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The Kinetics and Mechanism of the Reaction of Uranium(VI) with 8-Quinolinol and 8-Hydroxy-5-quinolinesulfonic Acid

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The kinetics of the reaction of uranium(VI) with 8-quinolinol and 8-hydroxy-5-quinolinesulfonate under the conditions of 1 : 1 chelate formation in the pH range 3.6—4.6 at different temperatures (20—30°C) and ionic strength $I = 0.1\ \mathrm{mol\,dm^{-3}}$ (KNO_3) have been studied. A dual path mechanism involving both $UO_2(aq)^{2+}$ and $UO_2(OH)(aq)^{+}$ and the partially deprotonated ligand (LH, LH^-) is consistent under the experimental conditions. The different rate constants under the condition of equilibrium have been determined. The results conform to $k_{obs}/B = k_1[H^+] + k_2K_h$;
where

$$B = \frac{1}{Q} + \frac{K_{a(1)}T_U}{([H^+] + K_{a(1)})(K_h + [H^+])};$$

K_h = hydrolysis constant of $UO_2(aq)^{2+}$; $K_{a(1)}$ = first deprotonation constant of the ligand, LH_2 (charges are omitted); k_1 and k_2 are the second order forward rate constants of $UO_2(aq)^{2+}$ and $UO_2(OH)(aq)^{+}$ respectively and Q is the equilibrium constant of the reaction, $UO_2^{2+} + LH \rightleftarrows UO_2L^+ + H^+$, where LH represents the partially deprotonated form of the ligand, 8-quinolinol and a similar reaction occurs for deprotonated 8-hydroxy-5-quinolinesulfonate (LH^-). Thermodynamic parameters for each of the steps have been determined. The results have been compared with those of recent findings in the interaction of cerium(IV) and iron(III) with these ligands. $UO_2(aq)^{2+}$ has been argued to react through a dissociative interchange (I_d) mechanism and its characteristic water exchange rate has been found as a rough estimate. Similarly for $UO_2(OH)(aq)^{+}$, a dissociative mechanism has been speculated.

The kinetics and mechanism of complexation of the d-block elements are now well documented[1,2] but the kinetic studies of such complexation reactions at the f-block centres such as uranium(VI) are scanty,[3—13] although the thermodynamic aspects of such complexation at uranium(VI) centre are well investigated. Very recently, the equilibria and kinetics of the interaction of iron(III)[14] (a d-block center) and cerium(IV)[15] (a f-block center) with the titled ligands have been reported and compared.[14] To extend and strengthen such comparative discussions of the kinetic behavior between the d- and f-block centres, the present investigation involving uranium(VI), a f-block centre which forms stable chelates[16,17] with the titled ligands has been chosen. Such chelates are of considerable interest from the stand point of analytical determination[18] of uranium. Though the thermodynamic aspects of such complexes are reported[16,17] but the kinetics of formation of these complexes do not appear to have been studied.

It is well-known that uranium(VI) ion exists in solution as an oxo-ion, UO_2^{2+} having the oxygen atoms at the axial positions and these axial positions are extremly inert,[19] while the equatorial positions are fairly labile[3—5,12,20,21] and the complexation occurs generally at the equatorial plane perpendicular to the uranyl group. Both dissociative (D)[5—11] and associative (A)[11—13] mechanisms have been found to operate in the ligand exchange process of uranyl complexes. $UO_2(aq)^{2+}$ is fairly prone to hydrolysis[22] in weakly acidic solution giving rise to different hydrolytic products including polymeric species. Existence of such different protolytic equilibria very often complicates[14,23] the kinetic interpretation. Though in ligand exchange studies[11] such protolytic equilibria at the uranyl centre are of no importance, but in formation reactions through the replacement of ligated water molecules, such equilibria are kinetically very important as in other systems.[14,15,23,24] Though the kinetic investigations at fairly strong acidities involving predominantly $UO_2(aq)^{2+}$ are reported[4,12] in some cases, but the kinetic results at the corresponding monohydroxo centre, $UO_2(OH)(aq)^{+}$ are virtually unavailable in literature. In the present investigation, in fairly weak acidities, it has been attempted to explore the kinetic behavior at both $UO_2(aq)^{2+}$ and $UO_2(OH)(aq)^{+}$ centers.

Experimental

Reagents and Materials : A stock solution of uranyl(VI) nitrate was prepared by dissolving recrystallized $UO_2(NO_3)_2{,}\cdot 6H_2O$ (A. R. Grade) in doubly distilled water in presence of known amount of dilute nitric acid to prevent the hydrolysis of uranium (VI) and was standardized volumetrically by the oxinate–bromate[18] method. The ligands (A. R. Grade) were recrystallized and weighed amounts were taken to prepare the solutions. All other chemicals used were of reagent grade. Doubly distilled water was used to prepare all the solutions.

Apparatus and Procedure : The spectra of the

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freshly prepared complexes in solution were recorded using a Carl-Zeiss Spectrophotometer (VSU-2P, Jena, Germany). The kinetic measurements were done in a Canterbury-model stopped-flow spectrophotometer (SF-3A, Hi-Tech, UK) coupled with an oscilloscope (Advance Instruments 1000A) and a microprocessor (Apple-II) with the help of which the pseudo-first order rate constants were calculated. The flow module of the SF-3A had arrangements for thermostatting (±0.05°C) the reacting solutions and the observation cell of the flow module. The kinetic runs were followed at λ=380 nm where the difference in absorbance between the complex formed and the starting materials is sufficiently high. The pH measurements were done with a systronics (India) pH meter-335. From the pH meter readings, $[H^+]$ values were calculated from a calibration curve obtained under the experimental conditions. To ensure the formation of only 1:1 metal complex and to maintain the pseudo-first order conditions at an ionic strength 0.1 $\mathrm{mol\,dm^{-3}}$ (KNO_3) in the pH range 3.6—4.6 in the temperature range 20—30°C, all the kinetic measurements were done in presence of excess metal ion.

Results and Discussion

8-Quinolinol (oxine) and 8-hydroxy-5-quinolinesulfonate form reddish yellow complexes with excess uranium(VI) in weakly acidic solutions. Under the experimental conditions (pH 3.6—4.6), from the known[25] values of pK_a of the protonated ligands ($LH_2^{+/\pm}$) for the processes, $LH_2^{+/\pm} \overset{K_{a(1)}}{\rightleftharpoons} /LH^{0/1-}+H^+$, $LH^{0/1-} \overset{K_{a(2)}}{\rightleftharpoons} /L^{1-/2-}+H^+$ (for 8-quinolinol, LH_2^+, $pK_{a(1)}=5.01$, $pK_{a(2)}=9.76$; for 8-hydroxy-5-quinolinesulfonate, $LH_2^\pm$, $pK_{a(1)}=3.92$, $pK_{a(2)}=8.12$ at 20°C, $I=0.1$ $\mathrm{mol\,dm^{-3}}$) it is evident that the ligands remain in equilibrium between LH_2 and LH (charges are omitted). On the other hand, from the known[22] values of hydrolysis constants (K_h) for the reaction $UO_2(aq)^{2+} \overset{K_h}{\rightleftharpoons} /UO_2(OH)(aq)^+ + H^+$, ($K_h=2.14\times10^{-5}$ at 25°C) it is reasonable to consider that within the experimental pH range, $UO_2(aq)^{2+}$ and $UO_2(OH)(aq)^+$ remain in equilibrium. The pK_a values[25] and K_h values[22] at other temperatures were obtained from the cited references.

For the formation of 1:1 complex, under the experimental conditions, T_U=total uranium(VI) concentration=(0.50—2.50)$\times10^{-3}$ $\mathrm{mol\,dm^{-3}}$; T_L=total ligand concentration=(0.50—1.00)$\times10^{-4}$ $\mathrm{mol\,dm^{-3}}$; pH=3.6—4.6 under the pseudo-first order conditions ($T_U/T_L \geq 10$), the experimental data are in conformity with the following reaction scheme :

$$LH_2^{+/\pm} \overset{K_{a(1)}}{\rightleftharpoons} LH^{0/1-} + H^+, \quad \text{(fast)}$$

$$UO_2(aq)^{2+} + LH^{0/1-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} /UO_2L^{+/0} + H^+, \quad Q = \frac{k_1}{k_{-1}}$$

$$K_h(-H^+) \downarrow\uparrow$$

$$UO_2(OH)(aq)^+ + LH^{0/1-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} /UO_2L^{+/0}, \quad \frac{Q}{K_h} = \frac{k_2}{k_{-2}}$$

Such a dual path mechanism has been found in the interaction of the titled ligands with iron(III)[14] and cerium(IV).[15] Considering the proton-transfer steps to be fast, the above scheme leads to the following rate equation,

$$k_{obs} = \frac{T_U K_{a(1)} \left(k_1[H^+] + k_2K_h\right)}{\left([H^+] + K_{a(1)}\right)\left([H^+] + K_h\right)} + \frac{\left(k_1[H^+] + k_2K_h\right)}{Q} \tag{1}$$

or,

$$\frac{k_{obs}}{B} = k_1[H^+] + k_2K_h \tag{2}$$

where,

$$B = \frac{T_U K_{a(1)}}{\left([H^+] + K_{a(1)}\right)\left([H^+] + K_h\right)} + \frac{1}{Q}$$

At fixed $[H^+]$, according to the Eq. 1, the plots of k_{obs} versus T_U (Fig. 1) gave straight lines with positive slopes and intercepts, from which the values of Q were calculated (Table 1) as follows,

$$Q = \frac{\text{slope}}{\text{intercept}} \times \frac{\left([H^+] + K_{a(1)}\right)\left([H^+] + K_h\right)}{K_{a(1)}} \tag{3}$$

By using these values of Q and proton dissociation constant[16,17] ($K_{a(2)}$), the stability constants ($\beta_1 = Q/K_{a(2)}$) can be estimated. Thus the estimated value

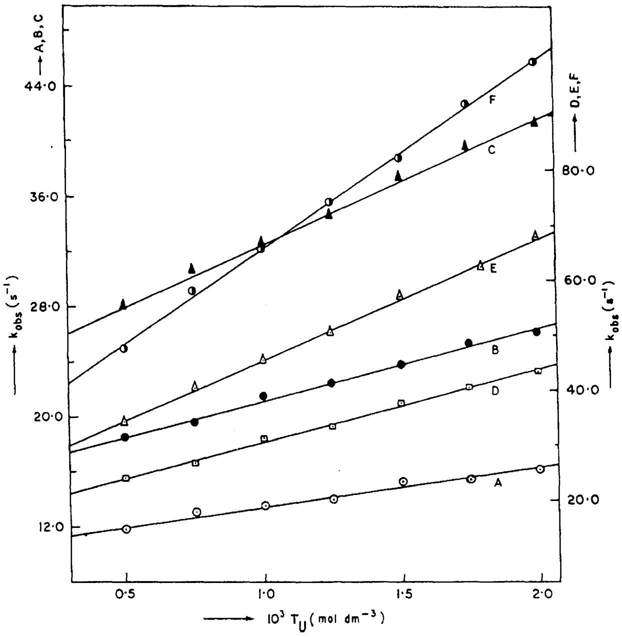

Fig. 1. Evaluation of the equilibrium constant (Q) from kinetic studies. (cf. Eqs. 1 and 3). T_U=(0.50—2.50)$\times10^{-3}$ $\mathrm{mol\,dm^{-3}}$; T_L=0.50$\times10^{-4}$ $\mathrm{mol\,dm^{-3}}$; $[H^+]=10^{-4}$ $\mathrm{mol\,dm^{-3}}$; I=0.1 $\mathrm{mol\,dm^{-3}}$ (KNO_3). A (20°C), B (25°C), and C (30°C) for uranium(VI)–8-quinolinol; D (20°C), E (25°C), and F (30°C) for uranium(VI)–8-hydroxy-5-quinolinesulfonate.

Table 1. Thermodynamic Parameters of the Process, $UO_2^{2+}+LH^{0/1-} \rightleftarrows UO_2L^{+/0}+H^+$, ($LH^0$ and LH^- Stand for Partially Deprotonated 8-quinolinol and 8-Hydroxy-5-quinolinesulfonate Respectively) from Kinetic Studies
$T_U=(0.50—2.50)\times10^{-3}$ mol dm^{-3}; $T_L=0.50\times10^{-4}$ mol dm^{-3}; $[H^+]=10^{-4}$ mol dm^{-3}; $I=0.1$ mol dm^{-3} (KNO_3).

Temp (°C)	Equilibrium constant, 10^2Q	
	Uranium(VI)–8-quinolinol	Uranium(VI)–8-hydroxy-5-quinolinesulfonate
20	34.27±1.25	17.20±0.80
25	40.36±1.40	20.25±1.00
30	46.40±1.20	24.40±1.10
ΔH, (kJ mol^{-1})	22.4±1.8	25.6±1.5
ΔS, (J K^{-1} mol^{-1})	67.6±4.4	72.6±4.8

($\log\beta_1=7.63$ at 25°C) for uranium(VI)–8-hydroxy-5-quinolinesulphonate is in fairly good agreement with the reported value[17] ($\log\beta_1=8.52$ at 25°C) obtained titrimetrically. Similarly, $\log\beta_1$ at 20°C for uranium(VI)–8-quinolinol becomes 9.38 from this kinetic study. From the Q values determined at different temperatures, the thermodynamic parameters, ΔH and ΔS were estimated (Table 1). In both cases, the equilibrium processes are mainly driven by the entropy factors, as the enthalpy changes are positive. From the Table 1, it is evident that with the increase of the pK_a values of the ligands, the equilibrium constant (Q) increases.

According to the Eq. 2, the plots of k_{obs}/B versus $[H^+]$ gave straight lines (Fig. 2) with positive slopes and intercepts from which k_1 and k_2 were evaluated. By using these values of forward rate constants along with those of Q, the backward rate constants k_{-1} and k_{-2} were calculated (Table 2). The activation parameters for each path were determined (Table 2) as usual by making the use of Eyring equation.[26]

From the Table 2, it is evident that the higher values of Q $(=k_1/k_{-1})$ for uranium(VI)-8-quinolinol than that of uranium(VI)-8-hydroxy-5-quinolinesulfonate system arise mainly due to the lower values of k_{-1} in the case of 8-quinolinol system. In each system, k_1 path is relatively unfavored with respect to k_{-1} path due to the higher values of $\Delta H^\ddagger$ in the forward path. It makes ΔH for Q positive and the process gets favored by the positive entropy factor. On the other hand, for $UO_2(OH)(aq)^+$, k_2 path is favored over the k_{-2} path mainly due to the lower values of $\Delta H^\ddagger$ in the forward path.

According to the Eigen mechanism,[27] the magnitude of overall rate constant (k) is given by $k=k_{ex}K_{OS}$ where K_{OS} is the outer-sphere association constant and k_{ex} is the first-order rate constant for water exchange at the metal centre. In the case of 8-quinolinol (LH), K_{OS} has been estimated as ca. 0.2 mol^{-1} dm^3 at 25°C for ion–molecular dipole interaction[28] and it can be computed with the Fuoss equation[29] in the cases where both the reactants are charged. In the case of 8-hydroxy-5-quinolinesulfonate (LH^-), the additional negative charge imparted by $-SO_3^-$ group at the remote site is expected not to introduce any electrostatic attraction in the outer-sphere association complex. Hence, it is reasonable to consider the magnitude of K_{OS} to be 0.2 mol^{-1} dm^3 as in the case of 8-quinolinol system. By using these K_{OS} values in the k_1 path, the estimated k_{ex} values (at 25°C) become 2.2×10^5 s^{-1} (for 8-quinolinol) and 1.8×10^5 s^{-1} (for 8-hydroxy-5-quinolinesulfonate). These values are fairly close to the reported[20] water exchange rate ($k_{ex}=9.8\times10^5$ s^{-1} at 25°C) at $UO_2(aq)^{2+}$. In fact, for a number of ligands (Table 3) having widely different basicities and structural features, the estimated water exchange rate (k_{ex}) lies in the range $(0.5—18.0)\times10^5$ s^{-1}. Thus it is reason-

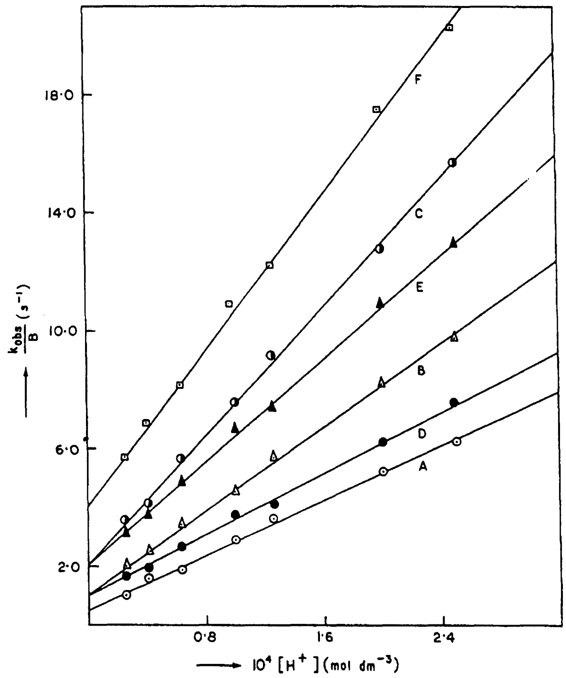

Fig. 2. Evaluation of k_1 and k_2 from kinetic studies (cf. Eq. 2). $T_U=(0.50—2.50)\times10^{-3}$ mol dm^{-3}; $T_L=(0.50—1.00)\times10^{-4}$ mol dm^{-3}; $T_U/T_L\geq10$; $[H^+]=(0.25—2.50)\times10^{-4}$ mol dm^{-3}; $I=0.1$ mol dm^{-3} (KNO_3). A (20°C), B (25°C), and C (30°C) for uranium(VI)-8-hydroxy-5-quinolinesulfonate; D (20°C), E (25°C), and F (30°C) for uranium(VI)-8-quinolinol.

Table 2. Kinetic Parameters of Interaction of Uranium(VI) with 8-Quinolinol and 8-Hydroxy-5-quinolinesulfonic Acid

$T_U=(0.50\text{—}2.50)\times10^{-3}$ mol dm^{-3}; $T_L=(0.50\text{—}1.00)\times10^{-4}$ mol dm^{-3}; $T_U/T_L\geq10$; $[H^+]=(0.25\text{—}2.50)\times10^{-4}$ mol dm^{-3}; $I=0.1$ mol dm^{-3} (KNO_3).

System	Temp °C	$10^{-4}k_1$ dm^3 mol^{-1} s^{-1}	$10^{-4}k_{-1}$ dm^3 mol^{-1} s^{-1}	$10^{-4}k_2$ dm^3 mol^{-1} s^{-1}	k_{-2} s^{-1}
Uranium(VI)–	20	2.60±0.05	7.86±0.12	7.33±0.09	2.80±0.06
8-quinolinol	25	4.32±0.10	10.80±0.15	9.34±0.10	5.04±0.05
	30	6.70±0.12	14.60±0.18	11.80±0.14	8.72±0.10
$\Delta H^\ddagger$ (kJ mol^{-1})		67.7±3.2	43.6±1.8	32.8±2.0	82.0±4.7
$\Delta S^\ddagger$ (J K^{-1} mol^{-1})		69.6±3.7	−3.6±0.5	−41.0±3.2	41.7±2.9
Uranium(VI)–	20	2.32±0.07	14.30±0.17	3.76±0.08	2.85±0.05
8-hydroxy-	25	3.60±0.06	18.00±0.20	4.70±0.12	5.01±0.12
5-quinolinesulfonate	30	5.50±0.12	22.91±0.28	5.90±0.15	8.33±0.15
$\Delta H^\ddagger$ (kJ mol^{-1})		61.5±2.9	32.5±2.2	30.8±1.8	77.1±3.8
$\Delta S^\ddagger$ (J K^{-1} mol^{-1})		47.4±3.1	−36.5±3.4	−53.6±3.5	25.0±1.4

Table 3. Specific Complex Formation Rate Constants (k_1) for Different Ligands for "$UO_2(aq)^{2+}$+Ligand" Reactions and Computed Water Exchange Rates (k_{ex}) at 25°C

Ligand (reactive form)	pK_a[a)]	$10^{-4}k_1$ dm^3 mol^{-1} s^{-1}	$10^{-5}k_{ex}$[b)] s^{-1}	Reference
8-Quinolinol (LH)	4.95, 9.67	4.32	2.20	This work
8-Hydroxy-5-quinolinesulfonate[c)] (LH$^-$)	3.86, 8.35	3.60	1.80	This work
4-(2-Pyridylazo) resorcinol (par) (LH_2)	3.14, 5.61	36.40	18.20	4
Chromotropic acid[c)] (LH^{3-})	5.40	71.40	3.57	5
Chromotrope 2B[c)] (LH_2^{2-})	8.59	1.06	0.53	5

a) pK_a values give the measure of basicities of the ligand sites involved in complexation. b) $k_{ex}=k_1/K_{OS}$; for ion-dipole interaction,[28] $K_{OS}=0.2$ mol^{-1} dm^3 and for the both the charged reactants, K_{OS} has been calculated by Fuoss[29] equation. c) The negative charge on sulfonato group at the remote site is expected not to introduce any electrostatic interaction.

able to conclude that at least for these ligands included in the Table 3, the dissociative (D) or dissociative interchange (I_d) mechanism operates.

The activation parameters (i.e. $\Delta H^\ddagger$ and $\Delta S^\ddagger$) determined (Table 2) are in fact composite ones[30] involving the ΔH and ΔS values of the corresponding outer-sphere association constants, deprotonation processes of the involved ligand, etc. A fairly good linear plot, $\Delta H^\ddagger$ versus $\Delta S^\ddagger$ (Fig. 3) for the k_1 path for different types of ligands indicates a similarity of mechanism for all these ligands.

Here it is worth mentioning that in $UO_2(aq)^{2+}$, the axial oxygen atoms are extremely inert[19] and remain unaffected during the substitution process. In the limiting S_N1 (or D) mechanism, the intermediate trigonal-bipyramid species having the D_{3h} symmetry is unfavored[20] from the stand point of participation of uranyl d- or f-orbitals in bond formation. But the dissociative interchange (I_d) mechanism can operate.[20]

The reported rate constants of complexation by SO_4^{2-}, SCN^-, $CH_3CO_2^-$, and $ClCH_2CO_2^-$ at the $UO_2(aq)^{2+}$ centre are 180, 290, 1050, and 110 dm^3 mol^{-1} s^{-1} respectively at 20°C. Apparently, these surprisingly small values indicate other mechanism[11,12] (probably, an associative mechanism) rather than the dissociative mechanism. But, here it is important to note that these complexation reactions were carried out at high UO_2^{2+} concentrations (0.28—0.01 mol dm^{-3}) in which range, polymerization of UO_2^{2+} ion may complicate the kinetic results as proposed by Ekstrom et al.[4]

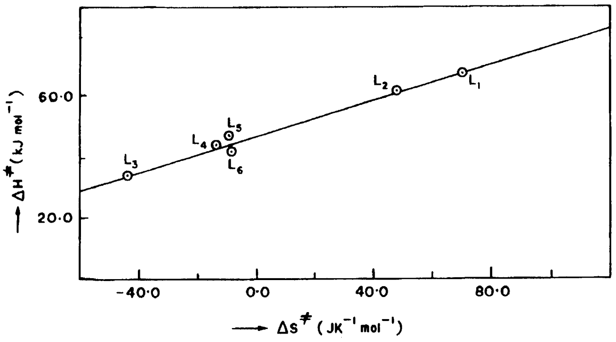

Fig. 3. $\Delta H^{\ddagger}$ versus $\Delta S^{\ddagger}$ (isokinetic plot) for k_1 path. L_1 = 8-quinolinol; L_2 = 8-hydroxy-5-quinolinesulfonate; L_3 = 4-(2-pyridylazo)resorcinol (par), Ref. 4; L_4 = chromotropic acid, Ref. 5; L_5 = chromotrope 2B, Ref. 5; L_6 = water, Ref. 20.

In fact, the rate constants of the above complexation reactions are similar to that determined[21] for the dimerization of the $UO_2(OH)(aq)^+$ species. However, both dissociative[5—11] and associative[11—13] mechanisms are known to operate in the ligand exchange process at the uranyl centre. But the governing factors to determine the mechanism are not yet fully clear[11] and it requires more extensive works in this discipline.

For the k_2 path, if the Eigen mechanism[27] is supposed to occur, then it leads to water exchange rate (k_{ex}) at the $UO_2(OH)(aq)^+$ centre 4.7×10^5 s^{-1} and 2.4×10^5 s^{-1} (taking $K_{OS}=0.2$ mol^{-1} dm^3 for ion–molecular dipole interaction) at 25°C for uranium(VI)–8-quinolinol and uranium(VI)–8-hydroxy-5-quinolinesulfonate systems respectively. Thus, these results show that the water exchange rate at $UO_2(OH)(aq)^+$ is expected to be in the order of 10^5 s^{-1} at 25°C. Unfortunately, the kinetic results at the monohydroxo centre of uranium(VI) are virtually unavailable in literature to confirm the conclusion. However, if the dissociative process occurs at $UO_2(aq)^{2+}$ center, then the operation of the same mechanism at the monohydroxo center is not unlikely. In fact, such a dissociative mechanism has been reported at the hydroxo species of cerium(IV)[15] and iron(III).[14,23,24]

The kinetic investigations with the titled ligands at iron(III),[14] cerium(IV),[15] and uranium(VI) reveal that in all cases, the dual path mechanism involving M^{n+} and $M(OH)^{(n-1)+}$ is working. For cerium(IV) and iron(III) though the k_1 path is sensitive (i.e. I_a mechanism) towards the nature of the entering ligands but the k_2-path is insensitive (i.e. I_d mechanism) towards the entering ligands. But for uranium(VI), both the k_1 and k_2 paths are found to involve I_d mechanism. Here it is worth mentioning that though for iron(III) system, k_2-path i.e. monohydroxo species is ca. 10^3 times more reactive than the k_1 path i.e. $Fe(aq)^{3+}$ species, but for the f-block centres i.e. cerium(IV) and uranium(VI), no such enhanced reactivity at the hydroxo center is noticed. Probably, it is a characteristic feature of the f-block elements and does not depend on the charge of the reactive center.

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