Orientations of $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ Complexes at a Reactive Separation in Water

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Abstract: A molecular dynamics simulation of ferrous and ferric ions in water has been performed to study the mutual orientations of the $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ complexes at a reactive separation of 5 Å in water. The study shows that although the conventional 3-fold 3-fold approach of the two hexaaquo octahedral complexes is the most dominant, the C_3 axes facing each other on the two complexes are not directed along the $Fe^{2+}-Fe^{3+}$ axis in aqueous solution. The extent of the dominance of different mutual orientations is presented.

Electron transfer reactions between transition metal complexes in polar solvents provide good examples for studying the distance dependence of electron transfer as well as in understanding the effects of polar solvent structure and dynamics on reaction rates and energetics.[1−3] However, the computation of the electronic factors associated with the theory of electron transfer rates requires an *a priori* knowledge regarding the favorable mutual ligand orientations of the two complexes in solution. In the case of the simplest symmetric electron exchange reaction between $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ complexes in water, the electronic matrix elements H_{AB}s associated with the electron transfer event were calculated for various geometries of the approaches of the two reactants to assess the relative weightage of each of the orientation to the primary electron exchange event.[4] It was found that the mutual approach along the 3-fold axes (C_3 axes) contributed most to the electron transfer rate at a favorable reactive encounter separation. These H_{AB}s have been used to estimate the bulk rate constant for this reaction.[2] The present paper investigates the dominance of various mutual ligand orientations of these complexes at a reactive separation in the solution medium. These mutual ligand orientations in the solution phase can be used in choosing the appropriate values of H_{AB}s for the calculation of bulk electron transfer rate constants.

In order to study the probable mutual ligand (in this case, H_2O) orientations, a molecular dynamics simulation was performed on a system containing ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions placed at a small reactive separation of 5 Å in water at a temperature of 298 K. Our system contained 300 water molecules in a cubic box of length 20.77 Å which corresponds to a density of 1 gm/cc. The positions of the Fe^{2+} and Fe^{3+} ions are held fixed on the x-axis of the coordinate frame such that the ions are 2.5 Å away from the origin, thus making an internuclear separation of 5 Å. The choice of 5 Å between the two complexes follows from an extensive theoretical analysis for this electron transfer reaction.[2] We used here a flexible model of Toukan and Rahman[5] for the water−water interactions. For the $Fe^{2+}-H_2O$ and the $Fe^{3+}-H_2O$ interactions, we employed the empirical functions proposed by Curtiss et al.[6] A molecule based spherical cut-off with half the box length as the cut-off distance was used to truncate the short range interactions of the ion−water and the water−water pairs. The long range interactions have been calculated by employing the reaction field technique and thus minimizing the edge polarization whose effects are well documented for a similar system.[3,7,8] The integration algorithm and other details of the simulation are the same as in our earlier work in which case we studied the solvent relaxation for this reaction.[9] After sufficient equilibration of the system, a production run for a duration of 300 ps was made using a time step of 0.0005 ps. Configurations were stored at an interval of 0.005 ps for analysis. During this period, we observed that the Fe^{2+} and the Fe^{3+} ions formed stable hexaaquo metal complexes, the geometries of which were of octahedral shape (Figure 1a). The average ion−oxygen distances for the Fe^{3+} and the Fe^{2+} complexes were 1.96 and 2.07 Å, respectively. These values are almost identical to the values from earlier simulations employing a different force field.[3,7]

The water molecules coordinating the ferrous ion (Fe^{2+}) and lying toward the ferric ion (Fe^{3+}) are labeled as 1, 2, and 3 as shown in Figure 1a. Similarly, the water molecules coordinating the Fe^{3+} ion and lying toward the Fe^{2+} are labeled as 1′, 2′, and 3′. The remaining water molecules are labeled as 4, 5, and 6 on the Fe^{2+} ion and 4′, 5′, and 6′ on the Fe^{3+} ion. The relevant axes of symmetry considered in this study for the two complexes are shown in Figure 1b. On the $Fe(H_2O)_6{}^{2+}$ complex, the unit vectors along the three 2-fold axes (C_2 axes) of symmetry (comprising the water molecules 1, 2, and 3) considered here

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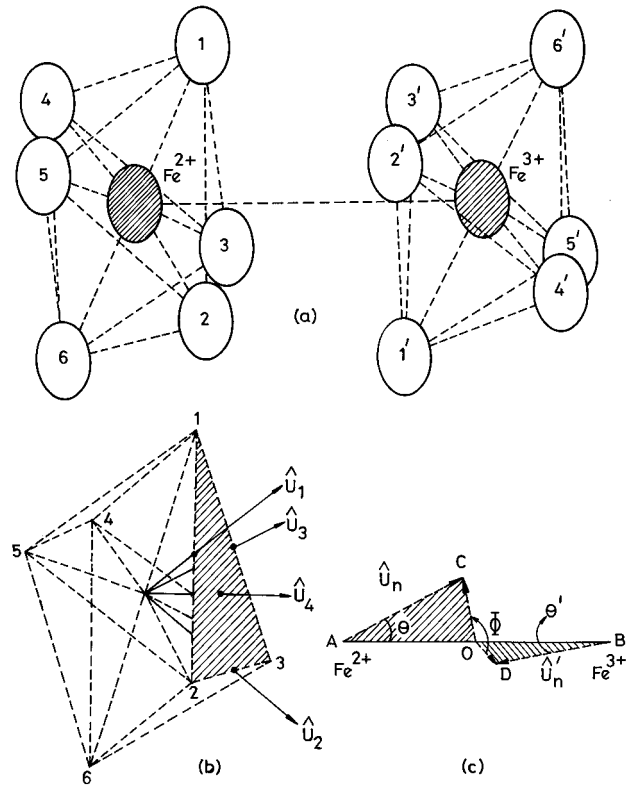

Figure 1. (a) An instantaneous configuration of water molecules around Fe^{2+} (left) and Fe^{3+} (right) ions which are separated by 5 Å in solution. Only the water oxygen positions are shown for clarity and numbered. The octahedral shape of the two complexes and the interionic axis are indicated with dotted lines connecting the atoms. (b) The unit vectors along the axes of symmetry $\hat{U}_1$, $\hat{U}_2$, and $\hat{U}_3$ (C_2 axes) and $\hat{U}_4$ (C_3 axis) on the Fe^{2+} complex are shown. The ligand configuration shown is obtained by a slight rotation (for better clarity) of the Fe^{2+} complex in Figure 1a. (c) The definitions of various angles θ, θ', Φ, and Ψ are discussed in the text. The angle Ψ (not shown) is the angle between a given pair of unit vectors $\hat{U}_n$ and $\hat{U}_n'$.

are $\hat{U}_1$, $\hat{U}_2$, and $\hat{U}_3$ and that on the 3-fold symmetry axis (C_3 axis) is $\hat{U}_4$. Similarly, the 2-fold unit vectors on the Fe^{3+} complex (comprising water molecules 1′, 2′, and 3′) are $\hat{U}_1'$, $\hat{U}_2'$, and $\hat{U}_3'$, and the 3-fold unit vector is $\hat{U}_4'$. We denote the corresponding C_2 and C_3 axes on the Fe^{3+} complex as C_2' and C_3', respectively. To estimate the alignment of the vectors $\hat{U}_n$s and $\hat{U}_n'$s ($n = 1-4$) along the $Fe^{2+}-Fe^{3+}$ vector, we define the angles θ and θ'. These are shown in Figure 1c. The angle Ψ is the angle between a given pair of $\hat{U}_n$ and $\hat{U}_n'$ which gives the extent of the mutual alignment of these vectors. Also defined in Figure 1c is the angle Φ which measures the dihedral angle between the planes OAC and OBD, where $\widehat{AC}$ and $\widehat{BD}$ are the vectors in the directions of $\hat{U}_n$s and $\hat{U}_n'$s, respectively. All these angles can be calculated in a simulation by taking the dot products of the relevant unit vectors involved.

During the course of the 300 ps simulation, we observed that the water molecules on the Fe^{3+} complex retained their orientational identities throughout the run (i.e., the molecules 1′, 2′, and 3′ were always facing the Fe^{2+} complex and the remaining waters namely 4′, 5′, and 6′ were facing away from the Fe^{2+} complex). However, the water molecules on the Fe^{2+} complex underwent occasional rearrangements after about a period of 60−80 ps in such a way that a new C_3 axis on an adjacent face orients toward the Fe^{3+} ion (i.e., a rotation of the Fe^{2+} complex through about 90°). In the present study, we focus our attention to a 70 ps period from the 300 ps trajectory during which the same pair of unit vectors $\hat{U}_4$ and $\hat{U}_4'$ (C_3 and C_3' axes) face each other. In other words, during the 70 ps period considered here, the water molecules 1, 2, and 3 remained in the interionic region.

Table 1. Average Values of Angles Ψ, θ, θ', and Φ over a 65 ps Segment (Excluding Initial 5 ps Data Shown in Figure 2) during the Simulation

pair of vectors ($\hat{U}_n - \hat{U}_n'$)	angle	water molecules in the interionic region (1, 2, 3 vs 1′, 2′, 3′)	water molecules away from the interionic region (4, 5, 6 vs 4′, 5′, 6′)
	Ψ	165.0 ± 6.4	164.7 ± 6.2
$\hat{U}_4-\hat{U}_4'$	θ	12.7 ± 5.9	13.8 ± 5.3
(C_3-C_3')	θ'	10.4 ± 3.0	10.6 ± 3.1
	Φ	100.2 ± 17.8	105.5 ± 13.0
	Ψ	146.8 ± 8.8	150.5 ± 8.4
$\hat{U}_3-\hat{U}_4'$	θ	31.4 ± 7.0	28.3 ± 6.9
(C_2-C_3')	θ'	10.4 ± 3.0	10.6 ± 3.2
	Φ	88.8 ± 27.5	95.0 ± 35.0
	Ψ	145.2 ± 4.8	147.9 ± 4.3
$\hat{U}_4-\hat{U}_3'$	θ	12.7 ±5.9	13.8 ± 5.3
(C_3-C_2')	θ'	41.9 ± 6.8	40.3 ± 7.0
	Φ	107.0 ± 25.0	107.0 ± 24.0

The average values of the angles Ψ, Φ, θ, and θ' for three of the mutual orientations, namely, C_3-C_3', C_2-C_3', and C_3-C_2' are shown in Table 1. The average angle Ψ (the angle between the orientation vectors) for the C_3-C_3' approach is 165 ± 6°, which is 15° away from an antiparallel arrangement. Also, the C_3 and C_3' axes make angles of 12.7 ± 6° and 10.4 ± 3.0°, respectively, with the ion−ion axis (the angles θ and θ' in Table 1). The dihedral angle Φ for the planes containing the C_3 and the C_3' and the ion−ion axis is 100.2 ± 17.8°, a nearly perpendicular arrangement. Thus, the C_3 and the C_3' axes are not aligned along the ion−ion axis, but slightly tilted away from it. The angles Ψ for the C_2-C_3' and the C_3-C_2' arrangements are 146.8 ± 8.8 and 145.2 ± 4.8, respectively.[10] These angles are smaller than the corresponding values for the C_3-C_3' arrangement indicating that the C_3-C_3' approach is the closest one to an antiparallel arrangement. The average value of the angles Ψ for C_2-C_2' approaches are not shown since these are even further from an antiparallel orientation.

The fluctuations in the cosine of the angle Ψ during the 70 ps period for the three mutual orientational arrangements, namely, C_3-C_3', C_2-C_3', and C_3-C_2' are plotted in Figure 2. The initial 5 ps period in this 70 ps segment represents a rearrangement of the Fe^{2+} complex so that the unit vector $\hat{U}_4$ on the C_3 axis of the Fe^{2+} complex is beginning to face the Fe^{3+} complex. After this rearrangement, the incoming new C_3 axis on the Fe^{2+} complex continued to face the Fe^{3+} complex throughout the rest of the 70 ps period considered in the Figure 2. The curve (a) represents the fluctuations in $cos(\Psi)$ between unit vectors $\hat{U}_4$ and $\hat{U}_4'$ (C_3-C_3' approach) of the two complexes. Similarly, the curve (b) represents the fluctuations in $cos(\Psi)$ between unit vectors $\hat{U}_3$ and $\hat{U}_4'$ (C_2-C_3' approach). The unit vector $\hat{U}_3$ is chosen since it is the most aligned vector with the ion−ion axis among the three C_2 axes on the Fe^{2+} complex. It is evident from Figure 2 (parts a and b) that these two mutual approaches fluctuate around a mean value except in a few time intervals where there is a sudden departure from the average value. For example, near 55 ps, values of $cos(\Psi)$ for the C_3-C_3' arrangement show a jump to higher values indicating that the unit vectors along the C_3 axes of the two complexes are moving away from the original nearly antiparallel arrangement. At the same time, the unit vectors for the C_2-C_3' arrangement shows a similar jump toward a near antiparallel arrangement. Such a rearrangement is clearly visible near 55

(10) Out of the three C_2 axes and the three C_2' axes, the one considered here is the most aligned C_2 and C_2' with the ion−ion axis (i.e., the one having the smallest value of θ and θ').

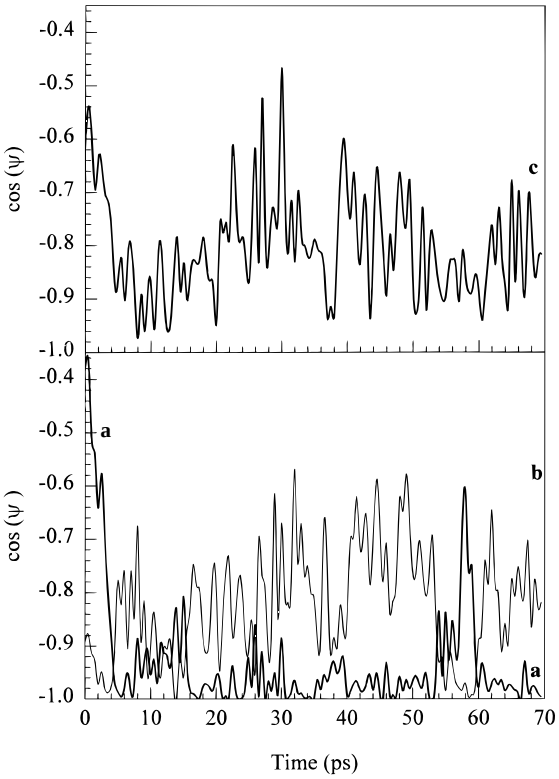

Figure 2. Fluctuations in cos(Ψ) for various mutual orientational arrangements of Fe^{2+} and Fe^{3+} complexes as a function of time. Curve (a) is for the fluctuation in cos(Ψ) for the mutual approach of C_3 axis on Fe^{2+} and C_3' axis on Fe^{3+} ions (abbreviated in the text as C_3-C_3' approach). Curves (b) and (c) are for the most oriented C_2-C_3' and C_3-C_2' approaches, respectively.

ps and to a lesser extent near 15 and 25 ps in Figure 2. Thus, it is obvious that each such rearrangement corresponds to an attempt of a rotation of the Fe^{2+} complex through about 90°. In other words, the complexes try to rearrange from one C_3-C_3' configuration to another C_3-C_3' configuration (with a new C_3 axis of an adjacent face of the Fe^{2+} octahedron) via an intermediate C_2-C_3' configuration. All such attempts in Figure 2 (a) and (b) are unsuccessful in the sense that the same C_3 axis on Fe^{2+} complex comes back to its original near-antiparallel orientation with the C_3' axis. However, during the entire 300 ps period of the simulation, we observed four rearrangements between one C_3-C_3' and another C_3-C_3' via an intermediate C_2-C_3' orientation. The curve (c) in Figure 2 corresponds to the fluctuation in *cos*(Ψ) for the C_3-C_2' approach. It is seen that although there are significant fluctuations in this arrangement, the C_3-C_2' alignment does not approach as near-antiparallel arrangements as observed in Figure 2 (parts a and b).

We also did a similar analysis for the water molecules 4, 5, and 6 and 4′, 5′, and 6′. The unit vectors on the symmetry axes of these molecules are directed away from each other. It is interesting to note from Table 1 that the average values of Ψ, Φ, θ, and θ' for the C_3-C_3' approach of these water molecules are nearly equal to those of 1, 2, and 3 and 1′, 2′, and 3′. This indicates that the mutual orientational preferences of the water molecules in the interionic region as well as outside the interionic region of the two clusters are identical.[11] This is interesting, since one expects that the water molecules outside the interionic region are in a different environment than those water molecules in the interionic region. This indicates the overall octahedral rigidity of the two complexes.

The main inference from this study is that although the conventional 3-fold 3-fold approach of the two hexaaquo octahedral complexes is the most dominant, the C_3 axes facing each other are not directed along the $Fe^{2+}-Fe^{3+}$ axis but are tilted from the ion−ion axis in the aqueous solution. Also, the planes containing these axes and the interionic axis are nearly perpendicular. There is an occasional rearrangement from one 3-fold 3-fold approach to another 3-fold 3-fold approach via an intermediate 2-fold 3-fold arrangement between the two complexes. We are currently investigating the orientational preferences of the two complexes at slightly larger separations.

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