

The Behavior of Microamounts of Americium in Aqueous Solution

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수용액중 극미량 Am의 거동

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Abstract

The behavior of micro amount of Am in aqueous solution were investigated with centrifugation method as a function of pH. In the studies described here, equilibration times were extended to 2-3 weeks to know the aging effect in radiocolloid formation. Also, the effect of the addition of foreign materials, e.g. silica gel and Fe^{3+} were examined as well as the effect of presence of concentrated electrolyte. In the results, Am appeared to be rapidly adsorbed on to impurity particles for $pH < 6$ and probably on the container walls by an ionic sorption process. The addition of foreign material increased the fraction of Am while the addition of concentrated electrolyte hindered the process. For $pH > 7$ Am behaved quite differently than for $pH < 6$. There appeared to be rapid sorption of some Am from solution probably on the container walls followed by partial desorption that occurred over a period of 1-2 days.

요 약

수용액중에 극미량의 Am의 거동이 pH변화에 따라 변화하는 것을 원심분리법으로 조사하였다. 이 연구에서 평형시간을 2~3주 연장, 방사성 콜로이드 형성에 있어서의 시간효과를 조사하였다. 또한 실리카겔 및 Fe^{3+} 등 외부 물질을 첨가하여 그 효과를 조사하였으며, 또한 진한 전해질물질의 효과도 아울러 조사하였다. 그 결과, pH 6에서 Am은 불순입자, 또는 용기벽과 이온 흡착과정으로 급속히 흡착이 일어났다. 외부물질의 첨가는 Am의 흡착을 촉진하였으며, 진한 전해질물질의 첨가로 흡착이 방해되었다. pH 7에서 Am은 pH 6조건과는 전혀 다른 거동을 나타내었다. 일부 Am은 용기 기벽에서 빠른 흡착이 일어났으며, 1~2일 후에 일부는 탈착되었다.

Introduction

A considerable number of papers have appeared in the literature concerning the physicochemical states of radioisotopes at trace concentration in

aqueous solution⁽¹⁻¹³⁾, however, a general description has not emerged and disagreements exist. These disagreements arise mainly because of different condition and methods used in the studies and, in some cases, because of difference in the interpretation of the some experimental

results.

In particular, several investigations^(14,15,16) have been devoted to the study of the state of ^{241}Am in aqueous solution at trace concentrations as a function of pH. A dispute followed the publication of result and explanation of the nature of possible colloidal formation^(17,18) e.g. adsorption of Am on near colloidal size particles of foreign material (pseudo colloids) versus the formation of colloids by Am itself (true colloids).

From the results of studies on the behavior of ^{241}Am at a concentration of $\sim 10^{-9}\text{M}$ as a function of pH using ultrafiltration, centrifugation, electromigration and direct adsorption techniques. Starik and Ginsburg concluded that the colloidal behavior of Am in aqueous solution at pH values between 6 and 8 resolved from the sorption of positively charged Am species on particles of foreign material, e.g. silicic acid particles, to form pseudo-colloids while true Am predominated at pH values greater than pH 9 where the solubility product for the formation of $\text{Am}(\text{OH})_3$ appeared to be exceeded⁽¹⁸⁾.

However, the results of recent experiments⁽¹⁹⁾ indicate that $\text{Am}(\text{OH})_3$ should not precipitate from 10^{-9}M Solution until pH 11. In order to predict the behavior of Am in aqueous systems in the state of Am at near neutral pH is needed.

Previous investigations of the behavior of Am as a function of pH involved measurements of the system for equilibration times of a few hours up to one or two days. In the studies described here, equilibration times were extended to 2~3 weeks. Also, the effects of the addition of foreign materials, e.g. silica gel and Fe^{3+} (which could be precipitated as $\text{Fe}(\text{OH})_3$), were examined as well as the effect of presence of concentrated electrolyte.

Experiment

Purification of Americium

Purification of the ^{243}Am used in these experiments was accomplished through the use of ion-exchange chromatography. Approximately 3 μgms of ^{243}Am was first adsorbed on to the top of a 3mm diameter by 10cm long Dowex 50 \times 8 cation-exchange resin column from a 0.1N HCl solution. The column was then washed with 3 column volumes of 0.1N HCl followed by 3 column volumes of 3N HCl, the Am^{3+} was then eluted from the column with 3 column volumes of 6N HCl the eluate was taken to near dryness and one ml of 10^{-5}M stock solution of Am prepared by dilution with 0.1N HCl. Alpha pulse height analysis of aliquots of the stock solution, showed the isotopic composition to be 99.8% ^{243}Am , 0.15% ^{241}Am and $10^{-4}\%$ ^{244}Cm by weight.

Method

Investigations of the state of isotopes at trace concentrations are hindered by the absence of methods for studying directly the states of extremely small dimensions and the possibility of altering the equilibria between the various forms that may coexist in solution by the measuring process itself. Of the various methods mentioned above that have been used to study the solutions of Am, precipitation by centrifugation followed by the direct measurement of the concentration of the Am in the bulk solution appears to be the least likely to affect the equilibria and was selected for these studies.

Procedures

To examine the behavior of Am as a function of pH, time and Am concentration, 25ml of 10^{-7}M and $4 \times 10^{-9}\text{M}$ solutions of Am were prepared by dilutions of portions of the stock solution with 0.1N HCl. The pH of these solutions were adjusted from about 1 to 10 in small pH increments by the addition of microliter amounts of concentrated NaOH (or concentrated HCl if back titration was necessary) so that the total solution volume did not change appreciably during the

process. The pH measurements were made with a Beckman model 7401 pH meter using a Beckman model 39505 micro-combination glass electrode. At each step in the pH adjustment, approximately 1.25ml of the solutions were withdrawn and placed in 1.5ml polyethylene centrifuge cones that were fitted with polyethylene stoppers.

These cones were then allowed to stand for up to 3 weeks. At various times during this period, the cones were centrifuged at 5000rpm for 10 minutes with a Beckman microfuge. After each centrifugation, 0.1ml aliquots of the supernates were taken, placed on 1-inch diameter platinum plates, evaporated to dryness with a heat lamp and flamed with a Bunsen burner to burn off residual solids. The alpha activity of each sample was measured with a conventional argon-methane gas flow proportional counter whose voltage was set for alpha particle detection. The percentages of Am precipitated by centrifugation were calculated from the values of the starting Am alpha activity in the solutions (A_i) and the alpha activity in the solution after each centrifugation (A_o), i.e.,

$$\% \text{ precipitated} = \frac{A_i - A_o}{A_i} \times 100$$

To examine the effect of foreign material and concentrated electrolyte, 25ml solutions of $10^{-7}M$ Am were also prepared, and they contain in addition to the Am, (1) 15mg/ml of finely divided silica gel, (2) 15mg/ml of silica gel plus 1M HN_4Cl , (3) $10^{-6}M$ ferric chloride, (4) $10^{-6}M$ ferric chloride plus 1M NH_4Cl and (5) $10^{-6}M$ ferric chloride plus 0.2M CaCl_2 . The pH of these solutions were adjusted as before and about 1.25ml aliquots again placed in 1.5ml centrifuge cones. These aliquots were allowed to stand for about 4 hours and were centrifuged and as sampled for Am as before.

The behavior of Am as a function of pH and time in solution that were not centrifuged was

also examined. Fifteen ml volumes of $10^{-7}M$ Am solutions of the pH values 5.3, 7.0, 8.7, and 11.0 were placed in glass centrifuge cones, stoppered and allowed to stand for about a week. At various times 0.1ml aliquots were taken from the top of each solution and the alpha activity determined as before.

Results and Discussion

Figure 1 shows the fraction of Am precipitated by centrifugation from a solution initially $4 \times 10^{-9}M$ in Am as a function of pH and time. The results obtained after 4 hours standing are quite similar to the results of Starik et al.⁽¹⁷⁾, i.e. a maximum of nearly 100% in the fraction precipitated at a pH of 6~6.5 and the fraction decreasing to ~20% at pH values near 4 and 8. However, the fraction precipitated increase dramatically with time for values of pH 8. The behavior suggests two different mechanisms for the precipitation. At a pH near 6, the particles were sufficiently large that they could be centrifuged from solution under the condition of our

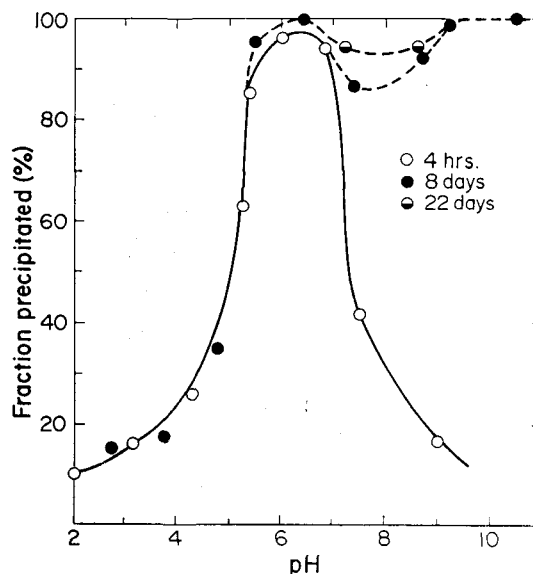


Fig. 1. Fraction Precipitated by Centrifugation of $4 \times 10^{-9}M$ Am against pH with Time.

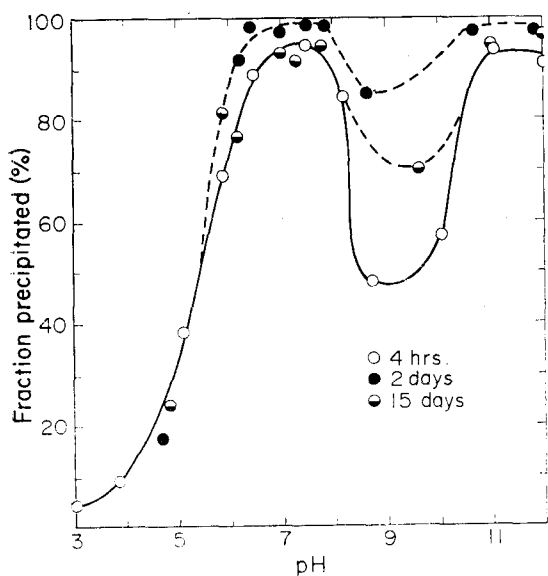


Fig. 2. Fraction Precipitated by Centrifugation of $10^{-7}M$ Am against pH with Time.

experiments, while at pH values greater than 8 the particle were initially too small to be centrifuged from solution but appeared to grow in size with time.

Figure 2. shows the fraction precipitated by centrifugation for an initial Am solution concentration of $10^{-7}M$ as a function of pH and time. As was the case with the $4 \times 10^{-9}M$ Am solutions, a maximum of nearly 100% occurred in the fraction precipitated at a pH about 7 after 4 hours standing. Considerably more Am was precipitated after 4 hours standing in the pH range 8~10 than for the $4 \times 10^{-9}M$ solutions but again the fraction increased with time.

Figure 3. shows the fraction of Am centrifuged from solution after 4 hours standing for an initial Am concentration of $10^{-7}M$ as a function of pH when silica gel was present. The presence of silica gel increased the fraction precipitated for pH values less than 5 compared to the results shown in figures 1 and 2 and enhanced precipitation occurred at pH values near 2 and 4. Nearly complete precipitation occurred for pH values greater than about 7. When the

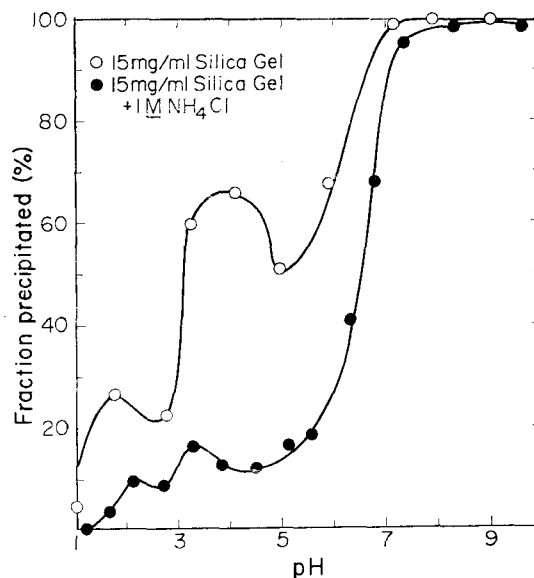


Fig. 3. Fraction Precipitated by Centrifugation of $10^{-7}M$ Am against pH with (a) 15mg/ml Silica Gel and (b) 15mg/ml Silica Gel and 1M NH_4Cl .

system was made in 1M NH_4Cl , precipitation was decreased for pH values less than 5 but remained the same for pH values greater than 7. The behavior of the Am at the lower pH values could be explained as due to the formation of pseudo colloids, i.e., the adsorption of positively charged Am species on the silica gel particle, as suggested by Starik⁽¹⁷⁾, this process should be hindered in the presence of 1 M NH_4^+ ion due to the competition of the Am ion with the more abundant NH_4^+ ions for charged sorption sites. For pH values greater than about 7, the presence of silica gel promoted the precipitation by centrifugation and the addition of NH_4Cl had no effect.

Figure 4 shows the fraction of Am precipitated by centrifugation as a function of pH for an initial Am concentration of $10^{-7}M$ and a ferric ion concentration of $10^{-6}M$ after 4 hours standing. Though not as pronounced as with silica gel, there is an enhancement in the fraction precipitated for pH values less than 5 with peaks at pH values of about 2 and 3.5. According to

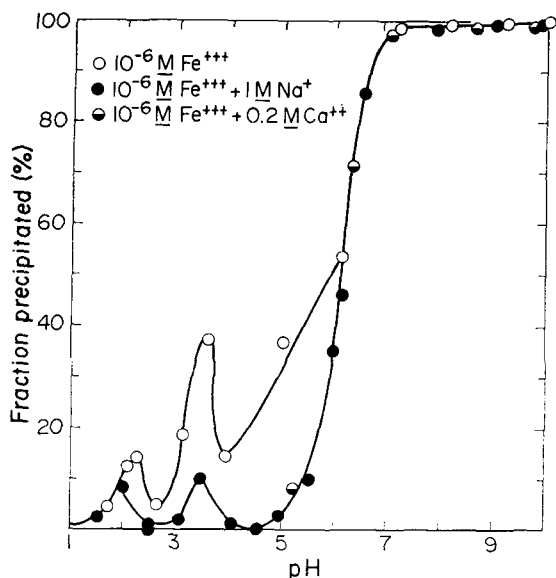


Fig. 4. Fraction Precipitated by Centrifugation of 10^{-7}M Am against pH with (a) 10^{-6}M Ferric Ion, (b) 10^{-6}M Ferric Ion and 1M NaCl, (c) 0.2M Ca Ion.

Baes and Mesmer⁽²⁰⁾, the solubility product of $\text{Fe}(\text{OH})_3$ should be exceeded for pH values greater than about 3 for a 10^{-6}M Fe^{+++} solution. As with silica gel, the presence of Fe^{+++} promoted the precipitation of Am for pH values greater than about 6. The inclusion of 1M Na^+ or 0.2M Ca^{++} ions to the system produced a decrease in the fraction precipitated for pH 5 but produced no change for pH 6.

Figure 5 shows the fraction of Am that remained in solution in the 15 ml glass cones for an initial Am concentration of 10^{-7}M and for pH values of 5.3, 7.0, 8.7 and 11.0 as a function of time. For pH=5.3, there was a decrease in the Am concentration to about 60% of the initial values in a few hours, probably due to adsorption on the container walls. The solution concentration then remained nearly constant for 6 days. For the other pH values, there was an initial decrease to 50~60% of the starting concentration in a few hours which was followed by an increase in the solution concen-

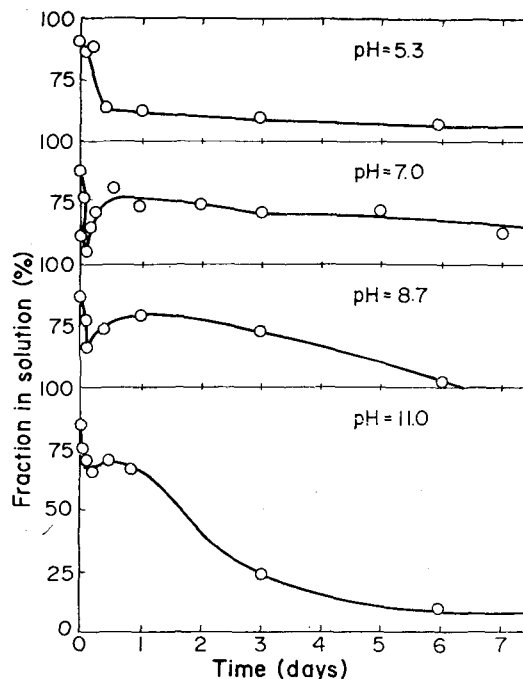


Fig. 5. Percent Fractions of 10^{-7}M Am in 5ml Centrifuge Cone at Various pH Time.

tration that peaked after about one day. The fraction of Am in the solution of pH=7 then decreased only slightly with time while the pH 8.7 and 11.0 solutions showed substantial decreases with time. For all four pH values, there appeared to be rapid adsorption of a large fraction of the Am on to the container walls or on impurities present in the solution. For pH values of 7.0, 8.7 and 11.0, some of this Am appeared to desorb back into solution over a period of about one day. For pH 8.7 and 11.0, this initial increase in Am concentration was followed by a slow disappearance of Am from solution by natural precipitation.

Conclusions

1. For $\text{pH} \leq 6$, Am appeared to be rapidly adsorbed on to impurity particles and probably on the container walls by an ionic sorption process. The addition of foreign material, silica gel

and iron, increased the fraction of Am in this state while the addition of concentrated electrolyte, i.e. cations that could compete with Am for negatively charged sorption sites, hindered the process. These results are consistent with the conclusion of Starik that the colloidal behavior of Am in trace concentration in solution for $\text{pH} \leq 6$ is determined by the adsorption of positively charged ions onto impurity particles in solution to form pseudocolloids.

2. For $\text{pH} \geq 7$, Am behaved quite differently from $\text{pH} \leq 6$. There appeared to be rapid sorption of some Am from solution probably on the container walls followed by partial desorption that occurred over a period of 1~2 days. The latter behavior may be associated with the slow formation and subsequent desorption of hydrolysis products of Am. The Am appeared to form particles of sufficient size to be precipitated by centrifugation only slowly over a period of several days. This process enhanced by the addition of both foreign material and concentrated electrolyte. It is tempting to conclude, as did Starik, that for $\text{pH} \geq 7$ the solubility product for the formation of $\text{Am}(\text{OH})_3$ was exceeded and particles of the hydroxide slowly formed to centrifugable size with time, i.e. the formation of true colloids of Am. The presence of foreign material and concentrated electrolyte could enhance the coagulation process. However, the result of reference⁽¹⁹⁾ suggest that the solubility produced for the formation of $\text{Am}(\text{OH})_3$ should not be exceeded until $\text{pH} \sim 9.5$ for the $4 \times 10^{-9}\text{M}$ solution and $\text{pH} \sim 8.5$ for the 10^{-7}M solution. If this is correct, then there is no ready explanation for the behavior of Am for the pH region 7~8. Hydrolysis species both monomeric and polynuclear, would be expected to be extensive in this pH region, however very little information is available as to their formation constants or behavior. Clearly, further studies are needed for $\text{pH} > 7$ in order to understand the behavior of

trace concentrations of Am in solution in this pH region.

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