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CONFIGURATIONAL MODEL OF METAL ION COMPLEX FORMATION IN WATER SOLUTIONS

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Конфігураційна модель утворення комплексів з металами у водних розчинах

І.В. Стасюк, О.В. Величко

Анотація. Запропоновано конфігураційну модель для квантово статистичного опису процесу утворення комплексів металів іонів у водному розчині. Особливу увагу звернено на утворення гідроксокомплексів. На основі запропонованої моделі можна визначити ряд хімічних характеристик реакції, зокрема функцію Б'єррума, парціальні мольні частки і константи утворення. Встановлено, що при зміні pH реакції розчину області існування різних форм комплексу залежать від різниці конфігураційних енергій та температури. Виявлено існування ефекту насичення, шо приводить до різкої зміни концентрації лігандів в розчині при проходженні концентрації іонів металу через певне значення. Досліджено залежність цього ефекту від температури та інших параметрів системи.

Configurational model of metal ion complex formation in water solutions

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Abstract. Configurational model for quantum statistical description of process of metal ion complex formation in water solution is proposed. Special attention is payed to 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 saturation effect which leads to sharp change of ligand concentration in solution when metal ion concentration crosses a certain value is found out. Dependence of this effect on temperature and other parameters of the system is investigated.

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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

$$M^{Z_M+} + nL^{Z_L-} \leftrightarrow (ML_n)^{Z_M-nZ_L}, \tag{1}$$

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, 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].

A lot of experiments are made where formation of hydroxocomplexes 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. [2]–[6]). 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 description 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 interaction of metal ion with ligand cations can be obtained on the basis of a simple Hamiltonian

$$\hat{H} = \sum_{ip} \lambda_p X_i^{pp} - \mu \sum_{ip} n_p X_i^{pp} , \tag{2}$$
$$p = 0, \ldots, p_{max} , \quad i = 1, \ldots, N_M ,$$

where X_i^{pp} is the projection operator of the complex i onto the configuration p, λ_p is the energy of the complex in the configuration p, n_p

is the number of ligands bounded to metal ion for this configuration, μ is the chemical potential of ligands, p_{max} is the maximal number of configurations for the complex and N_M is the number of metal ions.

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.

The Hamiltonian has a diagonal structure hence one can easily calculate thermodynamic functions of the model. The average values of projection operators (i.e. complex formation probability) are equal to

$$\langle X^{pp} \rangle = \frac{e^{-\beta(\lambda_p - n_p\mu)}}{\sum\limits_{q=0}^{p_{max}} e^{-\beta(\lambda_q - n_q\mu)}} = \frac{e^{\beta(\Delta_p + n_p\mu)}}{1 + \sum\limits_{q=1}^{p_{max}} e^{\beta(\Delta_q + n_q\mu)}}, \tag{3}$$

where $\Delta_p = \lambda_0 - \lambda_p$. If there are no isomer complexes (i.e. no states with the same number of ligands) $n_p = p$, values of $\langle X^{pp} \rangle$ correspond to the partial mole fraction of complexes with p ligands and p_{max} is the maximal possible number of ligands in the complex. Average number of ligands per complex $\overline{n}_L$ now can be expressed as

$$\overline{n}_L = \sum_p n_p \langle X^{pp} \rangle. \tag{4}$$

Thus the number of ligands bounded to metal ions is $N_L = \overline{n}_L N_M$.

3. Energies of complexes for hydroxide actinides

Usually the partial mole fraction of the complex ML_p is defined as

$$f_p = \frac{B_p C_L^p}{1 + \sum\limits_{q=1}^{p_{max}} B_q C_L^q}, \tag{5}$$

where B_p is the formation constant of the complex ML_p. In the case when $\beta\mu = \beta\psi + \ln C_L$, 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 (5), one can consider that

$$B_p = \exp\left(\beta(\Delta_p + p\psi)\right)$$

and

$$\Delta_p = \frac{1}{\beta} \ln B_p - p\psi. \tag{6}$$

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 1 there are presented calculated with use of formula (6) values of Δ_p for some species with formation constants measured in works [2]–[5].

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 [7,8]. A comprehensive study of this issue with account of associative interactions and with special attention payed to actinide solutions one can find in the works [9,10].

But for small concentration of species the expression for chemical potential μ could include only ideal gas and electrostatic interaction (in Debye–Hückel approximation) terms [11]:

$$\beta\mu = \beta\psi + \ln C_L, \tag{7}$$

where

$$\begin{aligned} \psi &= \ln\left(D\beta^{\frac{5}{2}}\right) - Kz^2 I^{\frac{1}{2}} \beta^{\frac{3}{2}}, \\ D &= P\left(\frac{2\pi\hbar^2}{m}\right)^{\frac{3}{2}}, \\ K &= \sqrt{2}e^3 \left(\frac{\pi}{v}\right)^{\frac{1}{2}} \varepsilon^{-\frac{3}{2}}, \end{aligned}$$

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,

Ion type	Number of OH^- groups p	B_p	Δ_p, cm^{-1}	Ref.
Pu^{4+}	1	$3.020 \cdot 10^{12}$	9433	[2]
	2	$1.900 \cdot 10^{24}$	18540	
	3	$3.415 \cdot 10^{35}$	27390	
	4	$2.669 \cdot 10^{46}$	36070	
	1	$3.5 \cdot 10^{13}$	9600	[5]
	2	$6.3 \cdot 10^{26}$	19000	
	3	$3.2 \cdot 10^{37}$	27300	
	4	$1.6 \cdot 10^{45}$	34200	
Am^{3+}	1	$3.6 \cdot 10^{7}$	7000	[3]
	2	$5.5 \cdot 10^{14}$	14000	
	3	$3.6 \cdot 10^{21}$	21000	
NpO_2^{2+}	1	$4.3 \cdot 10^{10}$	8000	[4]
	2	$1.6 \cdot 10^{19}$	15000	
	3	$3.1 \cdot 10^{23}$	20000	
Th^{4+}	1	$4.37 \cdot 10^{11}$	8860	[5]
	2	$2.19 \cdot 10^{22}$	17300	
	3	$9.12 \cdot 10^{32}$	25700	
	4	$4.07 \cdot 10^{43}$	34000	
PuO_2^{2+}	1	$4.0 \cdot 10^{10}$	8200	[5]
	2	$2.5 \cdot 10^{19}$	16000	
	3	$7.9 \cdot 10^{23}$	21000	
UO_2^{2+}	1	$1.0 \cdot 10^{9}$	7300	[5]
	2	$6.3 \cdot 10^{16}$	14000	
	3	$7.9 \cdot 10^{24}$	21000	

Table 1. Calculated values of Δ_p for actinide species.

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

$$\langle X^{pp} \rangle = \frac{C_L^p e^{\beta(\Delta_p + p\psi)}}{1 + \sum\limits_{q=1}^{p_{max}} C_L^p e^{\beta(\Delta_q + q\psi)}}. \tag{8}$$

One can consider two main cases for such model:

1. The value of concentration of ligands in 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 N_{Ltot} ($N_{Ltot} = N_L + N_{Lsol}$ where N_{Lsol} 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 (8)). In chemistry instead of concentration itself very often is used the p–function of concentration which is defined as

$$\mathrm{pL} = -\lg C_L,$$

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: $C_H C_{OH} = 10^{-14}$. Hence the pH reaction determines the C_L (C_{OH}) concentration. Dependence of partial mole fractions on the pH reaction of the solution is presented on the Fig. 1a and 1b. It should be noted that bare metal ion or fully occupied complex are dominative species in greater part of pH range. Bounds 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 Fig. 1a and 1b calculated with use of Δ_p sets from works [2] and [5] correspondingly. Comparatively small changes in Δ sets lead to appreciable shift of characteristic pH region of reaction and significant redistribution of partial mole fraction.

Chemical experiments are usually done at so called normal conditions at temperature $t = 25°$C. But as one can see on the Fig. 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 $t = 0 - 50°$C is usual and chemical properties of the same species can vary significantly.

4.2. Saturation effect

The second condition is more convenient recast as

$$C_{Ltot} = \overline{n}_L C_M + C_L, \tag{9}$$

where $C_M = N_M/N$, $C_L = N_{Lsol}/N$ and $C_{Ltot} = N_{Ltot}/N$ are corresponding concentrations, $N = N_M + N_L + N_{solv}$ is the number of all particles in the solution, N_{solv} is the number of solvent molecules. With use of expressions (4) and (8) the above equation can be solved numerically.

Results of numerical calculations are presented on the Fig. 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 Fig. 2b dependency 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 decreases from its saturation value C_{Ltot}. Degree of exhaustion of ligands in the solution depends on temperature and strength of the metal–ligand bond.

As one can see on the Fig. 2c the threshold concentration C'_M depends the on total concentration of ligands C_{Ltot}. Change of the C_{Ltot} 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_{Ltot} presented on the Fig. 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 $\mathrm{T} \to 0$ (Fig. 3a). The average value of ligands per complex $\overline{n}_L$ equals to 0 at $\mathrm{T} \to \infty$ and p_{max} at $\mathrm{T} \to 0$ (Fig. 3d), the concentration of ligands in solution C_L equals to C_{Ltot} at $\mathrm{T} \to \infty$ and $C_{Ltot} - p_{max} C_M$ at $\mathrm{T} \to 0$ (Fig. 3e). Both dependencies have a well defined region of changes and asymptotical behaviour at the temperature limits. For C_M slightly above the threshold

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 $\to 0$ the concentration of ligands in solution $C_L \to 0$ and the average number of ligands $\overline{n}_L = C_{Ltot}/C_M$ (Fig. 3d and 3e). For large C_M fully occupied complexes are practically absent and bare ions dominate in solution (Fig. 3c). 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.

5. Summary

Quantum statistical approach to the problem makes possible to investigate the system in the wide range of parameter 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.

6. Acknowledgement

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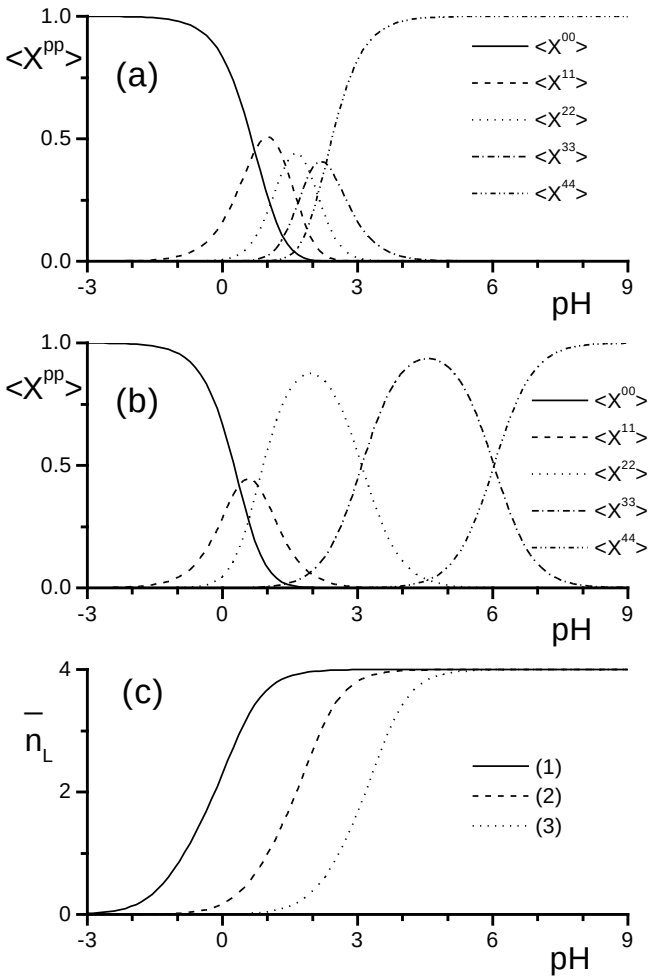

Figure 1. Dependence of metal cation complexation by OH^- groups on pH reaction of the solution. If not mentioned values of parameters are as follows: I=0.01, t=25°C, the Δ_p set is taken from Table 1 for Pu^{4+} [2].

(a,b) Partial mole fractions as a function of pH reaction; Δ_p sets for Pu^{4+} are taken from: (a) — Ref. [2], (b) — Ref. [5].

(c) Average number of ligands at different temperatures t: (1) — 0°C, (2) — 25°C, (3) — 50°C.

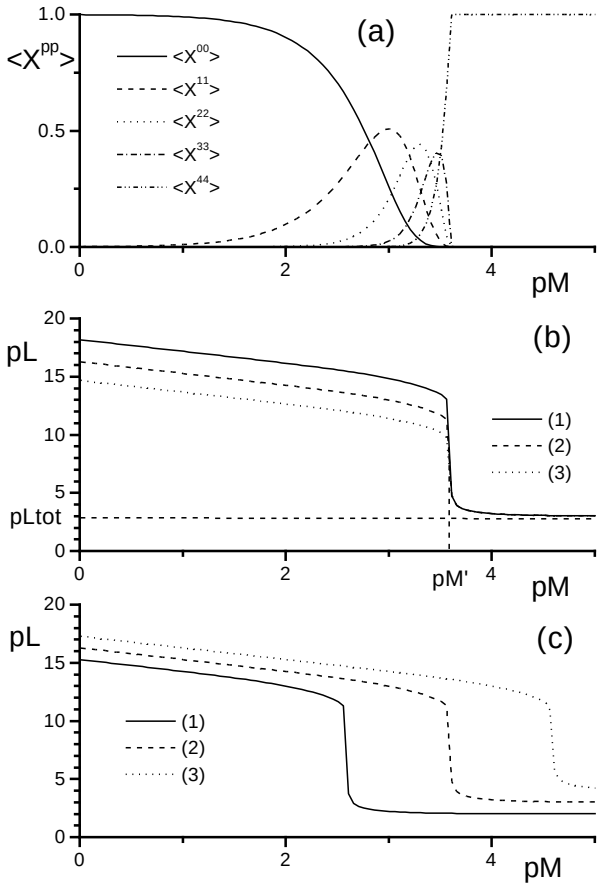

Figure 2. Saturation effect at variation of metal ion concentration C_M for the system with the fixed total concentration of ligands C_{Ltot}. If not mentioned values of parameters are the same as on the Fig. 1 except C_{Ltot}=1·10^{-3}.

(a) Partial mole fractions of different species of hydroxocomplex. Concentration of ligands (OH^- groups) at:

(b) different temperatures t: (1) — 0°C, (2) — 25°C, (3) — 50°C;

(c) different concentrations C_{Ltot}: (1) — 1·10^{-2}, (2) — 1·10^{-3}, (3) — 1·10^{-4}.

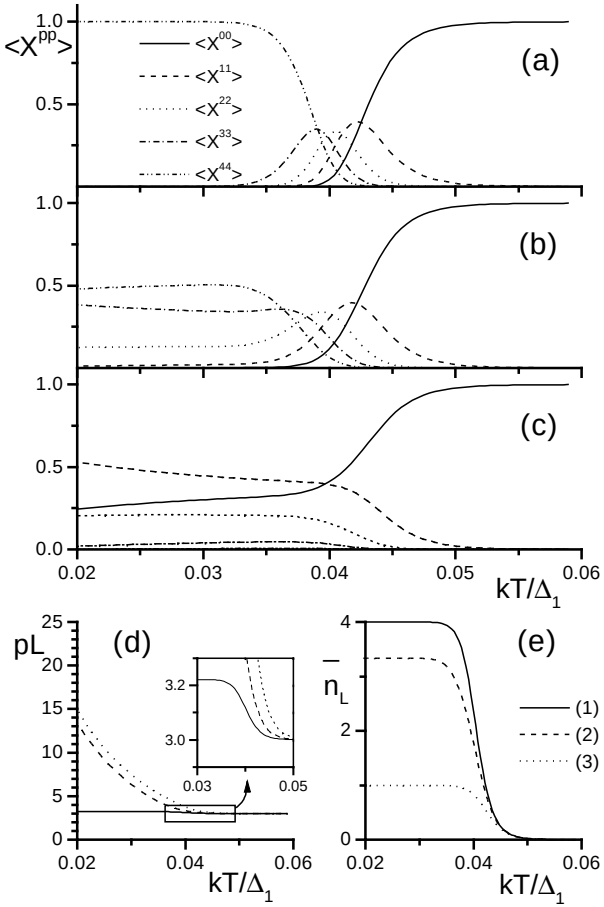

Figure 3. Influence of the saturation effect on temperature dependencies for the system with the fixed total concentration of ligands C_{Ltot}. Values of parameters are the same as on the Fig. 1 and the Fig. 2, temperature is given in dimensionless units.
Dependence of formation probabilities on temperature 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 $\overline{n}_L$ (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) — $C_M = 10^{-3}$.

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