

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 $I = 2$ 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

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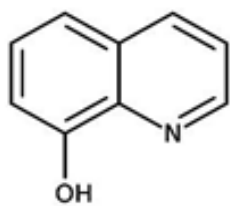
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Introduction

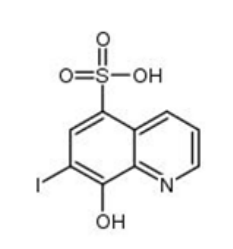
8-hydroxyquinoline, its derivatives and metal-ion complexes exhibit multifunctional properties, including antioxidant, antineurodegenerative, anticancer, anti-inflammatory and antidiabetic activities. The interest in 8-hydroxyquinolines and their metal complexes has grown in the last two decades exponentially 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 luminescent analysis, technologies for creating materials with photo- and electroluminescent properties for optoelectronics, photonics, chemo- and biosensors.^{3,4} 8-hydroxyquinoline is used in the *extraction and spectrophotometric determination of cerium(IV)*, and cerium(IV) is employed in the *oxydymetric 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 (H₂Fer) 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^{6,7} formed in the $Ce^{4+} - SO_4^{2-} - R$ systems with $R = HOxN$ and H_2Fer ,



HOxN



H₂Fer

Materials and procedure

Reagents

8-hydroxyquinoline (C₉H₇ON) and 8-hydroxy-7-iodoquinoline-5-sulfonic acid (C₉H₆O₄NIS) of the analytically pure grade and cerium(IV) sulfate tetrahydrate Ce(SO₄)₂·4H₂O of analytical reagent grade were used as starting materials. In all solutions, an ionic strength of $I = 2$ 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 ferroin⁵ 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 $l = 1$ cm and a KF-5 photoelectric colorimeter with a MEA-4 recording device and a temperature controlled case for standard cells with $l (10.00 \pm 0.01) \times 10^{-1}$ cm. The pH value was measured in the reaction mixture, after the recording of the optical density ($\tau \approx 1$ min and also $\tau \approx 10$ min), and in the cerium(IV) solutions with a DATA METER precision pH meter. 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 where the starting components were placed was turned upside down, was taken as the time of reaction onset, $\tau = 0$. Kinetic measurements were carried out at 515 nm, where the greatest increase in the differences $\Delta D^0 = D^0 - D_M$ and $\Delta \dot{D}^0 = \dot{D}^0 - \dot{D}_M$ were observed with increasing pH (D^0 is the initial value of the optical density of the reaction mixture at the initial time $\tau = 0$ found by linear extrapolation of the kinetic curves in the coordinates $\log D - \tau$, where their linearity took place; D_M the optical density of the metal ion

solution, $\dot{D}_M \approx 0$ is the rate of its change; and $-\dot{D}^0 \equiv \partial D / \partial \delta$, 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 $c_1^0 = -(\dot{D}^0 - \dot{D}_M) / (\dot{D}_\infty^0 - \dot{D}_M) c_M$ ($c_M \leq c_L$), 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 maximum value $-\dot{D}_\infty^0, s^{-1}$, of the rate $-\dot{D}^0, s^{-1}$, were found by means of the $-\dot{D}^0 - pH$ method.^{6,7} The initial rate of the redox decomposition of the complexes was estimated graphically on a semi-log grid using the slope ratio of line $-\dot{D}^0 = (D^0 - D^i) / (\tau^0 - \tau^i) = const$ (Figure 1) and calculated by the linear least squares method.

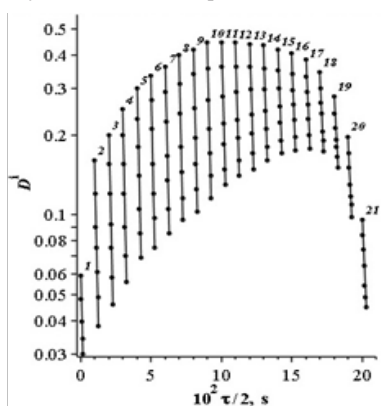


Figure 1 Pseudo first-order rate curves $D^i - \tau^i (\tau^{i+1} - \tau^i) = 5c, i = 1, \dots, 5 - 7$ for the $Ce^{4+} - SO_4^{2-} - H_2Fer$ system ($c_{M+L} = 9.53 \times 10^{-4}$ mol/L, $l = 2$, $T = 289.15$ K, $\lambda_{ef} = 515$ nm).

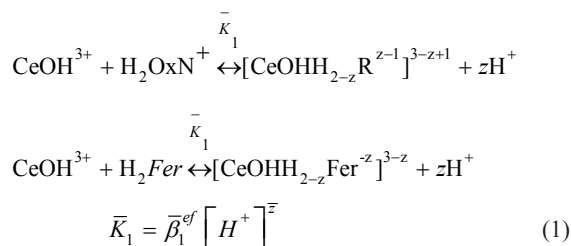
Results and discussion

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 $\Delta D^0 - N_L$ (N_L is the mole fraction of the ligand), adapted to the study of variable-valence metal complexes, and a kinetic analog of this method $(\log D)_\tau - N_L$, where $(\log D)_\tau \equiv \partial \log D / \partial \delta$.⁶ Figure 2 shows that in the systems $\log \bar{\beta}_1$ 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,⁸ 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.ⁱ

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 $\dot{D}^0 - pH$ method.⁶ The predominant form of cerium(IV) against the sulfate background at pH studied is the monohydroxo form $CeOH^{3+}$.⁷ 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



were established was estimated graphically as the slope of the dependence of $CeOH^{3+}$ on pH,

$$\log \bar{\beta}_n^{ef} = \log \bar{K}_n + z pH \quad (2)$$

as a result of comparison of two $\dot{D}^0 - pH$ data series.

Effective (depending on the pH value) stability constants $\bar{\beta}_n^{ef}$ were calculated using the equation

$$\bar{\beta}_1^{ef} = \frac{\bar{c}_1^0}{(c_M - \bar{c}_1^0)(c_L - \bar{c}_1^0)} \quad (3)$$

Figure 3 demonstrate that in the course of complexation a $CeOH^{3+}$ 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.

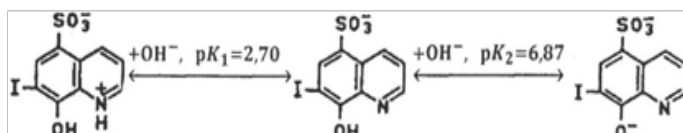
Stability constants

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



$$\bar{\beta}_1 = \bar{\beta}_1^{ef} f_2, f_2 = 1 + \sum_{i=1}^2 B_i [H^+]^i \quad (5)$$

the concentration stability constants $\bar{\beta}_1$ were calculated for each point of function $\log \bar{\beta}_1 = \log \bar{\beta}_1^{ef} + \log f_2$ and by averaging the values obtained according to series $\dot{D}^0 - pH$. Calculations were performed using the following logarithms of the cumulative protonation constants of the anionic species R^{m-} : $\log B_1 = pK_2 = 9,56, \log B_2 = \lg B_1 + pK_1 = 14,76, pK_1 = 5,20$ ($OxiN^-$);⁹ $\log B_1 = 6,87, \log B_2 = 9,57, pK_1 = 2,70$ (Fer^{2-}).¹⁰ Note that according to,^{10,11} the values of the dissociation constants K_1, K_2 obtained in¹⁰ for 7-iodo-8-hydroxyquinoline-5-sulfonic acid characterize the equilibria



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.¹² The averaged values of $\log \bar{\beta}_1$ determined using the method $\dot{D}^0 - pH$ were 15.54 ± 0.13 for the $[CeOHOxiN]^{2+}$ complex (Table 1) and 12.38 ± 0.11 for the complex $[CeOHFer]^+$ (Table 2).

The constancy of the calculated $\log \bar{\beta}_1$ value within the series $\dot{D}^0 - pH$ indicates that the basic equilibria in solution are taken into account correctly. Lower stability of the complex $[\text{CeOHFe}]^+$ compared to $[\text{CeOHOxiN}]^{2+}$ is due to the presence of the electron withdrawing groups (sulfonic acid group and iodine atom) in the molecule H_2Fer .

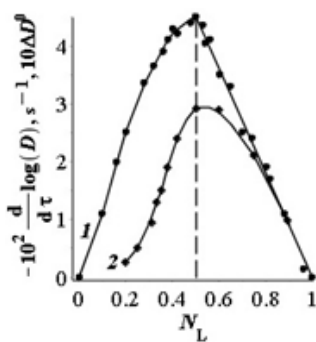


Figure 2 Diagrams: (1)

$\Delta D^0 - N_L (c_{M+L} = 9.53 \times 10^{-4} \text{ mol/L}, I = 2, T = 289.15 \text{ K}, \lambda_{ef} = 515 \text{ nm})$ for the system $\text{Ce}^{4+} - \text{SO}_4^{2-} - \text{H}_2\text{Fer}$, (2)

$\text{Ce}^{4+} - \text{SO}_4^{2-} - \text{H}_2\text{Fer} (c_M = c_L = 4.77 \times 10^{-4} \text{ mol/L}, I = 2, T = 289.15 \text{ K}, \lambda_{ef} = 515 \text{ nm})$ for the system $\text{Ce}^{4+} - \text{SO}_4^{2-} - \text{HOxiN}$.

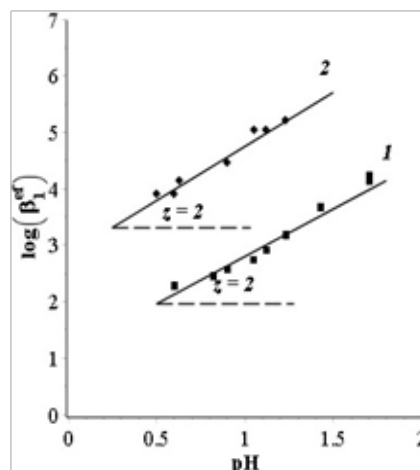


Figure 3 Diagrams of the dependence of the logarithm of the effective stability constant of complexes on the pH. System: (1)

$\text{Ce}^{4+} - \text{SO}_4^{2-} - \text{HOxiN} (c_M = 1.56 \times 10^{-4}, c_L = 4.69 \times 10^{-4} \text{ mol/L}, I = 2, T = 289.15 \text{ K}, \lambda_{ef} = 515 \text{ nm})$

(2) $\text{Ce}^{4+} - \text{SO}_4^{2-} - \text{H}_2\text{Fer} (c_M = c_L = 4.77 \times 10^{-4} \text{ mol/L}, I = 2, T = 289.15 \text{ K}, \lambda_{ef} = 515 \text{ nm})$.

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

$10\dot{D}^0, \text{s}^{-1}$	$10\Delta D^0$	pH	$10^4 c_1^0, \text{mol/L}$	$\log \bar{\beta}_1^{\text{ef}}$	$\log \bar{\beta}_1$
-0.16	0.13	0.6	0.12	2.27	15.83
-0.23	0.19	0.82	0.18	2.46	15.58
-0.28	0.23	0.9	0.22	2.57	15.53
-0.39	0.31	1.05	0.31	2.75	15.41
-0.51	0.42	1.12	0.4	2.91	15.43
-0.77	0.6	1.23	0.6	3.19	15.49
-1.28	1.03	1.43	1	3.68	15.58
-1.64	1.38	1.7	1.28	4.13	15.49

* $\log \bar{\beta}_1 = 15.54 \pm 0.13$.

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

$10\dot{D}^0, \text{s}^{-1}$	$10\Delta D^0$	pH	$10^4 c_1^0, \text{mol/L}$	$\log \bar{\beta}_1^{\text{ef}}$	$\log \bar{\beta}_1$
-0.38	3.46	0.5	2.86	3.9	12.47
-0.38	4.73	0.6	2.88	3.91	12.28
-0.34	4.07	0.63	2.59	4.15	12.46
-0.5	6.2	0.9	3.79	4.46	12.23
-0.55	6.48	1.05	4.16	5.05	12.53
-0.55	6.43	1.12	4.16	5.05	12.39
-0.56	6.63	1.23	4.25	5.21	12.33

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, $\log \bar{\beta}_1 = 15.54 \pm 0.13$ for $[\text{CeOHOxiN}]^{2+}$ and $\log \bar{\beta}_1 = 12.38 \pm 0.11$ for $[\text{CeOHFer}]^+$, 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 275.15–289.15 K.

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No.

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None

Conflict of interest

Author declares that there is no conflict of interest.

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