Theoretical Treatment of Fluoride Complexation of Element 104 in HF Solutions

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Recent experiments on fluoride complexation of element 104, Rf, in aqueous HF/HNO_3 solutions [1,2] have demonstrated an unexpected behaviour of Rf in comparison with that of Zr and Hf: Whereas all the elements are retained as cations on cation exchange resins (CIX) below 10^{-3} HF, no rise of the K_d value of Rf is observed up to 1M HF in contrast to Zr and Hf when sorbed by anion exchange resins (AIX). This observation was tentatively interpreted as a difference in the competition between NO_3^- with respect to $RfF_x^{(x-4)-}$ on the one hand, and to $ZrF_x^{(x-4)-}$ and $HfF_x^{(x-4)-}$ on the other hand, for the binding sites on the AIX.

To interpret the unexpected behaviour of Rf in HF/HNO_3 solutions, we have studied the complex formation of Zr, Hf, and Rf theoretically using the model applied by us for prediction of complexation of element 105, Db, and element 106, Sg, in aqueous solutions [3,4].

In HF/HNO_3 solutions at HF between 10^{-3} M and 10^{-2} M $HF/0.1$ M HNO_3, at pH$\cong$1, the complex formation can be described by the following equilibria

$$M(H_2O)_8^{4+} \Leftrightarrow MF(H_2O)_7^{3+} .. \Leftrightarrow .. MF_5(H_2O)^- \Leftrightarrow MF_6^{2-} \quad (1)$$
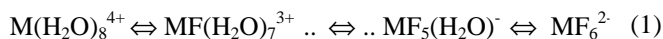
where M = Zr, Hf, and Rf. To predict the complex formation, the free energy change ΔG^r of equilibria (1) should be calculated. As an initial step, the following equilibrium was considered

$$M(H_2O)_8^{4+} + 6HF \Leftrightarrow MF_6^{2-} \quad (2)$$
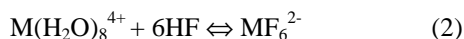
According to our model, ΔG^r of a reaction can be expressed as

$$-\Delta G^r / 2.3RT = \Delta \sum a_i + \Delta \sum a_{ij} - \Delta S, \quad (3)$$

where $\sum a_i = OP$ (overlap population) is a non-electrostatic metal-ligand contribution to molecular bonding, and $\sum a_{ij} = \sum BQ_iQ_j / d_{ij}\varepsilon$ is a sum of each pairwise electrostatic interaction. Here, d_{ij} is the distance between moieties i and j; Q_i and Q_j are their effective charges; ε is a dielectric constant, and B is an independent constant. ΔS of eq. (3) is a change in the entropy term. Q_i and OP are obtained as a result of the Mulliken population analysis of the electronic structures of the complexes on the right- and left-hand side of reaction (2) calculated using the fully relativistic Density Functional Method (DFT) [5].

Geometry and bond lengths (R_e) of $M(H_2O)_8^{4+}$ (D_{2d}-symmetry) and MF_6^{2-} (M = Zr, Hf, and Rf) were assumed on the basis of analysis of the structural data for Zr and Hf and from calculated R_e for some simpler Rf gas-phase compounds [6].

As a result of the calculations, energetic, as well as electronic density distribution parameters were obtained. The Q_M and OP values (Table 1) show an increase in covalence of each type of complexes from Zr to Rf.

Table 1. E^C, ΔE^C (in eV) and ΔOP for the complexation reaction $M(H_2O)_8^{4+} \Leftrightarrow MF_6^{2-}$

E^C	Zr	Hf	Rf
Q_M: $M(H_2O)_8^{4+}$	1.97	1.89	1.85
Q_M: MF_6^{2-}	0.94	0.85	0.75
E^C: $M(H_2O)_8^{4+}$	-53.34	-52.07	-50.92
E^C: MF_6^{2-}	-2.60	-1.18	0.23
ΔE^C	50.75	50.88	51.15
OP: $M(H_2O)_8^{4+}$	8.93	9.03	9.11
OP: MF_6^{2-}	2.11	2.38	2.49
ΔOP	-6.82	-6.65	-6.62

The calculated E^C, ΔE^C and ΔOP, are also shown in Table 1. ΔE^C being the predominant type of the metal-ligand interaction shows that Rf should form complexes similarly to those of Zr and Hf only at slightly higher HF concentrations, so that the sequence in the complex formation is Zr > Hf > Rf. Thus, Rf is expected to be extracted by AIX shortly after Hf, with the differences between the three elements being very small.

The theoretically obtained sequence for Zr and Hf is in agreement with the experimental sequence for the descending K_d values in the sorption by CIX and the rising K_d values in the sorption by AIX. It is also in agreement with the descending K_d values for Rf in relation to those of Zr and Hf in the CIX sorption. Taking into account the very small difference in ΔG^r for the complexes of Rf as compared to those of Zr and Hf, the absence of a rising K_d curve on AIX for Rf at higher HF concentrations cannot be explained by the complexation step, provided the same types of complexes are formed. It can, at best, be accounted for by the formation of different types of complexes and their different partition. As a plausible explanation, formation of the neutral H_2RfF_6 in $HF/0.1$ M HNO_3 could be suggested due to a probable preference of the RfF_6^{2-} complex for the protonation. Nevertheless, from the point of view of the electronic structure of the Rf complexes, it is hard to foresee a large difference between Zr and Hf on the one hand, and Rf on the other hand, whatever is the process. The hypothesis suggested here, as well as those discussed in ref. [2], will be considered in our further theoretical research.

References

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