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# Model description of the H–bonded transuranium complexes

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In the framework of configurational model it is established that regions of existence of various forms of actinide hydroxocomplexes at variation of solution pH depend on differences of configuration energies and temperature. Saturation effect is found out, which leads to a sharp change of ligand concentration. Model of the polymerization of ionic groups $UO_2[(OH)_2UO_2]_n^{2+}$ into chain structure via hydrogen bonds is proposed. The thermodynamic stability of such a formation is investigated depending on the number of links at different temperatures and at various boundary conditions.

**Key words:** *aqueous solutions, complex formation, polymerization*

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

## 1. Introduction

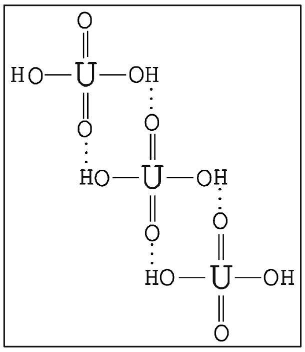


**Figure 1.** The schematic structure of polymer complex of uranile.

The first part of the work intends to propose a simple and reliable quantum statistical model for describing the actinide hydroxocomplex formation in aqueous solutions investigated in the range of experiments (see e.g. [1]–[4]), to make semiempirical estimation of complex configurational energies based on the experimental data and to investigate an effect of saturation in the process of complex formation for the solution with high concentration of metal ions.

The second part of the work is devoted to an investigation of polymer complexes of uranile $\mathrm{UO_2[(OH)_2UO_2]_n^{2+}}$ with sheet–like double bridges of ionic groups $\mathrm{OH^-}$ (Figure 1) [5]. Objects of such a type are formed under the influence of hydrolysis and radiolysis of electrolytic aqueous solutions. Our main purpose is to describe the thermodynamics of the polymerization process from the microscopic point of view allowing for the quantum–statistical character of distribution of protons on hydrogen bonds.

## 2. Configurational model of metal hydroxocomplexes

Main thermodynamic properties of the subsystem of metal ion interacting with ligand cations can be obtained based on a simple Hamiltonian

$$\hat{H} = \sum_{ip} \lambda_p X_i^{pp} - \mu \sum_{ip} n_p X_i^{pp} \ , \tag{1}$$

where $p$=0, …, $p_{\max}$, $i$=1, …, $N_{\mathrm{M}}$, $X_i^{pp}$ is the projection operator for the complex $i$ onto the configuration $p$ with the energy $\lambda_p$ and $n_p$ ligands bounded to metal ion, $\mu$ is the chemical potential of ligands, $p_{\max}$ is the maximal number of possible configurations for the complex and $N_{\mathrm{M}}$ is the full number of metal ions. The average values of projection operators (i.e. complex formation probabilities) are equal to

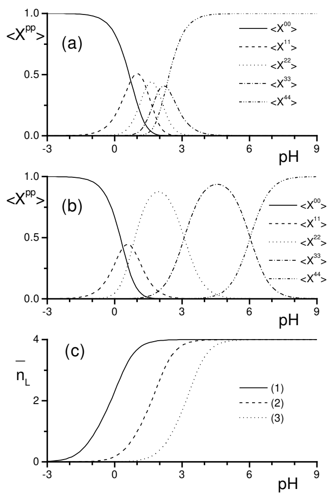
$$\langle X^{pp} \rangle = e^{\beta(\Delta_p + n_p \mu)} \Big/ \left[ 1 + \sum_{q=1}^{p_{\max}} e^{\beta(\Delta_q + n_q \mu)} \right] , \tag{2}$$

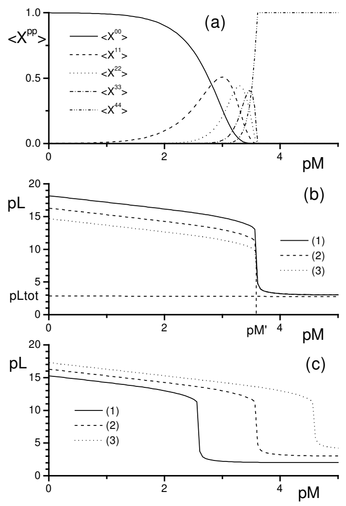
where $\Delta_p = \lambda_0 - \lambda_p$. If there is only one state with the given number of ligands $n_p = p$, the mean value $\langle X^{pp} \rangle$ correspond to the partial mole fraction of complexes with $p$ ligands. Average number of ligands per complex $\overline{n}_{\mathrm{L}}$ can be expressed as $\overline{n}_{\mathrm{L}} = \sum_p n_p \langle X^{pp} \rangle$. Thus the number of ligands bounded to metal ions is $N_{\mathrm{L}} = \overline{n}_{\mathrm{L}} N_{\mathrm{M}}$. Corresponding concentrations are to be defined as $C_{\mathrm{M}} = N_{\mathrm{M}}/N$, $C_{\mathrm{L}} = N_{\mathrm{Lsol}}/N$ and $C_{\mathrm{Ltot}} = N_{\mathrm{Ltot}}/N$, where $N = N_{\mathrm{M}} + N_{\mathrm{L}} + N_{\mathrm{solv}}$ is the total number of particles and $N_{\mathrm{solv}}$ is the number of solvent molecules.

For small concentration of metal ions the expression for chemical potential $\mu$ could include only ideal gas and electrostatic interaction (in Debye–Hückel approximation) terms: $\beta\mu = \beta\psi + \ln C_{\mathrm{L}}$, where the variable $\psi$ depends on: the mass of the ligand particle, pressure (here the atmospheric one), the ionic strength and the dielectric constant of the solution. Partial mole fraction is equal to corresponding complex formation probability and comparing their definitions one can see that $\Delta_p = \beta^{-1} \ln B_p - p\psi$, where $B_p$ is the formation constant of the complex $\mathrm{ML}_p$. By means of this expression the following values of energy parameters $\Delta_p$ have been calculated here based on the data of forming the constant measurement originated from the papers cited below: for $Pu^{4+}$ they are $\Delta_1$=9433 cm$^{-1}$, $\Delta_2$=18540 cm$^{-1}$, $\Delta_3$=27390 cm$^{-1}$ and $\Delta_4$=36070 cm$^{-1}$ [1], while data from [2] give the values 9600, 19000, 27300 and 34200 cm$^{-1}$ correspondingly; for $Th^{4+}$ they are 8860, 17300, 25700 and 34000 cm$^{-1}$ [2]; for $Am^{3+}$ — 7000, 14000 and 21000 cm$^{-1}$ [3]; for $UO_2^{2+}$ — 7300, 14000 and 21000 cm$^{-1}$ [2]; for $PuO_2^{2+}$ — 8200, 16000 and 21000 cm$^{-1}$[2]; for $NpO_2^{2+}$ — 8000, 15000 and 20000 cm$^{-1}$[4].

One can consider two main cases for such a model:

**1. Fixed concentration of ligands in solution (fixed pH value).** Regions of pH values, where particular forms of hydroxocomplexes exist, depend significantly on values of the $\Delta_p$ set (compare Figure 2a and 2b). Chemical experiments are usually done at so called normal conditions at temperature T=25°C. But as one can see in Figure 2c variation of temperature has a similar effect as variation of $\Delta_p$.



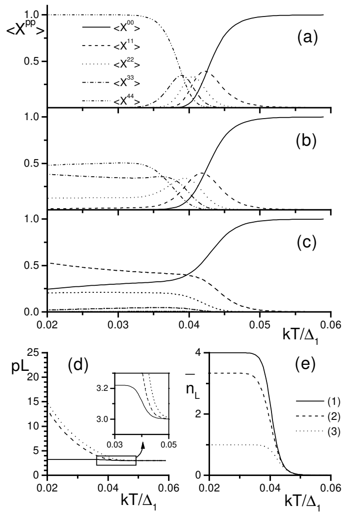




**Figure 2.** (left) Partial mole fractions (a,b) and average number of ligands (c) at different T ((1) – 0°C, (2) – 25°C, (3) – 50°C) as functions of the solution pH. I=0.01, T=25°C, the $\Delta_p$ set is calculated for $Pu^{4+}$ data from [1] (a,c) and [2] (b).

**Figure 3.** (centre) Saturation effect at variation of $C_{\rm M}$ for the system with fixed $C_{\rm Ltot}$: partial mole fractions (a); concentration of ligands at different T (b) ((1) – 0°C, (2) – 25°C, (3) – 50°C) and different $C_{\rm Ltot}$ (c) ((1) – $10^{-2}$, (2) – $10^{-3}$, (3) – $10^{-4}$). Values of parameters see Figure 2 except $C_{\rm Ltot}$=$10^{-3}$, pX$=-\lg C_X$.

**Figure 4.** (right) Influence of the saturation effect on temperature behaviour of the system with fixed $C_{\rm Ltot}$: dependencies of formation probabilities at different $C_{\rm M}$ ((a) – $10^{-4}$, (b) – $3{\cdot}10^{-4}$, (c) – $10^{-3}$), $\overline{n}_{\rm L}$ (d) and $C_{\rm L}$ (e) at different $C_{\rm M}$ ((1) – $10^{-4}$, (2) – $3{\cdot}10^{-4}$, (3) – $10^{-3}$) on temperature. Values of parameters see Figure 3.

**2. Saturation effect (fixed $N_{\rm Ltot}$ value).**

At fixed total number of ligands concentrations should satisfy the equation $C_{\rm Ltot}=\overline{n}_{\rm L}C_{\rm M}+C_{\rm L}$, which can be solved numerically. Saturation effect manifests itself by sharp decrease of the formation probability value of highly occupied forms of the hydroxocomplex and increase of the bare metal ion fraction with increase of concentration $C_{\rm M}$ (Figure 3a). When the concentration of metal ions $C_{\rm M}$ increases to the threshold value $C'_{\rm M}=p_{\rm max}C_{\rm Ltot}$ the concentration of ligands $C_{\rm L}$ rapidly decreases from its saturation value $C_{\rm Ltot}$ (Figure 3b). The threshold concentration $C'_{\rm M}$ depends on the total concentration of ligands $C_{\rm Ltot}$ (Figure 3c).

For fixed concentration $C_{\rm Ltot}$ at the concentration $C_{\rm M}$ below the threshold value lowering of temperature leads to a decrease of bare metal ion fraction from 1 to 0, as well as to the appearance of intermediate complex configurations and, finally, to the domination of fully occupied complexes at T→0 (Figure 4a). The concentration of ligands in solution $C_{\rm L}$ equals to $C_{\rm Ltot}$ at T→∞ and $C_{\rm Ltot}-p_{\rm max}C_{\rm M}$ at T→0 (Figure 4d) and the corresponding values of $\overline{n}_{\rm L}$ are 0 and $p_{\rm max}$ (Figure 4e). For $C_{\rm M}$ slightly above the threshold, behaviour of partial mole fractions changes significantly (Figure 4b). In this case at T→0 the concentration $C_{\rm L}$→0 and the average number of ligands is $\overline{n}_{\mathrm{L}}{=}C_{\mathrm{Ltot}}/C_{\mathrm{M}}$ (Figure 4d and 4e). For large $C_{\mathrm{M}}$ fully occupied complexes are not practically present and bare ions dominate in solution (Figure 4c).

## 3. Statistical model of double-bounded polymer chain

The model of a molecular complex, where pairs of hydrogen bonds join in series of ionic groups, is presented in Figure 1. A case is considered, when intermediate ionic groups and groups (A) and (B) at the ends of a polymer are the same regarding their properties.

The vectors $||k,l_k\rangle = |k;S^z_{k1},S^z_{k2}\rangle \quad (l_k = 1\ldots4)$ are introduced to describe the states of each double bridge (the eigenvalues $S^z_{kr} = \pm1/2$ of pseudospin component for $r$ hydrogen bond, $r=1,2$, on $k$ double bridge correspond to two equilibrium positions of proton on the bond).

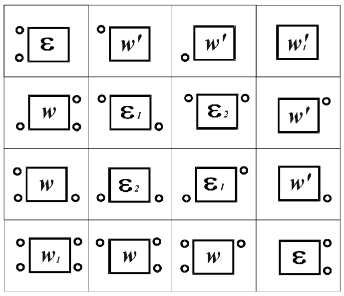



**Figure 5.** Energies of proton configurations.

Hamiltonian of a proton subsystem can be written in terms of Hubbard operators $X^{pq}_k = |k;p\rangle\,\langle k;q|$. It consists of two parts $\hat{H} = \hat{H}_{\mathrm{S}} + \hat{H}_{\mathrm{L}}$, where

$$\hat{H}^{\mathrm{S}}_m = (m+2)\varepsilon + \sum_{k=1}^{m}\sum_{pq} B^{pq}\hat{X}^{pp}_k\hat{X}^{qq}_{k+1} + \hat{H}^{\mathrm{A}}_1 + \hat{H}^{\mathrm{B}}_{m+1} \quad (3)$$

describes the short–range configurational interaction, and

$$\hat{H}^{\mathrm{L}}_m = -\frac{a^2(Ze)^2}{c^3}\sum_{\substack{l,l'=1\\(l\neq l')}}^{m+1}\frac{(\hat{X}^{11}_l-\hat{X}^{44}_l)(\hat{X}^{11}_{l'}-\hat{X}^{44}_{l'})}{|l-l'|^3} \quad (4)$$

is an electrostatic dipole–dipole long–range part (here $m$ is the number of intermediate ionic groups). The components of $\{B^{pq}\}$ matrix

$$\{B^{pq}\} = \begin{pmatrix} 0 & \frac{w'+w}{2}-\varepsilon & \frac{w'+w}{2}-\varepsilon & w'_1-\varepsilon-2\delta \\ \frac{w'+w}{2}-\varepsilon & \varepsilon_1-\varepsilon & \varepsilon_2-\varepsilon & \frac{w'+w}{2}-\varepsilon \\ \frac{w'+w}{2}-\varepsilon & \varepsilon_2-\varepsilon & \varepsilon_1-\varepsilon & \frac{w'+w}{2}-\varepsilon \\ w_1-\varepsilon+2\delta & \frac{w'+w}{2}-\varepsilon & \frac{w'+w}{2}-\varepsilon & 0 \end{pmatrix} \quad (5)$$

are expressed in terms of the energies of proton configurations in a potential minima near ionic groups (Figure 5).

By the terms $\hat{H}^{\mathrm{A}}_1 = \sum\limits_p \alpha_{\mathrm{A}p}\hat{X}^{pp}_1$ and $\hat{H}^{\mathrm{B}}_{m+1} = \sum\limits_p \alpha_{\mathrm{B}p}\hat{X}^{pp}_{m+1}$ the boundary effects are described; the $\alpha_{\mathrm{A,B}\,p}$ coefficients take certain values of configuration energies from the set of a possible one (Figure 5) depending on the number of protons joined outside to the boundary ionic groups; $Ze$ is the effective charge of proton, $a$ is the distance between potential minima on the hydrogen bond and $c$ is the distance between centres of ionic groups.

Calculating the free energy of a proton subsystem we use the expression

$$F_m = -\frac{1}{\beta}\ln Z_m\,; \quad Z_m = Z_m^{\mathrm{S}}\Big\langle \mathrm{e}^{-\beta \hat{H}_m^{\mathrm{L}}}\Big\rangle_{\mathrm{S}}\,, \tag{6}$$

where $Z_m^{\mathrm{S}} = Sp\left[\mathrm{e}^{-\beta \hat{H}_m^{\mathrm{S}}}\right]$ is partition function of the system with the short–range interactions only; $\langle\ldots\rangle_{\mathrm{S}}$ denotes the statistical average with Hamiltonian $\hat{H}_m^{\mathrm{S}}$.

The $Z_m^{\mathrm{S}}$ function is evaluated by means of transfer matrix method

$$Z_m^{\mathrm{S}} = \sum_{pq}\left[\hat{A}\Big(\mathrm{e}^{-\beta\hat{B}}\Big)^m\hat{D}\right]_{pq} = \sum_{pq}\left[\hat{A}\,\hat{U}\hat{\Lambda}^m\hat{U}^{-1}\hat{D}\right]_{pq}, \tag{7}$$

where $\hat{A} = \sum\limits_p \mathrm{e}^{-\beta\alpha_{\mathrm{A}p}}\hat{X}_{pp}$ and $\hat{D} = \sum\limits_p \mathrm{e}^{-\beta\alpha_{\mathrm{B}p}}\hat{X}_{pp}$. Transfer matrix $\mathrm{e}^{-\beta\hat{B}}$ is transformed into a diagonal form by means of a unitary transformation $\hat{U}^{-1}\mathrm{e}^{-\beta\hat{B}}\hat{U} = \hat{\Lambda}$.

Considering the small values of $\lambda = -\beta a^2(Ze)^2/c^3$ ($\beta = 1/kT$) parameter we use a cumulant expansion $\langle \mathrm{e}^{-\beta\hat{H}_m^{\mathrm{L}}}\rangle_{\mathrm{S}} = 1 - \lambda\langle\hat{H}_m^{\mathrm{L}}\rangle_{\mathrm{S}} + \frac{\lambda^2}{2}\left[\langle(\hat{H}_m^L)^2\rangle_{\mathrm{S}} - \langle\hat{H}_m^L\rangle_{\mathrm{S}}^2\right] - \ldots$ taking into account corrections of the first and second orders.

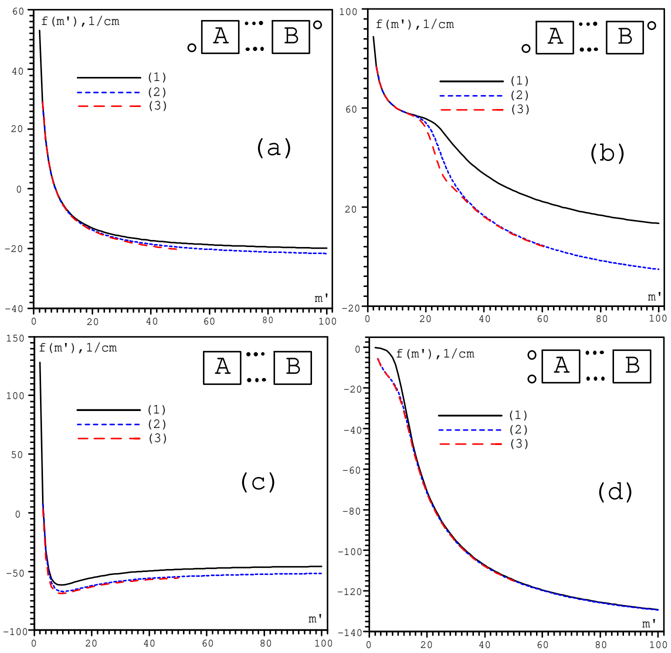



**Figure 6.** Free energy $f(m')$ per one ionic group as a function of $m'$: (1) – the contribution of the short–range interaction, (2) and (3) – the full free energy up to the first and second orders of cumulant expansion correspondingly. (a) – $T = 298$ K, $\varepsilon_1 = \varepsilon_2 = 125$ cm$^{-1}$, $w' = w = 800$ cm$^{-1}$; (b) – $T = 150$ K, $\varepsilon_1 = \varepsilon_2 = 125$ cm$^{-1}$, $w' = w = 800$ cm$^{-1}$; (c) – $T = 298$ K, $\varepsilon_1 = \varepsilon_2 = 125$ cm$^{-1}$, $w' = 200$ cm$^{-1}$, $w = 800$ cm$^{-1}$; (d) – $T = 298$ K, $\varepsilon_1 = \varepsilon_2 = 0$ cm$^{-1}$, $w' = w = 800$ cm$^{-1}$ ($\varepsilon = 0$).

The results presented below are obtained by means of numerical calculations. In Figure 6 the dependencies of free energy $f(m')$ per one ionic group on the length of polymer chain (number of ionic groups $m'$) for the different boundary conditions at various temperatures are shown.

We have used the values of energies of proton configurations $\varepsilon_1$ and $\varepsilon_2$ in the range $100\ldots150$ cm$^{-1}$; $w$ and $w'$ in the range $600\ldots800$ cm$^{-1}$ ($Ze = 1/4e$). These values are characteristic of the system with hydrogen bonds.

The parameters $a$ and $c$ were taken from structural data [6] ($a = 0.2$ Å and $c = 6.064$ Å). These distances are specific for hydrogen–bonded crystal compounds of uranile with different sorts of atom inclusion ($\lambda_{\mathrm{T=298K}} = -0.078$).

## 4. Summary

The configurational model is proposed for describing the H–bonded transuranium complexes in aqueous solutions, which gives a correct dependence of partial mole fractions of actinide hydroxocomplexes on the solution pH, temperature, etc. At high metal ion concentration a saturation effect can take place, which leads to the rapid change of the ligand concentration in the solution. If the metal ion concentration crosses the threshold value, suppression of complexes with high number of ligands at low temperature takes place due to exhaustion of ligands in solution.

For the proposed model of polymer chain, the dependence of free energy per one ionic group on the number $m'$ of groups is investigated. In some cases the non-monotonous character of dependencies $f(m')$ on $m'$ is discovered (see, for example, bends (Figure 6b) or minimum (Figure 6c) of $f(m')$ function). In almost all boundary conditions we observe the decrease of the free energy per one ionic group with the increasing number of ionic group $m'$. This gives an evidence that the formation of a polymer chain structure is thermodynamically advantageous.

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### Модельний опис трансуранових комплексів з водневими зв'язками

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В рамках конфігураційної моделі встановлено, що при зміні pH розчину області існування різних форм гідроксокомплексів залежать від різниці конфігураційних енергій та температури. Виявлено ефект насичення, що приводить до різкої зміни концентрації лігандів. Запропоновано модель полімеризації іонних груп $UO_2[(OH)_2UO_2]_n^{2+}$ в ланцюжки через водневі зв'язки. Вивчено стійкість таких утворень залежно від числа зв'язків при різних температурах та крайових умовах.

**Ключові слова:** *водні розчини, комплексоутворення, полімеризація*

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