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CONFIGURATIONAL MODEL OF METAL ION COMPLEX FORMATION IN WATER SOLUTIONS

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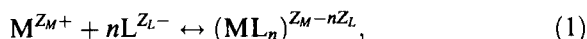
A configurational model for the quantum statistical description of the process of metal ion complex formation in water solution is proposed. Special attention is paid to the formation of hydroxocomplexes. In the framework of the model determination of such chemical characteristics of reaction as Bjerrum function, partial mole fraction and formation constants is made. It is established that regions of existence of different complex forms at variation of solution pH reaction depend on differences of configuration energies and temperature. Existence of a saturation effect which leads to a sharp change of ligand concentration in solution when the metal ion concentration crosses a certain value is established. Dependence of this effect on temperature and other parameters of the system is investigated.

Keywords: Configurational model; hydroxocomplexes; actinides

PACS numbers: 82.20.Db, 82.20.Hf, 82.30.b

1. INTRODUCTION

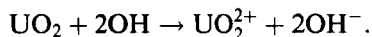
Complex formation reactions of metal ions and ligand groups are of great importance due to pollution of environment by heavy metal (including actinides) species. In general this type of reaction can be described as



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where M^{Z_M+} stands for a metal cation with valence Z_M , L^{Z_L-} corresponds to a ligand with valence Z_L and n is the number of ligands bounded to the cation.

Very often ligands are simply hydroxy anions OH^- . Then the reaction (1) is called hydrolysis which is a very common reaction. Ions H^+ and OH^- are known as very active reagents. For instance, investigations of destroyed 4-th unit of Chernobyl nuclear power plant show that stability of nuclear fuel containing glass-like mass depends on the presence of OH^- groups. The increase of OH^- content brings glassy medium stability down. Such species as H^+ and OH^- destroy the silicate matrix increasing the probability of active elements outflow from that into water [1]. From another side the process of alkalisation of uranium from nuclear fuel containing mass to water can run actively, because UO_2 reacts with OH radicals which are formed in the process of radiolysis and they are in excess in aqueous solutions:



Oxidation reactions of UO_2 by ion Fe^{3+} and radicals O and OH in water will be accompanied by the yield of uranyl ions to water. Further, uranyl UO_2^{2+} will be hydrolysed. The experimental investigations of the object's aqueous solutions of radioactive elements show that their pHs are usually in the intervals of $6.5 \div 7$ and $9 \div 10$. This stimulates hydrolysis processes and uranium leaking out from fuel containing masses. As a consequence concentration of uranium varies from 10 mg/l to 0.1 – 0.7 g/l [2, 3].

A lot of experiments are made where formation of hydroxo-complexes of actinides (ions U^{4+} , Pu^{4+} , Pu^{3+} , Am^{3+} , Th^{4+} , Np^{4+} , Np^{3+} etc.) and their compounds (such ions as UO_2^{2+} , PuO_2^{2+} , PuO_2^+ , NpO_2^{2+} , NpO_2^+ etc.) have been studied (see e.g. [4–8]). Such characteristics of the reaction as solubility product of solid forms, formation constants of different hydroxy species and appropriate partial mole fractions are usually measured as the result of the experiments.

Present work is intended to solve such aspects of the problem as to propose a simple and reliable quantum statistical model for descrip-

tion of metal ion complex formation in water solutions, to make semiempirical estimation of configurational energies on the basis of experimental data and to investigate an effect of saturation in complex formation for the solution with fixed concentration of species.

2. CONFIGURATIONAL MODEL

Main thermodynamic properties of the interaction of metal ion with ligand cations can be obtained on the basis of a simple Hamiltonian

$$\hat{H} = \sum_{ip} (\kappa_p - \mu_p) X_i^{pp}, \quad p = 0, \dots, n, \quad i = 1, \dots, N_M, \quad (2)$$

where X_i^{pp} is the projection operator of the complex i onto the configuration p , κ_p and μ_p are the energy and the chemical potential of the complex in the configuration p correspondingly, n is the maximal number of configurations for the complex and N_M is the number of metal ions. Further a simple model will be considered where the index p corresponds to the number of ligands bounded to the complex.

Despite its simplicity the Hamiltonian allows to describe main features of reaction of metal ion with ligand groups in water environment *e.g.*, the average number of ligands per complex (Bjerrum function), complex formation probability (partial mole fraction), reaction constants *etc.*

Since under the assumption that complexes do not interact, the partition function of the system can be presented as a product

$$\mathcal{Z} = \prod_p \mathcal{Z}_p,$$

where the partition function of the complexes with p ligands is

$$\mathcal{Z}_p = \sum_{N_p} \frac{1}{N_p!} Z_p^{N_p} e^{((\mu_p N_p)/\Theta)} = \exp(Z_p e^{(\mu_p/\Theta)})$$

with the partition function of the complex

$$Z_p = \frac{1}{h^3} \int e^{-(H_p/\Theta)} d\vec{p}_1 d\vec{q}_1 = \frac{V}{\lambda_p^3} e^{-\beta\kappa_p}, \quad \lambda_p = \hbar \sqrt{\frac{2\pi}{m_p \Theta}},$$

where m_p is the mass of the complex with p ligands. The great thermodynamical potential of the system is given by the expression

$$\Omega = -\Theta \ln Z = -\Theta \sum_p \ln Z_p = -\Theta \sum_p Z_p e^{(\mu_p/\Theta)},$$

through which the average number of complexes with p ligands can be expressed

$$\bar{N}_p = -\frac{\partial \Omega}{\partial \mu_p} = Z_p e^{(\mu_p/\Theta)}.$$

The total number of metal ions N_M and the number of ligands N_L bounded to metal ions are equal to

$$N_M = \sum_p \bar{N}_p, \quad N_L = \sum_p p \bar{N}_p.$$

Due to material balance $\mu_p = \mu_M + p\mu$, where μ_M and μ are the chemical potentials of "bare" metal ions and ligands correspondingly. The complex formation probability for the complex with p ligands is given by

$$\begin{aligned} w_p &= \frac{\bar{N}_p}{N_M} = \frac{Z_p e^{\beta\mu_p}}{\sum_{q=0} Z_q e^{\beta\mu_q}} = \frac{(V/\lambda_p^3) e^{-\beta\kappa_p} e^{\beta(\mu_M + p\mu)}}{\sum_{q=0} (V/\lambda_q^3) e^{-\beta\kappa_q} e^{\beta(\mu_M + q\mu)}} \\ &= \frac{m_p^{3/2} e^{-\beta\kappa_p} e^{\beta p\mu}}{\sum_{q=0} m_q^{3/2} e^{-\beta\kappa_q} e^{\beta q\mu}} = \frac{(m_p/m_0)^{3/2} e^{\beta(\Delta_p + p\mu)}}{1 + \sum_{q=1}^n (m_q/m_0)^{3/2} e^{\beta(\Delta_q + q\mu)}}, \end{aligned} \quad (3)$$

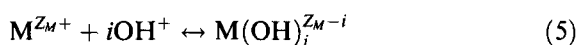
where $\Delta_p = \kappa_0 - \kappa_p$ and index "0" corresponds to the "bare" complexant, hence the average number of ligands per complex can be expressed as

$$\bar{n}_L = \sum_p p w_p; \quad (4)$$

this gives a useful relationship $N_L = \bar{n}_L N_M$.

3. ENERGIES OF COMPLEXES FOR HYDROXIDE ACTINIDES

The reaction of metal hydrolysis can be considered from two points of view: the “bare” metal ion as the complexant and the metal ion embedded by n water molecule as alternative one. In the framework of the first approach the OH^- groups are assumed to play the role of ligands in the reaction [7]



with reaction constant (named in this case as formation constant)

$$B_i = \frac{[\text{M}(\text{OH})_i]}{[\text{M}][\text{OH}]^i}.$$

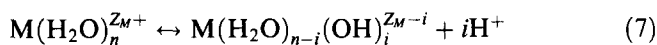
The total concentration of metal in solution is

$$C_M = [\text{M}] + [\text{MOH}] + \dots + [\text{M}(\text{OH})_n],$$

where n is the maximal possible number of OH^- groups bounded to metal ion; the partial mole fraction of $\text{M}(\text{OH})_p$ -type complex is equal to

$$f_p = \frac{[\text{M}(\text{OH})_p]}{C_M} = \frac{B_p[\text{OH}]^p}{1 + \sum_{i=1}^n B_i[\text{OH}]^i}. \quad (6)$$

Alternatively one can assume that the metal cation exists as the complex with n water molecules $\text{M}(\text{H}_2\text{O})_n^{Z_M+}$ and complexes with OH^- groups are formed by splitting out of hydrogen ions H^+ which are considered as ligands in the reaction [8]



with the reaction constant

$$K_i = \frac{[\text{M}(\text{H}_2\text{O})_{n-i}(\text{OH})_i][\text{H}]^i}{[\text{M}(\text{H}_2\text{O})_n]} = \frac{[\text{M}(\text{OH})_i][\text{H}]^i}{[\text{M}]}$$

The relation exists between constants B_i and K_i

$$K_i = (K_w)^i B_i,$$

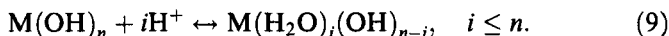
where $K_w = 10^{-14}$ is the ionic product of water. Now the total concentration of metal can be expressed as

$$C_M = [M(H_2O)_n] + [M(H_2O)_{n-1}OH] + \dots + [M(OH)_n],$$

and corresponding partial mole fraction of $M(H_2O)_{n-k}(OH)_k$ -type complex is equal to

$$\begin{aligned} f_p &= \frac{[M(H_2O)_{n-p}(OH)_p]}{C_M} \\ &= \frac{K_p [M(H_2O)_n][H]^{-p}}{[M(H_2O)_n](1 + K_1[H]^{-1} + \dots + K_n[H]^{-n})} \\ &= \frac{K'_{n-p}[H]^{n-p}}{K'_n[H]^n + K'_{n-1}[H]^{n-1} + \dots + 1} \\ &= \frac{K'_{n-p}[H]^{n-p}}{1 + \sum_{i=1}^n K'_i[H]^i}, \end{aligned} \quad (8)$$

where $K'_p = K_{n-p}/K_n$ (one should make the formal definition $K_0 = 1$); K'_p is the constant of the reaction



From the chemical point of view Eqs. (5), (7) and (9) are practically equivalent, because all of them describe the chemical equilibrium between metal ions and their hydroxides. But from the physical point of view the nature of the ligand (an OH^- group or a 17 times lighter hydrogen ion H^+ with more than two times smaller Δ_p energies) is important. It is obvious that the approach (7) leads to increase of complexant mass by the mass of nOH^- groups. Similarly to the definition of f_p (6) the partial mole fraction of $M(OH)_nH_p$ -type complexes (in other designation $M(H_2O)_p(OH)_{n-p}$) is given by

$$g_p = \frac{K'_p[H]^p}{1 + \sum_{i=1}^n K'_i[H]^i}. \quad (10)$$

In the case when $\beta\mu = \psi + \ln C_L$, where the explicit form of the variable ψ will be given in the next section, keeping in mind that partial mole fraction is equal to corresponding complex formation probability and comparing expressions (3) and (6), one can consider that

$$B_p = (m_p/m_0)^{3/2} \exp(\beta\Delta_p + p\psi)$$

and

$$\Delta_p = \frac{1}{\beta} (\ln[(m_p/m_0)^{3/2} B_p] - p\psi). \quad (11)$$

An analogical relationship can be established between K'_p and Δ_p for the H^+ ligands with use of expressions (3) and (10).

TABLE I Calculated values of Δ_p for actinide species

Ion type	p	OH^-		H^+		Ref.
		B_p	$\Delta_{p'} \text{ cm}^{-1}$	K'_p	$\Delta_{p'} \text{ cm}^{-1}$	
Pu^{4+}	1	$3.020 \cdot 10^{12}$	9412	$1.280 \cdot 10^3$	4080	[4]
	2	$1.900 \cdot 10^{24}$	18500	$7.119 \cdot 10^5$	7987	
	3	$3.415 \cdot 10^{35}$	27330	$1.132 \cdot 10^8$	11630	
	4	$2.669 \cdot 10^{46}$	35990	$3.747 \cdot 10^9$	14960	
	1	$3.5 \cdot 10^{13}$	9600	$2.0 \cdot 10^6$	5300	[7]
	2	$6.3 \cdot 10^{26}$	19000	$3.9 \cdot 10^9$	9270	
	3	$3.2 \cdot 10^{37}$	27300	$2.2 \cdot 10^{10}$	12000	
	4	$1.6 \cdot 10^{45}$	34100	$6.2 \cdot 10^{10}$	14600	
Am^{3+}	1	$3.6 \cdot 10^7$	7000	$1.5 \cdot 10^7$	6000	[5]
	2	$5.5 \cdot 10^{14}$	14000	$1.0 \cdot 10^{14}$	12000	
	3	$3.6 \cdot 10^{21}$	21000	$2.8 \cdot 10^{20}$	18000	
NpO_2^{2+}	1	$4.3 \cdot 10^{10}$	8000	$5.2 \cdot 10^9$	7000	[6]
	2	$1.6 \cdot 10^{19}$	15000	$1.4 \cdot 10^{15}$	11000	
	3	$3.1 \cdot 10^{23}$	20000	$3.2 \cdot 10^{18}$	15000	
Th^{4+}	1	$4.37 \cdot 10^{11}$	8770	$3.55 \cdot 10^3$	4050	[7]
	2	$2.19 \cdot 10^{22}$	17100	$8.52 \cdot 10^6$	8020	
	3	$9.12 \cdot 10^{32}$	25400	$1.70 \cdot 10^{10}$	12000	
	4	$4.07 \cdot 10^{43}$	33600	$3.89 \cdot 10^{12}$	15400	
PuO_2^{2+}	1	$4.0 \cdot 10^{10}$	8200	$3.2 \cdot 10^9$	6800	[7]
	2	$2.5 \cdot 10^{19}$	16000	$5.1 \cdot 10^{14}$	12000	
	3	$7.9 \cdot 10^{23}$	21000	$1.3 \cdot 10^{18}$	16000	
UO_2^{2+}	1	$1.0 \cdot 10^9$	7300	$8.0 \cdot 10^5$	5000	[7]
	2	$6.3 \cdot 10^{16}$	14000	$1.3 \cdot 10^{12}$	10000	
	3	$7.9 \cdot 10^{24}$	21000	$1.3 \cdot 10^{17}$	15000	

This expression is a very convenient tool to establish relationship between the model under discussion and chemical experiment results (namely to extract model parameters Δ_p from data of formation constant measurement). Unfortunately precision of formation constant measurement is rather poor, data from different sources can vary more than two times (relatively small change of energy difference Δ moves characteristic region of reaction to strongly acidic, alkaline or neutral solution). In the Table I there are presented calculated with use of formula (11) values of Δ_p for some species with formation constants measured in works [4–7] for both cases of OH^- and H^+ groups as ligands.

It should be pointed out, that in most cases the relation $\Delta_p = p\Delta_1$ is fulfilled with a rather good accuracy (nevertheless, it is necessary to recall mentioned above low precision of experiments). This fact allows to make the assumption, that all ligands are bounded in the same way (additively) and the correlation between ligands bounded to a complexant is small.

4. CONFIGURATION DISTRIBUTION FUNCTION

Detailed description of water solutions at arbitrary concentrations is itself a quite complicated problem. Chemical potentials of solvent and solutants should include terms taking into account finite size of particles, nonelectrostatic (*e.g.*, of Lennard–Jones type) and electrostatic interactions in solution. Special feature of water as the solvent with molecules of dipole structure is also considered in more sophisticated investigations [9, 10]. A comprehensive study of this issue with account of associative interactions and with special attention paid to actinide solutions one can find in the works [11, 12].

But for small concentration of species the expression for chemical potential μ could include only ideal gas contribution and electrostatic interaction (in Debye–Hückel approximation) terms [13]:

$$\beta\mu = \psi + \ln C_L,$$

where

$$\psi = \ln \left[P \left(\frac{2\pi\hbar^2}{m} \right)^{3/2} \beta^{5/2} \right] - \sqrt{2}e^3 \left(\frac{\pi}{v} \right)^{1/2} z^2 f^{1/2} \beta^{3/2},$$

m is the mass of the ligand particle, P stands for external pressure (assumed to be equal to the atmospheric one), e is an elementary charge, I is the ionic strength of the solution, z is the charge of the ligand, v is the volume per a solvent molecule and ε is the dielectric constant of the solution. Now expression (3) can be recast as

$$w_p = \frac{(m_p/m_0)^{3/2} C_L^p e^{\beta \Delta_p + p\psi}}{1 + \sum_{q=1}^n (m_q/m_0)^{3/2} C_L^q e^{\beta \Delta_q + q\psi}} \quad (12)$$

One can consider two main cases for such model:

1. The value of concentration of free ligands in the solution (pH reaction in the case of OH^- groups) is fixed which usually takes place in experiment.
2. The total number of ligands in the system (free and bounded to the complexant ligands) $N_{L\text{tot}}$ ($N_{L\text{tot}} = N_L + N_{L\text{sol}}$ where $N_{L\text{sol}}$ is the number of ligands in the solution) is fixed which usually takes place in natural environment.

4.1. Fixed Concentration of Ligands in Solution (Fixed pH Values)

Partial mole fractions explicitly depend on concentration of ligands (see expression (12)). In chemical notation instead of concentration itself the p -function of concentration is used very often

$$pL = -\lg C_L,$$

where C_L is the concentration of the L species. Common used example is the pH reaction of water solution (H stands for H^+ cation concentration). Concentration of hydroxy anions OH^- is in close relationship with H^+ concentration: $C_{\text{H}}C_{\text{OH}} = K_w$. Hence the pH reaction determines the $C_{\text{H}}(C_{\text{OH}})$ concentration. Dependence of partial mole fractions on the pH reaction of the solution is presented on the Figures 1a and 1b. It should be noted that bare metal ion or fully occupied complex are dominative species in greater part of pH range. Boundaries of pH regions, where particular forms of hydroxocomplex exist, depend significantly on values of the Δ_p set. This dependence is clear visible by comparison of Figures 1a and 1b calculated with use of Δ_p sets from works [4, 7] correspondingly. Comparatively small changes in Δ sets lead to appreciable shift of characteristic pH

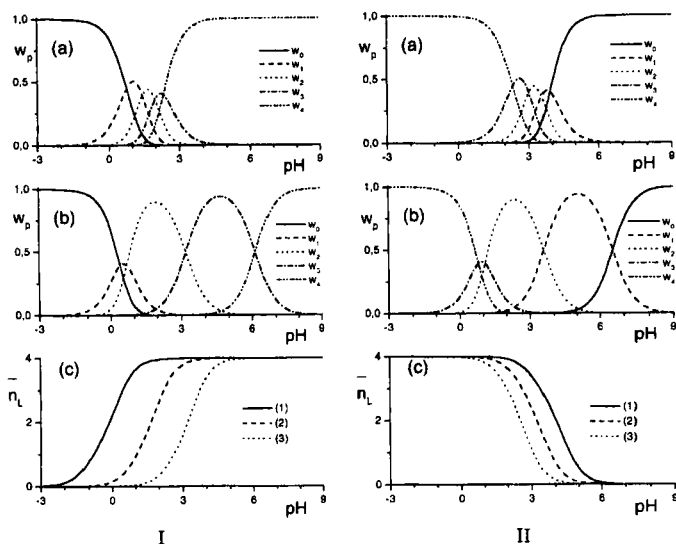


FIGURE 1 Dependence of metal cation complexation on pH reaction of the solution. If not mentioned values of parameters are as follows: $I=0.01$, $t=25^{\circ}\text{C}$, the Δ_p set is taken from Table I for Pu^{4+} [4]; (I) — $L=\text{OH}^-$, (II) — $L=\text{H}^+$.

- (a, b) Partial mole fractions as a function of pH reaction; Δ_p sets for Pu^{4+} are taken from:
 (a) — Ref. [4],
 (b) — Ref. [7].
 (c) Average number of ligands at different temperatures t : (1) — 0°C , (2) — 25°C , (3) — 50°C .

region of reaction and significant redistribution of partial mole fraction.

Chemical experiments are usually done at so called normal conditions at temperature $t=25^{\circ}\text{C}$. But as one can see on the Figure 1c variation of temperature has a similar effect as variation of Δ . Temperature effect is an important phenomena because in natural environment variation of temperature in the range $t=0-50^{\circ}\text{C}$ is usual and chemical properties of the same species can vary significantly.

4.2. Saturation Effect

The condition of the fixed total number of ligands is more convenient recast as

$$C_{L\text{tot}} = \bar{n}_L C_M + C_L, \quad (13)$$

where $C_M = N_M/N$, $C_L = N_{Lsol}/N$ and $C_{Ltot} = N_{Ltot}/N$ are corresponding concentrations, $N = N_M + N_{Lsol} + N_{solv}$ is the number of all particles in the solution, N_{solv} is the number of solvent molecules. With use of expressions (4) and (12) the above equation can be solved numerically in respect to the concentration C_L .

Results of numerical calculations are presented on the Figure 2. Saturation effect manifests itself by sharp decrease of the formation probability value of full occupied form of the hydroxocomplex and increase of the bare metal ion fraction with increase of concentration C_M (Fig. 2a). On the Figure 2b dependence of the concentration of ligands in the solution C_L on temperature t is depicted. It should be recall that increase of pM corresponds to decrease of the concentration C_M . The saturation effect which takes place at fixed total concentration of ligands C_{Ltot} is clear visible on the picture. When the concentration of metal ions C_M increases to the threshold value $C'_M = p_{max} C_{Ltot}$ the concentration of ligands C_L rapidly

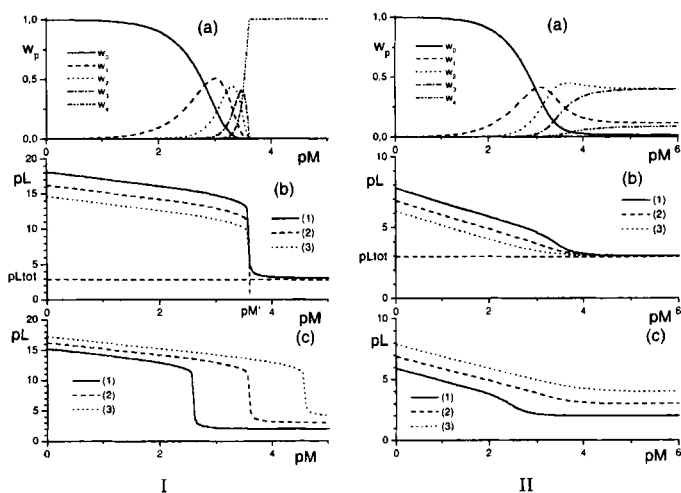


FIGURE 2 Saturation effect at variation of metal ion concentration C_M for the system with the fixed total concentration of ligands C_{Ltot} . If not mentioned values of parameters are the same as on the Figure 1 except $C_{Ltot} = 1 \cdot 10^{-3}$; (I) - $L = OH^-$, (II) - $L = H^+$.

(a) Partial mole fractions of different species of hydroxocomplex.

Concentration of ligands (OH^- groups) at:

(b) different temperatures t : (1) - $0^\circ C$, (2) - $25^\circ C$, (3) - $50^\circ C$;

(c) different concentrations C_{Ltot} : (1) - $1 \cdot 10^{-2}$, (2) - $1 \cdot 10^{-3}$, (3) - $1 \cdot 10^{-4}$.

decreases from its saturation value $C_{L_{tot}}$. Degree of exhaustion of ligands in the solution depends on temperature and strength of the metal-ligand bond. It should be noted that due to smaller configuration energies the region of sharp change is absent or less pronounced in the case of H^+ ligands. But it anyway appears all lowering of temperature (Fig. 2c–II).

The partial mole fraction of “bare” complexant increases at the increase of the complexant concentration in the solution for both cases. It takes place due to different nature of the complexant: M^{n+} for the case (I) and $M(OH)_n$ for the case (II). Hence cases (I) and (II) demonstrates different situations and one should not expect the reciprocal behaviour like in Figures 1a, b.

As one can see on the Figure 2c the threshold concentration C'_M depends on total concentration of ligands $C_{L_{tot}}$. Change of the $C_{L_{tot}}$ value does not change the shape of curves and affects the interval of C_L rapid change only.

Temperature effect at fixed total concentration of ligands $C_{L_{tot}}$ presented on the Figure 3 depends on quantity of metal ions. At concentration C_M below the threshold decrease of temperature leads to reduction of bare metal ion fraction from 1 to 0, appearance of other hydroxo species and, finally, domination of fully occupied complexes at $T \rightarrow 0$ (Fig. 3a). The concentration of ligands in solution C_L equals to $C_{L_{tot}}$ at $T \rightarrow \infty$ and $C_{L_{tot}} - p_{max}C_M$ at $T \rightarrow 0$ (Fig. 3d), the average value of ligands per complex \bar{n}_L equals to 0 at $T \rightarrow \infty$ and p_{max} at $T \rightarrow 0$ (Fig. 3e). Both dependencies have a well defined region of changes and an asymptotical behaviour at the temperature limits. For C_M slightly above the threshold the behaviour of partial mole fractions changes significantly (Fig. 3b). For example, the fully occupied complex fraction now has a maximum caused by competition of two factors: tendency of ligands to bound to complex at lower temperature and increased possibility to release ligands from the complex due to exhaustion of ligands in solution. In this case at $T \rightarrow 0$ the concentration of ligands in solution $C_L \rightarrow 0$ and the average number of ligands $\bar{n}_L = C_{L_{tot}}/C_M$ (Fig. 3d and 3e). For large C_M fully occupied complexes are practically absent and bare ions dominate in solution (Fig. 3c). In all cases the complex tends to decomposition at high temperature. The region of significant changes at variation of temperature could lay in the characteristic range for water solutions (say 0–100°C) at the appropriate Δ set.

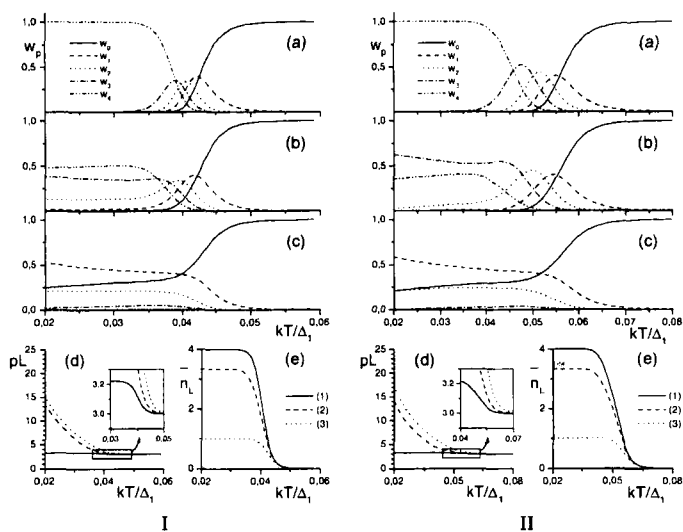


FIGURE 3 Influence of the saturation effect on temperature dependencies for the system with the fixed total concentration of ligands C_{Ltot} . Values of parameters are the same as on the Figure 1 and the Figure 2, temperature is given in dimensionless units; (I) - $L = OH^-$, (II) - $L = H^+$.

Dependence of formation probabilities on temperature at different C_M : (a) - $C_M = 10^{-4}$, (b) - $C_M = 3 \cdot 10^{-4}$, (c) - $C_M = 10^{-3}$.

Dependence of the average numbers of ligands per complex \bar{n}_L (d) and the concentration of ligands in solution C_L (e) on temperature at different C_M : (1) - $C_M = 10^{-4}$, (2) - $C_M = 3 \cdot 10^{-4}$, (3) - $C_M = 10^{-3}$.

Thus some conclusions of practical significance arise from above considerations in the case of the fixed total concentration of ligands: there is a narrow region of the metal concentration where \bar{n}_L and pH change rapidly; similar sharp changes of \bar{n}_L and pH occur in the certain region of temperature; at change of parameters (pH, temperature *etc.*) the "bare" metal or the fully occupied complex dominate in wide regions separated by the comparatively narrow zone of coexistence of various species.

5. SUMMARY

Statistical approach to the problem makes possible to investigate the system in a wide range of parameters including temperature and to describe qualitatively the process of transformation from one to

another complex configuration (redistribution of its partial mole fractions).

It is shown that in the case of hydroxocomplexes the region of the solution pH reaction, where coexistence of different complex species takes place, depends significantly on the difference of complex configuration energies, temperature and other model parameters.

If the total number of ligands is fixed, the saturation effect takes place due to exhaustion of ligands in the solution. This effect leads to the rapid change of the ligand concentration in the solution when the metal ion concentration crosses the certain threshold value. Another manifestation of the effect is suppression of partial fractions of complex species with high number of ligands at change of temperature in the low temperature limit due to exhaustion of ligands in solution.

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