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Abstract

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CHEMISTRY

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DETERMINATION OF THE COMPOSITION AND STABILITY CONSTANTS OF LEAD CHLORIDE COMPLEXES FROM EXPERIMENTS ON THE DISTRIBUTION OF A RADIOACTIVE ISOTOPE BETWEEN PRECIPITATE AND SOLUTION

(Presented by Academician V. I. Spitsyn, July 12, 1958)

V. G. Khlopin and his school (^{1}) established that, in the distribution of a microelement between the precipitate and the solution of an isomorphous compound of the macrocomponent, true thermodynamic equilibrium can be attained.

Let us consider cocrystallization as a reversible ion-exchange reaction of equal valence:

$$\mathrm{m_{lq}} + \mathrm{M_{sol}} leftarrows \mathrm{m_{sol}} + \mathrm{M_{lq}}.$$

The equilibrium constant of this reaction is

$$K = \frac{[\mathrm{m}]_{\mathrm{sol}}[\mathrm{M}]_{\mathrm{lq}}}{[\mathrm{m}]_{\mathrm{lq}}[\mathrm{M}]_{\mathrm{sol}}}. \tag{1}$$

In this equation m is the microelement, M the macroelement. The subscripts indicate the phase (solid and liquid) in which the ions are found; their activities are given in square brackets. However, if the concentration of the microcomponent in the solid phase is small and the ionic strength of the solution is maintained constant, then all activity coefficients are practically constant quantities. Therefore, concentrations may be used instead of activities, with all activity coefficients included in the equilibrium constant. Equation (1) is also applicable to the case of distribution of isomorphous ions of the microcomponent between the surface and the solution (primary ion-exchange adsorption).

V. G. Khlopin (^{1}) showed that the presence in an aqueous solution of ions that form complexes with one of the elements m or M causes a change in the "constant" of distribution. In what follows we shall call the distribution coefficient the quantity obtained when calculation is made by formula (1), when instead of the equilibrium concentration the analytical concentration determined experimentally is substituted.

The change in the distribution coefficient as a function of the concentration of the complex-forming ion indicates the existence of complex ions in solution. Examples of such an effect are given in the works of V. G. Khlopin and A. P. Ratner (^{2}) and of Keding (^{3}). In the latter case it can be shown that the change in D is determined mainly by a change in activity.

We have proposed a calculation method for determining the composition and stability constants of ion complexes. The distribution in the system SrSO_4—Pb^{212}—SO_4—HCl was studied. The experiments were carried out by the well-known method developed by V. G. Khlopin and his students (^{1,4,5}). If the experimental data are expressed by the formula

$$D = \frac{x}{y}\frac{1-y}{1-x} \tag{2}$$

(where x and y are the fractions of the micro- and macrocomponents in the precipitate, and $1-x$ and $1-y$ are the corresponding fractions in solution), then, in the absence of a complexing agent, $D_0 = K$; in the presence of a complexing agent, if analytical concentrations are substituted into formula (2), the distribution coefficient is a function of the concentration of the ions of the complexing agent. The calculations are substantially simplified if the macrocomponent does not form strong complex compounds with the ions of the complexing agent, and if basic or acid salts and complex ions do not enter into the lattice of the macrocomponent compound. When equilibrium is reached in the system we have chosen:

$$\mathrm{Pb}^{\bullet\bullet} + \mathrm{SrSO}_4 leftharpoons \mathrm{PbSO}_4 + \mathrm{Sr}^{\bullet\bullet}.$$

$$D_0 = \frac{[\mathrm{PbSO}_4][\mathrm{Sr}^{\bullet\bullet}]}{[\mathrm{Pb}^{\bullet\bullet}][\mathrm{SrSO}_4]}. \tag{3}$$

It has been shown that strontium ions do not form stable complex compounds with chloride ions. In the presence of chloride ions, which form complex ions of the type $[\mathrm{PbCl}_j]^{2-j}$, the distribution coefficient D will differ from the equilibrium constant D_0, since instead of the concentration of $[\mathrm{Pb}^{\bullet\bullet}]$ ions, which should enter equation (3), the analytical concentration will be substituted, in this case equal to $C_{\mathrm{Pb}} = [\mathrm{Pb}^{\bullet\bullet}](1 + \sum \beta_j [\mathrm{Cl}']^j)$, where β_j is the stability constant of the corresponding complex ions PbCl_j^{2-j}

$$\beta_j = \frac{[\mathrm{PbCl}_j^{2-j}]}{[\mathrm{Pb}^{\bullet\bullet}][\mathrm{Cl}']^j}. \tag{4}$$

Therefore the distribution coefficient is

$$D = \frac{[\mathrm{PbSO_4}][\mathrm{Sr}^{\bullet\bullet}]}{[\mathrm{SrSO_4}]C_{\mathrm{Pb}}} = \frac{[\mathrm{PbSO_4}][\mathrm{Sr}^{\bullet\bullet}]}{[\mathrm{SrSO_4}][\mathrm{Pb}^{\bullet\bullet}](1 + \sum \beta_j [\mathrm{Cl}']^j)} = \frac{D_0}{1 + \sum \beta_j [\mathrm{Cl}']^j}$$

or

$$\frac{D_0}{D} - 1 = \sum \beta_j [\mathrm{Cl}']^j. \tag{5}$$

As is seen, the basic equation (5) for calculating the composition and stability constants of complex compounds using the distribution law is analogous to the known equations for ion exchange and extraction. To determine j and β_j, it is necessary to obtain the dependence of D on the concentration of the complexing agent at constant ionic strength of the solution. The resulting data may be processed by any of the known methods ($^{6-9}$).

Experimental Part

The solubility of strontium sulfate labeled with S^{35} was first determined in solutions containing HCl and $\mathrm{HClO_4}$ in various ratios corresponding to an ionic strength equal to unity. As kinetic experiments showed, equilibrium "from below" was established rather rapidly—in 30–40 min (at a stirring rate of 1300 rpm). It was not possible to determine the solubility "from above," since extremely stable supersaturated solutions are obtained and the supersaturation was not removed over several days. Therefore, to solve the main problem, the distribution of Pb^{212} between the surface of the precipitate and a saturated solution of the given composition was studied.

In applying equations (2) and (3) to primary exchange adsorption, the concentration $[\mathrm{SrSO_4}]$ is proportional to the weight of the precipitate, which is valid when using a repeatedly recrystallized suspension; $[\mathrm{SrSO_4}] = ky$; the proportionality coefficient k may be combined with the constant D, then $Dk = D'$.

All the experimental data presented in Table 1 were obtained as the average of 4–7 determinations. The root-mean-square error for the solubility and D' values is, respectively, not more than 4.5 and 10%. From the data in the last column, the dependence of the function

Fig. 1

Figure 1: Fig. 1

Table 1

HCl concentration,* mol/l	Solubility of $SrSO_4$, g/l	D'	$\frac{\frac{D'_0}{D'} - 1}{[Cl']}$
0	1.94	0.39	
0.01	1.93	0.23	63
0.05	1.90	0.11	52
0.10	1.86	0.09	31
0.20	1.81	0.09	17
0.40	1.75	0.09	8
0.50	1.74	0.08	8
1.00	2.00	0.08	4

* Ionic strength of the solutions $\mu = 1$.

$$\frac{\frac{D'_0}{D'} - 1}{[Cl']}$$

on the concentration $[Cl']$ was plotted.

According to equation (5), this function should be increasing. Analysis of the curve obtained indicates the presence of a side process, as a result of which the value of D' decreases more slowly than follows from equation (5). This can be explained by secondary adsorption of negatively charged lead ions by the suspension, which is positively charged in acid solutions. The latter was confirmed by special adsorption experiments. However, in the region of low concentrations $[Cl']$, where adsorption of negatively charged complex ions may be neglected, calculation of the first constant becomes possible. Extrapolating the curve (Fig. 1) to its intersection with the ordinate axis, we obtain $\beta_1 = 65 \pm 9$; the value found does not differ substantially from that known in the literature (^{10}).

Fig. 1

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