

An Independent Method for Data Selection of Long-life Radionuclides (Actinides and Fission Products) in the Geosphere

By Marc Henry* and Thierry Merceron**

* Laboratoire de Chimie de la Matière Condensée, Université Pierre et Marie Curie, T. 54–55 E5,
4, Place Jussieu, F-75252 Paris Cedex 05, France

** Agence Nationale pour la gestion des Déchets RADioactifs (ANDRA), Route du panorama R. Schuman,
B.P. 38, F-92266 Fontenay-aux-Roses Cedex, France

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Abstract

An independent method for data selection of long-life radionuclides based on the electronegativity equalization principle is proposed to predict the speciation of metal cations as a function of the solution pH. Hydrolysis, condensation and complexation reactions of metal cations in aqueous media are, by this simple model, unified and can be analyzed in terms of electronegativities, oxidation states and coordination numbers with a specific PC software. This paper describes the thermodynamical basis and the underlying concepts of the model in relation to the aqueous actinide chemistry of elements such as U and Tc. It is then shown that the model could provide a complementary approach to existing softwares based on thermodynamic data bases allowing to make intelligent and reasonable choices for the various complexes to consider in complex geochemical codes.

1. Introduction

Water is a solvent able to transport any chemical element in simple ionic or complex form, owing to both its high dielectric constant and strongly protic nature. This explains the geological importance of aqueous solutions in the field of radionuclide migration (Allard *et al.*, 1984), but also their tremendous technological importance in the field of material synthesis (Henry *et al.*, 1992). To the best of our knowledge, the modelling of the chemical behavior of radionuclides in the atmosphere, hydrosphere or biosphere relies heavily, at the present time, on equilibrium thermodynamics. Consequently, most of the research done in this field is devoted to the determination of equilibrium constant and to the development of reliable data bases. If experimental equilibrium constants are not available, it becomes impossible to predict the speciation of a given cation without referring to a theoretical model which gives estimates of equilibrium constants. In both cases, the detailed chemical structure of the solute species is barely taken into account, leading to a whole range of empirical constants having no well-defined physical meaning. In the following we propose a new way of describing the chemical speciation of metallic cations in an aqueous medium which do not rely on the knowledge of equilibrium constants. This theoretical model uses parameters having well-defined physi-

cal meanings (oxidation states, coordination numbers, electronegativities) which are function of the detailed structure of the solute species. As speciation calculations require rather precise estimate of equilibrium constants (0.2–0.5 log units), this model is not quantitative enough to replace softwares based on well-referenced thermodynamic data bases. Its only aim is to show that from an electronegativity standpoint, severe restrictions exist on the composition of the first coordination sphere of cations if electronic equilibrium with the surrounding medium is to be reached. This qualitative model thus provide a completely data base-independent and complementary approach which could be of great help for making intelligent choices among a wide range of potential chemical species.

2. The Partial Charge Model (PCM)

The model is based upon the electronegativity equalization principle (EEP) proposed by Sanderson (1951). According to this principle, electronegativities of atoms within any chemical compound have to equalize to the same value upon chemical bonding. This comes from the fact that electronegativity χ is the electronic version of the thermodynamic chemical potential $\mu = \partial G / \partial N$ (Parr *et al.*, 1978):

$$\chi = -\mu_e = - \left. \frac{\partial E}{\partial N} \right|_z \quad (1)$$

Experiments show that for atoms the variation of the total energy E with the number of electrons N can be well approximated through a quadratic relationship (Iczkowski and Margrave, 1961):

$$E = E_0 + \chi^0(Z-N) + \frac{1}{2} \eta(Z-N)^2 \quad (2)$$

where E_0 is the energy of the neutral atom of atomic number Z , χ^0 its electronegativity and η the atomic hardness (Parr and Pearson, 1983) which is inversely proportional to the covalent radius (Mortier *et al.*, 1985). According to (1) and (2) the electronegativity of an atom depends on its charge $q = Z - N$ through:

$$\chi = - \left. \frac{\partial E}{\partial N} \right|_z = \chi^0 + \eta q \quad (3)$$

In a chemical compound having n atoms and a total electrical charge z , the electronegativity of each atom i varies according to (3): $\chi_i = \chi_i^0 + \eta_i q_i$. In that case the EEP states that at equilibrium all electronegativities have to be equal: $\chi_i = \langle \chi \rangle \forall i = 1, \dots, n$, with $\langle \chi \rangle$ the so-called mean electronegativity of the compound. Applying the charge conservation constraint to Equation (3) and introducing the atomic softness $\sigma = 1/\eta$ (Yang and Parr, 1985) leads to:

$$\sum_{i=1}^n q_i = z \Leftrightarrow \sum_{i=1}^n \sigma_i (\langle \chi \rangle - \chi_i^0) = z \Rightarrow \langle \chi \rangle = \frac{\sum_{i=1}^n \sigma_i \chi_i^0 + z}{\sum_{i=1}^n \sigma_i} \quad (4)$$

From a practical point of view, a choice have to be made concerning the electronegativity and hardness scales to use in conjunction with (4). We have checked that the Allred-Rochow scale (Little and Jones, 1960), (Batsanov, 1968), (Zhang, 1982) where electronegativity is proportional to the ratio of the nuclear effective charge Z_{eff} computed according to Slater rules to the square of the Pauling covalent radius r_{cov} ($\chi \propto Z_{\text{eff}}/r_{\text{cov}}^2$) is well-suited for our needs. Moreover, as the covalent radius is a good estimate for atomic size, the hardness could be approximated on this particular scale as $\eta = \sigma^{-1} = k\sqrt{\chi^0}$, with k an empirical constant to be determined from known partial charges distributions. Choosing the HX series ($X = \text{F, Cl, Br and I}$) with $q_{\text{H}} = -q_{\text{X}} = q$ derived from dipolar moment data (0.416, 0.177, 0.121 and 0.059 respectively) leads to $k = 1.36$ (Henry *et al.*, 1992). Consequently with (4) and the approximation $\sigma_i = (1.36\sqrt{\chi_i^0})^{-1}$, it becomes possible to compute the partial charge on any atom for a given stoichiometry.

Relations (4) may also be used to handle atomic groups rather than atoms as softnesses are additive. According to (4), any atomic group G having m atoms, has a global softness σ_G and a mean electronegativity χ_G given by:

$$\sigma_G = \sum_{i=1}^m \sigma_i = \sum_{i=1}^m (1.36\sqrt{\chi_i^0})^{-1} \quad (5)$$

$$\text{and } \chi_G = \left(\sum_{i=1}^m \sqrt{\chi_i^0} \right) \div (1.36\sigma_G).$$

Consequently if the group G is part of a compound having a mean electronegativity $\langle \chi \rangle$, its partial charge may be calculated according to:

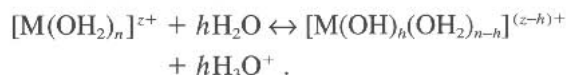
$$q(\langle \chi \rangle, \chi_G) = \sum_{i=1}^m q_i = \sum_{i=1}^m \frac{\langle \chi \rangle - \chi_i^0}{1.36\sqrt{\chi_i^0}} = \sigma_G (\langle \chi \rangle - \chi_G). \quad (6)$$

For example the water molecule H_2O is characterized on the Allred-Rochow scale ($\chi_{\text{O}}^0 = 3.5$ and $\chi_{\text{H}}^0 = 2.1$) by $\sigma_w = \sigma_{\text{O}} + 2\sigma_{\text{H}} = (1.36\sqrt{3.5})^{-1} + 2(1.36\sqrt{2.1})^{-1} = 1.408$ and a mean electronegativity $\chi_w = (\sqrt{3.5} + 2\sqrt{2.1}) \div (1.36\sigma_w) = 2.491$. Consequently, the par-

tial charge on the aquo group should always be computed as $q(\text{H}_2\text{O}) = 1.408(\langle \chi \rangle - 2.491)$ if $\langle \chi \rangle$ is the mean electronegativity of the given compound.

3. Hydrolysis of cations

In aqueous solutions cations M^{z+} are solvated through dipolar water molecules leading to aquo-ions $[\text{M}(\text{OH}_2)_n]^{z+}$. According to the EEP charge transfer should occur within this new complex in order to equalize all electronegativities to the same level. To check this point let us compare the partial charge on the hydrogen atoms in the water molecule $q(\text{H}) = 0.507(2.491 - 2.1) = +0.20$ and in a solvated complex such as $[\text{Ni}(\text{OH}_2)_6]^{2+}$ for example. Using $\chi_{\text{Ni}}^0 = 1.80$ for the electronegativity of the nickel atom we find: $\langle \chi[\text{Ni}(\text{OH}_2)_6]^{2+} \rangle = 2.671$, i.e. $q(\text{H}) = +0.29$. This higher positive partial charge suggests that water bound to the Ni^{2+} cation should be more acidic than pure water. Consequently, spontaneous deprotonation of aquo complexes could occur according to



As the mean electronegativity of the solvated proton H_3O^+ is 2.909, the mean electronegativity of the solvent $\langle \chi_{\text{aq}} \rangle$ should increase as the pH decreases. A quantitative treatment using the Allred-Rochow scale leads to the following relationship (Henry *et al.*, 1992):

$$\langle \chi_{\text{aq}} \rangle = 2.732 - 0.035 \text{ pH}. \quad (7)$$

Now, a simple equalization between the mean electronegativity of the solvent given by (7) and the mean electronegativity of the hydrolyzed complex $[\text{M}(\text{OH})_h(\text{OH}_2)_{n-h}]^{(z-h)+}$ leads to an analytical relationship linking the hydrolysis ratio h to the pH of the aqueous solution:

$$\langle \chi[\text{M}(\text{OH})_h(\text{OH}_2)_{n-h}]^{(z-h)+} \rangle = \frac{\sigma[\text{M}(\text{OH}_2)_n^{z+}]\langle \chi[\text{M}(\text{OH}_2)_n^{z+}] \rangle - h\sigma_{\text{H}^+}\chi_{\text{H}^+}}{\sigma[\text{M}(\text{OH}_2)_n^{z+}] - h\sigma_{\text{H}^+}} = \langle \chi_{\text{aq}} \rangle$$

that is to say:

$$h = \frac{q\{\langle \chi_{\text{aq}} \rangle, \langle \chi[\text{M}(\text{OH}_2)_n^{z+}] \rangle\}}{q\{\langle \chi_{\text{aq}} \rangle, \langle \chi(\text{H}^+) \rangle\}}. \quad (8)$$

According to this relationship, the hydrolysis ratio h of any element M in aqueous solutions is governed by three main parameters:

- i) The oxidation state z .
- ii) The hydration number n .
- iii) The pH of the solution.

Of these three parameters the most difficult to handle is the hydration number n which may not be constant over the whole range of pH. A typical case is encountered with the Al^{3+} cation for which ^{27}Al NMR points to the formation of an hexa-aquo octahedral complex $[\text{Al}(\text{OH}_2)_6]^{3+}$ in acidic solutions and to a tetrahydroxo tetrahedral complex $[\text{Al}(\text{OH})_4]^-$ under basic conditions

Table 1. Electrostatic energies of $[\text{Al}(\text{OH})_h(\text{OH}_2)_{n-h}]^{(3-h)+}$ complexes for $0 \leq h \leq 4$ and $4 \leq n \leq 6$

| Complex | <i>n</i> | $\langle \chi \rangle$ | <i>q</i> (Al) | <i>q</i> (O) | <i>E_n</i> (kcal · mol ⁻¹) |
|--|----------|------------------------|---------------|--------------|--|
| $[\text{Al}(\text{OH}_2)_6]^{3+}$ | 6 | 2.754 | +0.78 | -0.29 | -86 |
| $[\text{Al}(\text{OH})(\text{OH}_2)_5]^{2+}$ | 6 | 2.676 | +0.73 | -0.32 | -63 |
| $[\text{Al}(\text{OH})_2(\text{OH}_2)_4]^+$ | 6 | 2.588 | +0.68 | -0.36 | -29 |
| $[\text{Al}(\text{OH})_3(\text{OH}_2)_3]^0$ | 6 | 2.488 | +0.62 | -0.40 | +19 |
| $[\text{Al}(\text{OH})_4(\text{OH}_2)_2]^-$ | 5 | 2.487 | +0.62 | -0.40 | -34 |
| $[\text{Al}(\text{OH})_5(\text{OH}_2)]^{2-}$ | 6 | 2.373 | +0.55 | -0.44 | +80 |
| $[\text{Al}(\text{OH})_4(\text{OH}_2)]^-$ | 5 | 2.344 | +0.53 | -0.45 | +20 |
| $[\text{Al}(\text{OH})_3]^{3-}$ | 4 | 2.295 | +0.50 | -0.47 | -21 |

(Akitt, 1989). Very simple electrostatic arguments could explain why such a reduction of the coordination number should occur as the pH increases, providing that coordination changes are governed by enthalpic contributions. According to the Coulomb law the electrostatic energy associated to a system of two charges q_1e and q_2e separated by a distance d in the vacuum is given by:

$$E = \frac{e^2}{4\pi\epsilon_0} \times \frac{q_1q_2}{d} = 332 \frac{q_1q_2}{d(\text{\AA})} \text{ kcal} \cdot \text{mol}^{-1}. \quad (9)$$

Considering only metal and oxygen atoms, elementary geometric considerations show that if d is M-O mean bond length in \AA , the total electrostatic energy of an octahedron E_6 , a trigonal bipyramid E_5 and a tetrahedron E_4 are in kcal · mol⁻¹:

$$E_6 = 332 \{6q(\text{M})q(\text{O})/d + q(\text{O})^2[12/d\sqrt{2} + 3/2d]\} = 332q(\text{O})[6q(\text{M}) + 10q(\text{O})]/d$$

$$E_5 = 332 \{5q(\text{M})q(\text{O})/d + q(\text{O})^2[6/d\sqrt{2} + 3/d\sqrt{3} + 1/2d]\} = 332q(\text{O})[5q(\text{M}) + 6.5q(\text{O})]/d$$

$$E_4 = 332 \{4q(\text{M})q(\text{O})/d + 6\sqrt{3}q(\text{O})^2/2d\sqrt{2}\} = 332q(\text{O})[2q(\text{M}) + 3.67q(\text{O})]/d.$$

Table 1 compares the total electrostatic energies computed with $d = 2 \text{\AA}$ for hydrolyzed $[\text{Al}(\text{OH})_h(\text{OH}_2)_{n-h}]^{(3-h)+}$ complexes such as $0 \leq h \leq 4$ and $4 \leq n \leq 6$. It is obvious to see with such simple geometric considerations that the octahedral coordination of aluminum is stable ($E_6 < 0$) for positively charged complexes ($h \leq 2$) and unstable ($E_6 > 0$) for neutral or negatively charged complexes ($h \geq 3$). This table shows also that the reduction of the coordination from 6 to 5 for the $h=3$ complex and from 6 to 4 for the $h=4$ complex stabilizes the system in agreement with NMR measurements.

As a conclusion for the role of the hydration number n , we will use in conjunction with Equation (8) two numbers N_{max} and N_{min} for acidic ($\text{pH} < 7$) and basic conditions ($\text{pH} > 7$) which will define two hydrolysis ratio h_a and h_b , and the equilibrium hydrolysis ratio h will be given by: $h = \min(h_a, h_b)$. Moreover, we will assume that the $[\text{M}(\text{OH})_h(\text{OH}_2)_{n-h}]^{(z-h)+}$

mononuclear hydrolyzed precursor should be the predominant species in the solution providing that the following condition: $\text{pH}(h-0.5) \leq \text{pH} \leq \text{pH}(h+0.5)$ is fulfilled. With such a condition, it becomes possible to draw, using Equation (8), theoretical electronegativity-based speciation diagrams for any element in a given oxidation state.

4. Uranium

Uranium has an Allred-Rochow electronegativity of 1.22 and can be found under four main oxidation states: +3, +4, +5 and +6. Among these four values, the +4 and +6 states are the most common being characterized by five typical coordination numbers $n = 6, 7, 8, 9$ and 12 (Shannon and Prewitt, 1976). A survey of the crystal chemistry of U^{IV} shows that in most cases the uranium atom is found in eightfold or ninefold coordination (Wells, 1984). Consequently, the value $N_{\text{max}} = 9$ should be representative of the hydration number of U^{IV} under acidic conditions. For the basic side with $d(\text{U}-\text{O}) = 2.5 \text{\AA}$ we compute $E_6\{[\text{U}(\text{OH})_5(\text{OH}_2)]^-\} = +9 \text{ kcal} \cdot \text{mol}^{-1}$ ($\langle \chi \rangle = 2.364$, $q(\text{U}) = +0.74$ and $q(\text{O}) = -0.45$) and $E_5\{[\text{U}(\text{OH})_5]^{2-}\} = -93 \text{ kcal} \cdot \text{mol}^{-1}$ ($\langle \chi \rangle = 2.329$, $q(\text{U}) = +0.72$ and $q(\text{O}) = -0.46$), meaning that $N_{\text{min}} = 5$ is the right choice. Having fixed the values of N_{min} and N_{max} we can compute the mean electronegativities and softnesses of the solvated form of U^{IV} :

$$\sigma[\text{U}(\text{OH}_2)_6^{4+}] = 13.331$$

$$\text{and } \langle \chi[\text{U}(\text{OH}_2)_6^{4+}] = 2.729$$

$$[\text{U}(\text{OH}_2)_5^{3+}] = 7.699$$

$$\text{and } \langle \chi[\text{U}(\text{OH}_2)_5^{3+}] = 2.903.$$

Inserting these values into (8) leads to:

$$h_a = \frac{-0.062 + 0.467 \text{ pH}}{0.679 + 0.018 \text{ pH}}$$

$$\text{and } h_b = \frac{1.276 + 0.270 \text{ pH}}{0.679 + 0.018 \text{ pH}}$$

these two hyperbola crosses ($h_a = h_b$) at $\text{pH} \approx 6.8$, and applying the $h \pm 0.5$ criterion leads to the speciation diagram drawn in Figure 1. Let us now change the oxidation state of uranium from 4 to 6. According to the crystal chemistry of U^{VI} $N_{\text{max}} = 7$ or 8 (Wells, 1984) and we have to focus on the value of N_{min} . For a $[\text{M}(\text{OH})_7]^-$ complex having a regular pentagonal bipyramidal coordination, geometric considerations leads to:

$$E_7 = 332 \{7q(\text{M})q(\text{O})/d + q(\text{O})^2[10/d\sqrt{2} + 5 \times 2/d(\sqrt{5} + 1) + 5 \times 2/d(\sqrt{10} - 2\sqrt{5}) + 1/2d]\} = 332q(\text{O})[7q(\text{M}) + 14.91q(\text{O})]/d.$$

For $[\text{U}(\text{OH})_7]^-$, we compute $\langle \chi \rangle = 2.428$, $q(\text{U}) = +0.78$, $q(\text{O}) = -0.42$ and assuming $d = 2.5 \text{\AA}$ leads

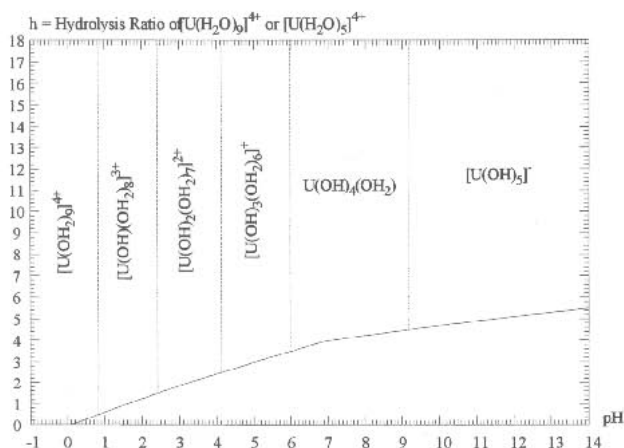


Fig. 1. Theoretical electronegativity-based speciation diagram for U^{IV} in aqueous solutions drawn from Equation (8) with $\chi(U) = 1.22$, $N_{min} = 5$, $N_{max} = 9$ and $z = 4$.

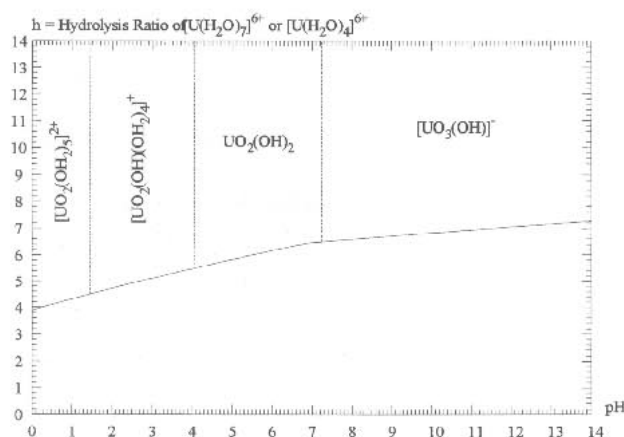


Fig. 2. Theoretical electronegativity-based speciation diagram for U^{VI} in aqueous solutions drawn from Equation (8) with $\chi(U) = 1.22$, $N_{min} = 4$, $N_{max} = 7$ and $z = 6$.

to $E_7 = +45 \text{ kcal} \cdot \text{mol}^{-1}$. Removing one water molecule leads to $[U(OH)_5]^-$ with $\langle \chi \rangle = 2.412$, $q(U) = +0.77$, $q(O) = -0.43$ and $E_6 = -18 \text{ kcal} \cdot \text{mol}^{-1}$. For U^{VI} $N_{min} = 6$ is thus a possible choice but implies the existence of an $h = 8$ complex $[UO_2(OH)_4]^{2-}$ with $\langle \chi \rangle = 2.245$, $q(U) = +0.66$, $q(O) = -0.49$ and $E_6 = +61 \text{ kcal} \cdot \text{mol}^{-1}$. For $[UO_3(OH)_2]^{2-}$: $\langle \chi \rangle = 2.150$, $q(U) = +0.60$, $q(O) = -0.53$ and $E_5 = +31 \text{ kcal} \cdot \text{mol}^{-1}$, but for the totally deprotonated complex $[UO_4]^{2-}$: $\langle \chi \rangle = 1.936$, $q(U) = +0.46$, $q(O) = -0.61$ and $E_4 = +32 \text{ kcal} \cdot \text{mol}^{-1}$. The correct choice for U^{VI} should then be $N_{min} = 4$ leading to Figure 2.

According to these two diagrams (Fig. 1 and 2) the least hydrolyzed species of U^{IV} and U^{VI} in acidic solutions should be respectively a tetravalent $[U(OH)_2]^{4+}$ and a divalent $[U(OH)_4(OH_2)_4]^{2+}$ cation in agreement with experimental findings (Baes and Mesmer, 1976). Let us notice that on structural grounds (Wells, 1984) the $[U(OH)_4(OH_2)_4]^{2+}$ complex should be rewritten $[UO_2(OH_2)_6]^{2+}$ (uranyl cation). For our model this makes no difference as Equation (5) by construction cannot make the difference between two

Table 2. Electrostatic energies of $[TcO_x(OH)_{6-2x}]^-$ and $[TcO_x(OH)_{5-2x}]^-$ complexes ($0 \leq x \leq 3$)

| Complex | n | $\langle \chi \rangle$ | $q(Tc)$ | $q(O)$ | E_n (kcal $\cdot \text{mol}^{-1}$) |
|----------------------|-----|------------------------|---------|--------|---|
| $[Tc(OH)_6]^-$ | 6 | 2.476 | +0.27 | -0.40 | +158 |
| $[TcO(OH)_4]^-$ | 5 | 2.471 | +0.27 | -0.40 | +83 |
| $[TcO(OH)_2]^-$ | 4 | 2.462 | +0.27 | -0.41 | +30 |
| $[TcO_3]^-$ | 3 | 2.438 | +0.25 | -0.42 | -2 |
| $[Tc(OH)_5(OH_2)]^-$ | 6 | 2.428 | +0.36 | -0.42 | +142 |
| $[Tc(OH)_5]^-$ | 5 | 2.411 | +0.35 | -0.43 | +75 |
| $[TcO(OH)_3]^-$ | 4 | 2.380 | +0.33 | -0.44 | +21 |
| $[TcO_2(OH)]^-$ | 3 | 2.310 | +0.30 | -0.47 | -7 |

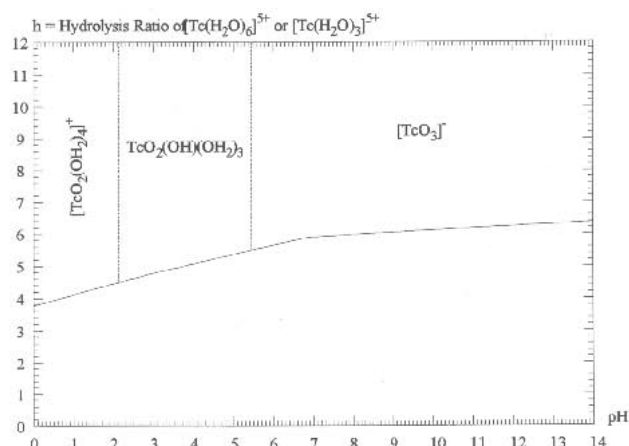


Fig. 3. Theoretical electronegativity-based speciation diagram for Tc^V in aqueous solutions drawn from Equation (8) with $\chi(Tc^V) = 1.96$, $N_{min} = 3$, $N_{max} = 6$ and $z = 5$.

such isomers which have exactly the same rough formula. For the most basic species, our model predicts anionic forms $[U(OH)_5]^-$ for U^{IV} and $[UO_3(OH)]^-$ for U^{VI} . Despite the fact that complexes such as $[U(OH)_5]^-$ has been invoked in literature (Baes and Mesmer, 1976), experimental evidence of anionic forms of uranium is still very poor. Here, the confrontation with experiments is not so easy as these species should be in equilibrium with highly insoluble solid phases such as UO_2 and $UO_2(OH)_2 \cdot nH_2O$. The characterization of the solute species is thus impaired by kinetic factors and low solubility. It may thus be possible that our model goes wrong in that case, and we have to wait for decisive but difficult experiments at very high pH to draw a final conclusion invalidating our model.

5. Technetium

A second example is provided by the element technetium which can exist under three oxidation state $z = +4$, $+5$, and $+7$ having an Allred-Rochow electronegativity of 2.33, 1.96 and 1.77 respectively (Zhang, 1982). The highest oxidation state Tc^{VII} is known only in fourfold coordination. Consequently, for that partic-

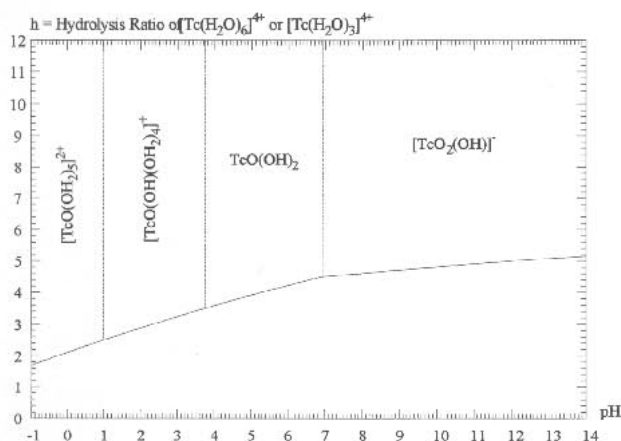


Fig. 4. Theoretical electronegativity-based speciation diagram for Tc^{IV} in aqueous solutions drawn from Equation (8) with $\chi(\text{Tc}^{\text{IV}}) = 1.77$, $N_{\text{min}} = 3$, $N_{\text{max}} = 6$ and $z = 4$.

ular case $N_{\text{min}} = N_{\text{max}} = 4$, and relation (8) predicts that the only stable complex over the whole range of pH is the pertechnetate ion $[\text{TcO}_4]^-$, in good agreement with experimental data (Baes and Mesmer, 1976). For Tc^{V} and Tc^{IV} structural data suggests $N_{\text{max}} = 6$ for acidic conditions, while Table 2 show that N_{min} should be set equal to 3 in both cases ($E_3 = 332q(\text{O})[3q(\text{M}) + 1.73q(\text{O})]/d$). Figures 3 and 4 give the corresponding speciation diagrams which predict that under the most acidic conditions Tc^{V} should form a monovalent cation $[\text{TcO}_2(\text{OH}_2)_4]^+$, while Tc^{IV} gives rise to a divalent one $[\text{TcO}(\text{OH}_2)_5]^{2+}$. Again these predictions seem to be in good agreement with experimental findings (Baes and Mesmer, 1976).

6. Conclusion

We have tried to show in this short paper that it is indeed possible to have an *a priori* good estimate of radionuclide speciation in pure aqueous medium through the use of the partial charge model, without referring to equilibrium constants. This model allows to derive quite general relationships such as relations (5) or (8) which have been used in two particular cases (uranium and technetium) but which nevertheless apply over the whole periodic table. In order to go one step further towards the prediction of radionuclide speciation in the geosphere, the possible complexation by the counter-anions (chloride, nitrate, sulphate, carbonate, phosphate, silicate) and the possible condensation reactions of monomeric hydrolyzed complexes $[\text{M}(\text{OH})_h(\text{OH}_2)_{n-h}]^{(z-h)+}$ must be considered. This has already been done and we refer interested readers to the original literature (Henry *et al.*, 1992). Another point which have been recently solved (Henry and Taulelle, 1993) is the elaboration of a partial charge model which allows to distinguish between structural

isomers. Among points which still remain to be solved are the influence of temperature and pressure and the prediction of Pourbaix diagrams. Anyway, in its most simple form the partial charge model is a very useful tool which allows to make intelligent and reasonable choices for the various complexes to consider for those which have to deal with very complex geochemical codes. The fact that our model do not rely on existing thermochemical data bases, but has still a very well-founded thermochemical basis (we equalize atomic electronegativities rather than macroscopic chemical potentials) is a very promising feature to perform cross-checking among a huge amount of data. Moreover, the structural nature of our approach allows to make a full use of new promising techniques (X-ray diffraction, EXAFS-XANES, multinuclear solution or solid-state NMR, IR-Raman spectroscopy ...) in parallel with more classical approaches based on analytical chemistry methods. Finally, we wish to inform the interested readers that PC softwares are under development and will be available in a very near future.

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