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Abstract

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The Influence of the Radius and Charge of an Ion on Extraction

(The Position of Elements in Separation Series)

In the preceding communication (1), two separation series were presented for extraction with tributyl phosphate—one for the nitrates of the lanthanides and yttrium, and the other for the nitrates of thorium(IV), uranyl (UO_2^{2+}), and cerium(IV). It was shown that in many cases the position in these series does not depend on the concentration of the substances being separated. An element (ion) situated to the left in the series, under repeated extraction, accumulates in the aqueous phase (raffinate) and can be obtained in it in pure form. An element (ion) situated farther to the right accumulates in the extract (organic phase) and can be isolated in pure form in a single operation only in those cases when, in distribution coefficient and in its ability to displace from the organic phase, it considerably surpasses its companion or all accompanying substances. Such is the position with cerium(IV), which displaces from the organic phase all rare-earth elements (r.e.e.) (III), thorium, and even uranyl compounds (1). Therefore it is easy to obtain cerium(IV) in pure form in the extract even when all r.e.e. (III) are present in the aqueous phase (2,3,4).

The separation series of the r.e.e. (III) fully coincides with their arrangement in the periodic system (follows the atomic number), and this has been shown by many experiments both for individual elements and for their groups (cerium and yttrium) in individual separations, as well as in the course of repeated extraction (3,5). When r.e.e. (III) are washed out of the extract by an aqueous solution of the heavy r.e.e. (III) or Ce(IV), the direct order of their appearance in the aqueous phase should be observed, i.e., the reverse of that known in elution with a complexing agent in ion-exchange chromatography (6). All this can readily be predicted, since these processes are explained analogously—the strength of complex compounds of the r.e.e. (III) increases as the radius of the element ion decreases. Under the action of organic solvents, such a complex compound is the solvate and, obviously, the element (ion) possessing the strongest solvate will accumulate in the organic phase. The element that gives a less strong solvate, or does not form one at all, will accumulate in the aqueous phase (raffinate).

On the relationship between the stability of complex compounds of the lanthanides and actinides and the reciprocal of the ionic radius of the r.e.e. (III) (see, for example, (7), p. 48). The heat of hydration of r.e.e. (III) ions monotonically follows the atomic number and is inversely proportional to the ionic radius (14), vol. 1, pp. 159-160). A stability series is also known for complex compounds of other trivalent elements; namely, strengthening is observed with decreasing ionic radius: La $<$ Y $<$ Sc $<$ Al. In accordance with this, yttrium should be placed in our series after lanthanum, and, taking its ionic radius into account, after gadolinium (around holmium), which was established long ago, in particular by us (3). The arrangement in the second separation series during extraction, namely: ThIV—UO_2^{2+}—Ce(IV), can likewise be explained from the same standpoint–the strength of the solvates; thus, the ionic radius of Th(IV) is taken to be 7% larger than that of cerium(IV), and therefore the greater strength of the solvates of cerium(IV) is obvious. Special

our studies (8) showed the possibility of obtaining pure thorium in the raffinate when it is washed out with an aqueous solution of cerium(IV) from a combined extract; the position of Ce(IV) to the right of Th(IV) in the series also follows from the distribution and separation diagrams for $Th(NO_3)_4$–$Ce(NO_3)_4$–HNO_3–H_2O–$(C_4H_9O)_3PO$ (1,8). The latter method of establishing the position of elements in the series is important in that it simultaneously shows the independence of this position in the series from any change in the concentrations of the given system.

The greater stability of uranyl complex compounds in comparison with thorium(IV) is well known. If this situation is extended to the solvates formed by these two members of the series, then the position of uranyl to the right of thorium will be quite natural. Specially studied distribution and separation diagrams for $Th(NO_3)_4$–$UO_2(NO_3)_2$–H_2O–$(C_4H_9O)PO$ (1) showed that thorium does indeed accumulate in the raffinate, while uranyl nitrate accumulates in the extract, independently of the concentration of the extracted salts. The displacement of thorium by uranyl nitrate from the organic phase into the aqueous phase is interesting in many respects.

The question of which of the two ions, Ce(IV) or $UO_2^{\cdot\cdot}$, will occupy the rightmost position in this series, i.e., which of them has the stronger solvates, is difficult to decide from general considerations, and therefore the distribution and separation diagrams of the system $UO_2(NO_3)_2$–$Ce(NO_3)_4$–H_2O–$(C_4H_9O)_3PO$ (1,9) were studied. It turned out that, independently of the concentration of both substances, cerium(IV) accumulates in the extract and uranyl nitrate in the raffinate. But the difference in the values of the distribution and separation coefficients is relatively small (1), i.e., the strength of their solvates differs little.

Thus, understanding the position of the individual members for each series considered separately proved possible from the simplest point of view (the strength of the solvates) and only in two or three cases out of 20 did the problem have to be solved on an experimental basis.

At first glance, the problem of uniting (conjugating) the two series seems more complicated. It will be necessary to solve the same question of the stability of complexes for ions not only of different size, but also of different valence, namely 3, 4, and 6. The amount of experimental material here is much smaller, and there is not yet a single distribution and separation diagram for a system with one lanthanide and one actinide element. It was already noted earlier in this article that Ce(IV) salts out all rare-earth elements (III) from the organic phase into the aqueous phase. Thus, cerium(IV) lies to the right of all in the series for rare-earth elements (III). It remains to decide the place of thorium(IV), considering that the place for uranyl has more or less been determined, namely after thorium and before cerium(IV), because of the closeness in stability of the solvates with the latter (see above).

The strength of the solvates of lanthanum and nitric acid is close (somewhat greater for nitric acid), which determines the complexity of the distribution and separation diagrams for the system HNO_3–$La(NO_3)_3$–H_2O–$(C_4H_9O)_3PO$ (1,10). Meanwhile, the difference in the strength of the solvates of the same nitric acid and thorium is very significant and leads to large separation coefficients (1,11). Thus, there is no doubt that the strength of the solvates of lanthanum and thorium(IV) is very different and greater for thorium. This also follows from the smaller radius (by 10%) and the greater charge of the thorium ion. Above, a series of stability of complex compounds was given for trivalent ions: La $<$ Y $<$ Sc $<$ Al; on this basis, the strongest solvates should be expected for aluminum. In our previous work (12), a curve is given for salting out aluminum nitrate with thorium nitrate from the organic phase (isoamyl alcohol). This may serve as an indication that thorium(IV) in the combined series may be located to the right of yttrium and all yttrium rare-earth elements (III). Confirmation of the same may be provided by the series of stability of complex compounds for other purposes, considered by A. A. Grinberg and K. B. Yatsimirskii (13). For the elements included in it, approximately

equal ionic radii, while the charge increases from one to four, namely

Na $<$ Ca $<$ Y $<$ Th.

Thus, the position of thorium (IV) in the combined separation series to the right of all the rare-earth elements (III) appears probable from many points of view and on the basis of a number of direct and indirect experimental data; after thorium (IV) in the joint series should follow the uranyl ion and cerium (IV). For confirmation of the expectations concerning the influence of the uranyl ion on the extraction of rare-earth elements (III), see (15).

The series given above, Na $<$ Ca $<$ Y $<$ Th, also has a more general significance for the extraction of nitrates. Nitric-acid sodium is practically not extracted into TBP. As was shown by investigations by I. I. Yakovlev in our laboratory of the system $NaNO_3$–$Ca(NO_3)_2$–H_2O–$(C_4H_9O)_3PO$, calcium nitrate already begins to be extracted into tributyl phosphate, but, admittedly, together with a noticeable amount of water (16). The distribution coefficient for yttrium for small amounts reaches 6, while for thorium it attains large values with a smaller dependence on its own concentration. Both of the latter salts are extracted without water.

Thus, the hydrates are more stable than the solvates for sodium nitrate; for divalent calcium the stabilities of hydrates and solvates are commensurate, while for trivalent yttrium and especially for tetravalent thorium the solvates with TBP are significantly more stable than their hydrates.

The foregoing indicates that much work still remains to be done, both on distribution and separation diagrams and on the thermochemistry of extraction processes, in order to illuminate the numerous questions that have arisen concerning the joint separation series in extraction for the lanthanides and actinides. But even now it is emerging with considerable definiteness:

La . . . HNO_3 . . . Sm . . . Gd . . . Y . . . Yb . . . Lu . . . ThIV . . . $UO_2^{\cdot\cdot}$ . . . CeIV.

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