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REGULAR ARTICLE

On the combined use of discrete solvent models and continuum descriptions of solvent effects in ligand exchange reactions: a case study of the uranyl(VI) aquo ion

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Abstract Modeling of the solvent is important when using quantum chemical methods for the assignment of mechanisms from experimental studies of the exchange of water between metal aquo ions and the bulk solvent. In the present study, we have investigated if and how the mechanisms for water exchange in the $UO_2(OH_2)_5^{2+}$–H_2O system is affected by the choice of chemical models for the second coordination sphere and physical models for describing the cavity in conductor-like polarizable continuum (CPCM) models. In the first case, we have compared models with one and five waters in the second coordination sphere. For both models, we have compared cavities in which each atom is assigned one spherical cavity and one in which the water molecules are described by a single spherical cavity (the United Atom model). There are significant differences in the relative energy of dissociative and associative intermediates; however, they are not large enough to affect the conclusion that the water exchange proceeds through an associative/interchange mechanism.

Keywords Actinide · Quantum chemistry · Solvent models · Water exchange

1 Introduction

Experimental investigations of ligand exchange reactions provide information on the rate equation, the rate constant and activation parameters of the reaction studied. The rate-equation is used to deduce possible stoichiometric mechanisms for the reaction, but does not provide any information of the intimate mechanism, that is the molecular details of the events along the reaction coordinate. For reactions in solution, information of this type can only be obtained by comparing experimental activation parameters with calculated values obtained through a combination of chemical and quantum chemical models. We have previously discussed [1] the experimental [2] water exchange reaction (1) using a simple model where the water-exchange takes place between the first and second coordination spheres, reaction (2).

$$[UO_2(^*OH_2)_5]^{2+}(H_2O) \rightleftharpoons [UO_2(OH_2)_5]^{2+}(H_2{}^*O) \qquad (1)$$

$$\left[UO_2^*OH_2(OH_2)_4\right]^{2+}(H_2O)_5 \rightleftharpoons \left[UO_2(OH_2)_5\right]^{2+} \times (H_2{}^*O)(H_2O)_4 \qquad (2)$$

Perspective views of reactants and intermediates are shown in Figs. 1 and 2.

In this communication, we will explore how sensitive the mechanistic conclusions are for variations in the

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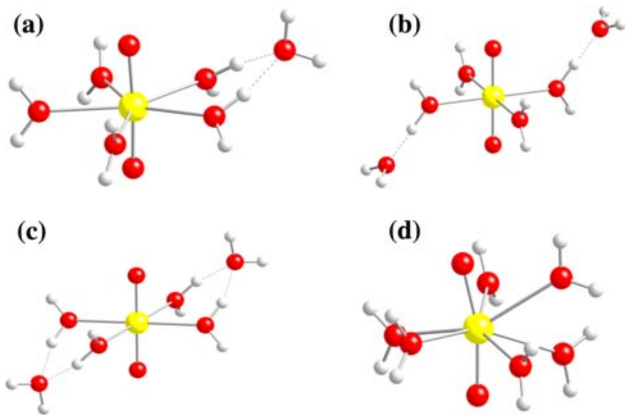

Fig. 1 Perspective views for the six-water model: **a** reactant, D-intermediates with the second-sphere water molecules either bound to the first-sphere water molecules by **b** one hydrogen bond or **c** two hydrogen bonds, and **d** the A-intermediate

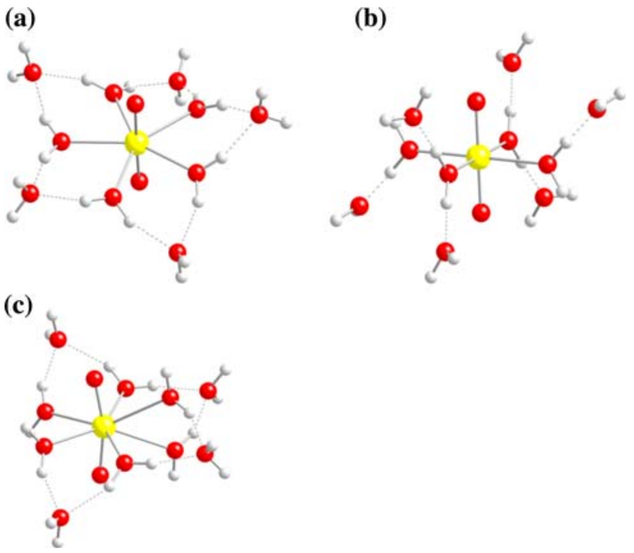

Fig. 2 Perspective views for the ten-water model: **a** reactant, **b** D-intermediate, and **c** the A-intermediate

composition of the second coordination sphere by comparing models with a total of six and ten water molecules.

The water-exchange reaction has been studied experimentally by Farkas et al. [2], providing information on the activation parameters. The water exchange reaction has also been investigated in many studies by means of theoretical methods [1, 3–21]. In these studies, different quantum chemical methods have been used, both DFT [3–6, 10–15, 18, 20, 21] and ab initio methods [1, 3, 6, 11, 17–19]. The intimate mechanism has been discussed both by Farkas et al. [2] and in a number of quantum chemical studies [1, 3–6, 12–15, 18]. The preferred mechanism was selected by comparing the activation energy for the dissociative (D), associative (A) and interchange (I) reaction paths. The model reaction takes place as an exchange of water between the first and second coordination spheres using a conductor-like polarizable continuum model (CPCM) [22] to describe the bulk solvent. The values of the reaction energies vary somewhat, depending on the quantum chemical method used and this point has been discussed in one of our previous studies [23], as well as by others [3, 6, 11, 18].

The chemical model with a single water molecule in the second coordination sphere is a gross simplification and it seems important to investigate if, and how much, the different activation parameters vary with the number of water molecules in the second sphere. Different codes use different CPCM models to describe the solvent cavity and these models seem to give different results, a point that has been discussed previously by Gutowski and Dixon [11]. However, they addressed the issue by considering only the possibility of a dissociative water-exchange reaction path as proposed by the analysis of the HEXS experiments [24, 25]. The present communication addresses the question for both the associative and dissociative reaction mechanisms.

2 Theory

2.1 The cluster models

The uranyl(VI) aquo ion is five-coordinated (See Refs. [24–26] and references therein), in order to saturate the second hydration sphere a minimum of five and a maximum of ten additional water molecules are needed. In the first case, all second sphere water molecules are bonded through double hydrogen bonds (thus acting as bridges between the first shell water ligands) and in the second case through single hydrogen bonds to the water molecules in the first hydration sphere.

The smallest model that can be used to describe both the associative/interchange and dissociative water exchange reaction involves six water molecules (Eq. 1), one of which is located in the second sphere in the reactant. This model is unbalanced in the sense that the water molecules in the first sphere have quite different chemical surroundings. A more balanced model is obtained with ten water molecules, five in the first and five in the second hydration sphere. In order to ensure a fully saturated second hydration sphere in the reactant, a total of 15 water molecules would be needed, but this would not provide a complete second hydration sphere for the associative intermediate that requires 18 water molecules.

It is not realistic to use large models in the study of ligand exchange reactions, not so much because of the size of the calculations but because of the number of possible minima and transitions states grow with the number of water molecules in the model, and it is therefore important to establish the minimum size for a chemically reasonable model for such studies. In the present context, we will also assess how the number of hydrogen bonds between the first and second coordination spheres may affect the reaction energies.

We have investigated the associative and dissociative reactions with the six- and ten-water models. The model with ten water molecules is still somewhat too small to allow a saturated first hydration sphere for both the reactant and the intermediates, more water molecules would be needed for this purpose.

For the reactant and the D-intermediate in the six-water model there are, as indicated above, two possible configurations of the second sphere water, one with a single, the other with a double hydrogen bond. Bühl et al. [12–15] found using Car-Parinello calculations based on BLYP, that the single bonded configuration gives the lowest energy for the D-intermediate and this result has been verified both at the B3LYP and the MP2 levels [23]. However, it is not a priori clear whether the single or the double hydrogen bonded model for the D-intermediate is best suited to describe the reaction. In a recent article, Tsushima [5] has suggested that the second sphere water molecule in the reactant also binds to the first sphere with a single hydrogen bond. We have explored this possibility in the present study but we have not been able to reproduce Tsushima's results.

2.2 Solvent effects

Solvent effects strongly influence the reaction energies in the ligand exchange reactions of uranyl(VI) in a water solvent as reported in several previous studies [1, 11–15] and these effects must be accounted for. An estimate of the solvent effects can be obtained from models where the solvent is described by a polarizable dielectric continuum. In the simplest models, such as the Born approximation, the solute is enclosed in a sphere and the solvent effect can be calculated directly from a simple formula [27]. In more advanced models, the cavity has a shape which is adapted to the geometrical form of the solute. The original ansatz used in the shape adapted conductor-like polarizable continuum model (CPCM) [22] was to associate individual spheres to all atoms in the solute, but later the idea of united atoms [28] (UA0) was introduced, where one spherical cavity is used for compound systems such as water. We have compared the individual atom approach, using the UFF radii [29] as implemented in Gaussian03 [30], with the united atom approach, and found significant differences for the reaction energies between them in some cases.

3 Computational details

All geometries were optimized at the B3LYP level in gas phase. The geometry optimizations are quite time consuming, in particular for the ten-water model and for this reason, the geometry optimization of the ten-water model was performed in two steps; the structures were first optimized using the GGA DFT functional BLYP [31–33] with the efficient RI-DFT method [34, 35], and in a second step, the geometry was refined using the hybrid functional B3LYP [33, 36–38]. The numerous local minima made it necessary to use C_2 symmetry constraints for the A- and D-intermediates, while the reactant could be optimized without symmetry constraints. The geometries for the six-water model were optimized directly with B3LYP, using the symmetry constraints C_s for the reactant, C_2 for the A-intermediate and C_{2h} for the D-intermediate. All structures are minima since no imaginary frequencies were found. The TURBOMOLE 5.10 [39, 40] package was used in all geometry optimizations.

A small core relativistic ECP of the Stuttgart type [41, 42] was used for uranium together with the associated segmented basis set [14s13p10d8f1g]/(10s9p5d4f1g) [43]; oxygen and hydrogen were treated at the all electron level with a triple-zeta valence plus polarization (TZVP) basis set suggested by Schäfer et al. [44, 45].

In a previous article [23], it was shown that GGA DFT functionals as well as hybrid functionals such as B3LYP, give inaccurate reaction energies for water exchange reactions, while MP2 performs much better. However, geometries are well described with B3LYP [46, 47], and the reaction energies were therefore calculated at the MP2 level with B3LYP optimized geometries. For water, all electrons except O(1s) and for uranyl, the electrons in the doubly occupied σ_u, σ_g, π_u and π_g orbitals plus the 6s and 6p of uranium and the 2s orbitals of the oxygen atoms were correlated in the MP2 calculations, Gaussian03 was used throughout those calculations. In a previous method study [23], we found no significant Basis Set Superposition Errors (BSSE) either at the DFT or at the MP2 levels for the six-water model, and consequently we do not expect any significant BSSE effects on the complexes investigated in the present study.

The solvation effect from the bulk water was obtained using CPCM. The cavity surrounding the solute is described in different ways in the different quantum chemical codes, for example COSMO [48], implemented in TURBOMOLE, uses the individual atom approach, while both this and the united atom approach are implemented in Gaussian03 and in the Molcas package [49], with the united atom approach as the default setting. However, the default radius of the cavity for water molecules differs between the codes. We have calculated the reaction energies for the associative and dissociative intermediates using both the individual and the united atom approach with Gaussian03. The enthalpy corrections were obtained in gas phase, at the B3LYP level; B3LYP generally gives good geometries and vibrational frequencies. The enthalpy correction was subsequently added to the electronic reaction energies obtained with CPCM both at the MP2 and at the B3LYP levels. The frequency calculations were performed with TURBOMOLE.

4 Results

In this section, we compare the six- and ten-water models, where the reactant and the dissociative and associative intermediates are $[UO_2(OH_2)_5]^{2+}$, $(H_2O)_r$, $[UO_2(OH_2)_4]^{2+}$, $(H_2O)_d$ and $[UO_2(OH_2)_6]^{2+}$, $(H_2O)_a$, respectively, with $r = 1$ or 5, $d = 2$ or 6 and $a = 0$ or 4. The comparison is done both in gas phase and in a solvent, the latter described by CPCM models using either the individual or the united atom approach.

4.1 Geometry and bond distances

Table 1 shows bond distances in the model with six water molecules; the corresponding structures are shown in Fig. 1. The geometries agree, not surprisingly, with those reported previously [23]. The main difference between the D-intermediates with single and double hydrogen bonds is that in the former the U–OH_2 distance for the water with the single hydrogen bond to the second sphere is significantly shorter than the remaining ones, 2.37 versus 2.46 Å.

The bond distances for the model with ten water molecules are given in Table 2 and the corresponding structures are shown in Fig. 2. The bond distances in the first coordination sphere are not significantly different between the reactant and the A-intermediate; in the D-intermediate all five-second-sphere water molecules are linked to the first coordination sphere with a single hydrogen bond and the structure and bond distances are again close to those in the D-intermediate with a single hydrogen bond in the six-water model.

Table 2 Geometries of the reactant, A and D-intermediates in the ten-water model, optimized at the B3LYP level in gas phase

Complex	$d(U–O_{yl})$	First sphere		Second sphere	
		$N(U–OH_2)$	$d(U–OH_2)$	$N(U–OH_2)$	$d(U–OH_2)$
Reactant	1.76	5	2.46–2.49	2	4.35–4.38
				3	4.25–4.28
A-int.	1.77	4	2.47–2.50	2	4.24
		2	2.65	2	4.49
D-int	1.76	2	2.35	4	4.44
		2	2.41	2	4.59

Distances are in Angstroms. $N(U–OH_2)$ designates the number of U–OH_2 bonds

4.2 Reaction energies

All reaction energies have been calculated at the B3LYP or MP2 level, but for reasons discussed in detail in [23], MP2 values (given in Table 3) are judged more reliable than B3LYP ones (reported in Table 4), and unless specifically stated, reaction energies used in the following sections were obtained at the MP2 level. As described in the previous section, enthalpies were estimated by adding correction obtained at the B3LYP level

The reaction enthalpies for the formation of A-intermediates for the ten- and six-water models in gas phase are 36 and 37 kJ/mol, respectively. The effect of the solvent is to decrease these energies to 12 and 17 kJ/mol, respectively, using the CPCM model with the united atom approach, and to 31 and 34 kJ/mol, respectively, using the individual atom approach.

The reaction enthalpies in gas phase for the formation of the D-intermediate shows larger differences between the six- and ten-water models. The reaction enthalpy for the

Table 1 Geometries of the reactant, A and D-intermediates in the six-water model, optimized at the B3LYP level in gas phase

Complex	$d(U–O_{yl})$	First sphere		Second sphere	
		$N(U–OH_2)$	$d(U–OH_2)$	$N(U–OH_2)$	$d(U–OH_2)$
Reactant	1.75	5	2.48–2.51	1	4.26
A-int.	1.76	4	2.50–2.54		
		2	2.64		
D-int. (2 H-bonds)	1.75	4	2.42	2	3.93
D-int. (1 H-bond)	1.75	2	2.37	2	4.46
		2	2.46		

Distances are in Angstroms. $N(U–OH_2)$ designates the number of U–OH_2 bonds

Table 3 Reaction enthalpies in kJ/mol computed at the MP2 level for the six- and ten-water models in gas phase and in the CPCM solvent model both with the individual atom model or the united atom model

Model	Associative reaction		Dissociative reaction		
	10 H_2O	6 H_2O	10 H_2O	6 H_2O (2 H-bonds)	6 H_2O (1 H-bond)
Enthalpy correction	1	0.3	−8	0	−4
Gas phase	36	37	39	35	12
Individual atom model	31	34	62	37	31
United atom model	12	17	31	63	33

Included in the table are also the enthalpy corrections (enthalpy–reaction energy in gas phase, see text)

Table 4 Reaction enthalpies in kJ/mol computed at the B3LYP level for the six- and ten-water models in gas phase and in the CPCM solvent model both with the individual atom model or the united atom model

Model	Associative reaction		Dissociative reaction		
	10 H_2O	6 H_2O	10 H_2O	6 H_2O (2 H-bonds)	6 H_2O (1 H-bond)
Gas phase	49	44	16	21	−8
Individual atom model	47	43	43	24	14
United atom model	28	27	12	49	15

The enthalpy corrections (enthalpy–reaction energy in gas phase, see text) are shown in Table 3

latter is 39 kJ/mol, while the enthalpies obtained with six water molecules are 35 and 12 kJ/mol for the models with double and single hydrogen bonds, respectively, illustrating the larger stability of the latter.

In the solvent, using the individual atom approach, the enthalpy for the D-intermediate for the ten-water model is increased to 62 kJ/mol. The reaction energy for the six-water model with double hydrogen bonding increased by 2–37 kJ/mol, while the increase on the single bonded model is larger, from 12 to 31 kJ/mol. The united atom approach gives quite different results. The reaction enthalpy for the ten-water complex is decreased to 31 kJ/mol, while it is decreased to 63 and 33 kJ/mol for the six-water model with double and single hydrogen bonds, respectively.

5 Discussion

Based on these results, there are two issues to discuss, both highly relevant for the choice of physical/chemical models and the estimate of the uncertainty in quantum chemical calculations of reaction energies for reactions in solution.

1. Which of the two approaches used to describe the solvent cavity is better suited to describe water exchange reactions, the individual atom or the united atom approach?
2. Is the hydrogen bonding between the first and second coordination sphere best described using a single hydrogen bond from the second sphere donor to the first sphere acceptor, or a double hydrogen bond with the second sphere water as a bridge between two-first-sphere acceptors?

In this section, we will only refer to the MP2 results shown in Table 3.

The D- and A-intermediates cannot be identified experimentally and accordingly, there are no experimental data for their enthalpy of reaction from the precursor. However, there is experimental information for the activation enthalpy for the water exchange reaction [2]. In a previous communication [1], we have shown that the activation barriers surrounding the intermediates are low, hence, the experimental activation enthalpy is a good estimate of the reaction enthalpy between the reactant and the intermediates. The experimental activation enthalpy for water exchange is 26 kJ/mol [2] and we have used this quantity for comparison with the calculated reaction enthalpies. The calculated reaction enthalpies can of course also be used to select the proper mechanistic pathway. In ref. [1], it was concluded that the associative pathway is preferred in the water exchange reaction, and with the above assumptions the same conclusion can be drawn from the results in Table 3. The A-intermediate has a significantly lower reaction enthalpy than the D-intermediate in the ten-water model, using both the individual and the united atom approach for the solvent interactions. In the six-water model, the united atom approach also results in a lower reaction enthalpy for the A-intermediate, while the individual atom approach gives approximately the same enthalpy for both intermediates. It should be noted that there are no known examples of stable compounds with only four small ligands in the equatorial plane of the uranyl(VI) ion [26].

The calculated electronic reaction enthalpies from reactant to intermediate for the associative reaction in both the ten- and the six-water models obtained with individual atom approach are very close to, albeit somewhat larger, than the experimental activation enthalpy. Lower reaction energies, by 15–20 kJ/mol, are obtained with the united atom approach.

Turning to the dissociative reaction path, the picture is more scattered. The individual atom approach gives similar reaction enthalpies for the six-water model with both single and double hydrogen bonds, but a poor agreement with the reaction enthalpy obtained with the ten-water model. With the united atom approach, the agreement between the six-water single hydrogen bond model and the ten-water model is excellent, while the reaction enthalpy obtained with the two hydrogen bond model is much higher.

Let us first discuss the solvent models. The poor agreement between the ten- and six-water models obtained with the individual atom approach is noteworthy, and indicates a problem with this model. Contrary to expectations, the associative and the dissociative reaction paths have almost equal reaction energies. The united atom approach gives an overall better agreement between the six- and ten-water models and also allows a comparison with earlier studies. However, this is quite unexpected since the united atom approach is an approximation of the individual cavity model.

Turning to the second question, which bonding mode in the six-water model is best suited to describe the reaction? In a recent article, Tsushima [5] found that the reactant with a single hydrogen bond was 22 kJ/mol more stable than the corresponding model with two hydrogen bonds using B3LYP and CPCM, with solvent parameters from UAHF [28]. We have optimized the reactant, both in gas phase and in the solvent, to investigate this possibility. We find that the reactant model with double hydrogen bond is 8 kJ/mol more stable in gas phase, while the two models are essentially equivalent in a solvent, the difference in enthalpy being below 1 kJ/mol. The results were independent of whether the geometry optimization was made in gas phase or in the solvent. A model with two hydrogen bonds is also consistent with the ten model results.

For the dissociative intermediate, it appears that the single hydrogen bond model is to be preferred. This conclusion is based on the geometry optimizations, where both models have single hydrogen bonds. In addition, there is close agreement between the six- and ten-water models with united atom cavities. The actual mode of bonding between the first and second coordination sphere is not known, but as there is a very large excess of water compared to the solute, it is not unreasonable that single hydrogen bonding is preferred.

The reaction energies have been calculated based on geometries optimized in gas phase. However, the results in Tables 1 and 2 show that the geometries are sensitive to the solvent effects and this may cause the scattered reaction energies for the dissociative intermediate. In order to investigate this we have re-optimized a number of geometries in the CPCM solvent using both individual and united atom cavities. The differences in reaction energies based on geometries optimized in gas phase or in the solvent are minor, at most 2 kJ/mol for the small model and 7 kJ/mol for the larger one.

Reaction enthalpies obtained at the B3LYP level are shown in Table 4. It is interesting to note that the solvent effect, regardless of the ansatz (the solvent effects are shown in parenthesis in Tables 3 and 4), is almost the same at the MP2 and the B3LYP levels. This means that the solvent effect calculated at the B3LYP level is a useful approximation also when other methods have been used.

Gutowski and Dixon [11] have investigated several cavity parameters and cavity shapes for both PCM and CPCM. They find a difference between UA0 and the UFF, where the latter is equivalent to our individual cavity approach. They note that UFF gives a larger solvent effect than UA0 by 11 kJ/mol on the reaction

$$\left[\mathrm{UO_2(H_2O)_4}\right]^{2+} + \mathrm{H_2O} \rightleftharpoons \left[\mathrm{UO_2(H_2O)_5}\right]^{2+}$$

This result is in between our corresponding results for the single and double hydrogen bond models. However, the results are not directly comparable since we use quite different models. Gutowski and Dixon [11] have also studied the reaction

$$\left[\mathrm{UO_2(OH_2)_4}\right]^{2+}, (\mathrm{H_2O})_n \rightleftharpoons \left[\mathrm{UO_2(OH_2)_5}\right]^{2+}(\mathrm{H_2O})_{n-1},$$

with $n = 8$ and 11.

In gas phase, their reaction energies are 29 and 44 kJ/mol, respectively, in fair agreement with our result obtained using the ten-water model. They report a solvent effect of 19 and 16 kJ/mol with UA0, in agreement with our results for the six-water single hydrogen-bond model but in disagreement with our ten-water model where the solvent effect was −8 kJ/mol. We have no explanation for this result, but it is surprising that the solvent effect is still so large with a saturated second hydration sphere. In our experience, it is also quite difficult to find global minima for models with so many water molecules. Gutowski and Dixon [11] did not investigate structures involved in the associative pathway.

Other groups, among them Siboulet et al. [10] have investigated the influence of a second hydration shell on geometries and Raman frequencies, also Shamov and

Schreckenbach [16] have studied hydration of uranyl(VI) and uranyl(V) with up to 17 water molecules. These studies are not directly related to the problems addressed in the present study though.

6 Conclusions

In the present study, we have shown that in the chemical model used to describe the water exchange reaction in solvated uranyl(VI), the water molecule(s) in the second hydration sphere is(are) linked with one hydrogen bond to the first hydration sphere in the dissociative intermediate, and with two hydrogen bonds in the reactant. We have so far not been able to decide unequivocally if the united atom cavities are to be preferred over individual atom cavities in CPCM.

We also conclude, in agreement with previous studies, that the reaction path is associative in the water exchange reaction in uranyl(VI), and that the reaction is satisfactorily described by the minimalistic six-water model single hydrogen bond model. The same conclusion was obtained from the six-water model containing two hydrogen bonds [1]. From the results of the present study, it appears that the two hydrogen bond model is indeed useful albeit less accurate than the one with a single hydrogen bond between the second sphere water and a coordinated water in the first coordination sphere.

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