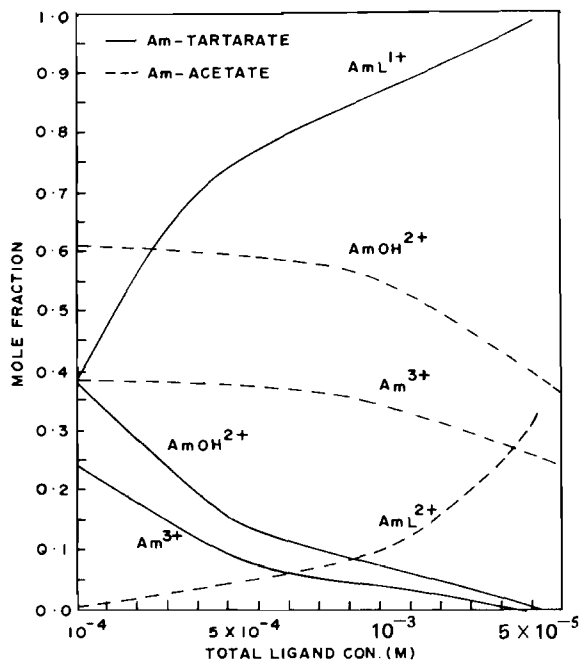
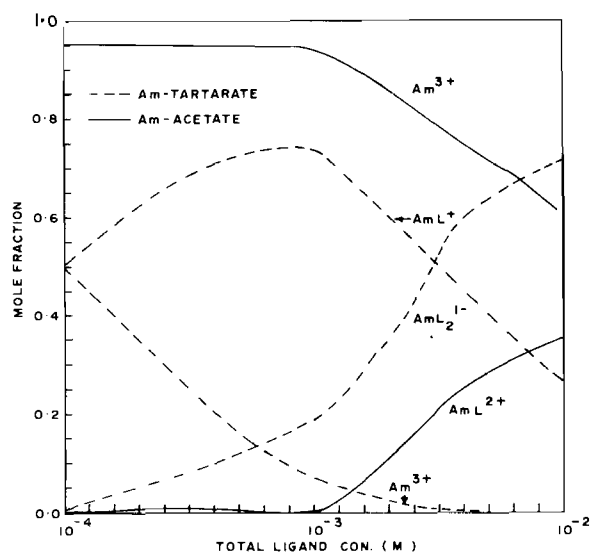Fig. 4. Mole fraction of Am(III) as a function of ligand concentration at pH 7.

Fig. 5. Speciation of Am(III) as a function of ligand concentration at pH 4.

the range 10^{-4} to 10^{-3} M, $AmOH^{2+}$ and Am^{3+} are the dominating species in the presence of acetic

acid, with least contribution from complexation. In the case of tartaric acid, because of its chelating nature, the main species is the AmL^{1+} complex with suppression of hydrolysis as the ligand concentration increases. In the case of solutions at pH = 4.0, the concentration of the complex ion increases with increasing concentration of the ligand.

Acknowledgement

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