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ANION-EXCHANGE STUDIES WITH ACTINIUM AND LANTHANIDES
IN NITRATE SOLUTIONS

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ANION-EXCHANGE STUDIES WITH ACTINIUM AND LANTHANIDES
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In a previous paper we reported that the lanthanides are slightly adsorbed by anion-exchange resins such as Dowex-1 from concentrated HNO_3 solution¹. Further experiments with praseodymium have shown that this element adsorbs more strongly on Dowex-1 from nitrate solutions than from HNO_3 media². This adsorption was found to increase with the nature of the cation of the supporting nitrate solution in the order: $\text{H} < \text{NH}_4 < \text{Li} < \text{Ca} < \text{Cu} < \text{Fe} < \text{Al}$.

These results were extended by Y. Marcus for a number of lanthanides and successful separations between these elements were achieved with the anion-exchange resin in LiNO_3 media³.

In the present communication we report a study on the anion-exchange behaviour of actinium, undertaken with the aim of separating trace-amounts of this rare earth-like element from weighable quantities of its homologue lanthanum.

The separation between actinium and lanthanum was investigated in $30 \times 0.24 \text{ cm}^2$ columns of Dowex-1, 8% DVB, 50-100 mesh, in the ni-

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tric form. Actinium 228 (MsTh II, β , γ , 6.13 h. period) was extracted from Radium 228 (MsTh I, β , 6.7 y. period) according to the procedure of Haissinsky⁴. The purity of the radioelement was controlled by period measurements and from its gamma-energy spectrum, determined in a NaI(Tl) scintillation spectrometer. Activity measurements were made in a scintillation counter. Lanthanum nitrate, prepared from its oxide (Johnson, Matthey Specpure), was detected colorimetrically using sodium alizarine sulphonate⁵.

The nitrates were dissolved in concentrated LiNO_3 solution and introduced in the column. Elution was carried with more dilute LiNO_3 and its course followed by sampling the effluents in volumes of 3 ml., which were analysed radiometrically for actinium and colorimetrically for lanthanum. The results obtained in a typical experiment are shown in Fig. 1. In this experiment 3 ml of a 8.5 M LiNO_3 solution with tracer actinium and 30 mgs of $\text{La}(\text{NO}_3)_3$ were slowly introduced in the column, which had been pretreated with 8.5 M LiNO_3 . Elution was carried with 4.3 M LiNO_3 at a flow rate of 0.4 cm/min. (See Fig. 1).

From column experiments and equilibrium measurements with actinium the following values were obtained for the distribution coefficient $D_v \left(\frac{(\text{Ac})_{\text{resin}}}{(\text{Ac})_{\text{sol.}}} \times \frac{\text{vol. sol.}}{\text{vol. resin}} \right)$ as a function of the molarity of

LiNO_3						
M_{LiNO_3}	2.5	3.1	3.6	4.0	4.4	5.6
D_{Ac}	1.7	3.1	5.1	6.1	10.2	17.5
D_{La}	-	5	10	-	20	-

The results of Marcus have shown that the adsorption of the lanthanides by the anion-exchange resin, at a fixed LiNO_3 concentra-

tion, increases in the sequence $\text{Yb} < \text{Tb} < \text{Eu} < \text{Sm} < \text{Pm} < \text{Nd} < \text{Pr} < \text{Ce} < \text{La}$, which is also the order of increasing ionic radius or increasing basicity in the series³. The adsorption position of Ac in this sequence falls approximately between Sm and Nd. This is somewhat unexpected, since the ionic radius of $\text{Ac}(+3)$ (1.11 Å) is larger than that of $\text{La}(+3)$ (1.06 Å) and its chemical properties are in general those of a more basic element⁶. Moreover, we found that the adsorption positions of the lower homologues of lanthanum, Y and Sc, are approximately at those expected from their relative basicities: $\text{Sc} < \text{Yb} < \text{Y} < \text{Tb} < \dots < \text{La}$.

An anomalous behaviour of Ac with respect to its basicity was reported many years ago by M. Curie and S. Takvorian⁷. These authors observed that during the fractional crystallization of the lanthanon magnesium double nitrates all Ac present concentrates between Sm and Nd instead of accumulating with the more basic fractions. The remarkable analogy with the adsorption position of Ac suggests that the solubility of these double nitrates may be correlated to the adsorption of the lanthanides by the anion-exchange resin. Thus, the solubility of these salts (grs/100 ml H_2O) increases in the order⁸ $\text{La} < \text{Ce} < \text{Pr} < \text{Nd} < \text{Sm}$, which is the reverse of the adsorbabilities of these elements by the resin. Crystalline double nitrates are not obtained with the heavier lanthanides, which is consistent with their low adsorbabilities.

A meaning for these correlations can be given by assuming that the adsorption by the anion-exchange resin is determined by the stability of the nitrate complexes. On this basis, the solubility of the double nitrates of the lanthanides and of actinium decreases with the increase in the tendency toward the formation of nitrate com-

plexes in the series. Similar relations between solubility and complex stability have been reported by Williams for the nitrates of the alkali-earth metals⁹.

A comparison between the anion-exchange behaviour of actinium and americium (+3) (0.99 \AA^3) shows that these elements adsorb from LiNO_3 solutions in the order $\text{Ac} < \text{Am}$. Spectrophotometric and ion-migration studies¹⁰ suggest that $\text{Am} (+3)$ is more complexed by the nitrate ion than $\text{Pu} (+3)$. The adsorbability of these actinides will probably fall in the sequence $\text{Ac} < \text{Pu} < \text{Am}$, which is the order of decreasing ionic radius in the series and the reversal of that observed with the lanthanides. Differences in the tendency toward complex formation between elements of comparable ionic radius such as the lanthanides and the actinides have been attributed to modifications in the character of the metal ligand bonds in the two series¹¹. For the nitrate systems, useful information about this question could be derived from systematic studies on the infra-red spectra of the double nitrates of the lanthanides and of actinides with a bivalent cation, analogous to those done by Gatehouse, Livingstone and Nyholm for $\text{Zn}_3\text{Pr}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ and other nitrate complexes¹².

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