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Binding of Pertechnetate to Uranyl(VI) in Aqueous Solution. A Density Functional Theory Molecular Dynamics Study

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According to constrained Car–Parrinello molecular dynamics simulations and thermodynamic integration, the free binding energy between uranyl hydrate and pertechnetate in aqueous solution is significantly lower than that between uranyl and nitrate, namely, by 1.7 kcal mol^{-1}. This is the first study of the differential binding of these two ligands to uranyl, which can have implications for the separability of uranium and technetium during the reprocessing of nuclear waste.

Efficient separation of radionuclides from nuclear waste is a prerequisite for their reuse or storage. One problem during extraction of uranium from spent nuclear fuel, e.g., in the PUREX process,[1] is the rather poor separation from technetium. Under the oxidizing conditions of this process (dissolution in concentrated nitric acid), both elements are present in the forms of uranyl(VI), UO_2^{2+}, and pertechnetate, TcO_4^-. It has been shown recently by X-ray crystallography[2] and ^{99}Tc NMR spectroscopy[3] that both ions can form addition complexes, which can persist in an organic solvent. It has been suggested that this complex formation may be the reason for the poor separability of both ions because they could be simply extracted together into the organic phase. In the presence of suitable scavenger ligands, typically phosphine oxides R_3PO, uranyl can be extracted in the form of complexes of the type $UO_2(NO_3)_2(R_3PO)_2$. It is conceivable that, in such complexes, pertechnetate could replace nitrate. Alternatively, complexes of the type $UO_2(TcO_4)_2(R_3PO)_3$ could form.[2] In any event, the TcO_4^- ligand would have to compete with nitrate, which is present in huge excess. As a first step toward the assessment of the relative affinities of the two ligands toward uranyl, we have now computed the relative binding energies of NO_3^- and TcO_4^- ions with uranyl hydrate in water. To this end, we employed constrained Car−Parrinello molecular dynamics (CPMD)[4] simulations and pointwise thermodynamic integration,[5] a protocol that we had used successfully to reproduce thermodynamic and kinetic properties of aqueous uranyl(VI) hydrate.[6]

Reasonably well equilibrated solutions of the expected additional products, $[UO_2(H_2O)_4(\eta^1\text{-}XO_n)]^+$ (**1**, $XO_n = NO_3$; **2**, $XO_n = TcO_4$) were prepared in a periodic water box, employing the same methods and parameters[7] as those in our previous studies.[6] The mean U−O(X) bond distances are 2.46(9) and 2.44(8) Å for **1**[6e] and **2**, respectively (over 3 and 4 ps, respectively, of unconstrained simulation). We have recently shown with the same computational protocol that the monodentate five-coordinate complex **1** is the preferred species for uranyl mononitrate in water and that bidentate

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[1] For instance, see: (a) McKibben, J. M. *Radiochim. Acta* **1984**, *36*, 3. (b) Wilson, P. D., Ed. *The Nuclear Fuel Cycle*; Oxford University Press: Oxford, U.K., 1996.

[2] Sarsfield, M. J.; Sutton, A. D.; May, I.; John, G. H.; Sharrad, C.; Helliwell, M. *Chem. Commun.* **2004**, 2320.

[3] Sutton, A. D.; John, G. H.; Sarsfield, M. J.; Renshaw, J. C.; May, I.; Martin, L. R.; Selvage, A. J.; Collision, D.; Helliwell, M. *Inorg. Chem.* **2004**, *43*, 5480.

[4] Car, R.; Parrinello, M. *Phys. Rev. Lett*. **1985**, *55*, 2471.

[5] For instance, see: Sprik, M.; Ciccotti, G. *J. Chem. Phys*. **1998**, *109*, 7737 and references cited therein.

[6] (a) Bühl, M.; Diss, R.; Wipff, G. *J. Am. Chem. Soc*. **2005**, *127*, 13506. (b) Bühl, M.; Kabrede, H.; Diss, R.; Wipff, G. *J. Am. Chem. Soc*. **2006**, *120*, 6357. (c) Bühl, M.; Kabrede, H. *Inorg. Chem*. **2006**, *45*, 3834. (d) Bühl, M.; Kabrede, H. *ChemPhysChem* **2006**, *7*, 2290. (e) Bühl, M.; Diss, R.; Wipff, G. *Inorg. Chem*. **2007**, *46*, 5196.

[7] CPMD simulations were performed with the CPMD program (CPMD. version 3.9.2; copyright by IBM Corp. and Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany), the gradient-corrected BLYP functional (Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098; Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785), and norm-conserving Troullier−Martins pseudopotentials (Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993; Kleinman, L.; Bylander, D. M. *Phys. Rev. Lett.* **1982**, *48*, 1425); see ref 6a and the Supporting Information for further details concerning construction and validation of the pseudopotentials for uranium and technetium, respectively. Periodic boundary conditions and a cubic cell (lattice constant 13.0 Å) were used that contained **1** (or **2**) and an additional 54 (or 53) water molecules, yielding a density of around 1.1, typical for uranyl complexes (e.g., uranyl nitrate) with similar concentration. The complexes were oriented in the box in such a way that the U−O(X) bond, the reaction coordinate, was aligned roughly parallel to the long diagonal of the box. For **1**, the last snapshot from the unconstrained simulation from ref 6e was used as the starting point, and for **2**, NO_3^- and one H_2O were manually replaced with TcO_4^-. Kohn−Sham orbitals were expanded in plane waves up to an energy cutoff of 80 Ry. Molecular dynamics (MD) simulations were run in the *NVT* ensemble using a single Nosé−Hoover thermostat set to 320 K (in order to increase the mobility of the liquid, which tends to be too sluggish at 300 K with most generalized gradient approximations, see: VandeVondele, J.; Mohamed, F.; Krack, M.; Hutter, J.; Sprik, M.; Parrinello, M. *J. Chem. Phys.* **2005**, *122*, 014515), a fictitious electronic mass of 600 au, and a time step of 0.121 fs. To maintain this time step, H was substituted with D.

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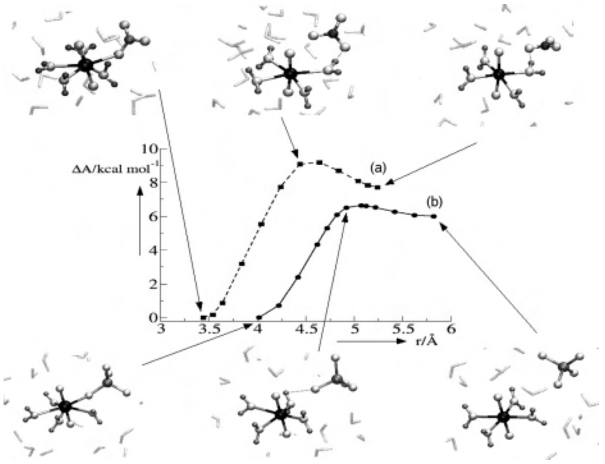

Figure 1. Change in the free energy, ΔA, upon dissociation of the nitrate and pertechnetate ligands from **1** (dashed line, curve a) and **2** (solid line, curve b), respectively, together with selected typical snapshots from the trajectories. Reaction coordinates are the U−N and U−Tc distances, respectively.

species are less stable, by up to 2.8 kcal mol^{-1}.[6e] For **2**, we assume the same basic structure, in line with the η^1-binding mode and five-coordination observed or inferred for uranyl pertechnetate complexes.[2,3,8]

We then used the U−O(X) distance as the reaction coordinate, elongating it in steps of 0.2 Å and running constrained CPMD simulations at each point until the mean constraint force was reasonably well converged.[9] This procedure was continued until the anionic ligand was incorporated into the second coordination sphere, forming contact ion pairs $[UO_2(H_2O)_4]^{2+}XO_n^-$ with near-zero forces on the constraint. Numeric thermodynamic integration of the resulting mean forces affords the Helmholtz free-energy profiles depicted in Figure 1.

We first turn to the nitrate complex. Formation of the contact ion pair with uranyl tetrahydrate according to

$$[UO_2(H_2O)_4(NO_3)]^+ \rightarrow [UO_2(OH_2)_4]^{2+}NO_3^- \qquad (1)$$

is computed to be endergonic by $\Delta A = 7.7 \pm 0.5$ kcal mol^{-1} (curve a in Figure 1). With the same protocol, water dissociation from uranyl hydrate

$$[UO_2(OH_2)_5]^{2+} \rightarrow [UO_2(H_2O)_4]^{2+} + H_2O \qquad (2)$$

had been found to be endergonic by $\Delta A = 8.7$ kcal mol^{-1}.[6a] When the driving force for complete dissociation of the ion pair on the right-hand side of eq 1 is neglected, a free energy of $\Delta A = 1.0$ kcal mol^{-1} is thus obtained[10] for the displacement reaction

$$[UO_2(OH_2)_5]^{2+} + NO_3^- \rightarrow [UO_2(H_2O)_4(NO_3)]^+ + H_2O \qquad (3)$$

From the experimental binding constant of nitrate and uranyl,[11] a free energy of $\Delta G° = -0.4 \pm 0.2$ kcal mol^{-1} can be inferred for this process. Even though the theoretical estimate has the wrong sign, it is well within the accuracy of ca. 2.5 kcal mol^{-1} established previously[6c,d] for the methodology employed, and the fact that nitrate binds only weakly to uranyl is very well reproduced. The theoretical estimate can be further refined by taking the aforementioned driving force for ion-pair separation into account. According to a very simple model from the literature, the equilibrium constant for dissociation of a hydrated contact ion pair (or outer-sphere complex) composed of a dication and a monoanion into the infinitely separated constituents can be estimated as $\log K = -0.74$,[12] from which a Gibbs free energy of $\Delta G = +1.0$ kcal mol^{-1} can be calculated. Subtracting this correction from our ΔA value for eq 3,[13] we arrive at an estimate of ca. 0 kcal mol^{-1} for this process, in good accord with the experiment. Even though this degree of agreement is certainly fortuitous to some extent (given the potential shortcomings of density functional theory and the limitations in the system size and simulation times), it is further testimony to the capability of the CPMD-based approach to capture the essentials of uranyl chemistry in aqueous solution.

For the pertechnetate complex **2**, formation of the corresponding contact ion pair with uranyl tetrahydrate is computed to be endergonic by $\Delta A = 6.0 \pm 0.4$ kcal mol^{-1} (curve b in Figure 1). This value is significantly lower, by 1.7 kcal mol^{-1}, than that of the analogous nitrate complex. Thus, pertechnetate is predicted to form an even weaker complex with uranyl than nitrate. Following the same lines as those discussed above for nitrate,[10] the free binding energy of pertechnetate according to

$$[UO_2(OH_2)_5]^{2+} + TcO_4^- \rightarrow [UO_2(H_2O)_4(TcO_4)]^+ + H_2O \qquad (4)$$

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(8) In the gas phase, the computed driving forces for the process $[UO_2(H_2O)_4(\eta^1\text{-L})]^+ \rightarrow [UO_2(H_2O)_3(\eta^2\text{-L})]^+ + H_2O$ are, e.g., $\Delta E =$ 13.4 and 22.2 kcal mol^{-1} for L = NO_3 and TcO_4, respectively, at the BLYP/LANL2DZ(U)/SDD/(Tc)/6-31G** level. There is thus no evidence for a chelating propensity of pertechnetate.

(9) Within 2−3 ps after 0.5 ps of equilibration, the standard deviation for the running average during the last picosecond was 4×10^{-4} au or less, similar to the degree of convergence documented in Figure S1 of the Supporting Information of ref 6a. The standard deviations from each point were used to estimate upper and lower limits for the integral of the (numeric) thermodynamic integration. Each new point was continued from the final, equilibrated configuration of the previous one, using 2000 steps of continuous slow growth to increase the constrained distance.

(10) We discuss relative energies of selected points on a free-energy surface rather than reaction mechanisms. Such energies are, at least in principle, independent of the chosen path. The actual displacement reaction (eq 3) may well follow an associative mechanism, as in the case of water exchange at uranyl (cf. ref 6c and literature cited therein).

(11) Extrapolated to standard conditions, a value of $\log \beta_1{}^0 = 0.30 \pm 0.15$ has been recommended for the equilibrium constant in the aqueous system $UO_2^{2+} + NO_3^- \rightleftharpoons UO_2NO_3^+$. See: Grenthe, I.; Fuger, J.; Konings, R. J. M.; Lemire, R. J.; Muller, A. B.; Nguyen-Trung, C.; Wanner, H. In *Chemical Thermodynamics Vol. 1: Chemical Thermodynamics of Uranium*; Wanner, H., Forest, I., Eds.; Elsevier: Amsterdam, The Netherlands, 1992.

(12) For instance, see: Morel, F. M. M.; Hering, J. G. *Principles and Applications of Aquatic Chemistry*; John Wiley & Sons: New York, 1993; p 399, where a simple expression from statistical considerations of electrostatic interactions between ions in a dielectric continuum was used for this estimate. In principle, but evidently not in practice, this process could be modeled by prolonging the path in Figure 1 to infinity.

(13) Because volume changes are very small in the condensed phase, ΔG and ΔA should be very similar.

is estimated to be $\Delta A = +2.7$ kcal mol^{-1} (+1.7 kcal mol^{-1} with the correction for ion-pair separation).

As mentioned above, the *absolute* accuracy of free energies obtained with the CPMD-based protocol so far is ca. 2.5 kcal mol^{-1} relative to the experiment. The computed difference in the uranyl binding energies between nitrate and pertechnetate, $\Delta A = +1.7$ kcal mol^{-1} for eq 5,

$$[UO_2(OH_2)_4(NO_3)]^+ + TcO_4^- \rightarrow [UO_2(H_2O)_4(TcO_4)]^+ + NO_3^- \quad (5)$$

is of the same order of magnitude. This *relative* change in the binding energy, however, should be more reliable because of the identical setup for both systems and the expected cancellation of systematic errors. From this value and from the experimental data of uranyl nitrate,[11] the following binding constant for uranyl pertechnetate can be inferred:

$$UO_2^{2+} + TcO_4^- \rightleftharpoons UO_2TcO_4^+, \qquad \log \beta_1^{\,0} = -0.95 \qquad (6)$$

With this weak binding constant, TcO_4^- to a large degree resembles ClO_4^-, which essentially does not bind at all to uranyl in aqueous solution. The most significant consequence of this result is that pertechnetate cannot compete with nitrate for coordination to aqueous uranyl hydrate, i.e., that formation of uranyl pertechnetate complexes in the nitric acid phase during the PUREX process can safely be excluded. Such complexes therefore have to be formed in the organic phase (or at its boundary) during extraction. While this result might have been intuitively anticipated from aqueous uranyl chemistry, we now substantiate it by the first dedicated, computational evidence for the differential binding of the relevant ligands.

It would be desirable to simulate the reaction paths from Figure 1 in an organic solvent (or better yet, at an aqueous/organic interface), which would be of more immediate relevance for the actual coextraction of the two radionuclei under the experimental conditions. Unfortunately, the concomitant need for larger boxes and longer simulation times would render CPMD simulations prohibitively expensive at present.[14] Modeling the corresponding free energies in vacuo is also not easily possible because pristine **1** proved unstable in an unconstrained CPMD simulation,[6e] precluding the construction of a reaction path in the gas phase corresponding to that in Figure 1. Static optimizations[15] indicate an even weaker relative binding of TcO_4^- vs NO_3^- in the gas phase or with a polarizable continuum model (PCM), illustrated by the reaction energies of $\Delta E = +28.2$ kcal mol^{-1} (gas phase) or +15.3 kcal mol^{-1} (PCM) for the reaction in eq 5.

What is, finally, the reason for the different binding strengths of pertechnetate and nitrate? It is quite likely that electrostatic interactions are of paramount importance. From atomic charges computed for pristine TcO_4^- and NO_3^-, it would appear that the former should bind stronger to a cationic center because the O atoms are more negatively charged than those in the latter (e.g., −0.64e vs −0.56e for TcO_4^- and NO_3^-, respectively, using natural population analysis).[15] On the other hand, the electrostatic potential (ESP) around the O atoms is more negative in NO_3^- than in TcO_4^- (see the graphical representation in Figure S1 of the Supporting Information). For nitrate, the minima of the ESP in the valence shell around the O atoms roughly coincide with the positions of the in-plane lone pairs (at ca. 1.2 Å from the O atom and at an angle of ca. 100° with the N atom). For TcO_4^-, the most negative ESP values in the corresponding region are smeared out in a toroidal area about the O atoms (at ca. 1.3 Å from the O atom and 110−120° with the Tc atom). The corresponding minimal ESP values (at the BLYP level)[15] amount to −0.28 and −0.20 au for NO_3^- and TcO_4^-, respectively, qualitatively consistent with the relative binding strengths of both ions toward uranyl in the gas phase and in water. In this context, it is interesting to note that for phosphines the analogous quantity, namely, the minimum of the ESP near the lone-pair position, has been correlated with the binding strength toward transition metals.[16] Similar studies for the binding of O-donor ligands to uranyl could be rewarding.

In summary, we have computationally reproduced the binding constant between uranyl and nitrate in aqueous solution, using a quantum-chemical method that takes the effects of solvation and dynamics explicitly into account. With the same approach, we have for the first time predicted the corresponding binding constant between uranyl and pertechnetate, a quantity that has implications for the separability of the two radionuclides during reprocessing of nuclear waste. We have presented strong evidence that in water the affinity toward uranyl is significantly smaller for pertechnetate than for nitrate. To what extent this result is transferable to other extractable uranyl complexes and organic solvents is an interesting question worth being further pursued. Within the limitations of present-day density functionals concerning their quantitative accuracy, CPMD simulations can now be used to study *and predict* structures and thermodynamic quantities of uranyl species in aqueous solution.

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Supporting Information Available: Details concerning construction and validation of the pseudopotential for Tc, as well as plots of the ESP values around the ligands. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) For classical MD simulations of uranyl extraction, see, e.g.: Baaden, M.; Schurhammer, R.; Wipff, G. *J. Phys. Chem. B* **2002**, *106*, 434.

(15) Computed at the BLYP/LANL2DZ(U)/SDD(Tc)/6-31G** level using *Gaussian 03*; see the Supporting Information for details. PCM single-point computations employed the parameters of water.

(16) (a) Suresh, C. H.; Koga, N. *Inorg. Chem.* **2002**, *41*, 1573. (b) Review: Kühl, O. *Coord. Chem. Rev.* **2005**, *249*, 693.