Stability constants of cerium(IV) complexes with 8-hydroxyquinoline and 8-hydroxy-7-iodoquinoline-5-sulfonic acid

Abstract

Thermodynamic stability of cerium(IV) complexes formed in the initial stage of oxidation of 8-hydroxyquinoline and 8-hydroxy-7-iodoquinoline-5-sulfonic acid by cerium(IV) sulfate were studied spectrophotometrically and pH-potentiometrically with the aid of differential kinetic methods at an ionic strength \( I = 2 \text{ mol/L} \) within the pH range of 0.5–2.5 in a sulfuric acid medium and at temperatures of 275.15–289.15 K. Composition of these complexes, the form of organic ligand existence therein, and their stability constants were determined.

Keywords: 8-hydroxyquinoline, 8-hydroxy-7-iodoquinoline-5-sulfonic acid, cerium, coordination compounds, stability constants

Introduction

8-hydroxyquinoline, its derivatives and metal-ion complexes exhibit multifunctional properties, including antioxidant, antineurodegenerative, anticancer, anti-inflammatory and antidiabetic activities. The interest in 8-hydroxyquinolines and their metal complexes has grown in the last two decades exponentially as they are privileged structures for the design of new drug candidates that exert a host of biological effects on various targets.\(^1\),\(^2\)

The derivatives of 8-hydroxyquinoline and their compounds with rare earth elements (REE) are widely used in analytical chemistry. The luminescent properties of REE complexes with 8-hydroxyquinoline and its derivatives are employed in luminescence analysis, technologies for creating materials with photo- and electroluminescent properties for optoelectronics, photonics, chemo- and biosensors.\(^1\),\(^4\)

8-hydroxyquinoline is used in the extraction and spectrophotometric determination of cerium(IV), and cerium(IV) is employed in the oxydmetric determination of 8-hydroxyquinoline.\(^5\)

However, there are no data on the thermodynamic stability of cerium(IV) complexes with 8-hydroxyquinoline (HOxN) and 8-hydroxy-7-iodoquinoline-5-sulfonic acid (H\(_2\)Fer) in the literature. In this paper, the kinetic analogues of the thermodynamic methods for investigating the formation of variable-valence metal complexes are applied to the study of the stability of cerium(IV) complexes\(^6\) formed in the \( Ce^{4+} - SO_4^{2−} - R \) systems with \( R = HOxN \) and \( H_2Fer \).

Materials and procedure

Reagents

8-hydroxyquinoline (C\(_7\)H\(_6\)ON) and 8-hydroxy-7-iodoquinoline-5-sulfonic acid (C\(_{12}\)H\(_{7}\)ONIS) of the analytically pure grade and cerium(IV) sulfate tetrahydrate Ce(SO\(_4\))\(_2\)·4H\(_2\)O of analytical reagent grade were used as starting materials. In all solutions, an ionic strength of \( I = 2 \text{ mol/L} \) \( (c_{SO_4} = 0.67 \text{ mol/L}) \) was generated with analytical reagent grade ammonium sulfate. The initial solutions were prepared from precisely weighed portions. The content of cerium(IV) in a freshly prepared solution of cerium(IV) sulfate was determined by back titration with Mohr’s salt in the presence of ferroin\(^7\) before and after an experiment.

Instrumental analysis

The optical density was recorded in time using a SPECORD UV VIS recording spectrophotometer equipped with a temperature-controlled cell holder for rectangular quartz cells with an optical path length \( l = 1 \text{ cm} \) and a KF-5 photoelectric colorimeter with a MEA-4 recording device and a temperature controlled case for standard cells with \( l = (10.00±0.01) \times 10^{-3} \text{ cm} \). The pH value was measured in the reaction mixture, after the recording of the optical density, after an experiment.

In the measurements, the concentration scale was used. The glass electrode was calibrated against HCl solutions of known concentration at \( I = 2 \), since the pHs measured did not exceed 3.0–3.5. Buffer solutions were used for the initial correction of the pH-meter scale. The instant at which the mixing vessel whereto the starting components were placed was turned upside down, was taken as the time of reaction onset, \( t = 0 \). Kinetic measurements were carried out at 515nm, where the greatest increase in the differences \( D^0 = D^0 - D^M \) and \( D^0 = D^0 - D^A \) were observed with increasing pH (\( D^0 \) is the initial value of the optical density of the reaction mixture at the initial time \( t = 0 \)) found by linear extrapolation of the kinetic curves in the coordinates log \( D - t \), where their linearity took place; \( D^M \) the optical density of the metal ion...
solution, $D_M \approx 0$ is the rate of its change; and $-\dot{D}^0 = \frac{\partial D}{\partial \phi}$, $s^{-1}$, is the initial rate of the redox decomposition of the complexes). The initial equilibrium concentration of the cerium(IV) complexes were determined at the instant of time $\tau = 0$ according to formula $c_i^0 = -(\dot{D}^0 - D_M)/D_\infty$, where $c_M$ and $c_L$ are the concentrations of test solutions of cerium (IV) and ligands (HOxIN and $H_2Fer$). Here and below, the line above the symbol stands for the value determined by kinetic means. 

The predominant form of cerium(IV) is the mole fraction of the ligand), adapted to the fer system of its change; and was found by means of the $D^0 - pH$ method. The initial rate of the redox decomposition of the complexes was estimated graphically on a semi-log grid using the slope ratio of line $-D^0/(\tau - \tau') = const$ (Figure 1) and calculated by the linear least squares method.

Results and discussion

Composition of complexes

The metal: Ligand molar ratio in the complex formed at the time of mixing the solutions was established by the isomolar series method $D^0 - N_i$ (where $N_i$ is the molar fraction of the ligand), adapted to the study of variable-valence metal complexes, and a kinetic analog of this method ($\log D_\infty$). Figure 2 shows that in the systems $\log R_\infty$ complexes characterized by a metal:ligand ratio of 1:1 (mol/mol) are formed at the initial time. The obtained data agree with the data of kinetic studies, which indirectly indicate the formation of 1:1 (mol/mol) intermediate complexes in the course of oxidation of 8-hydroxyquinoline and 8-hydroxy-7-iodoquinoline-5-sulfonic acid by cerium(IV) in perchlorate medium.

Ligand speciation

The form in which organic ligands were present in the complex was determined by analyzing the property--$pH$ diagrams (Figure 3) by the $D^0 - pH$ method. The predominant form of cerium(IV) against the sulfate background at pH studied is the monohydroxy form CeOH$^{1+}$. The number of protons $z$ displaced from the cationic form $HR^+ = H_2OxN^-$ of the molecule $R = HOxIN$ and the zwitterionic molecule $H_2Fer$ by the cerium(IV) ion when equilibria

\[
\text{CeOH}^{1+} + H_2OxN^- \rightleftharpoons \text{CeOHH}_2R^{2+} \rightleftharpoons \text{CeOHH}_2\text{Fer}^{2+} \rightleftharpoons \text{CeOHFe}^{+}
\]

were established was estimated graphically as the slope of the $pH$ dependence of $CeOH^{1+}$, $\log \beta_n$ for $\tau = 0$ according to formula

\[
\log \beta_n = \log \tau_\infty + \tau pH
\]

as a result of comparison of two $D^0 - pH$ data series. Effective (depending on the pH value) stability constants $\beta_n$ were calculated using the equation

\[
\beta_n = \frac{c_M - c_N}{c_L - c_N}
\]

Figure 3 demonstrate that in the course of complexation a CeOH$^{1+}$ ion displaces two protons ($z = 2$) from $H_2OxN^-$ and $H_2Fer$. The latter can be accompanied by the formation of chelate complexes and the closure of the 5-membered cycles.

Stability constants

For the complexation equilibrium with anionic species $R^{m-} = OxIN^-$, $Fe^{2-}$ ($m = 1, 2$),

\[
\text{CeOH}^{3+} + R^{m-} \rightleftharpoons \text{CeOHHR}^{(3-m)-}
\]

the concentration stability constants $\beta_n$ were calculated for each point of function $\log \beta_n = \log \beta_1 + \log f_k$ and by averaging the values obtained according to series $D^0 - pH$. Calculations were performed using the following logarithms of the cumulative protonation constants of the anionic species $R^{m-}$: $log \beta_1 = pK_2 = 9, 56, log \beta_2 = pK_1 = 14, 76, pK_1 = 5, 20(OxIN^-)^9$, $log \beta_2 = 6, 87, log \beta_2 = 9, 57, pK_1 = 2, 70(Fe^{2+})^{10}$. Note that according to $10, 11$ the values of the dissociation constants $K_1, K_2$ obtained in $10$ for 7-ido-8-hydroxyquinoline-5-sulfonic acid characterize the equilibrium

\[
\text{CeOH}^{1+} + H_2OxN^- \rightleftharpoons K_1[H_2OxN^-] + zH^+
\]

The confidence interval for average values of these thermodynamic characteristics, along with the optical parameters of the complexes, was calculated at a sample size of $N = 14 - 16$ with a confidence level of 0.95 using the STATOBRABOTKA statistical processing program. The averaged values of $\log \beta_i$ determined using the method $D^0 - pH$ were 15.54±0.13 for the [CeOHOxIN] complex (Table 1) and 12.38±0.11 for the complex [CeOHFe] (Table 2).
The constancy of the calculated $\log \beta$ value within the series $D^0 - \varphi H$ indicates that the basic equilibria in solution are taken into account correctly. Lower stability of the complex $[\text{CeOHFer}]^{2+}$ compared to $[\text{CeOHOxiN}]^{2+}$ is due to the presence of the electron withdrawing groups (sulfonic acid group and iodine atom) in the molecule $\text{H}_2\text{Fer}$.

**Table 1** Stability constants of the complex $[\text{CeOHOxiN}]^{2+}$ determined by the $D^0 - \varphi H$ method $D^0_0 = 2.03 \times 10^{-2} \text{ s}^{-1}$, $c_L = 4.69 \times 10^{-4}$ mol/L, $D^0_0 = 0.162$, $I = 2$, $T = 289.15 \text{ K}$, $\lambda_{ef} = 515 \text{ nm}$, $l = 1 \text{ cm}$

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<th>$10 D^0_0, \text{ s}^{-1}$</th>
<th>$10 \Delta D^0$</th>
<th>$\varphi H$</th>
<th>$10^4 \epsilon^0_1, \text{ mol} / L$</th>
<th>$\log \beta_1$</th>
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$* \log \beta_1 = 15.54 \pm 0.13$.

**Table 2** Stability constants of the complex $[\text{CeOHFer}]^{2+}$ determined by the $D^0_0 - \varphi H$ method ($c_M = c_L = 4.77 \times 10^{-4} \text{ mol} / L$, $D^0_0 = 6.30 \times 10^{-2} \text{ s}^{-1}$, $D^0_0 = 0.745$, $I = 2$, $T = 289.15 \text{ K}$, $\lambda_{ef} = 515 \text{ nm}$, $l = 1 \text{ cm}$)

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<th>$\varphi H$</th>
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Conclusion

Thus, the compositions of the cerium(IV) complexes with 8-hydroxyquinoline and 8-hydroxy-7-iodoquinoline-5-sulfonic acid and also their stability constants, $\log \beta_1 = 15.54 \pm 0.13$ for [CeHOxIN]$^{2+}$ and $\log \beta_1 = 12.38 \pm 0.11$ for [CeOHFer]$^{+}$, were determined spectrophotometrically and pH-metrically by the kinetic analogues of the thermodynamic methods for investigating the formation of variable-valence metal complexes at an ionic strength $I = 2\text{mol/L}$ in a sulfuric acid medium and a temperatures of 275.15–289.15K.

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None

Conflict of interest

Author declares that there is no conflict of interest.

References