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PRECIPITATION OF METAL HYDROXIDES FROM AQUEOUS SOLUTIONS AS A RESULT OF SPONTANEOUS CONDENSATION OF POLYNUCLEAR HYDROXOCOMPLEXES

Background. Generally, it is assumed that the formation of a solid phase (precipitate) happens when the activities of the involved ions would exceed those defined by the thermodynamic solubility product. However, in case of precipitation of metal hydroxides, this is a simplification, and the real pattern is more complicated, since metal ions form strong mono- and polynuclear hydroxocomplexes in a solution. Formation of such complexes, especially those with zero charge, should result in the deviation from the common solubility product rule.

Objective. The aim of this paper is to develop a precipitation model, which takes into account the effect of the formation of the hydroxocomplexes on the solubility of a metal hydroxide. Eventually, this solubility includes the sum of the concentrations of metal ions, and all neutral, positively and negatively charged hydroxocomplexes involved in all equilibria in aqueous solution.

Methods. We assume that formation of the solid precipitate is the result of spontaneous condensation of polynuclear neutral hydroxocomplexes when their concentrations in a solution exceed a certain critical value. These critical concentrations can be estimated from the consideration of all equilibria with the assumption that the equilibrium constants for the formation of neutral polynuclear complexes when their nuclearity increases by one are approximately equal and do not significantly depend on the size of the particle.

Results. Using this approach, we developed the model, which predicts spontaneous condensation with formation of a precipitate. Also, we calculated the dependencies of $\text{pH}-\log C_M$ for precipitation of various divalent cation hydroxides. It was shown that there exist minimal concentrations, below which no precipitates are formed at any pH value.

Conclusions. Such approach also explains the nature of linear correlations between logarithms of solubility products and stability constants of neutral complexes described in literature. These results are important for the development and optimization of industrial wastewater treatment processes.

Keywords: solubility; metal hydroxides; metal hydroxocomplexes.

Introduction

Precipitation of metal hydroxides is used in technological processes such as preparation of various oxide materials [1] and removal of harmful metals from wastewaters [2, 3, 4–6]. Thus, for such practical applications, it is important to understand the conditions for precipitation of sparingly soluble species from solutions. It is also important for a student who studies Analytical Chemistry. Generally accepted is the assumption that the formation of a deposit occurs when the product of the activities (concentrations) of ions exceeds the solubility product. In case of hydroxide deposit formation $\text{M}^{2+} + 2\text{OH}^- = \text{M}(\text{OH})_2\downarrow$, it is $C_M C_{\text{OH}}^2 \geq K_s$, where C_M is the total concentration of M in a solution and K_s is the solubility product. In this paper, we shall demonstrate that this condition is only simplification which is valid at rather high concentrations of metal ions. The reason is the formation of hydroxocomplexes in the solution.

Problem statement

The aim of this paper is the development of the theoretical model which takes into account the formation of polynuclear complexes and comparing the predictions of this model with the available experimental data.

Theory

It is generally assumed that the value of solubility product (K_s) must be attained for a deposit to form. In case of metal hydroxide precipitation, this condition is

$$C_M c_{\text{OH}} \geq K_s. \quad (1)$$

Or, in terms of pH,

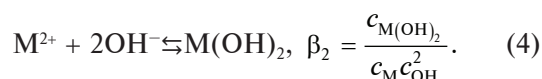
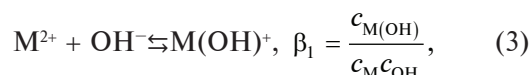
$$\log C_M \geq 28 - 2\text{pH} - pK_s, \quad (2)$$

where p means, as usual, $-\log$.

Thus, knowing the value of solubility product, the pH of a deposit formation can be calculated for each concentration of the solution.

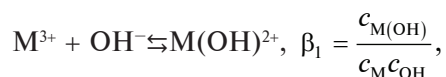
We will further show that the condition (1) or (2) is a simplification and the real pattern is more complicated.

In acidic solutions, ions M^{2+} exist in form of aquacomplexes $[M(H_2O)_6]^{2+}$. As the acidity of the solution decreases (pH increases), mixed aquahydroxocomplexes begin to form by substitution one or more water molecules with hydroxyl ions in the inner sphere of the complexes. When writing the reaction of their formation, the water molecules are usually omitted, and the corresponding equilibria are represented as follows:



The equilibrium constants β_1 (3) and β_2 (4) are generally known as *formation constants* or *stability constants* of the complexes.

Similarly, for M^{3+} cations



The $M(OH)_2$ and $M(OH)_3$ complexes, which are not charged, can “condense” to form polynuclear complexes:



Similarly, for M^{3+} cations



The reactions (5, 6) are the outer sphere interactions in which each polynuclear complex joins one molecule of mononuclear particle thus increasing its nuclearity by one. The equilibrium constants (condensation constants) for M^{2+} complexes

$$K_{c2} = \frac{c_{M_n(OH)_{2n}}}{c_{M_{n-1}(OH)_{2n-2}} c_{M(OH)_2}} \quad (7)$$

and

$$K_{c3} = \frac{c_{M_n(OH)_{3n}}}{c_{M_{n-1}(OH)_{3n-2}} c_{M(OH)_3}}. \quad (8)$$

We believe that the equilibrium constants (7, 8) should not significantly depend on the number of metal atoms in each polynuclear complex. It follows from thermodynamic considerations. The basic thermodynamic equation for temperature dependence of equilibrium constant is

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}, \quad (9)$$

where ΔH is the enthalpy change and R universal gas constant.

Applying this equation to the “condensation constants” (7, 8) and integrating, we obtain

$$\ln K_{c(n)} = \frac{-\Delta H_n}{RT} + const, \quad (10)$$

where ΔH_n is the enthalpy change for each of the reactions (5) or (6), and integrating *const* depends on the entropy change and reference system chosen.

Two new oxygen bridge bonds are formed in each of the reactions (5), and their energies should be approximately equal. The entropy changes also should not differ significantly (one particle is formed from two particles in each reaction of the sets (5) and (6)). The same reasoning should be valid also for the set of the reactions where three new oxygen bridge bonds are formed. Thus, we believe that the independence of the constants (7) and (8) on the number of equilibrium should be a good approximation. Of course, the condensation constants for $M(OH)_2$ and $M(OH)_3$ must be different because of the difference of enthalpy changes. If we denote the energy of one oxygen bridge bond formation as h and assume it approximately independent on the nature of the inner sphere metal cation, then $\Delta H_{(2)} \approx 2h$ and $\Delta H_{(3)} \approx 3h$. Thus, the ratio $\log K_{c(3)}/\log K_{c(2)}$ is expected to be about 1.5 if the effect of entropy change is neglected.

Further analysis is given for the M^{2+} cations assuming that all constants (10) are equal. Under this assumption, concentration of each polynuclear complex can be related to the concentration of mononuclear particle $M(OH)_2$:

$$c_{M_n(OH)_{2n}} = K^{n-1} c_{M(OH)_2}^2, \quad (11)$$

Where K is the equilibrium constant for each of the reaction (8). We shall call it “condensation constant”.

Total concentration of metal in solution when the deposit is not yet formed is equal to the sum of concentrations of aqua complexes M^{2+} , mononuclear hydroxocomplexes $M(OH)^+$ and $M(OH)_2$, and polynuclear complexes $M_n(OH)_{2n}$. It can be represented as

$$C_M = c_M + \beta_1 c_M c_{OH} + \beta_2 c_M c_{OH}^2 (1 + \beta_2 K c_M c_{OH}^2 + \beta_2^2 K^2 c_M^2 c_{OH}^4 + \beta_2^3 K^3 c_M^3 c_{OH}^6 + \dots)$$

or in more concise form

$$C_M = c_M + \beta_1 c_M c_{OH} + \beta_2 c_M c_{OH}^2 \left(\sum_0^{\infty} K^i \beta_2^i c_M^i c_{OH}^{2i} \right). \quad (12)$$

A series in brackets (12) is geometric progression [7]. It converges when $K\beta_2 c_M c_{OH}^2 < 1$. In this case we obtain (13)

$$C_M = c_M + \beta_1 c_M c_{OH} + \frac{\beta_2 c_M c_{OH}^2}{1 - K\beta_2 c_M c_{OH}^2}. \quad (13)$$

A series diverges when $K\beta_2 c_M c_{OH}^2 \geq 1$.

One can see that the behaviour of the considered system is rapidly changed when the above-mentioned parameter attains the critical value equal to 1. Such event when properties of a system suddenly and sharply change is usually known as bifurcation [8].

Thus, the product $K\beta_2 c_M c_{OH}^2$ can be considered as a bifurcation parameter of the system. When it attains the value 1, the system sharply changes, and the deposit of hydroxide is formed.

So, the condition for the deposition of hydroxide is

$$c_M c_{OH}^2 \geq \frac{1}{K\beta_2}. \quad (14)$$

Comparing (1) and (14), we must conclude that the right term of (14) should be equal to the solubility product:

$$K_s \geq \frac{1}{K\beta_2}. \quad (15)$$

Two conclusions can be made from the analysis above.

1. Solubility product depends on the value of condensation constant and second formation constant of the hydroxocomplex (15).

2. Equation (14) rather than simplified formula (1) must be used as the criterion for the formation of deposit.

To use the criterion (14), concentration of free M^{2+} ions (c_M) must be known. In order to calculate its value, we assume that most of the metal in pre-deposition state is still in form of mononuclear complexes and concentration of polynuclear complexes is negligibly small. Then

$$C_M = c_M + \beta_1 c_M c_{OH} + \beta_2 c_M c_{OH}^2$$

and

$$c_M = \frac{C_M}{1 + \beta_1 c_{OH} + \beta_2 c_{OH}^2}. \quad (16)$$

Substituting (16) into (14) and taking into account (7), we obtain the formula for calculation of the pH of the hydroxide deposit formation at any concentration of the solution. Examples of such calculations are given in the next section.

Experimental verification

The values of stability constants and solubility products, which are necessary for calculations, were experimentally determined long ago and tabulated in many chemical handbooks. Table 1 below contains the data taken from [9].

Table 1. Reference data for main cations M^{2+}

Cations	$\log\beta_2$	pK_s	$\log\beta_1$	$\log C_s$	$\log C_{\min}$
1	2	3	4	5*	6**
Cd	8.33	13.66	4.17	-3.5	-5.3
Ni	8.55	14.7	4.97	-3.5	-6.0
Co	9.0***	14.8	4.4	-2	-5.5
Pb	10.8	14.92	6.9	-1	-4.2
Fe	9.77	15	5.56	-3	-5.2
Zn	11.3	17.15	4.4	-4.8	-5.8
Cu	13.68	19.66	7	-4	-6.1
UO ₂	18.6	22	9.8	-1.5	-3.4
Hg	21.7	25.52	10.3	-2.5	-3.9
Sn	20.64	26.2	11.86	-1.5	-5.5

* Lowest concentrations when simplified formula (1) can be used.

** Critical concentration values when hydroxide deposits do not form at any pH.

*** The value $\log\beta_2 = 4.6$ is given in literature. Evidently, this is a mistake. Most probably, 4.6 is logarithm of not total but stepwise second formation constant. Assuming this, we obtain the value given in the table.

Considering the data of Table 1, one can notice that as pK_s increases the $\log\beta_2$ also increases. That is, the correlation between these values is expected. This correlation is shown in Fig. 1.

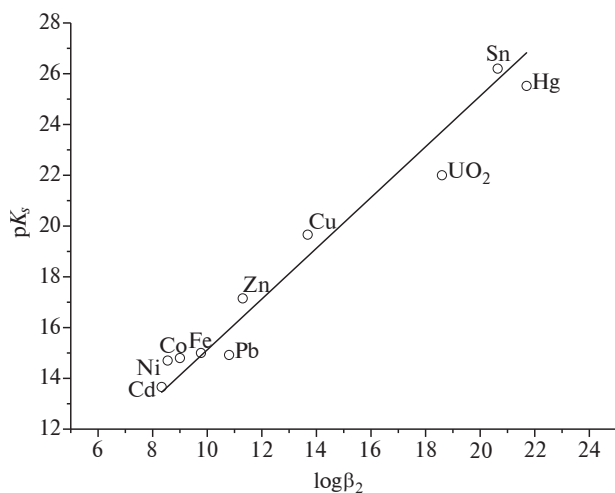


Fig. 1. Correlation between the values of solubility product and second stability constant of hydroxides $M(OH)_2$

We can see that the strong ($R = 0.9566$) linear correlation between pK_s and $\log\beta_2$ does exist:

$$pK_s = \log\beta_2 + (5.12 \pm 0.31). \quad (17)$$

Evidently, it proves that the condensation constant is not significantly influenced by the number of reactions (8), as well as by the cation nature, as it was expected from the thermodynamic consideration above. Then, from (17), the value of condensation constant is equal to (18):

$$\log K_{c(2)} = 5.12 \pm 0.31. \quad (18)$$

Using the value of this universal constant, we can predict the unknown values of second stability constant for the cations for which the solubility products are known. Some of such predicted values are given in Table 2.

Table 2. Predicted values of second stability constants for some cations M^{2+} which solubility products are known

Cation	pK_s	$\log\beta_2$
Be	21.2	16.1
HfO	34.5	29.4
Mg	10.74	5.63
Mn	12.72	7.62
Pt	35	30
PuO_2	20.5	15.4
TiO	29	24
VO	22.13	17

Similar pattern is observed for M^{3+} hydroxides. To build the correlation for these cations, the values of $\log\beta_3$ and solubility products pK_s were taken from [10].

In this case the strong ($R = 0.9263$) linear correlation between pK_s and $\log\beta_3$ also exists (Fig. 2). From the correlation of Fig. 2, one can obtain (19)

$$pK_s = \log\beta_3 + (7.26 \pm 0.46). \quad (19)$$

Hence, the condensation constant is equal to (20)

$$\log K_{c(3)} = 7.26 \pm 0.46. \quad (20)$$

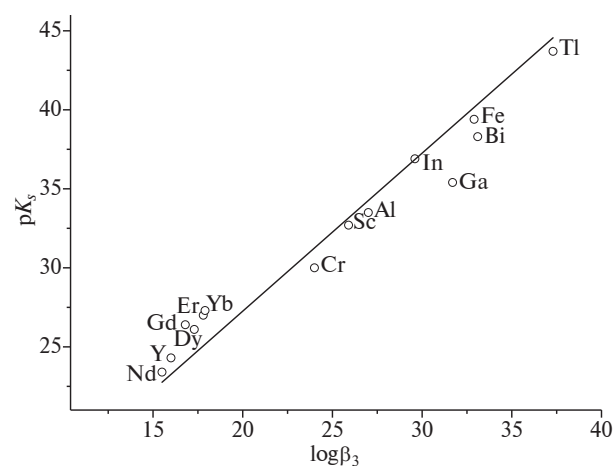


Fig. 2. Correlation between the values of solubility product and second stability constant of hydroxides $M(OH)_3$

It is worthwhile to note that the ratio $\log K_{c(3)}/\log K_{c(2)} = 1.42$, which is in agreement with the thermodynamic considerations (see above). If we, as before, assume that enthalpy of formation one new oxygen bridge bond (h) and entropy change does not depend on the nature of cation (at least approximately), then we can calculate the enthalpy from the condensation constants using equation (10):

$$2.3(\log K_{c2} - \log K_{c3}) = \frac{h}{RT}. \quad (21)$$

As follows from (21), $h = -12.1$ kJ.

The linear correlations between logarithms of solubility products and stability constants of neutral hydroxocomplexes were first described in [11, 12] in forms of purely empirical linear equations $\log\beta = a - b\log K_s$ ($a = -11.44$, $b = -1.290$ for $M(OH)_2$ [11]; $a = -13.12$, $b = -1.184$ for $M(OH)_3$ [12]). The author did not discuss the physical meaning of the empirical coefficients a and b .

The attempt was made [13] to establish the origin of the correlations. The authors correctly assumed that the coefficients b should always be 1 and attributed coefficient a to the concentration (activity) of neutral hydroxide molecules in equilibrium with the hydroxide deposit in the solution. However, the authors admit that they do not understand the reason why this activity is constant for each hydroxide.

In our opinion, the guess [13] is reasonable. In terms of our model, where the coefficient a is equal to the reverse condensation constant, at larger values of n in equilibria (8) or (9), the concentrations of $M_{n-1}(\text{OH})_{2n-2}$ and $M_n(\text{OH})_{2n}$ species (8) or $M_{n-1}(\text{OH})_{3n-3}$ and $M_n(\text{OH})_{3n}$ (9) should be approximately equal. Thus, as follows from (10) and (11), $1/K_c \approx c_{M(\text{OH})_2}$ for M^{2+} and $c_{M(\text{OH})_3}$ for M^{3+} cations.

We believe that our model explains the origin of linear correlations in a more natural way. Moreover, it permits to calculate the values of pH when a hydroxide begins to form a precipitate as a function of concentration of a metal in a solution. For such calculations, the values of all stability constants (not only neutral complexes) must be known. Such data are not available for M^{3+} cations. Thus, we performed the calculations only for M^{2+} cations.

Dependence between the concentration and pH of the deposit formation can be calculated using formulae (13–15). Using them and replacing the concentration of hydroxyl ions by pH, we obtain the working formula for such calculations:

$$C_M = \log K_s + \log(10^{28-2\text{pH}} + 10^{\log \beta_1 + 14 - \text{pH}} + 10^{\log \beta_2}). \quad (22)$$

The dependence (22) should have two asymptotes: at low pH values the first term in brackets prevails and we obtain the straight line corresponding to the simplified formula (2); at high pH when the last term in the brackets prevail the asymptote is minimal constant concentration when no deposit is formed at any pH values. This minimum concentration should approximately be equal to $1/K$, that is

$$-\log C_{\min} \approx \log K. \quad (23)$$

The calculations were performed for each cation of Table 1. The examples of calculated dependencies pH of deposition – concentration are shown in Fig. 3 for the precipitation of cadmium and iron hydroxides. Such dependencies for other cations are similar.

As follows from the calculations, at higher concentrations and lower pH, simplified formula (2) can be applied instead of more complicated dependency (22). The low limits of concentrations where the formula (2) is applicable are given in column 5 of Table 1. There are also the minimal critical values of concentration. Below these values, no deposits are formed at any pH. These critical concentrations are given in column 6 of Table 1. As follows from Table 1, the formula (22) is a better approximation than the currently accepted relation (1). It is valid for most of the cations except for UO_2^{2+} and Hg^{2+} . Both cations slightly fall out of the correlation in Fig. 1.

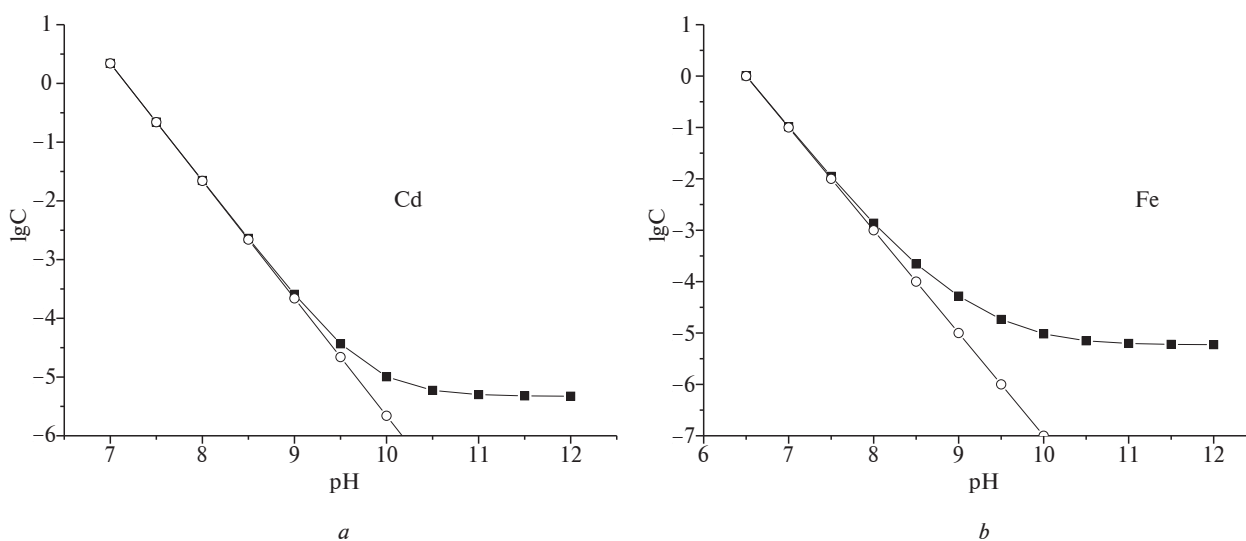


Fig. 3. pH dependencies of deposition – concentration for Cd^{2+} (a) and Fe^{2+} (b) ions

Conclusions

The model was proposed where precipitation of metal hydroxides begins at certain critical values of pH and concentrations by means of spontaneous condensation of neutral polynuclear hydroxocomplexes – this phenomenon can be considered as a bifurcation event. The condensation constant was introduced. It depends very weakly on the nature of cations, which was substantiated thermodynamically and proved experimentally.

As follows from the model, the commonly accepted criterion (1) for the formation of the hydroxide deposits is a simplification that can be

used at concentrations about 10^{-3} mol/l or higher. At lower concentrations, the pH of deposition deviates significantly due to the formation of hydroxocomplexes.

Moreover, the lower limit of the concentrations exists (about 10^{-5} – 10^{-6} mol/l) where deposits are not formed at any pH values. These features should be taken into account when considering the formation of hydroxide deposits for the purposes of analytical determinations of metal cations in aqueous solutions and practical applications such as removal of metal cations from industrial waste solutions.

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Ю. Андрійко, О.О. Андрійко

ОСАДЖЕННЯ ГІДРОКСИДІВ МЕТАЛІВ ІЗ ВОДНИХ РОЗЧИНІВ ЯК НАСЛІДОК СПОНТАННОЇ КОНДЕНСАЦІЇ ПОЛІАДЕРНИХ ГІДРОКСОКОМПЛЕКСІВ

Проблематика. Заведено вважати, що творення твердої фази (осаду) відбувається тоді, коли активності іонів перевищать значення, визначені термодинамічним добутком розчинності. Однак у випадку осадження гідроксидів металів, це є спрощенням, і реальна картина буде складнішою через утворення в розчині міцних моно- та поліядерних комплексів. Утворення таких комплексів, особливо з нульовим зарядом, буде призводити до відхилень від правила добутку розчинності.

Мета дослідження. Розробити модель осадження, що враховує вплив гідроксокомплексів на розчинність гідроксиду металу. Зрештою, ця розчинність є сумою концентрацій іонів металу, нейтральних, позитивно та негативно заряджених гідроксокомплексів, що беруть участь у всіх встановлених у розчині рівновагах.

Методика реалізації. Розроблення моделі осадження з припущенням, що утворення твердого осаду відбувається внаслідок спонтанної конденсації нейтральних поліядерних гідроксокомплексів, коли їх концентрації перевищать певне критичне значення. Ці критичні концентрації можна оцінити, аналізуючи всі рівноваги в розчинах і припускаючи, що константи рівноваги утворення нейтральних поліядерних комплексів є приблизно однаковими та суттєво не залежать від розміру частинок, коли їхня "ядерність" збільшується на одиницю.

Результати дослідження. Створено модель, що передбачає можливість спонтанної конденсації з утворенням осаду. Розраховано залежності $pH - \log C_M$ для осадження гідроксидів дво валентних катіонів і встановлено, що існують деякі мінімальні концентрації, нижче яких не утворюються осади за будь-яких значень pH.

Висновки. Сформований підхід дав змогу пояснити природу лінійних кореляцій між логарифмами добутків розчинності та константами стійкості нейтральних комплексів, описаних у літературі. Отримані результати є важливими для розроблення й оптимізації промислових процесів очищення стічних вод.

Ключові слова: розчинність; гідроксиди металу; гідроксокомплекс металів.

Ю. Андрийко, А.А. Андрийко

ОСАЖДЕНИЕ ГИДРОКСИДОВ МЕТАЛЛОВ ИЗ ВОДНЫХ РАСТВОРОВ КАК РЕЗУЛЬТАТ СПОНТАННОЙ КОНДЕНСАЦИИ ПОЛИЯДЕРНЫХ ГИДРОКСОКОМПЛЕКСОВ

Проблематика. Принято считать, что образование твердой фазы (осадка) происходит тогда, когда активности ионов превысят значения, определенные термодинамическим произведением растворимости. Однако в случае осаждения гидроксидов металлов это является упрощением, и реальная картина будет сложнее из-за образования в растворе прочных моно- и полиядерных комплексов. Образование таких комплексов, в особенности с нулевым зарядом, будет приводить к отклонениям от правила произведения растворимости.

Цель исследования. Разработать модель осаждения, которая учитывает влияние гидроксокомплексов на растворимость гидроксида металла. В итоге эта растворимость является суммой концентраций ионов металла, нейтральных, положительно и отрицательно заряженных гидроксокомплексов, которые принимают участие во всех установившихся в растворе равновесиях.

Методика реализации. Разработка модели осаждения с предположением, что образование твердого осадка происходит вследствие спонтанной конденсации нейтральных полиядерных гидроксокомплексов, когда их концентрации превысят определенное критическое значение. Эти критические концентрации можно оценить, анализируя все равновесия в растворах и предполагая, что константы равновесия образования нейтральных полиядерных комплексов приблизительно одинаковы и существенно не зависят от размера частиц, когда их "ядерность" увеличивается на единицу.

Результаты исследования. Разработана модель, которая предусматривает возможность спонтанной конденсации с образованием осадка. Рассчитана зависимость $\text{pH}-\log C_M$ для осаждения гидроксидов двухвалентных катионов и установлено, что существуют некоторые минимальные концентрации, ниже которых не образуются осадки при любых значениях pH.

Выводы. Сформированный подход позволил объяснить природу линейных корреляций между логарифмами произведений растворимости и константами устойчивости нейтральных комплексов, описанных в литературе. Полученные результаты важны для разработки и оптимизации промышленных процессов очистки сточных вод.

Ключевые слова: растворимость; гидроксиды металлов; гидроксокомплексы металлов.

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