Kinetics and Equilibria of the Interaction of 8-Hydroxyquinoline with Gallium(III) in Water and Sodium Dodecyl Sulfate Solution

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Received: September 4, 2008; Revised Manuscript Received: November 27, 2008

The kinetics and equilibria of binding of gallium(III) to the 8-hydroxyquinoline (HQ) have been investigated in water and in the presence of sodium dodecyl sulfate (SDS) micelles. Moreover, the pK_{A1} and pK_{A2} of HQ and first hydrolysis constant of Ga^{3+} ion have been measured in water and SDS solution. The analysis of the kinetic and thermodynamic behavior reveals that the reactive form of Ga(III) is $GaOH^{2+}$ in both cases. Although in water the only bound form of Ga(III) appears to be the deprotonated complex GaL, evidence for stabilization of the protonated form, GaHL on the micelle surface and stabilization of Ga^{3+} with respect to $GaOH^{2+}$ is provided by the kinetic behavior in SDS. The addition of SDS at concentrations around the critical micellar concentration, results in a large enhancement of the rate of complex formation. The large catalytic effect produced by the SDS micellar solution provides a promising basis for the extraction of gallium from water using the HQ/SDS system. A procedure for gallium(III) extraction and recovery based on ligand modified-micellar enhanced ultrafiltration method, using the HQ/SDS system, is described.

Introduction

There is much interest in the study of the complexation of trivalent cations of group XIII, particularly in relation to their use in biology and medicine. The most important application of Ga(III) is in nuclear medicine;[1,2] the radioactive isotope of gallium, ^{67}Ga, is able to reveal some particular pathologies like tumors or inflammations, and it is also useful to check the functioning of human organs. Moreover, trivalent gallium(III) is capable of inhibiting tumor growth. The metal is administered bound to ligands able to stabilize gallium against hydrolysis and to favor membranes permeation.[3] In this context, the knowledge of the modes of interaction of gallium ions with metal receptors is of great importance to optimize the design and synthesis of better radiopharmaceuticals. Whereas the mechanism of metal−ligand interaction has been widely investigated and quite well elucidated in the case of divalent metal ions, the position of trivalent cations is less clear. This is mainly due to the extensive hydrolysis and polymerization of these cations, which leads to the formation of several reactive species[4] and seriously limits the range of acidity that can be investigated. In addition, the distribution of the metal and the ligand among differently protonated forms introduces proton ambiguity,[5] which often makes it impossible to unequivocally associate a given experimental rate constant to a given reaction path.

Moreover, knowledge of the equilibria and mechanisms of metal complex formation (and dissociation) reactions could be of crucial importance to predict efficient procedures for extraction and recovery of metals, particularly when the extraction process is made using micellar pseudophases. In micellar extraction, an anionic surfactant is added to the stream containing the cation to be removed. The surfactant forms highly charged aggregates (micelles) onto which the metal cations can be bound. The micellar extraction process consists of three steps. The first one where the metal is concentrated on the micellar pseudophase; in the second step the micellar pseudophase is separated from the aqueous pseudophase through ultrafiltration or other separation techniques; during the third and final step the metal is stripped off the micellar pseudophase. The trapping of metal ions on the micellar pseudophase can be achieved in two different ways: (1) by exchange of the multivalent metal ions with the monovalent counterion of anionic micelles and (2) by complexation of metal ions through a complexing agent (extractant) bound to the surface or solubilized into the core of the micelle. In the first case, metal ions are attracted to the negatively charged micelle surface by electrostatic interaction; the subsequent ultrafiltration step is called micellar enhanced ultrafiltration (MEUF). We are interested in the latter method where the extent of the metal ion binding depends on the stability constant of the metal-extractant complex, in strong similarity with classical solvent extraction. In this case the ultrafiltration step is referred to as ligand modified-micellar enhanced ultrafiltration (LM-MEUF).

Beside the fact that it is generally undesirable to use organic solvents in extraction processes, because of the associated environmental hazards, there are significant advantages in using a micellar solution over a two-phase water−organic solvent system for the extraction process. The micelles are distributed uniformly through the medium as very small aggregates and no stirring of the medium is required, because the system is a single homogeneous macrophase. Moreover, micelles are able to solubilize ligands with hydrophobic residues that can react with metal ions present on the metal surface where the reaction will be facilitated as the result of a local concentration effect on both reactants.

8-Hydroxyquinoline (HQ) and many of its derivatives have been extensively used as chelating reagents in analytical chemistry[6] and the two main fields of application of HQ are extraction and fluorometric determination of metal ions. Fluorescent quinolinium derivatives are used to detect and quantify the presence of Cl^- ions in cells.[7]

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10.1021/jp8078666 CCC: $40.75
Published on Web 01/15/2009

In the present article we report on kinetics and equilibria of the binding of gallium(III) to HQ in pure water and in aqueous solution containing micelles of sodium dodecyl sulphate (SDS). The aim of the investigation is to elucidate the mechanisms of complex formation in the two different media and enable us to gain useful information for the optimization of a procedure for gallium extraction.

Experimental Section

Materials. All reactants were analytical grade. The ligand 8-hydroxyquinoline (HQ) and the surfactant sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich and used as received. Sodium perchlorate and sodium chloride were obtained from Fluka. Gallium perchlorate was prepared by dissolution of a known weight of the pure metal in a known excess of perchloric acid. The dissolution process is very slow due to hydrogen overvoltage; hence, the metal was put in contact with a platinum wire and the solution was slightly warmed. This procedure led to a dramatic increase in the speed of dissolution. The concentrations of gallium(III) stock solutions were checked by EDTA titration[8] and found to coincide with those calculated from the weight of the dissolved metal. All the other stock solutions were prepared by dissolving weighed amounts of the relevant reagent in doubly deionized water, which was also used as a reaction medium. The ultrafiltration membranes, supplied by Millipore (Amicon), were made of regenerated cellulose (filter code YM 3) of diameter 44.5 mm and with a molecular weight cut off (MWCO) of 3KD. The membranes were pretreated and stored according to the method recommended by Millipore (Amicon).

Instrumentations and Methods. All measurements were made at 25 ± 0.1 °C. The pH measurements were made using a Metrohm 713 instrument. The pH of the solutions was adjusted by adding small amounts of concentrated HCl or NaOH. The cmc of SDS was checked by electrical conductivity. In the absence of added salt (or divalent metal ions) the value at 25 °C was 7.9×10^{-3} M, which is in excellent agreement with literature data.[9−11]

A Perkin-Elmer Lambda 35 spectrophotometer was used for spectral measurements. Spectrophotometric titrations were performed by adding with a microsyringe (Mitutoyo) increasing volumes of gallium perchlorate solution to 2.0 mL of the ligand solution directly in the spectrophotometric cell, keeping constant both the acidity and the ionic strength. The titration curves were analyzed according to an iterative procedure used by Hynes and Diebler.[12]

The time course of Ga(III)/HQ complex formation and dissociation reaction was monitored by the stopped-flow method using a Biologic SFM-300 mixing unit connected to a spectrophotometric line by optical fibers as already described.[13] Complex formation experiments were performed by mixing solutions of the ligand with solutions of gallium perchlorate whose concentration, C_M, was varied keeping the conditions $C_M \geq 10C_L$. Measurements in the presence of SDS were performed by mixing solutions of metal and ligand, each containing the same micelle concentration with no added ionic strength. Complex dissociation experiments were performed by mixing a solution containing a mixture of HQ 4×10^{-4} M and gallium perchlorate 4×10^{-4} M at pH = 3.0 with a solution of the desired HCl concentration. The kinetic curves were monoexponential and were analyzed using a nonlinear least-squares procedure provided by a multivariate analysis software (Jandel-AISN). The time constants used to evaluate the kinetic parameters are average values from at least six repeated experiments which displayed a maximum spread of 10%.

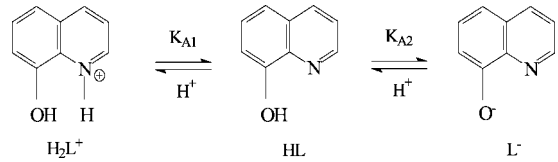


Figure 1. Protonation equilibria of 8-hydroxyquinoline (HQ).

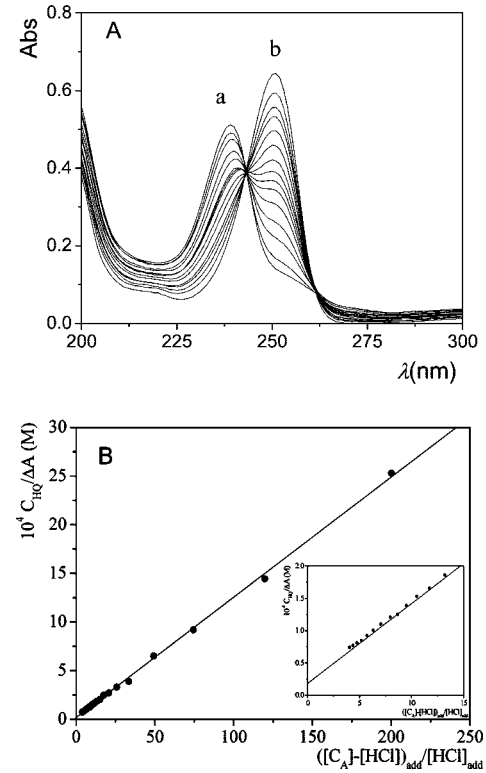


Figure 2. Determination of pK_{A1} of HQ in water ($I = 0.2$ M ($NaClO_4$), $T = 25$ °C). (A) Absorption spectra of HQ at different pH values, $C_{HQ} = 2 \times 10^{-5}$ M, $C_a = 1 \times 10^{-3}$ M. Spectrum a, recorded at pH = 8, shows the peak due to the neutral ligand. Spectrum b, recorded at pH = 2.7, shows the peak due to the protonated ligand (H_2L^+). (B) Analysis of a spectrophotometric titration at $\lambda = 251$ nm according to eq 1. The inset shows an enlargement of the plot in the vicinity of the intercept.

The ultrafiltration experiments were carried out in a batch stirred cell (Amicon, model 8050) with a capacity of 50 mL and an effective membrane area of 13.4 cm^2. Ultrafiltration was performed as follows: 20 mL of solution containing the metal, the ligand and surfactant micelles was passed through the ultrafiltration cell under a 2 bar nitrogen pressure. The metal−ligand complex adsorbed on the micelles remains in the retentate (2.5 mL), whereas the aqueous phase containing uncomplexed ions crosses the membrane, costituting the permeate (17.5 mL). Then, the retentate is mixed with the stripping solution (12.5 mL) and a second ultrafiltration is performed to recover the displaced metal ion in the final collected permeate (12.5 mL). Shortly after the conclusion of the procedure the ultrafiltration membranes were flushed with deionized water and, if necessary, they were regenerated according to the method recommended by Millipore (Amicon). The amounts of metal ions extracted or recovered by ultrafiltration were assessed through atomic absorption spectroscopy using a Perkin-Elmer HGA-800 apparatus. Samples were atomized in an air/acetylene flame. The reproducibility of concentration measurements was within ±2%.

TABLE 1: Acid Dissociation Constants for 8-Hydroxyquinoline in Water and in SDS at 25 °C

	pK_{A1}	pK_{A2}	K_{H1}	$pK_{NaH_2PO_4}$
H_2O	4.68 ± 0.14^a	11.31 ± 0.03^a	$(3.0 \pm 0.5) \times 10^{-4}$ (M)^a	7.2^b
SDS (0.02 M)	6.80 ± 0.03^a	11.62 ± 0.02^a	$(5.8 \pm 1.4) \times 10^{-5}$ (M)^a	6.95 ± 0.02^c
SDS (0.04 M)	6.77 ± 0.02^a	11.64 ± 0.03^a		6.78 ± 0.02^c

[a] This work. [b] From ref 27. [c] From potentiometric titrations.

Results

Acid Dissociation Equilibria in Water. 8-Hydroxyquinoline, also denoted as H_2L^+ when appropriate, is a weak diprotic acid (Figure 1).

The pK_{A1} of HQ has been measured by exploiting the proton exchange reaction between H_2L^+ and acetate ions. Spectrophotometric titrations were carried out by adding calibrated amounts of HCl to a cell containing a known amount of HQ and an excess of CH_3COONa. Figure 2A shows the HQ spectra recorded in the pH range from 8 to 2.7 during a titration. The absorbance values at 251 nm have been analyzed according to eq 1

$$\frac{C_{HQ}}{\Delta A} = \frac{1}{\Delta\varepsilon} + \frac{1}{K\Delta\varepsilon} \times \frac{[C_A - [HCl]_{add}]}{[HCl]_{add}} \qquad (1)$$

where C_{HQ} is the analytical concentration of HQ, C_A is that of sodium acetate and $[HCl]_{add}$ is the concentration of added HCl. The absorbance variation is defined as $\Delta A = A\text{bs} - \epsilon_{HL}C_{HQ}$ whereas $\Delta\epsilon = \epsilon_{H_2L} - \epsilon_{HL}$. K represents the equilibrium constant of proton exchange process between H_2L^+ and CH_3COO^-, and it is defined as $K = K_{HA}/K_{A1}$. The analysis of a typical titration according to eq 1 is shown in Figure 2B. Using the pK_{HA} value of acetic acid of 4.51 ± 0.02 at $I = 0.2$ M and $T = 25$ °C (derived from the literature value at $I = 0$ M and $T = 25$ °C[14] with the help of the Davies[15] equation), the pK_{A1} value of HQ reported in Table 1 has been obtained. Its value is in agreement with the literature data ($pK_{A1} = 4.88$).[16]

The evaluation of pK_{A2} of HQ has been performed by adding known amounts of NaOH to a solution of HQ. In this case the absorbance data were collected at 239 nm and have been analyzed using eq 2

$$\frac{C_{HQ}}{\Delta A} = \frac{1}{\Delta\varepsilon} + \frac{1}{K\Delta\varepsilon} \frac{1}{[NaOH]_{add}} \qquad (2)$$

where $[NaOH]_{add}$ is the concentration of added sodium hydroxide, $\Delta\epsilon = \epsilon_{HL} - \epsilon_L$ and $K = K_{A2}/K_W$. The pK_{A2} value (Table 1) is lower than the literature value ($pK_{A2} = 10.38$).[17] The spectra recorded in the pH range from 8 to 12.7 and the analysis of a titration according to eq 2 are reported in Figure 1S (Supporting Information).

Complex Formation Equilibria in Water. The interaction between Ga(III) and HQ in aqueous solution is revealed by spectral changes in the UV region (Figure 3). At constant pH the equilibria could be described by the apparent complex formation reaction 3:

$$M_f + L_f \rightleftharpoons ML_T \qquad (3)$$

where M_f and L_f are the total concentrations of uncomplexed metal ($[M_f] = [M^{3+}] + [MOH^{2+}]$) and ligand ($[L_f] = [H_2L^+] + [HL] + [L^-]$), whereas ML_T is the total complex concentration ($ML_T = [MH_2L^{4+}] + [MHL^{3+}] + [ML^{2+}]$). Further

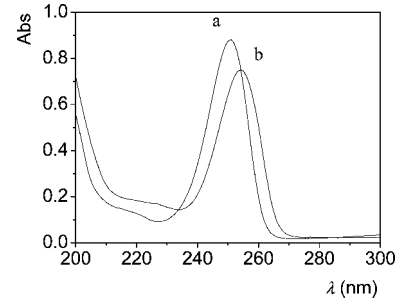
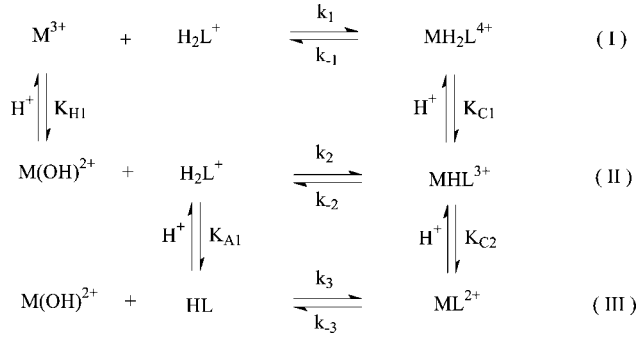


Figure 3. Absorption spectrum of the system Ga(III)/HQ in water: (a) HQ 2×10^{-5} M; (b) HQ 2×10^{-5} M + $Ga(ClO_4)_3$ 2×10^{-2} M. $[H^+] = 7.8 \times 10^{-3}$ M, $I = 0.2$ M ($NaClO_4$), $T = 25$ °C.

SCHEME 1



hydrolyzed and polymeric forms of Ga(III) have not been included in the above sums because in the investigated range of pH their concentration could be neglected.[4]

Under conditions of metal excess ($C_M \geq 10C_L$) only 1:1 complexes are formed. The equilibrium constant, K_{app}, of reaction 3 was evaluated for different pH values (in the range between 2.1 and 2.7) by titrations of HQ with $Ga(ClO_4)_3$ at 250 nm, according to a procedure already described.[12] The values of K_{app} were found to decrease as $[H^+]$ increases. The analysis of the equilbria and kinetics (described below) has been based on a general reaction pattern (Scheme 1) which includes possible interaction between the metal and ligand forms which prevail under the experimental conditions.

According to Scheme 1, the acidity dependence of K_{app} is given by eq 4

$$\frac{K_{app}}{\alpha_{H_2L}\beta_M} = K_1 + \frac{K_2K_{H1}}{[H^+]} + \frac{K_3K_{H1}K_{A1}}{[H^+]^2} \qquad (4)$$

where $K_1 = k_1/k_{-1}$, $K_2 = k_2/k_{-2}$ and $K_3 = k_3/k_{-3}$ are the equilibrium constants of the individual steps I, II and III respectively, whereas K_{H1} is the first hydrolysis constant of Ga^{3+} ion. The molar fractions of the ligand, α_{H_2L}, and metal, β_M, are defined as $\alpha_{H_2L} = [H_2L^+]/[L_f] = [H^+]/(K_{A1} + [H^+])$, and $\beta_M = [M^{3+}]/[M_f] = [H^+]/(K_{H1} + [H^+])$.

A plot of $K_{app}/\alpha_{H_2L}\beta_M$ vs $1/[H^+]$, according to eq 4, is shown in Figure 4. The value of K_{H1} at $I = 0.2$, has been evaluated in a first approximation by using the relationship $\log K_{H1} = -2.6$

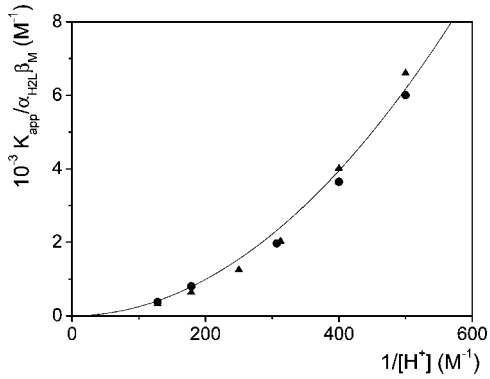


Figure 4. Dependence of the apparent equilibrium constant K_{app} for the Ga(III)/HQ system in water on hydrogen ion concentration at $I = 0.2$ M ($NaClO_4$), $T = 25$ °C: (●) data from spectrophotometric titrations; (▲) data from kinetic measurements (k_f/k_d). The continuous line is based on eq 4.

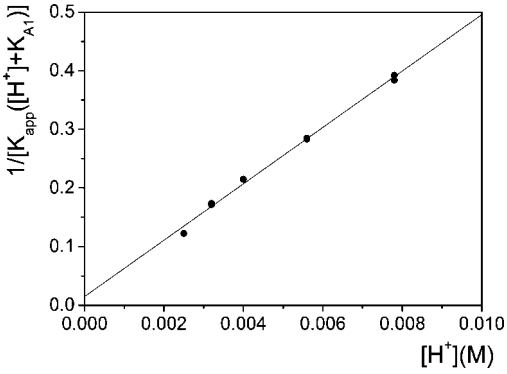


Figure 5. Plot according to eq 5 showing the dependence of the equilibria on acidity for the Ga(III)/HQ system in water.

$- 2.044I^{1/2}/(1 + I^{1/2})$.[15] Least-squares analysis of the data shows that the third term of eq 4 is by far the most important and its evaluation yields $K_3K_{A1}K_{H1} = (2.36 \pm 0.05) \times 10^{-2}$ M. Subsequently, neglecting the terms K_1 and K_2K_{H1} and introducing the expressions for α_{H_2L} and β_M into eq 4, one gets eq 5

$$\frac{1}{K_{app}([H^+] + K_{A1})} = \frac{1}{K_3K_{A1}} + \frac{[H^+]}{K_3K_{H1}K_{A1}} \qquad (5)$$

which enables us to evaluate K_{H1} as the ratio intercept/slope of the linear fit shown in Figure 5. The value of K_{H1} is reported in Table 1. From the slope of the plot of Figure 5, using K_{A1} and K_{H1}, one obtains $K_3 = (3.3 \pm 1.7) \times 10^6$ M whereas the plot of Figure 4 yields $K_3 = (3.7 \pm 1.9) \times 10^6$ M. The average value of K_3 is reported in Table 2.

Complex Formation Kinetics in Water. The kinetics of complex formation have been investigated under pseudo first-order conditions ($C_M \geq 10C_L$) at different pH values in the range 2.1−2.7 and $I = 0.2$ M. The curves are monoexponential (Figure 6A) and their analysis provided the amplitude and time constant, $1/\tau$, of the corresponding kinetic effect. Experiments at constant pH and varying the metal concentration show a good linearity of $1/\tau$ versus C_M (Figure 6B). Thus, a linear interpolation of the experimental data according to eq 6

$$1/\tau = k_d + k_fC_M \qquad (6)$$

would provide the values of the apparent complex formation (k_f) and dissociation (k_d) rate constants of reaction 3.

According to Scheme 1, the dependencies of k_f and k_d on [H$^+$] should be given by eqs 7 and 8, respectively

$$k_f = \left(k_1 + \frac{k_2K_{H1}}{[H^+]} + \frac{k_3K_{H1}K_{A1}}{[H^+]^2}\right)\alpha_{H_2L}\beta_M \qquad (7)$$

$$k_d = \left(k_{-3} + \frac{k_{-2}[H^+]}{K_{C2}} + \frac{k_{-1}[H^+]^2}{K_{C1}K_{C2}}\right)\gamma_{ML} \qquad (8)$$

where K_{C1} and K_{C2} are the acid dissociation constants of MH_2L^{4+} and MHL^{3+}, respectively, whereas $\gamma_{ML} = [ML^{2+}]/[ML_T] = K_{C1}K_{C2}/([H^+]^2 + K_{C1}[H^+] + K_{C1}K_{C2})$. The equilibrium results indicate that ML^{2+} is the prevailing complexed species, hence $\gamma \cong 1$. Figure 7A shows the acidity dependence of the forward rate constant. The data fit according to eq 7 shows that the values of k_1 and k_2K_{H1} are indistinguishable from zero whereas $k_3K_{A1}K_{H1} = (6.9 \pm 0.4) \times 10^{-4}$ M s^{-1}.

Concerning the process of complex dissociation the dependence of k_d/γ_{ML} vs [H$^+$], shown in Figure 7B, does not display a definite dependence on [H$^+$]; therefore, the second and third term of eq 8 can be neglected, whereas the back rate constant of step (III), k_{-3}, was evaluated as the mean value of k_d. The values of the individual rate constants, k_3 and k_{-3}, so obtained are collected in Table 2.

The equilibrium constant of reaction 3, K_{app}, has been evaluated from the kinetic costant ratio, k_f/k_d and the values so obtained (Figure 4, triangles) are in good agreement with those provided by the static experiments.

Complex Dissociation Kinetics in Water. The reaction of metal dissociation from the ligand (stripping reaction) has been investigated by addition of HCl to the metal complex previously formed by mixing $Ga(ClO_4)_3 = 4 \times 10^{-4}$ M and HQ = 4×10^{-4} M at pH = 3. The ionic strength was 1 M. The time course of the stripping reaction was monitored at $\lambda = 250$ nm exploiting the change of absorbance shown in Figure 3. In the stripping experiments the maximum contribution of k_fC_M to $1/\tau$ (eq 6) is only 0.28%; hence, it has been neglected. Under these circumstances it turns out that $1/\tau = k_d$. The dissociation path associated with k_{-3}, already detected in the complex formation experiments, is revealed by the stripping experiments as well. A plot of k_d/γ_{ML} vs [H$^+$] shows a straight line with zero slope (Figure 7C) from which, according to eq 8, a value of k_{-3} in agreement with that derived from the analysis of the complex formation process has been obtained (Table 2).

Acid Dissociation Equilibria in SDS. Prior to investigate the equilibria and kinetics in micellar solution the extent of HQ adsorption on SDS micelles was evaluated. Mixtures of HQ 1×10^{-5} M in SDS 0.02 M were prepared at pH 4.1 and then the two phases were separated by ultrafiltration. The absorbance of HQ collected in the permeate (aqueous phase) after ultrafiltration was compared with the absorbance of a solution of HQ 1×10^{-5} M at equivalent pH value in the absence of surfactant. It has been found that 82% of the ligand molecules are retained by the micelles.

The acid dissociation of HQ has been investigated in the presence of SDS micelles. Spectrophotometric titrations were carried out by adding calibrated amounts of a HCl solution containing SDS to a cuvette containing known amounts of a HQ and Na_2HPO_4 solution with the same concentration of SDS as that of the titrating solution. Figure 2SA (Supporting Information) shows some of the spectra recorded during a titration performed in SDS 0.02 M. The absorbance values at

TABLE 2: Reaction Parameters for the Ga(III)/Hydroxyquinoline System in Water and in SDS at 25 °C

	$10^2K_3K_{A1}K_{H1}$, M	$10^{-6}K_3$, M^{-1}	$10^4k_3K_{A1}K_{H1}$, M^{-1} s^{-1}	$10^{-5}k_3$, M^{-1} s^{-1}	10^2k_{-3}, s^{-1}	k_{-2}/K_{C2}, M^{-1} s^{-1}
H_2O	2.36 ± 0.05	3.5 ± 1.9 4.1 ± 2.2[a]	6.9 ± 0.4	1.1 ± 0.6	2.5 ± 0.5 2.8 ± 0.3[b]	
SDS	0.028 ± 0.001	30 ± 11	0.062 ± 0.004	6.7 ± 2.5	2.3 ± 0.1 3.6 ± 1.1[b]	0.28 ± 0.06[b]

[a] From kinetics. [b] From stripping reaction.

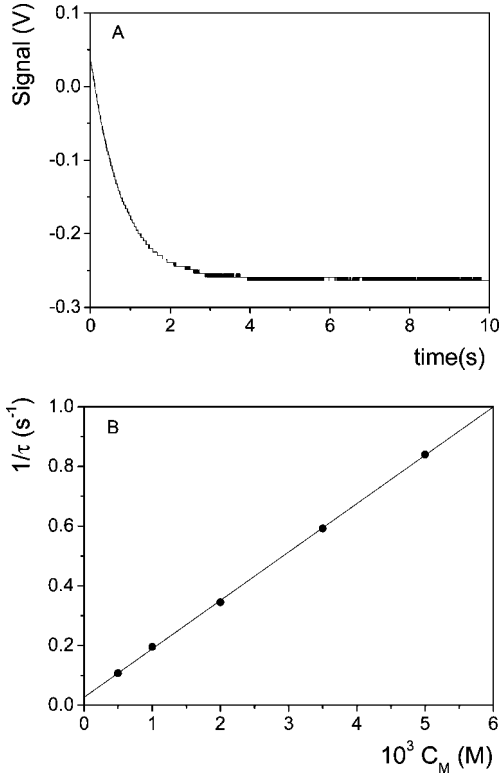


Figure 6. Kinetic behavior of the Ga(III)/HQ system in water. (A) Stopped flow curve of the complex formation process: $C_L = 2 \times 10^{-5}$ M, $C_M = 2.0 \times 10^{-2}$ M, $I = 0.2$ M ($NaClO_4$), pH = 2.5, $\lambda = 250$ nm, $T = 25$ °C. (B) Dependence of the time constant, $1/\tau$, vs total metal ion concentration: $C_L = 2 \times 10^{-5}$ M, $I = 0.2$ M ($NaClO_4$), pH = 2.7, $\lambda = 250$ nm, $T = 25$ °C.

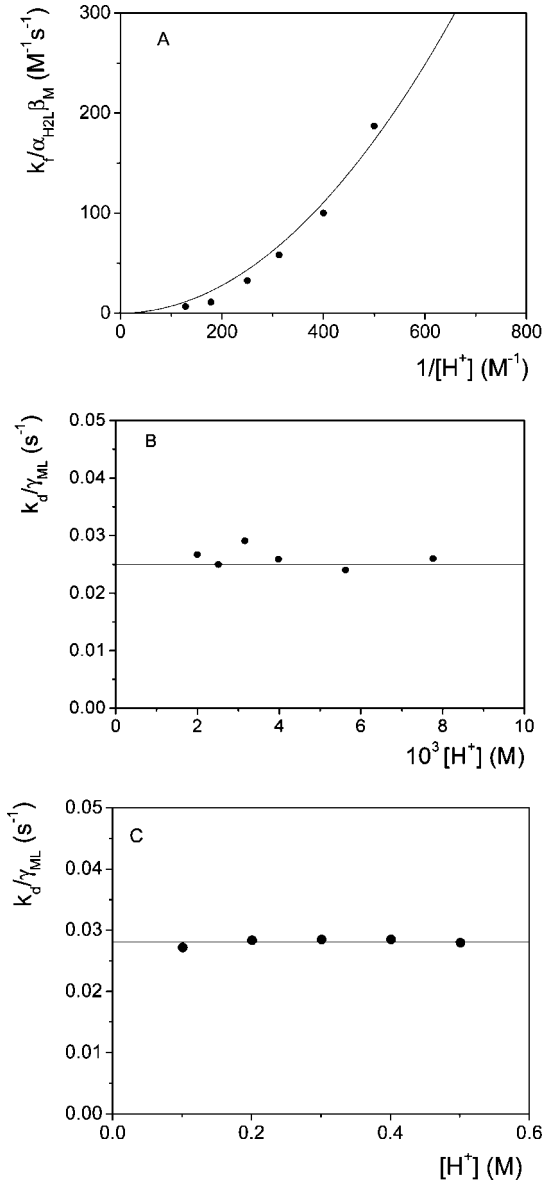


Figure 7. Kinetic behavior of the Ga(III)/HQ system in water. $I = 0.2$ M ($NaClO_4$), $T = 25$ °C. (A) Dependence of the forward rate constant, k_f, on hydrogen ion concentration; the continuous line is based on eq 7. (B) Dependence of the back rate constant, k_d, on hydrogen ion concentration. (C) Dependence of the rate constant of the stripping reaction, also denoted as k_d, on hydrogen ion concentration.

253 nm were analyzed according to eq 1 where now $C_A = C_{Na_2HPO_4}$ and $K = K_{NaH_2PO_4}/K_{A1}$. Figure 2SB (Supporting Information) shows the analysis of a titration curve in SDS solution. The acid dissociation constant of sodium dihydrogen phosphate ($K_{NaH_2PO_4}$) has been determined in SDS 0.02 and 0.04 M by means of pHmetric titrations, which have been performed by adding calibrate amounts of NaOH to a solution of NaH_2PO_4 containing SDS. Using the value for $K_{NaH_2PO_4}$ measured in SDS (Table 1), the value of K_{A1} in SDS has been obtained and reported in Table 1 as pK_{A1}.

The determination of pK_{A2} (Table 1) in the presence of SDS has been performed as in water with the difference that the solution of HQ to be titrated and NaOH contained equal concentration of SDS. Figure 3SA (Supporting Information) shows a titration curve and Figure 3SB (Supporting Information) the data analysis based on eq 2.

Complex Formation Equilibria in SDS. The interaction between Ga(III) and HQ is revealed by spectral changes in the UV region also in SDS micellar solution (Figure 4S, Supporting Information). The equilibrium constant, K_{app}, of reaction 3 has been evaluated for different pH values by spectrophotometric titrations performed at 253 nm in the pH range 3.7−4.5, which includes $[H^+]$ concentrations equivalent to those of the experiments in water. Spectrophotometric titrations were carried out in the absence of added salt by progressively adding calibrated amounts of $Ga(ClO_4)_3$ in SDS 0.02 M to a solution of HQ previously brought to the same concentration of surfactant and $[H^+]$.

Scheme 1 was assumed as suitable to represent the overall binding process in SDS as well. Thus, the dependence of K_{app} on $[H^+]$ would be given by eq 4. The analysis of the $K_{app}/\alpha_{H_2L}\beta_M$ versus $1/[H^+]$ plot (Figure 8) shows that, as in water, $K_{app}/\alpha_{H_2L}\beta_M$

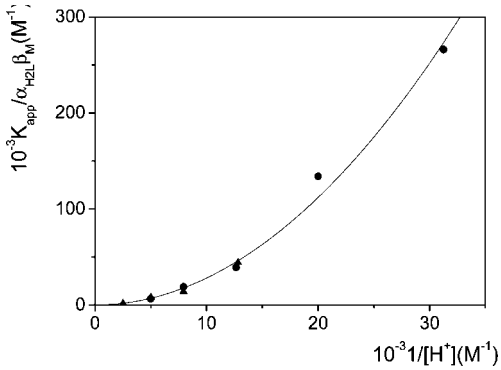


Figure 8. Dependence of the apparent equilibrium constant K_{app} on the acid concentration for the system Ga(III)/HQ in the presence of SDS 0.02 M, $T = 25$ °C: (●) data from spectrophotometric titrations; (▲) data from kinetic measurements (k_f/k_d). The continuous line is based on eq 4.

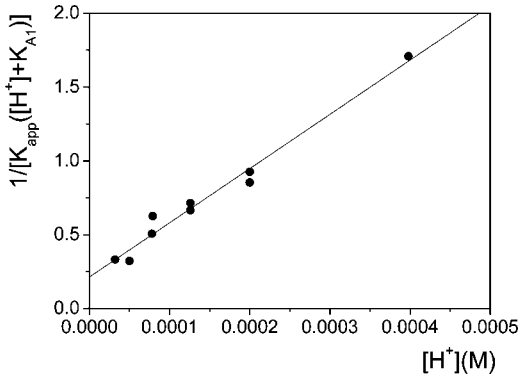


Figure 9. Plot according to eq 5 showing the dependence of the equilibria on acidity for the Ga(III)/HQ system in SDS 0.02 M.

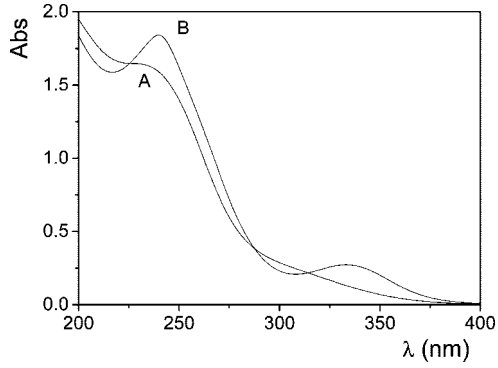


Figure 10. Absorption spectrum of $Fe(ClO_4)_3$ 4×10^{-4} M: (A) pH 2, $T = 25$ °C; (B) pH 3.7, [SDS] = 0.02 M, $T = 25$ °C.

$= K_3K_{A1}K_{HI}/[H^+]^2$. The values of α_{H_2L} and β_M have been calculated using the K_{A1} and K_{HI} value measured in SDS (Table 1). The value of K_{HI} in SDS has been obtained using eq 5, as shown in Figure 9; the related plot provides the value of K_{HI} in SDS reported in Table 1 and that of K_3 reported in Table 2.

It should be noted that the value of K_{HI} measured in SDS 0.02 M is lower than the value found in water (Table 1). This result indicates that in the presence of SDS the hydrolysis of Ga^{3+} is reduced. To confirm this finding, we recorded the UV spectra of Fe(III) both in pure water and in SDS 0.02 M (Figure 10); actually the hydrolytic behavior of iron(III) is similar to that of gallium(III), but the former species allows its hydrolysis to be monitored by spectral changes. The absorption spectrum of an aqueous solution of $Fe(ClO_4)_3$ 4×10^{-4} M recorded at pH = 2 is shown in Figure 10 (spectrum A). It shows two

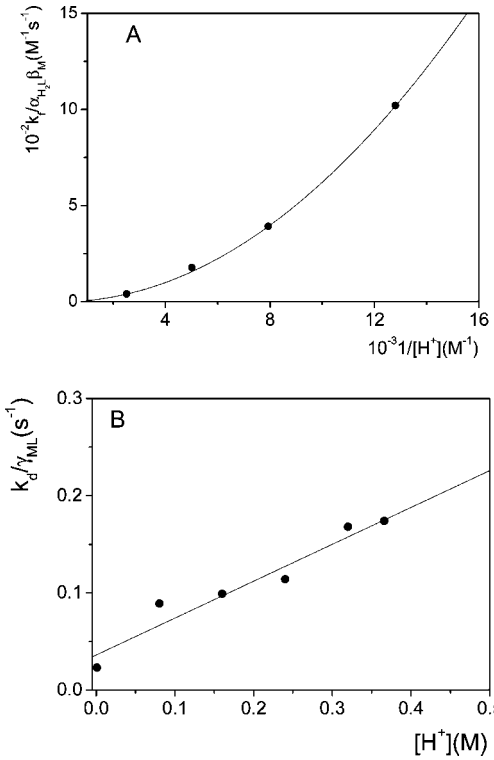


Figure 11. Kinetic behavior of the Ga(III)/HQ system in SDS 0.02 M, $T = 25$ °C. (A) Dependence of the forward rate constant, k_f, on hydrogen ion concentration. (B) Dependence of the rate constant of the stripping reaction, k_d, on hydrogen ion concentration.

shoulders at about 240 and 300 nm that should be ascribed respectively to the species Fe^{3+} and $Fe(OH)^{2+}$.[18] Figure 10 shows also the spectrum of the same iron solution recorded in SDS 0.02 M at the equivalent pH of 3.7 (spectrum B). The band centered at 240 nm, corresponding to the Fe^{3+} species, is definitely more intense compared to that of spectrum (A), thus revealing that the addition of SDS micelles does inhibit the hydrolysis of Fe^{3+}, and suggests that also the hydrolysis of Ga^{3+} is repressed by SDS. It should be noted that a band centered at 334 nm can be observed in spectrum B; this band is due to the formation of the highly charged $Fe_2(OH)_2^{4+}$dimer,[19] which is stabilized by the negative charges present on the micelle surface.

Complex Formation Kinetics in SDS. The kinetic curves, recorded under pseudo first-order conditions ($C_M \geq 10C_L$) were monoexponential (Figure 5SA, Supporting Information). A plot of $1/\tau$ versus the metal concentration at constant [SDS] (Figure 5SB, Supporting Information) again shows a good linear trend from which the k_f and k_d values have been determined. The plot of $k_f/\alpha_{H_2L}\beta_M$ versus $1/[H^+]$ displays a parabolic trend (Figure 11A). The data fit according to eq 7 yields the reaction parameter $k_3K_{A1}K_{HI} = (6.2 \pm 0.4) \times 10^{-6}$ M s^{-1} at [SDS] = 0.02 M, whereas the terms k_1 and k_2K_{HI} give a negligible contribution to k_f. The dissociation constant k_d was found to be independent of $[H^+]$ and because the static study shows that the species MH_2L^{4+} and MHL^{3+} (Scheme 1) could be neglected, the parameter γ_{ML} in eq 8 can be set equal to one. Hence, according to eq 8, from complex formation kinetics one can conclude that $k_d = k_{-3}$. The values of k_3 and k_{-3} are collected in Table 2. The values of K_{app} obtained from kinetics as the ratio of k_f/k_d are in good agreement with the titrations data (Figure 8).

Complex Dissociation Kinetics in SDS. The complex dissociation reaction (stripping) in SDS has been studied using the same modalities as in water. Increasing amounts of HCl in

SDS 0.02 M were added to an equimolar solution of HQ and $Ga(ClO_4)_3$ in SDS 0.02 M prepared at pH = 4.3, where the complex is largely formed. In this case, because in stripping experiments the different runs were performed at different HCl concentrations and in the absence of added salt, it turns out that the ionic strength is different for each stripping experiment. To separate the effect of $[H^+]$ on the reaction rate from a possible ionic strength effect, all the values of k_d have been reduced to $I = 0.01$ M using the Davies equation[15] and considering k_{-3} independent of ionic strength, according to step III.

Unlike the reaction in water, the process of complex dissociation in the presence of SDS displays a reaction path proportional to $[H^+]$. A plot of k_d/γ_{ML} vs $[H^+]$ shows a good linear increase (Figure 11B). Least-square analysis of the data according to eq 8 yields the reaction parameters k_{-2}/K_{C2} and k_{-3} (Table 2). Thus, the stripping reaction in SDS micelles reveals that at relatively high acidity levels step II, involving MHL^{3+}, becomes operative in addition to step III.

Micellar Catalysis. In the presence of SDS, Ga^{3+} and $GaOH^{2+}$ ions will be attracted electrostatically by the negatively charged micelle surface, whereas the ligand will be attracted by hydrophobic forces. Under these circumstances, the reaction on the micelle surface is favored as the result of a local concentration increase of both reactants.

The dependence of k_f and k_d on SDS concentration has been studied by investigating the complex formation process at constant pH (3.9) at different surfactant concentrations. Figure 12A shows the effect of SDS on the rate of complex formation. The values of k_f in SDS solution are greater than in water and the maximum rate enhancement is obtained for a surfactant concentration corresponding to 0.006 M. This effect can be quantitatively explained in terms of reactants accumulation on the micelle surface. As the SDS concentration is increased, a progressive reduction of the k_f values is observed, due to the increase of the micelle surface over which the reactant distribution occurs, thus producing a dilution effect. The k_d dependence on [SDS] displays a trend similar in shape to that of k_f (Figure 12B), but of more modest amplitude. The dependence of k_f/k_d ($=K_{app}$) on [SDS] is shown in Figure 12C.

Extraction and Recovery of Gallium(III) by LM-MEUF. For the metal extraction process to be significant, the SDS concentration must be higher than the cmc and the metal/ligand ratio must be such that almost all the metal is present in its complexed form. Under these circumstances the trapped metal complex is retained by the ultrafiltration membrane together with the micelles. Solutions for extraction experiments containing equimolar amounts of 4×10^{-4} M Ga(III) and HQ were prepared at pH 4.3 in SDS 0.02 M. Under these conditions the extent of complex formation is about 82%, as evaluated on the basis of the value of the stability constant of the Ga/HQ complex. The Ga^{3+} content in the retentate was always very high (≥96%), an extraction efficiency greater than 82% suggests that gallium binds to the micelle not only in the complexed form but also as free metal ion owing to electrostatic interaction with the micelle surface.

Metal recovery is also based on an ultrafiltration procedure. After the micellar phase (retentate) was separated from the liquid matrix (permeate) in the extraction procedure, the retentate, containing the micelles loaded with the metal complex, was treated with suitable amounts of strong acid (stripping reaction) to produce dissociation of the metal from the ligand. A second ultrafiltration step is then performed which allows to separate the metal containing phase (the permeate in this case) from the ligand containing phase (the retentate). Although the yield of recovered metal increases by increasing the acidity of the stripping solution,[20] it must be emphasized that $[H^+]$ levels higher than 0.1 M, besides damaging the membrane, are not desirable for the environment. For this reason we have found it profitable to replace most of the acid by NaCl or $MgCl_2$ because we found that added Na^+/Mg^{2+} ions can expell the metal from micelles almost as efficiently as H^+ ions.

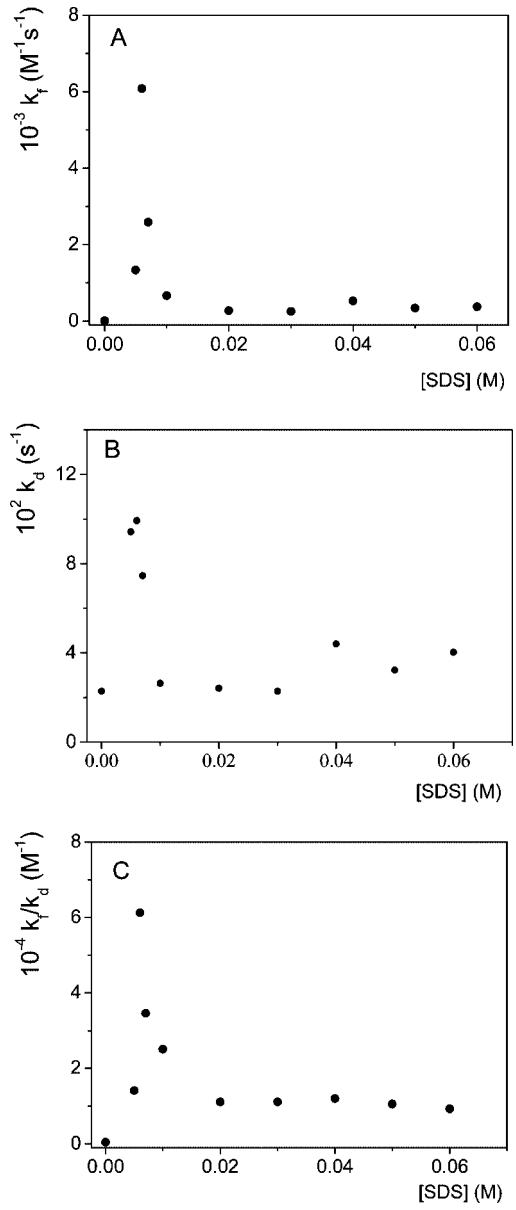


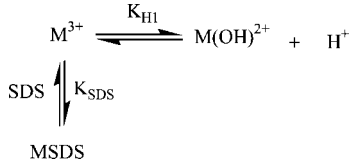
Figure 12. Micellar catalysis at pH = 3.9, $T = 25$ °C. (A) Dependence of the forward rate constant k_f on the SDS concentration. (B) Dependence of the back rate constant, k_d, on the SDS concentration. (C) Dependence of the equilibrium constant expressed as k_f/k_d on the SDS concentration.

A series of experiments was done by varying the salt type and the salt concentration at pH 0.1 M. The addition of salt solutions strongly increases the metal recovery efficiency. Actually the yield increases from 6% in the absence of salt, to 66% with NaCl and to 69% with $MgCl_2$ 0.2 M.

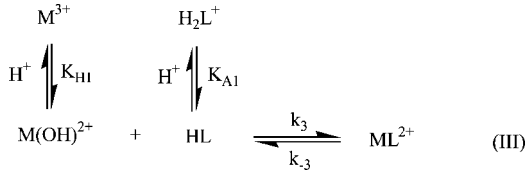
Discussion

Table 1 shows that the pK_{A1} value of HQ increases by about two units on going from water to SDS solution. Similar behavior

SCHEME 2



SCHEME 3



has been observed for different ligands.[21,22] The apparent pK_{A1} shift could be associated with the higher local concentration of the hydrogen ions at the micelle surface, which inhibits the acid dissociation reaction of the ligand. With the help of the pK_A shift, ΔpK_A, the pH value on the micelle surface could be evaluated by applying the relationship pH(SDS) = pH(measured) − ΔpK_A.[23]

The first hydrolysis constant of Ga^{3+} ion K_{H1} measured in SDS 0.02 M results to be lower than the value in pure water by a factor of about 5 (Table 1). As in the case of the ligand, we could explain this result assuming that the value of K_{H1} measured in the presence of SDS could be influenced by the higher local hydrogen ion concentration on the micelle surface, where the gallium has been attracted; this effect resulting in an apparent decrease of K_{H1}. Alternatively, possible chemical interaction between Ga(III) and SDS could be considered, as in Scheme 2.

Under these circumstances the observed hydrolysis constant, $K_{H1observed}$, will be reduced according to the relationship

$$K_{H1observed} = K_{H1}/(1 + K_{SDS}[SDS])$$

Because the formation of an inner sphere complex has been observed for In(III) and SO_4,[13] it is reasonable that, owing to the numerous negative charges on the SDS micelle and to the increased charge density of the smaller gallium ion, compared to indium, the Ga−SDS complex could be even more stable than the indium−sulfate complex.

Concerning the complex formation, the study in water shows that with HQ neither step I nor step II of Scheme 1 gives noticeable contributions to the metal binding process. This finding could be justified taking into account the repulsion between M^{3+} or MOH^{2+} and H_2L^+, which reduces the probability of encounters between these particles. Thus, the reaction pattern for Ga(III) complexation by HQ in water reduces to Scheme 3.

A correct analysis of the result requires that the rate constant should be normalized for the charge and ionic strength effects. This is accomplished by converting the experimental second order rate constant k into a first order rate constant k^*,[24] which refers to the conversion step of the outer-sphere complex into the corresponding inner-sphere complex. If the gallium complexation reaction follows the interchange dissociation mechanism I_d, in which the metal ion reactivity is independent of the ligand nature, the relationship $k^* \cong k_{H_2O}$ should hold, where k_{H_2O} is the rate constant for water exchange at the metal ion. The value of k^* for the complexation reaction of $GaOH^{2+}$ with neutral HQ has been evaluated through the relationship $k^* = k/K_{OS}$,[24,25] where K_{OS} is the ion-pair formation constant. The value of $k^* = 3.4 \times 10^5\ s^{-1}$ does not display definite variations on changing the ligand, moreover it is quite similar to the rate constant for water exchange at $[Ga(H_2O)_5OH]^{2+}$ ($k_{H_2O} = 3.4 \times 10^5$ to $3.4 \times 10^5\ s^{-1}$).[26] This result suggests that HQ binds to $Ga(OH)^{2+}$ according to an interchange dissociative mechanism (I_d).

The dependence of k_f on the SDS concentration (Figure 12A) displays the typical shape that reveals the occurrence of the "catalysis" effect.[11,21] The catalysis effect on the forward reaction expressed as $k_f(SDS)/k_f(H_2O)$ is 968, being $k_f(SDS)$ the maximum value of k_f (Figure 12A). Compared to previously studied systems, Ni^{2+}/PADA ($k_f(SDS)/k_f(H_2O) = 283$), Cd^{2+}/PADA ($k_f(SDS)/k_f(H_2O) = 67$)[21] and Ga^{3+}/PAR ($k_f(SDS)/k_f(H_2O) = 16$),[22] the rate enhancement for the Ga(III)/HQ system is very high. An explanation for this behavior could be found by considering that gallium is a trivalent ion, and therefore, it will strongly concentrate on the anionic SDS micelles.

The catalysis effect has been found for k_d as well but it is much less pronounced (Figure 12B); actually, the complex dissociation through path III (k_{-3}), being monomolecular, does not profit by the localized "concentration effect"; in contrast, dissociation through path II (k_{-2}/K_{C2}) involves reactive encounters between ML^{2+} and H^+, and should be sensitive to SDS, thus justifying the observed rate enhancement.

The maximum catalysis effect was observed for a SDS concentration equal to 0.006 M, which is lower than the cmc value. This result could be ascribed either to the presence of premicellar aggregates or to a slight reduction of the surfactant cmc due to the presence of charged species in solution. The latter hypothesis should be preferred because the cmc of SDS has been recently measured in the presence of $Ga(ClO_4)_3$ 2×10^{-4} M at pH 3 and found to be 0.0056 M.[22]

Conclusions

A combination of kinetic and thermodynamic methods has been employed to investigate the mechanism of Ga(III) binding to 8-hydroxyquinoline (HQ) in aqueous and SDS micellar solution. The reactive species is $GaOH^{2+}$ in both systems. However, the SDS micelles exert a strong accelerating effect on the complex formation step. The equilibria involved in the overall reaction are also affected by the presence of SDS. In particular the protonated complex (MHL^{3+}) and the hexaquo ion $Ga(H_2O)_6^{3+}$ are stabilized on the micelle surface.

Supporting Information Available: Figures showing the determination of pK_{A2} of HQ in water and SDS 0.04 M, the determination of pK_{A1} of HQ in SDS 0.02 M, the UV absorption spectrum of the system Ga(III)/HQ in SDS solution, the kinetic behavior of the Ga(III)/HQ system in SDS 0.02 M. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP8078666