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THE MODEL OF METAL OXIDE PARTICLE FORMATION FROM WATER SOLUTIONS OF SALTS

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Abstract. The model describing the formation of metal oxide particles from water solutions of salts was suggested. Dependence of instability constants of metal complexes and ionization constants of oxygen containing inorganic acids on the electron density upon the central ion or atom allows to calculate these values for metal hydroxides. Equations describing the number of metal ions in polyion, the concentration of polyions in solution, the number of metal ions in primary metal oxide particles and their concentration in the system were suggested.

Keywords: metal oxide particles, metal complexes, polyions, model.

1. Introduction

Metal oxide particles are well known for their use in the information bearers [1], magnetic liquids [2], biological, medical analysis and diagnostics [3], catalysis [4, 5] and scavenging of metal ions from industrial wastewater [6]. Wide usage of these materials provides investigations in the field of metal oxide stable dispersions obtaining by different physical and chemical methods [7-9]. The most prospective method of synthesis of metal oxide dispersions with definite size particles is the homogeneous nucleation from salt solutions in the presence of different natural stabilizers [10, 11].

Particle formation includes the stages of reaction of water soluble metal ions with hydroxyl ion, functional groups of stabilizers or insoluble metal salts [12], primary homogeneous nucleation with formation of water soluble polyions or particles including a few metal ions [13] and secondary nucleation provides nanosized particles or crystallites. Metal oxide microparticles are formed at the aggregation of crystallites when the concentration of the stabilizer is low or it is effectless [2, 14]. The size and the shape of metal oxide crystallites are determined by the first and second stages of the process. Therefore investigation and modeling of these stages are very important for obtaining metal oxide dispersions with a definite particle size.

2. Results and Discussion

The first stage of metal oxide particle formation from the solutions of their salts is the formation of hydroxide complexes of metal ions. The reaction of complex formation proceeds in some stages according to the scheme:

$$[Me(H_2O)_6]^{n+} OH^- \rightarrow [Me(OH)(H_2O)_5]^{(n-1)+} + H_2O \qquad (K_1) \quad (1)$$

$$[Me(OH)(H_2O)_5]^{(n-1)+} + OH^- \rightarrow [Me(OH)_2(H_2O)_4]^{(n-2)+} + H_2O \qquad (K_2) \quad (2)$$

$$[Me(OH)_2(H_2O)_4]^{(n-2)+} + OH^- \rightarrow [Me(OH)_3(H_2O)_3]^{(n-3)+} + H_2O \qquad (K_3) \quad (3)$$

The values of the equilibrium constants decrease at the increase of the substitution degree of number of water molecules by OH^- ions in complexes. Dependence of pK_n on the number of OH^- ions in the complex can be described by a straight line according to Eq. (4) in the first approximation, as it is shown in Fig. 1 for example.

$$pK_n = A + Bn \qquad (4)$$

where $pK_n = -\log(K_1 K_2 .... K_n)$, A and B are constants, n is the number of hydroxyl ions in the complex.

The values of and were calculated for metal complexes with ammonium, hydroxyl, iodide, chloride, fluorine ions, ions of organic acids, amine and hydroxyl containing organic compounds according to experimental data [15-17]. The correlation constants of the straight lines were higher than 0.9 in all cases. It is needed to note that the constants of dissociation of inorganic multi based acids can be described by Eq. (4) too.

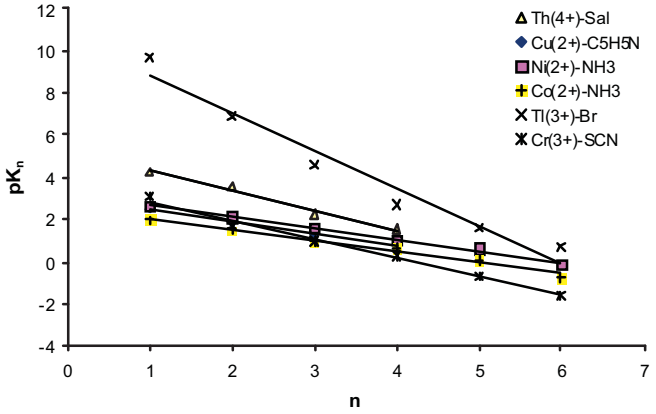

Fig. 1. Dependence of pK_n on the number of addends in the metal complex

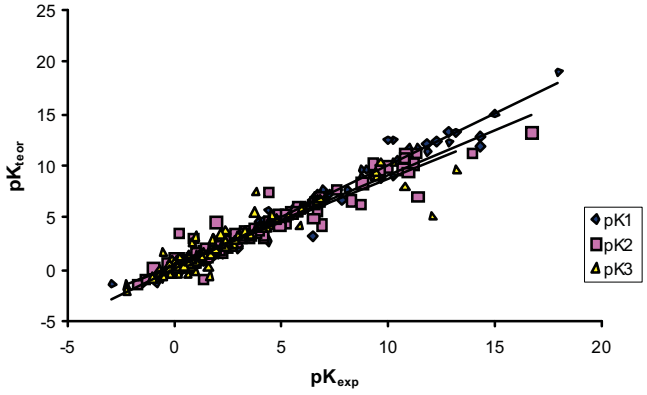

Fig. 2. Dependence of pK_n calculated according to Eq.(4) and experimental data taken from [15-17]

Table 1

Correlation coefficients, the tangent of the intercept on the ordinate axis and the slope angles of straight lines for dependence of theoretical and experimental pK_n

pK_n	R^2	h	tgα
pK_1	0.975	-0.07±0.16	1.00±0.12
pK_2	0.933	0.4±0.3	0.9±0.2
pK_3	0.870	0.4±0.5	0.8±0.3

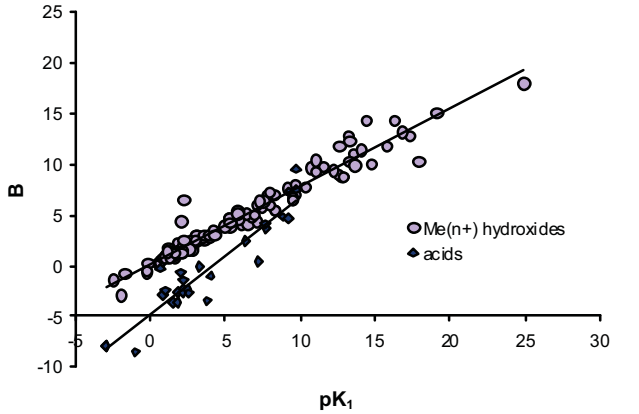

Fig. 3. Dependence of B value calculated according to the Eqs. (5) and (6) on pK_1 for metal hydroxyl complexes and pK_{d1} for oxygen containing inorganic acids

Deviation from linearity of experimental constants can be bound by the formation of dimmer or polymer metal ions according to the reaction

$$2[Me(H_2O)_m]^{n+} + L = [Me(H_2O)_{m-l} - L - Me(H_2O)_{m-l}]^{2n+} + 2H_2O,$$

where one metal ion in dimmer ion looses more than one water molecule in each stage of the new complex formation. Therefore experimental equilibrium constant must be changed according to equation $K = K_{exp}[H_2O]^l$, where K_{exp} is an experimental equilibrium constant of the complex formation, I is the number of water molecules lost by one metal ion at the formation of a new complex. Linear dependence of experimental data according to Eq. (4) is good when aqua metal complexes loose each number of water molecules in each stage of the new complex formation.

Theoretical values of pK_n were calculated according to Eq. (4) and the dependence of theoretical and experimental values of pK_n are presented in Fig.2. The values of the correlation constants and constants of straight lines are presented in Table 1.

Fig. 2 and Table 1 show that the values of the intercepts on the ordinate axis are close to zero and the slope angles of straight lines are close to 1. Therefore Eq. (4) can be used for calculation of values of the formation of different metal complexes and multi basic acids.

An increase of values of leads to the increase in the values of B. It is bound evidently with the increase of the degree of bond covalence when the number of hydroxyl ions or other addends in the complex rises. The dependence of B values on values for complexes or values for alkalis or multi basic acids can be described by straight lines (Fig. 3):

$$B_{com} = 0.766pK_1 + 0.242 \quad R^2 = 0.946 \qquad (5)$$

$$B_{acid} = 1.16pK_{d1} - 4.77 \quad R^2 = 0.886 \qquad (6)$$

We assume that the degree of bond covalence depends on the electron density in the central ion or charged atom that can be calculated according to Eq. (7):

$$d = (z_a - z_i)/r_i^3 \qquad (7)$$

where z_a is the number of the central ion or atom or the number of protons in its nucleus, z_i is the ion charge or the degree of oxidation of the central atom, r_i is the ion radius according to Polling [18].

Relationship between the values of pK_1 or pK_{d1} and the values of can be described by the straight line for instability constants of complexes (Figs. 4, 5) and ionization constants for alkali metal hydroxides as well as multi basic oxygen containing acids (Fig. 4). The correlation coefficients and parameters of straight lines are presented in Table 2.

Table 2

The values of the correlation coefficients, the tangent of the slope angles of straight lines and the intercept on the ordinate axis for lines in Figs. 4 and 5

Compound	R^2	Intercept	tg α
Metal hydroxide	0.837	-2.6±0.4	0.18±0.03
Oxygen containing inorganic acids	0.801	15.7±2.0	-0.041±0.018
EDTAA(3-)	0.733	-1.85±0.60	0.22±0.08
EDTAA(4-)	0.836	0.92±0.23	0.325±0.06

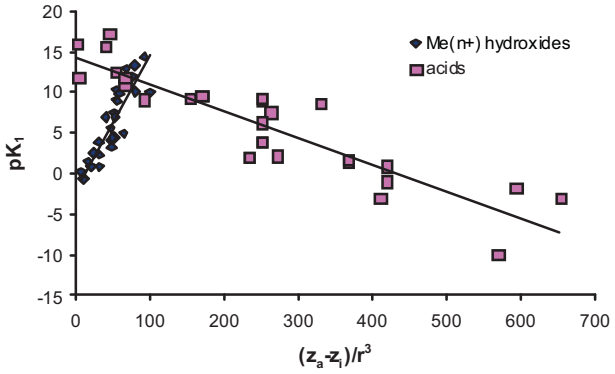

Fig. 4. Dependence of pK_1 for metal hydroxides and pK_{d1} for oxygen containing inorganic acids on $(z_a - z_i)/r_i^3$ value

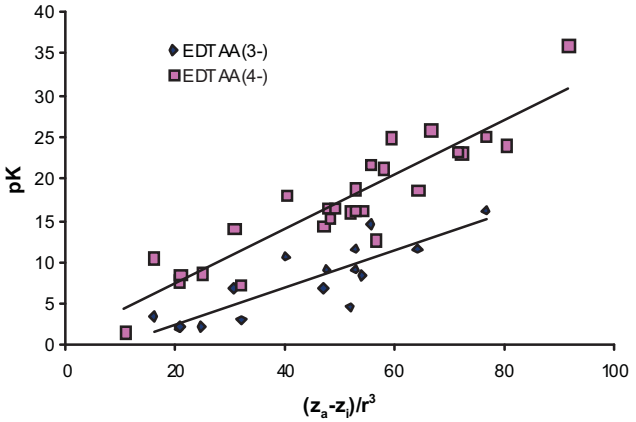

Fig. 5. Dependence of pK_1 for metal complexes with ethylene diamine tetraacetic acid on $(z_a - z_i)/r_i^3$ value at different pH. Experimental data were taken from [16]

Table 3

pK_n and pK_{dn} values calculated according to Eqs. (8) and (9) and experimental data of pK_n for ferric and ferrous ions

Ion	n in pK_n	pK_n (exp)	pK_n (according to Eq.(8)	pK_{dn} (according to Eq.(9)
Fe^{3+}	1	11.87	11.31	11.80
Fe^{3+}	2	21.17	20.21	20.72
Fe^{3+}	3	30.67	29.10	29.63
Fe^{2+}	1	5.56	5.94	12.79
Fe^{2+}	2	9.77	10.73	22.85
Fe^{2+}	3	9.67	15.52	32.91

It is needed to note that we used formal values of the electron number near central ion or charged atom that can be only the first approximation. This real value depends on the covalence degree of the bond between the central atom and oxygen as well as on the treatment between electrons of oxygen atoms in some compounds.

However we can make a few conclusions from these dependences:

- The values of pK_1 and pK_{d1} of metal hydroxides increase with the increase of $(z_a - z_i)/r_i^3$ values till 80–90. Therefore the covalence degree of Me–O bonds rises in this case.

- The values of pK_{d1} of oxygen containing inorganic acids increase with the decrease of $(z_a - z_i)/r_i^3$ values till 40–50. Therefore the covalence degree of O–H bonds rises when the electron density decreases.

- The values of pK_1 and pK_{d1} for metal hydroxides and acids are close to each other in the field of $(z_a - z_i)/r_i^3$ values from 60 to 90. The covalence degree of Me–O and H–O bonds are close to each other for these metal ions. Therefore metal hydroxides in this region have alkali and acidic properties depending on the reaction conditions.

Eqs. (8) and (9) for calculation of pK_n and pK_{dn} based on $(z_a - z_i)/r_i^3$ values were obtained from Eqs. (4)-(7) and constants in Table 2.

For metal hydroxides:

$$pK_{dn} = (0.181 + 0.139(n-1))(z_a - z_i)/r_i^3 - \\ -(2.56 + 1.72(n-1)) \quad (8)$$

For oxygen containing inorganic acids:

$$pK_{dn} = (0.0333 + 0.0386(n-1))(z_a - z_i)/r_i^3 + \\ +(14.35 + 11.87(n-1)) \quad (9)$$

These constants were calculated for ferric and ferrous ions and their comparison with experimental data show satisfactory results (Table 3).

The formal concentrations of hydroxyl containing complexes can be calculated according to Eqs (10)-(13) obtained from the schemes (1)-(3).

$$[Me(H_2O)_6^{n+}] = [Me^{n+}]_o/(1 + 10^{pK1}[OH^-] + \\ +10^{pK2}[OH^-]^2 + 10^{pK3}[OH^-]^3 \quad (10)$$

$$[Me(OH)(H_2O)_5^{(n-1)+}] = 10^{pK1}[OH^-][Me(H_2O)_6^{n+}] \quad (11)$$

$$[Me(OH)_2(H_2O)_4^{(n-2)+}] = 10^{pK2}[OH^-]^2[Me(H_2O)_6^{n+}] \quad (12)$$

$$[Me(OH)_3(H_2O)_4^{(n-3)+}] = 10^{pK3}[OH^-]^3[Me(H_2O)_6^{n+}] \quad (13)$$

Fig. 6 shows the dependence of concentration of ferric ion and its hydroxyl containing complexes on pH calculated according to the constants from Table 3.

As it is shown above, the values of pK_n and pK_{dn} for hydroxyl containing complexes of ferric ion are close to each other. Therefore they can be formed inside salts or oxides according to the reactions:

$$2[Fe(OH)(H_2O)_5^{2+}] \leftrightarrow [(H_2O)_x Fe - O - Fe(H_2O)_x^{4+}] \\ +2(5-x)(H_2O) \quad (14)$$

$$2[Fe(OH)(H_2O)_5^{2+}] + m[Fe(OH)_2(H_2O)_4^+] \leftrightarrow \\ \leftrightarrow [(H_2O)_x Fe^{2+} - (O - Fe^+)_m - Fe^{2+}(H_2O)_x^{(4+m)+}] \\ +(10-2x+4m)H_2O \quad (15)$$

where x = 2–10 depends on the medium pH.

Ferric ions in these polyions are charged and they must be soluble in water at short values of m. The reaction (16) leads to the formation of insoluble particles. These particles can be stabilized by the charged complexes according to the reaction with $[Fe(OH)_2(H_2O)_4]^+$ on their surface.

$$m[Fe(OH)_3(H_2O)_3] = [Fe(OH)O]_m + 4m(H_2O) \quad (16)$$

$$[Fe(OH)O]_m + y[Fe(OH)_2(H_2O)_4]^+ \leftrightarrow \\ \leftrightarrow [Fe_{(m+y)}(OH)_{2y}(H_2O)_{xy}]^{y+} + y(4-x)H_2O \quad (17)$$

When the concentration of $[Fe(OH)_2(H_2O)_4]^+$ is very low the particles can be stabilized by a weak dissociation of hydroxyl groups on the particle surface or by adsorption of water soluble ions from the mixture.

The distribution of $[Fe(OH)_2(H_2O)_4]^+$ complexes between the water soluble polyions and insoluble particles can be described by Eq. (18):

$$f = [Fe(OH)_2(H_2O)_4^+]/k_1[Fe(OH)_3(H_2O)_3] + \\ +[Fe(OH)_2(H_2O)_4^+]) \quad (18)$$

where f is a distribution coefficient, k_1 is the constant depended on the reaction conditions: temperature, rate of reagent batching.

The number of ferric ions in polyion depends on the formal concentration of hydroxyl containing complexes in the mixture according to reactions (14) and (15):

$$n_{polyion} = ([Fe(H_2O)_6^{3+}] + [Fe(OH)(H_2O)_5^{2+}] + \\ +f[Fe(OH)_2(H_2O)_4^+])/([Fe(H_2O)_6^{3+}] + \\ +0.5[Fe(OH)(H_2O)_5^{2+}]) \quad (19)$$

Fig. 7 shows that the number of ferric ions in polyion increases at the increase of the medium pH reaching maximum. The maximum number of ferric ions in polyion depends on f value. Experimental data [19-21] show that this number changes really from 2 to 10–12 at the increase of pH. Therefore the value of k_1 must be in the field of 0.1–0.3. The linear length of polyion can be changed from 2 to 6 nm at the increase of pH in this case.

The concentration of polyions was calculated according to Eq. (20):

$$[Polyion] = ([Fe^{3+}]_o - [Fe(OH)_3] - \\ -(1-f)([Fe(OH)_2(H_2O)_4^+])/n_{polyion} \quad (20)$$

Fig. 8 shows that the concentration of polyions decreases sharply with the increase of pH from 1 to 5. It is evidently bound with the substitution of water molecules by OH^- ions in polyions, decrease of their charges and aggregation of polyions with the formation of insoluble ferric oxide particles. Polyions are hard molecules and their conformational changes are difficult. Therefore only a small part of hydroxyl groups in polyions can form oxide bonds in aggregates and ferric oxide aggregate contains a great number of OH groups and water molecules.

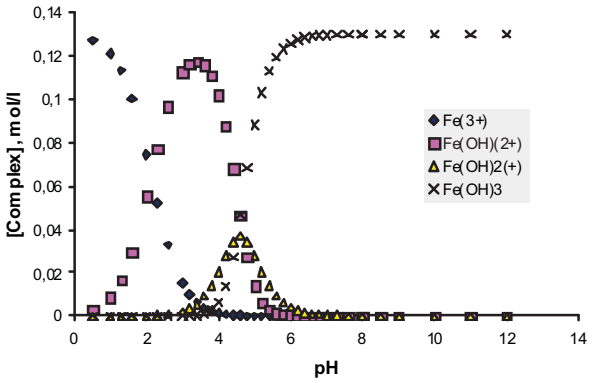

Fig. 6. Relationship between the formal concentrations of hydroxyl containing ferric complexes in the solution and pH

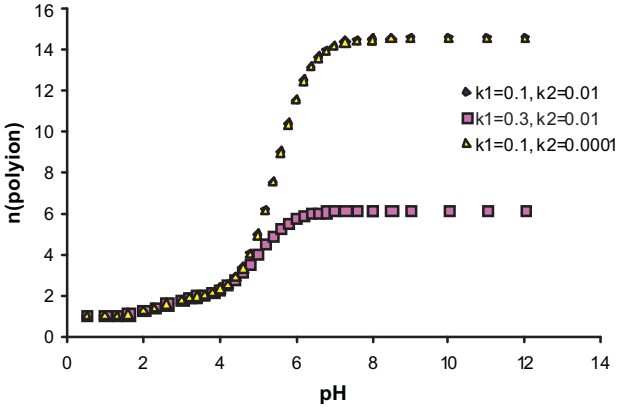

Fig. 7. Dependence of ferric ions number in polyion calculated according to Eq.(19) on the solution pH at different values of k_1 and k_2

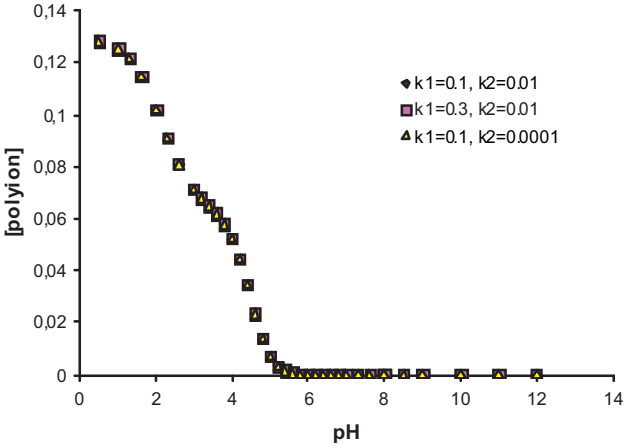

Fig. 8. Relationship between the polyions concentration in the solution calculated according to Eq. (20) and its pH at different values of k_1 and k_2

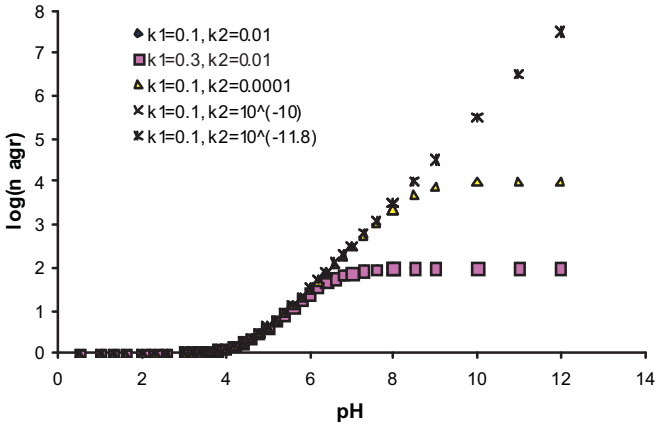

Fig. 9. Dependence of the logarithm of ferric ions number in primary ferric oxide particle calculated according to Eq. (21) on the solution pH at different values of k_1 and k_2

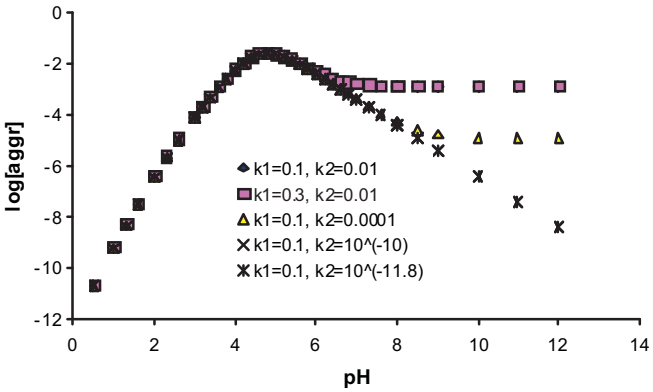

Fig. 10. Relationship between the logarithms of primary ferric oxide particles concentration in the system calculated according to Eq. (22) and its pH at different values of k_1 and k_2

The number of ferric ions in aggregate can be calculated according to Eq. (21):

$$n_{aggr} = ([Fe(OH)_3] + (1-f)[Fe(OH)_2(H_2O)_4^+])/((1-f)[Fe(OH)_2(H_2O)_4^+] + k_2[Fe(OH)_3]) \quad (21)$$

where k_2 is the constant describing dissociation of Fe–OH groups on the aggregate surface and efficiency of binding water soluble ions by ferric ion on the particle surface that stabilized aggregates or crystallite.

Fig. 9 shows that ferric ion number in aggregate increases with the increase of pH from 4 to 8–12. The maximum number of ferric ions in aggregate reaches 10^8–10^9 at pH close to 12 and the value of k_2 more than 10^{-10}. This value of k_2 is close to the constant of acidic dissociation of ferric ion (Table 3, first line). Therefore ionized ferric ions on the particle surface can be the stabilizers of the aggregates. The size of the aggregates

or crystallites containing 10^8–10^{10} ferric ions is between 40 and 100 nm that is close to the experimental data [2, 14].

The number of aggregates in the unit volume can be calculated according to Eq. (22):

$$[\text{Aggregate}] = ([Fe^{3+}]_o - [Fe(OH)(H_2O)_5^{2+}] - \\ - f([Fe(OH)_2(H_2O)_4^+]) / n_{aggr.} \quad (22)$$

Fig. 10 shows that the concentration of ferric oxide particles increases till the maximum at pH is close to 5, then it slowly decreases reaching the constant value at pH more than 9. The decrease of k_2 value leads to the increase of the number of ferric ions in the aggregate and the decrease of the aggregate concentration in the minimum at pH close to 12. Therefore this constant describes the properties of interface layer of crystallites stabilized by ferric ions in the system. The maximum on the aggregate concentration curve (Fig. 10) does not depend on the value of k_2 and evidently corresponds to the point of the aggregation of polyions with the formation of ferric oxide crystallites insoluble in water.

4. Conclusions

Equation for estimation of dissociation constants of oxygen containing bases and acids based on the dependence of electron density in the central ion is presented. It is shown that calculated constants are in satisfactory accordance with experimental data and allow to calculate concentrations of ions forming at hydrolysis. Equations describing polyions from metal hydroxides formation are elaborated and the process of formation of metal hydroxide particles is calculated.

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МОДЕЛЬ УТВОРЕННЯ ЧАСТИНОК ОКСИДІВ МЕТАЛІВ У ВОДНИХ РОЗЧИНАХ ЇХ СОЛЕЙ

Анотація. *Запропонована модель, яка описує утворення частинок оксидів металів у водних розчинах їх солей. Залежність констант нестійкості комплексів металів, констант йонізації неорганічних кислот, що містять кисень, та гідроксидів металів від електронної густини на центральному йоні або атомі кислотного залишку, дає можливість розрахувати значення цих констат. Запропоновані рівняння, що описують число йонів металу в полійоні, число йонів металу в первинних частинках оксиду металу і їх концентрації в системі в залежності від pH середовища.*

Ключові слова*: частинки оксиду металу, комплекси металів, полійони, модель.*