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DIAGRAMS AND SEPARATION SERIES IN EXTRACTION

Extraction rays (L) in a number of cases converge at one point (pole), corresponding to the composition of the substance extracted from the aqueous phase. This may be a compound of simple composition, for example HNO_3, or a complex compound, for example $HFeCl_4 \cdot 6H_2O$. In the first case, a sufficiently pure single component may be extracted into the extract*, while in the second, no separation occurs in the extract. But in all cases the extraction rays end on one of the coordinate axes, which means that one of the components is obtained in concentrated form in the raffinate. It has long been known that components can accumulate separately in the raffinate and in the extract, and the purpose of the present article is an attempt to find the laws governing this separation.

When acid is present in the aqueous phase, either divergence of the extraction rays occurs (there is no pole), or they become curved (^{1}). In the first case, salt and acid pass into the extract in a variable ratio which, however, remains constant for each ray and does not change from ray to ray. This case is usually observed in the region of elevated acid concentrations (three rays in Fig. 1 *I*). Curvature of the ray is observed near the coordinate axis, when little of the extracted component remains and it can no longer prevent the second component from passing into the extract (salting it out from it (^{2})). However, this curvature of the ray does not prevent it from reaching the coordinate axis, i.e., the concentration of the second component in the raffinate. The concentration of one or another component in the raffinate, when the complex extracted from the aqueous phase has a complex composition (for example, $HFeCl_4 \cdot 6H_2O$), depends on the composition of the initial solution. Thus, in Fig. 1 *IV* two rays are shown (a and b), and the compositions of the initial solutions are indicated by crosses. Ray a gives a raffinate enriched in component B, while ray b gives one enriched in component A: this is the excess of one or the other component remaining after extraction of the complex $HFeCl_4 \cdot 6H_2O$.

In a number of systems (Fig. 1 *II* and 1 *IV*) the extraction rays end in the region of slight extraction (^{3},^{4}), where separation is impossible; in drawings II and IV these regions are bounded by limiting extraction rays c and are designated H.

Fig. 1

Figure 1: Fig. 1

The above follows from the phase equilibria studied by us in extraction. In the present article a new type of extraction diagrams is proposed, in which, in the delamination region, in rectangular coordinates (^{1}), instead of the distribution coefficient, the separation coefficients $\beta = K'_{\text{distrib}}/K''_{\text{distrib}}$** are plotted. In doing so, we sought to make the value of β greater than unity (when $\beta \leqslant 1$, there is no separation, or the substance accumulates in the raffinate). In naming the systems (see Table 1), the component passing into the extract is written first and is plotted on the abscissa axis, while the component accumulating in the raffinate is written second and is plotted on the ordinate axis. Of the extraction systems we have studied (^{1}), 9 are considered here, in which the extraction into the organic phase of two components has been studied in sufficient detail. It turned out that four types of separation diagrams stand out rather clearly (Fig. 1).

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* The other components are present in the extract as an irregular impurity.

** A separation diagram for the system $Ce(NO_3)_4$—$Th(NO_3)_4$—H_2O—TBF was constructed as early as 1960 in the dissertation of Yu. A. Afanas' eva (^{5}).

Fig. 1

Type I (Fig. 1 *I*)–the course of the isolines of the separation coefficient β does not depend, or depends only slightly, on the concentration of the second component, and therefore they run perpendicular to the abscissa axis; as the concentration of the extracted component decreases, the value of β increases (the horizontal direction of the feathered arrow).

Table 1

No.	System	β max.	β min.	Diagram type	Source
1	$Th(NO_3)_4$–$Ce(NO_3)_4$–H_2O–	256	3.6	I	(5)
2	$UO_2(NO_3)_4$–$Ce(NO_3)_4$–H_2O–	4.65	0.9	I	(6)

No.	System	β max.	β min.	Diagram type	Source
3	HNO_3–$UO_2(NO_3)_4$–H_2O–	27000	3.5	I	(7)
4	HNO_3–$Ce(NO_3)_4$–H_2O–	234	1.91	I^1	(8)
5	HNO_3–$Th(NO_3)$–H_2O–	51.4	2.3	I^1	(9)
6	HNO_3–$UO_2(NO_3)_2$–H_2O–	222.0	1.6	I^2	(10)
7	$La(NO_3)_3$–HNO_3–H_2O–	12.3	0.4	II	(1)
8	$Th(NO_3)_4$–$UO_2(NO_3)_2$–H_2O–	41.4	7.3	III	(1)
9	HCl–$FeCl_3$–H_2O–$(C_2H_5)_2O$	232	0.1	IV	(4)

Type II (Fig. 1 *II*)—the value of β increases with increasing concentration of the component accumulating in the raffinate (see the direction of the feathered arrow). This phenomenon is analogous to salting-out* when considering $K_{\text{distr.}}$. The isolines of β intersect the abscissa axis at an acute angle.

Type III (Fig. 1 *III*)—the values of β decrease with increasing concentration of the component accumulating in the raffinate (see the direction of the feathered arrow); closed curves and curves with a maximum for the isolines of β are very curious. It should be noted that the maxima of these curves lie quite well on one smooth curve going toward the abscissa axis.

* By analogy with a salting-out agent, these substances may be called separating agents.

Type IV (Fig. 1 IV) is intermediate between types II and III and is singled out specially in view of the fact that here there is a rare possibility of concentrating both components in the raffinate (rays *a* and *b*), as was stated above. In the region of ray *a* the values of β are greater than unity; for ray *b* they are less than unity, as was to be expected, since different components accumulate in the raffinate.

Types I^1 and I^2 are intermediate between I and II: with increasing concentration of the component passing into the extract, the isolines of β bend. In the case of I^2, part of the β isolines is cut off by the saturation branches of the solubility curve in the aqueous phase.

Table 1 gives examples of extraction systems with their assignment to one or another type of separation diagram. The maximum and minimum values of β are also given.

The existence of type I separation diagrams (Fig. 1 I) makes it possible to assume so great a strength of the solvates $Ce(NO_3)_4$ that an increase in the concentration of thorium or uranium nitrates does not significantly affect the separation. Practically, in system No. 1 (Table 1), the β isolines in the upper part of the diagram deviate somewhat to the right, i.e., separation improves at the very highest concentrations of thorium nitrate.

In system No. 2 the β isolines form with the abscissa axis an angle somewhat smaller than 90°. There are many grounds for believing that the solvates of uranyl nitrate are only slightly inferior in strength to the solvates of CeIV. Hence, in particular, follow the small values of β, smaller than for the case of thorium and CeIV (by up to 50 times), and even a reversal of the separation at high concentrations, when, to be sure, β in one case becomes less than unity (0.96).

Systems Nos. 3–6 are of interest in that in all cases nitric acid accumulates in the raffinate, irrespective even of the extractant (DEHP or TBP). In TBP the maximum values of β for nitric acid and uranyl nitrate or Ce IV nitrate are approximately the same (up to 220), while for thorium nitrate they are four times smaller. One may suppose that thorium nitrate displaces nitric acid from the extract to a lesser extent. For lanthanum nitrate and nitric acid (system No. 7) the mutual influence upon transfer to the extract is approximately the same, but, judging from the extraction rays, lanthanum nitrate nevertheless accumulates in the raffinate. The minimum value of β lies at high concentrations of nitric acid.

Uranyl nitrate relatively easily displaces thorium nitrate into the raffinate. But in this case (system No. 8) the maximum value of β is not near the ordinate axis, as in all other cases, but near the abscissa axis at medium concentrations of uranyl nitrate (Fig. 1 III).

From the foregoing we obtain that by changing the concentration of the components for TBP it is not possible to reverse the extraction separation, for example in the sense of changing accumulation of a component in the raffinate to accumulation in the extract*, and from this follows the possibility of constructing a series for extraction analogous to the electromotive series for metals. We propose to call it the **extraction separation series**. In this series any substance standing to the left of a given one will accumulate in the raffinate, and one standing to the right—in the extract.

This series for nitrates and tributyl phosphate is represented in the form

$$\begin{array}{l}\text{Nitrates, insoluble}\\ \text{in the organic phase}\end{array} \left\| \; \cdots H_2O \cdots La \cdots HNO_3 \cdots Th \cdots UO^{\cdot\cdot} \cdots CeIV. \right. \tag{1}$$

From consideration of it, in particular, it follows that by the action of an aqueous solution of $Ce(NO_3)_4$ one can displace from the extract all other substances entering into it. Thus, in addition to other conditions, by selection of a second extracted component it is possible to direct the separation of the substance taken,

* For the 20 systems studied, no case was observed in which the pole of the extraction rays shifted from one coordinate axis to the other ([1]).

i.e., to accumulate it, as desired, in the raffinate or in the extract. For example, thorium nitrate will accumulate in the extract in the presence of nitric acid of any concentration or of lanthanum nitrate. But in the presence of CeIV nitrate or uranyl nitrate, thorium will concentrate in the raffinate. Displacement from the extract by nitric acid is clearly shown in [12,13].

Earlier, together with A. A. Sorokina [2], we established the displacement from the organic phase into the aqueous phase of the cerium rare earths and of both groups of rare-earth elements by cerium(IV) nitrate. Its action is so striking that it is easy to separate from indicator amounts of the daughter product Ce^{144}, namely from Pr^{144} [11]. Here, by analogy with what was set forth above, our results for concentrated HNO_3 can be expressed in the form of the following separation series

$$La \ldots Pr \ldots Sm \ldots Y \ldots Ho \ldots Yb \ldots Lu \ldots Ce\,IV, \tag{II}$$

which obeys the same rules as series (I). It should be noted that the sum of the yttrium earths, at its total concentration of 5%, reduces by half the extraction into the extract not only of Nd and Sm, but also of Y and Ho. The extraction of Yb is reduced by this addition only by 30%; Ce IV readily reduces the extraction of Ho by half, etc.

In order to link these two separation series into one general series for actinides, it is necessary to find the place for nitric acid, thorium nitrate, and uranyl nitrate. Undoubtedly, thorium is located to the right of the cerium rare-earth elements, while uranyl nitrate immediately precedes Ce IV. Even with these assumptions, the general series requires further study and refinement.

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