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## Abstract

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# ON THE ORDER OF ARRANGEMENT OF ZONES

# IN PRECIPITATION CHROMATOGRAMS

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The aim of the present work is to derive relations, in as general a form as possible, that predict the sequence of precipitation and the order of arrangement of zones in precipitation chromatograms. The formulation of such a problem is due to the insufficient development of this question in the literature devoted to precipitation chromatography ($^{1-3}$), especially as regards the influence of the ratio of the concentrations of the chromatographed ions and of the concentration of the precipitating ion on the sequence of arrangement of precipitate zones.

First of all let us consider the question of the sequence of precipitation under static conditions. We have a system consisting of ions $A_i^{z_i+}$, each of which is capable of giving a sparingly soluble compound with a common precipitating ion $B^{z_0-}$, also introduced into the system:

$$\frac{z_0}{s_i}A_i^{z_i+} + \frac{z_i}{s_i}B^{z_0-} \rightleftarrows (A_i)_{z_0/s_i}B_{z_i/s_i}\downarrow;$$

$s_i$ is the common divisor of the values $|z_0|$ and $|z_i|$ (the stoichiometric divisor).

A sparingly soluble compound is formed when, in solution, the product of the activities of the ions composing it exceeds the solubility product $L_i$

$$L_i^{s_i} = a_i^{z_0}a_0^{z_i} = (f_ic_i)^{z_0}(f_0c_0)^{z_i}, \tag{1}$$

where $a_i$ are the activities of the ions, $f_i$ are activity coefficients, and $c_i$ are equilibrium molar concentrations ($a_i = f_ic_i$); the index $i$ corresponds to the precipitated ions and their precipitates, while the subscript zero corresponds to the precipitating ion.

This excess can be characterized by the value of the supersaturation factor $\Pi_i$, equal to the ratio of the product of the activities (concentrations) of the ions in the initial state (denoted by the superscript zero) to the product of the ion activities at equilibrium, i.e., to the solubility product

$$\Pi_i = (f_i c_i^0)^{z_0} (f_0 c_0^0)^{z_i} / L_i^{s_i}. \tag{2}$$

Precipitation is possible when $\Pi_i > 1$, and the first ion $A_i$ to begin precipitating in the given system will be the one that produces the greater supersaturation of the solution in the system, i.e., one should consider the ratio of supersaturations

$$\Pi_{12} = \Pi_1 / \Pi_2 = (f_1 c_1^0 / f_2 c_2^0)^{z_0} (f_0 c_0^0)^{z_1 - z_2} L_2^{s_2} / L_1^{s_1}. \tag{3}$$

In a three-component system, when $\Pi_{12} > 1$ the precipitate $A_1B$ is formed first, and when $\Pi_{12} < 1$ the precipitate $A_2B$ is formed. In the case $\Pi_{12} = 1$, both ions initially precipitate simultaneously; however, during precipitation the concentration ratio will change in such a way that the value of $\Pi_{12}$ will decrease when $z_1 > z_2$, and increase when $z_1 < z_2$, i.e., conditions are created for preferential precipitation of the ion with the lower valence.

Thus, in the general case the order of precipitation depends both on the ratio of the initial concentrations of the ions being precipitated and on the magnitude of the initial concentration of the precipitating ion (in the case when the precipitated ions have different valences). For a given ratio of the initial concentrations of two precipitated ions $c_1^0/c_2^0$, there is a value of the concentration of the precipitating ion, $c_{0,\mathrm{inv}}^0$, at which inversion of the order of precipitation of these two ions occurs. The quantity $c_{0,\mathrm{inv}}^0$ can be calculated from the condition $\Pi_{12} = 1$:

$$c_{0,\mathrm{inv}}^0 = \frac{1}{f_0} \left[ \left( \frac{f_2 c_2^0}{f_1 c_1^0} \right)^{z_0} \frac{L_1^{s_1}}{L_2^{s_2}} \right]^{1/(z_1 - z_2)}. \tag{4}$$

If $z_1 > z_2$, then for $c_0^0 > c_{0,\mathrm{inv}}^0$ the precipitate $A_1B$ is formed first, while for $c_0^0 < c_{0,\mathrm{inv}}^0$ the precipitate $A_2B$ is formed. For the case $z_2 > z_1$ we obtain the reverse relations.

A clear confirmation of the considerations expressed can be obtained, for example, in the following simple experiment. To a solution containing the ions $\mathrm{Cl}^-$ and $\mathrm{CrO}_4^{2-}$, a solution of $\mathrm{AgNO}_3$ of various concentrations is added dropwise. Knowing the values of the solubility products of the precipitates AgCl and $\mathrm{Ag_2CrO_4}$ ($1.78 \cdot 10^{-10}$ and $1.1 \cdot 10^{-12}$) (4), for an equimolar mixture of $\mathrm{Cl}^-$ and $\mathrm{CrO}_4^{2-}$ from equation (4) we obtain $c_{\mathrm{Ag,inv}}^0 \simeq 6 \cdot 10^{-3}\, M$; moreover, for $\mathrm{AgNO}_3$ solutions with concentrations lower than the calculated critical value, formation first of an AgCl precipitate and then of $\mathrm{Ag_2CrO_4}$ is expected, whereas at a higher concentration of $\mathrm{AgNO}_3$ the reverse is expected. Indeed, in the first case a white precipitate (AgCl) is formed first, while in the second case the color of the precipitate at the first instant is red ($Ag_2CrO_4$); however, with this arrangement of the experiment the color of the precipitate in the second case quickly changes to white, since the concentration of $Ag^+$ in the course of precipitation rapidly falls below the critical value and the order of precipitation changes to the opposite one, while the initially formed $AgCrO_4$ precipitate dissolves when there is a deficiency of $Ag^+$.

In an analogous manner one can calculate the critical ratio of the initial concentrations of the precipitated ions at which, in the given system, a change in the sequence of precipitation occurs:

$$\left(\frac{c_1^0}{c_2^0}\right)_{\text{inv}} = \left(\frac{L_1^{s_1}}{L_2^{s_2}}\right)^{1/z_0} \frac{f_2}{f_1} \left(f_0 c_0^0\right)^{(z_2 - z_1)/z_0} . \tag{5}$$

It follows from this equation that only in the case of equal-valence precipitated ions ($z_1 = z_2$) is the ratio of their initial concentrations at which inversion of the precipitation sequence may occur a constant quantity independent of the concentration of the precipitating ion. Experimental confirmation of the inversion of the order of precipitation under such conditions was given by St. Ivanov (2).

The sequence of arrangement of zones in precipitation chromatograms depends, as is known, on the order in which the corresponding ions precipitate (3). The law of constancy of solubility products, on the basis of which the order of precipitation of ions in a given system is determined, is a general law, independent of the conditions under which precipitation is carried out. Therefore, everything said above about the order of precipitation under static conditions is in principle also valid for the case of precipitation under dynamic conditions. However, the distinctive nature of dynamic conditions leaves its mark on the character of the precipitation processes.

Let us consider a variant of ion-exchange precipitation chromatography often used in practice. In this variant, a solution of the electrolyte $AM$ is passed through a support that is an ion exchanger ($R$) and is saturated with the ion $B^-$. The first stage of the complex process is ion exchange:

$$\mathrm{R{-}B} + \mathrm{A}^+ + \mathrm{M}^- \rightleftharpoons \mathrm{R{-}M} + \mathrm{B}^- + \mathrm{A}^+.$$

As a result, the ion $B^-$, which subsequently performs the function of the precipitating ion, passes from the ion-exchanger (carrier) phase into the solution. The concentration of the ion $B^-$ in the solution increases, and as soon as a certain supersaturation of the solution with respect to the solubility product is reached, a precipitate $AB$ begins to form. If a mixture of electrolytes $A_1M$, $A_2M, \ldots (A_{iM})$ is introduced into the column, then precipitates of the corresponding sparingly soluble compounds $A_{iB}$ will be formed in the order in which their solubility products are reached. In the present case it is more appropriate to introduce into consideration the value of the maximum concentration of the precipitating ion $B^-$ at which it can still remain in solution together with the ion $A_i^+$ (bearing in mind that the concentration of the latter is equal to its concentration in the initial chromatographed solution $c_i^0$):

$$c_{0,i} = \frac{L_i^{s_i/z_i}}{f_0 \left(f_i c_i^0\right)^{z_0/z_i}}. \tag{6}$$

The order of precipitation, and consequently the order of the zones in the precipitation chromatogram, will follow the order of increasing values of $c_{0(i)}$, associated for each ion $A_i$ with its initial concentration. The value of the reacting concentration of the precipitating ion in the method under consideration for obtaining a precipitation chromatogram is not directly controlled by the experimenter, and the sequence of precipitation can in principle be changed only by changing the ratio of the concentrations of the chromatographed ions in the initial solution. For the corresponding calculations one may take the ratio

$$\frac{c_{0(1)}}{c_{0(2)}} = \frac{L_1^{s_1/z_1}}{L_2^{s_2/z_2}} \frac{\left(f_2 c_2^0\right)^{z_0/z_2}}{\left(f_1 c_1^0\right)^{z_0/z_1}}. \tag{7}$$

It should be noted that, because of the large difference in the values of the solubility products, the indicated route for obtaining inversion of the sequence of precipitation zones is in many cases practically infeasible; this circumstance is very valuable from a practical point of view.

Precipitation-chromatographic separation is often carried out by another method as well: the chromatographed solution is introduced into a column containing a mechanical mixture of an inert carrier and a sparingly soluble precipitating agent. This method differs from that considered above only in the mechanism of the first stage of the process—in the present case it is the simple dissolution of the precipitating agent; the indicated difference essentially changes nothing in the question of the order of precipitation, since in both cases the concentration of the precipitating ion increases in the direction from 0 to $c_{0(i)}$.

Only the reverse method of obtaining a precipitation chromatogram differs substantially from the preceding methods; in this method a solution of the precipitating agent is introduced into a column containing a mixture of ions. In this case, to determine the order of precipitation, instead of the quantity $c_{0(i)}$ one should consider the analogous quantity

$$c_{i(0)} = \frac{L_i^{s_i/z_0}}{f_i \left(f_0 c_0^0\right)^{z_i/z_0}} \tag{8}$$

and the ratio

$$\frac{c_{1(0)}}{c_{2(0)}} = \left(\frac{L_1^{s_1}}{L_2^{s_2}}\right)^{1/z_0} \frac{f_2}{f_1} \left(f_0 c_0^0\right)^{(z_2-z_1)/z_0} . \qquad (9)$$

Since, when the method of obtaining a precipitation chromatogram is changed from the direct to the reverse one, a very substantial change occurs in the ratio of the concentrations of all ions (for systems consisting of one and the same set of ions), it is legitimate to expect an inversion of the sequence-

of the arrangement of the precipitate zones. For example, in the system of ions $Cl^- + CrO_4^{2-}$ and $Ag^+$, with the direct method of obtaining the chromatogram (the initial concentration of the solution is $0.1\,M$ for each anion), according to equation (7) the ratio $c_{Ag^+(Cl^-)} : c_{Ag^+(CrO_4^{2-})} = 2 \cdot 10^{-5} < 1$; the formation of an AgCl precipitate in the first zone and of $Ag_2CrO_4$ in the second is predicted. With the reverse method, for a solution of $Ag^+$ with concentration $c^0 = 0.1\,M$, from equation (9) we obtain the ratio $c_{Cl^-(Ag^+)} : c_{CrO_4{}^{2-}(Ag^+)} = 16 > 1$, i.e., the sequence of zones in the chromatogram should change. Experiment (for example, in paper chromatography technique) fully confirms the arrangement predicted by calculation.

On the basis of the considerations discussed, the following conclusions may be drawn. The order of precipitation, which determines the sequence of zones in precipitation chromatograms, generally depends both on the ratio of the concentrations of the ions being separated and on the magnitude of the concentration of the precipitating ion. However, under the specific conditions for carrying out precipitation-chromatographic separation of ions, the possibilities available to the experimenter for inverting the order of arrangement of the zones are often very limited. Using equations (6), (8) or (7), (9), one can predict the order of succession of the zones in precipitation chromatograms.

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*Note: Figure translations are in progress. See original paper for figures.*