SALTING-OUT COEFFICIENTS, CURVES, AND DIAGRAMS IN EXTRACTION

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The distribution coefficient introduced by Nernst describes sufficiently fully the basic process of extraction and other similar methods, in which two phases and one distributed component participate. However, when not one but two or more substances are distributed, a whole series of new questions arises, connected with their influence on one another. Such questions include the measure of the change in extraction or separation when, for example, a fourth component is introduced into a ternary system. Of particular importance is establishing the dependence of the magnitude of salting-out on the concentration of this fourth component.* We have introduced a new coefficient for distribution systems whose component number is equal to four or more. The essence of this salting-out coefficient is seen from the following expression:

$$\frac{K_{\text{dist}}^{\text{IV}}}{K_{\text{dist}}^{\text{III}}} = K_{\text{salt}}^{\text{IV}},$$

the Roman numerals in the subscripts are an indication of the component number of the system to which the distribution and salting-out coefficients refer; of course, the distribution coefficients are taken at one concentration of the substance being distributed. Experience in the application of salting-out coefficients has shown that they may be: a) greater than unity—extraction in the quaternary system is greater than in the ternary system—the phenomenon of salting-out from the aqueous phase; b) less than unity—extraction in the quaternary system is less than in the ternary system—the phenomenon of salting-in (salting-out from the organic phase); c) equal to unity, i.e., the fourth component does not affect the distribution.

For $K_{\text{salt}} \geq 1$ we propose the subscript "w," i.e., $K_{\text{salt}}^{\text{w}}$ ("w" is the initial letter of the word "water" phase), since it is usually accepted that salting-out of this type proceeds from the aqueous phase.

For $K_{\text{salt}} \leq 1$ the subscript "o" is proposed, since it has been shown that the decrease in extraction (salting-in) proceeds through the organic phase ([1,5]), salting-out occurs precisely from it. $K_{\text{salt}}^{\text{o}}$ is often more conveniently replaced

Fig. 1. Salting-out curves $K^{\mathrm{v}}_{\mathrm{sal}}$ for $\mathrm{La(NO_3)_3}$ with salting-out agent $\mathrm{NH_4NO_3}$.

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by the reciprocal value $1/K^{\mathrm{o}}_{\mathrm{salt}}$; let us note in advance that salting-out and salting-in may proceed simultaneously, pass one into the other, etc.

Of interest are the dependences of $K^{\mathrm{w}}_{\mathrm{salt}}$ and $K^{\mathrm{o}}_{\mathrm{salt}}$ on the concentration of the fourth component. The curves expressing this dependence are called **salting-out curves**.

Salting-out curves have been obtained by us for 12 quaternary systems, in which one, two, or more components are extracted into the organic phase: acids, salts of actinides, lanthanides, iron, etc.; the extractants are tributyl phosphate, BEDP, and ether; the acids are nitric and hydrochloric; the salting-out agents are ammonium nitrate, lanthanum nitrate, ferric chloride, etc. The variety of substances entering into the systems studied ([1,2]), and the considerable number of systems, allow us to consider that the conclusions obtained have general significance.

* A ternary distribution system is described sufficiently fully by the distribution coefficient and its change with the concentration of the extracted ion.

First of all, we shall give several definitions based on the concept of the salting-out coefficient.

A **salting-out agent** is a component of a quaternary system for which $K^{\mathrm{v}}_{\mathrm{sal}} \gg 1$. It is usually chosen so that it does not pass into the organic phase. The component of a quaternary system for which $K^{0}_{\mathrm{sal}} \leqslant 1$ is called the **second subordinate** component.

The component of a quaternary system that causes salting out of the second component is called the **dominating** component, or the **dominant**. For the dominant itself $K_{\mathrm{sal}} = 1$, but it may undergo salting out from the aqueous phase (see below), which does not contradict its dominant position in the organic phase and its ability to salt out specifically from this phase. For quaternary systems, the processes in extraction are more numerous and more varied than for ternary systems, and they are well described by salting-out coefficients and curves.

Fig. 1. Salting-out curves $K^{\mathrm{v}}_{\mathrm{sal}}$ for $\mathrm{La(NO_3)_3}$ with salting-out agent $\mathrm{NH_4NO_3}$. 1 –4%, 2 –7.8%, 3 –14.5%, 4 –20 and 33.5% $\mathrm{La(NO_3)_3}$

At present it has been possible to establish three regularities for the dependence of K_{sal} on the concentration of the fourth component:

1. Direct proportionality between $K^{\mathrm{v}}_{\mathrm{sal}}$ and the concentration of the salting-out agent
   ($K^{\mathrm{v}}_{\mathrm{sal}} = a + bC_{\mathrm{sal}} \gg 1$).

2. $K_{\text{sal}}^{\text{v}}$ for the dominant is usually equal to unity.* In this case there is no salting out from the organic phase of the dominant itself, and only its salting out from the aqueous phase is possible (5).
3. For K_{sal}^{0} of the second component, the dependence on the concentration of the dominant is complex and usually passes through a minimum.

The salting-out curves for $K_{\text{sal}}^{\text{v}}$ are indeed rectilinear, and as an example we present them in Fig. 1 for the system NH_4NO_3—$La(NO_3)_3$—H_2O—TBP. The lower the concentration of the distributed substance ($La(NO_3)_3$), the greater the slope of the curves, i.e., the greater the salting-out. For 35% lanthanum solutions the salting-out curves run almost horizontally, i.e., they depend very little on the concentration of the salting-out agent.

A rectilinear course of the curves of salting out from the aqueous phase has also been noted for the following systems (the salting-out agent is given first):

$$NH_4NO_3\text{—}UO_2(NO_3)_2\text{—}H_2O\text{—TBP}; \tag{1}$$

$$La(NO_3)_3\text{—}HNO_3\text{—}H_2O\text{—TBP}; \tag{2}$$

$$HCl\text{—}FeCl_3\text{—}H_2O\text{—}(C_2H_5)_2O. \tag{3}$$

It should be noted that for system (2) there are two cycles of change in the angle of slope of the salting-out curves: cycle I –from 0 to 37% HNO_3, and cycle II –from 37 to 70% HNO_3. This is one of the reasons for the complexity and peculiarity of this system (3). The situation is also interesting in the third system: with HCl as the salting-out agent, the change in K_{sal} follows a strictly rectilinear law; the salting-out curves from the aqueous phase for the salting-out agent $FeCl_3$ of the same system change slope, as indicated above, but are not straight lines, and a number of them pass through a maximum. The explanation here is the same as for the two salting-out cycles in system (2): the transfer into the extract of two components and the presence of their mutual influence in the organic phase (the dominants are ferric chloride and nitric acid).

For the salting out of cerium nitrate (the dominant) by thorium nitrate (the second component), regions of local increase are observed at low–

* That is, only the concentration of the dominant itself determines its K_{dist}, independently of the content of the second extracted component.

···concentrations. The rectilinear horizontal segments of these curves are also located at $K_{\text{sal}}^{\text{aq}} > 1$.

In addition to the case indicated, salting-out from the aqueous phase of the dominant component is observed in the system $UO_2(NO_3)_2$—$Th(NO_3)_4$—H_2O—TBP, etc.

$K_{\text{sal}}^{\text{aq}} = 1$ for the dominant components (given first) is observed for the following systems:

$$\text{UO}_2(\text{NO}_3)_2\text{—HNO}_3\text{—H}_2\text{O—TBP}; \tag{4}$$

$$\text{UO}_2(\text{NO}_3)_2\text{—HNO}_3\text{—H}_2\text{O—BEDP}; \tag{5}$$

$$\text{Th}(\text{NO}_3)_4\text{—HNO}_3\text{—H}_2\text{O—TBP}; \tag{6}$$

$$\text{Ce}(\text{NO}_3)_4\text{—HNO}_3\text{—H}_2\text{O—TBP}. \tag{7}$$

For these dominant components the isolines K_{dist} of the distribution diagram in rectilinear coordinates are straight lines running perpendicular to the abscissa axis (6).

Unusually complex are the distribution diagrams of the second components, and as an example we present system (4). The salting-out curves K_{sal}^0 for it (4) pass, for all concentrations, through a minimum (Fig. 2),

Fig. 2

Fig. 3

Fig. 2. Curves K_{sal}^0 for HNO_3 in the system $\text{UO}_2(\text{NO}_3)_2\text{—HNO}_3\text{—H}_2\text{O—TBP}$: 1–5%, 2–10-30%, 3–50% HNO_3

Fig. 3. Salting-out diagram (K_{sal}^0) for HNO_3, dominant component—$\text{UO}_2(\text{NO}_3)_2$

and for $1/K_{\text{sal}}^0$ this will be a maximum. The presence of a maximum is also characteristic of the distribution curve of nitric acid alone (the ternary system). All this leads to the complexity of distribution diagrams of this type (the presence of closed regions of the K_{dist} "valley," etc.). In addition, the maxima of the salting-out curves for $1/K_{\text{sal}}^0$ in each system are located at different concentrations of the dominant component and differ in shape and magnitude.

In systems where two dominant components close in strength of action are encountered (for example, uranium and thorium nitrates), the salting-out curve $1/K_{\text{sal}}^0$ first follows an exponential, and then, at high contents, passes into a horizontal plateau (manifestation of the influence of the concentration of the second component). But for the system $\text{Ce}(\text{NO}_3)_4\text{—UO}_2(\text{NO}_3)_2\text{—H}_2\text{O—TBP}$, where the dominant components are even closer in strength of action, the salting-out curves ($1/K_{\text{sal}}^0$) are rectilinear, which leads to distinctive diagrams

distribution of both extracted substances (the isolines run at an obtuse angle to the abscissa).

The absolute dominant is $Ge(NO_3)_4$ ([2,5]), and the second (subordinate) component is always water (for more detail, see the separation series in extraction ([2])).

Salting-out curves may also be considered as isoconcentrates for $K^{\mathrm{w}}_{\mathrm{sal}}$ or K^{0}_{sal} in a new type of **salting-out diagrams**. On the composition field of a ternary aqueous system, the values of $K^{\mathrm{w}}_{\mathrm{sal}}$ or K^{0}_{sal} are plotted and, by drawing isolines for their equal values, these diagrams are obtained (see Fig. 3 for K^{0}_{sal} of nitric acid in system 4).

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