

Stability Constants of Zinc and Cadmium Complexes with 1,2,3,4-Tetrahydro-8-Hydroxyquinoline in Aqueous Solution

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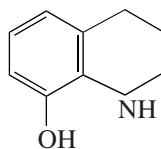
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Abstract—The stability constants β of Zn^{2+} and Cd^{2+} complexes with 1,2,3,4-tetrahydro-8-hydroxyquinoline (HTOq) in aqueous solution were determined by pH-metric titration in combination with computer-assisted simulation of presumed equilibria. According to the data obtained, HTOq is inferior to 8-hydroxyquinoline in complexing ability.

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In [1], it has been found that hydrogenation of 8-hydroxyquinoline (HOq) in positions 1, 2, 3, and 4 weakens the acid properties of the heterocyclic N atom and virtually does not affect the acid-base characteristics of the OH group in 1,2,3,4-tetrahydro-8-hydroxyquinoline (HTOq).



According to spectrophotometric data, HTOq (like HOq) reacts with Cu^{2+} , Zn^{2+} , and Cd^{2+} ions to give insoluble complexes of these metals [3]. When the dissociation constants of a ligand change, the stability constants β of its complexes should be expected to change as well. In [4], it has been found that HTOq is less toxic than HOq and hence can be of interest for determination and microconcentration of metal ions [5, 6], or as a safe reagent precipitant of heavy metal cations in water detoxication [7].

The goal of this study was to determine the constants of complexation between 1,2,3,4-tetrahydro-8-hydroxyquinoline and Zn^{2+} and Cd^{2+} ions in aqueous solution by potentiometric titration.

EXPERIMENTAL

1,2,3,4-Tetrahydro-8-hydroxyquinoline was prepared by catalytic hydrogenation of 8-hydroxyquinoline and identified from T_m values and ^1H NMR spectra [4]. The salts ZnSO_4 and CdSO_4 (analytical grade) were recrystallized from water. Commercial chemicals HCl (1.19 g/cm³), KOH, and KCl (reagent grade) were used without preliminary purification. The concentrations of

the initial solutions of KOH (0.1 mol/l) and HCl (0.3 mol/l) were determined according to standard procedures. The concentrations of Zn^{2+} and Cd^{2+} solutions (0.087 mol/l) were determined by complexometric titration [8]. The initial solutions of HTOq (0.5, 1, and 2 mmol/l) were prepared from a precisely weighed sample in an equimolar amount (or in a small excess) of HCl. The titrate contained HTOq (0.2, 0.4, and 0.6 mmol/l), a salt of the M^{2+} ion ($\text{M} = \text{Zn}$ or Cd ; $c_{\text{HTOq}} : c_{\text{M}} = 1 : 5$ to $5 : 1$), and KCl as a supporting electrolyte (pH 3.7–4.7). The titrant contained KOH (2, 4, and 6 mmol/l) and KCl. All solutions of HTOq were prepared from deaerated distilled water immediately before titration in calibrated vessels and kept in the dark.

Titration was carried out in a temperature-controlled cell at 298 ± 0.2 K; the ionic strength was constant ($I = 0.01$) for pH 4–8. The volume of an added titrant was measured with a microburette. The emf of a circuit consisting of an ESL-43-07 glass electrode and an EVL-1M3.1 silver-chloride electrode was measured on an OP-211/1 ionometer. The electrodes were calibrated against standard buffer solutions. The potential was measured with an accuracy of ± 1 mV. The spectra of solutions were recorded on an SF-46 spectrophotometer (cell length 1 cm, water as a reference solution).

RESULTS AND DISCUSSION

Variations in the pH of solutions of $\text{HTOq} \cdot \text{HCl}$ and $\text{HTOq} \cdot \text{HCl} \cdot \text{M}$ ($\text{M} = \text{Zn}^{2+}$ or Cd^{2+} ; $c_{\text{HTOq}} : c_{\text{M}} = 1 : 3$) with the number of moles of alkali added per mole of the ligand ($c_{\text{KOH}}/c_{\text{HTOq}}$) are shown in Fig. 1. It can be seen that complexation with Zn^{2+} or Cd^{2+} cations begins at pH > 5.5, when the ligand is almost com-

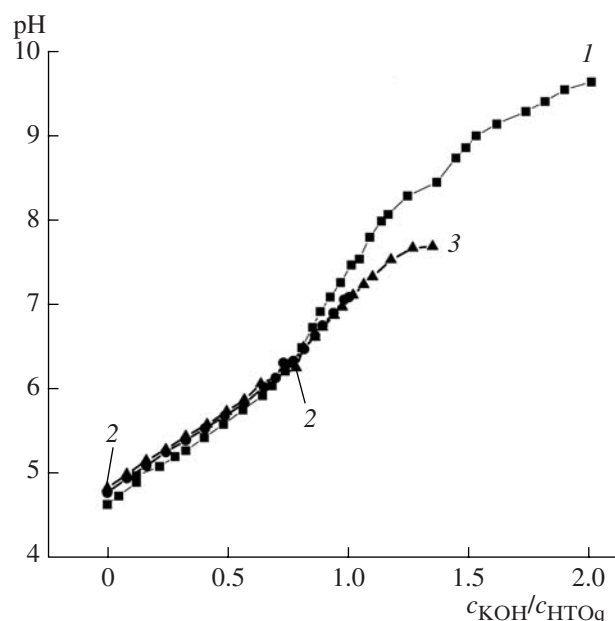


Fig. 1. Titration curves for solutions of $\text{HTOq} \cdot \text{HCl-M}$ with 0.002 M KOH as a titrant ($c_{\text{HTOq}} = 0.2$ mmol/l, $c_{\text{HCl}} = 0.2$ mmol/l, $c_{\text{M}} = 0.6$ mmol/l): (1) 0, (2) Zn^{2+} , and (3) Cd^{2+} .

pletely titrated in the first step ($c_{\text{KOH}}/c_{\text{HTOq}} > 0.75$) and its dominant form is HTOq :



The reaction occurs with release of protons. The titration curves of solutions $\text{HTOq} \cdot \text{HCl-M}$ (Fig. 1, 2, 3) are shifted to the acid region relative to the titration curve of the solution $\text{HTOq} \cdot \text{HCl}$ (Fig. 1, 1).

The electronic absorption spectra of solutions of the complexes $\text{Cd}(\text{TOq})_n^{(2-n)}$ and $\text{Zn}(\text{TOq})_n^{(2-n)}$ are shown in Fig. 2. The optical density A at a given wavelength λ was determined from the additivity condition by the equation

$$A_{\text{M}(\text{TOq})_n} = A - A_{\text{HTOq}} - A_{\text{M}}, \quad (2)$$

where A_{HTOq} , A_{M} , and A are the optical densities of solutions of the ligand, the metal, and the system ligand + metal, respectively. Since the optical densities were determined from difference (2), only four positive values were obtained for $A_{\text{Zn}(\text{TOq})_n}$ (Fig. 2). The absorption peaks of the complexes appear at 410–420 nm. In [3], it was assumed from the shift of λ_{max} that the stability of the complexes with HTOq in aqueous solution changes in the order $\text{Cu}^{2+} > \text{Zn}^{2+} \geq \text{Cd}^{2+}$. It can be seen in Fig. 2 that $A_{\text{Cd}(\text{TOq})_n}$ is much greater than $A_{\text{Zn}(\text{TOq})_n}$. Provided that the molar absorption coefficients ε of the com-

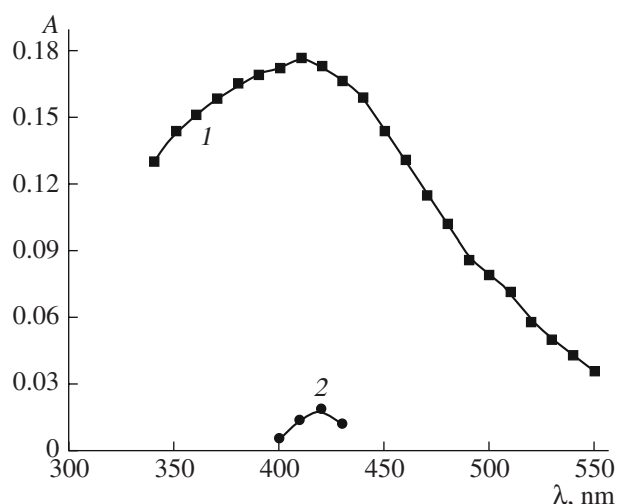


Fig. 2. Electronic absorption spectra of solutions of (1) $\text{Cd}(\text{TOq})_n^{(2-n)}$ and (2) $\text{Zn}(\text{TOq})_n^{(2-n)}$ for $c_{\text{HTOq}} = c_{\text{M}} = 1$ mmol/l; $\text{pH} > 5.5$.

plexes are equal, one can expect that $\log \beta_{\text{Cd}(\text{TOq})_n}$ will be greater than $\log \beta_{\text{Zn}(\text{TOq})_n}$.

To calculate the stability constants of the complexes, the potentiometric data were processed on an IBM/PC with the PHMETR program [9]. The mathematical model included the following equilibria:



Reaction (8) does not contribute greatly to the parameters in question because, according to calculations, the formation of metal hydroxides does not exceed 0.003%. Using given concentrations of the basic species (M^{2+} , TOq^- , and H^+), known constants of reactions (3)–(5) [1], our potentiometric data, and calibration data for the glass electrode, we calculated function F :

$$F = \sum_{i=1}^n (\text{p}[\text{H}^+]_{\text{exp}} - \text{p}[\text{H}^+]_{\text{calc}})_i^2, \quad (9)$$

where $[\text{H}^+]_{\text{exp}}$ and $[\text{H}^+]_{\text{calc}}$ are the experimental and calculated (in the context of the given model) equilibrium concentrations of hydrogen ions and n is the number of measurements (the weight factors were ignored because all measurements were believed to be equally accurate). The minimum of the criterial function F cor-

Table 1. Values of the criterial function F_{\min} in the calculation of the stability constants of the complexes in the system $\text{HTOq} \cdot \text{HCl-M}$ ($\text{M} = \text{Zn}^{2+}$ and Cd^{2+}) with different ratios $c_{\text{HTOq}} : c_{\text{M}}$

c_{HTOq} , mol/l	$c_{\text{HTOq}} : c_{\text{M}}$	$\log \beta_1$	$\log \beta_2$	$F_{\min} \times 10^2$
HTOq · HCl-Zn²⁺				
0.2	1 : 5	3.81 ± 0.04	8.15 ± 0.17	0.3847
			8.91 ± 0.08	0.5737
0.2	5 : 1	3.91 ± 0.02		0.6083
		2.73*	8.96	0.7575
0.4	1 : 3		9.02 ± 0.10	0.5826
		4.97 ± 0.17		1.1765
		3.22 ± 0.12	7.91 ± 0.19	1.7433
			8.13 ± 0.07	4.1582
		3.44 ± 0.04		3.4200
HTOq · HCl-Cd²⁺				
0.2	1 : 5	2.46 ± 2.3	8.78 ± 0.08	1.2763
			8.80 ± 0.03	8.3327
0.2	1 : 1	3.98 ± 0.04		1.2701
		4.80 ± 0.08		7.9814
0.2	5 : 1		10.05 ± 0.04	0.67851
		3.48*	10.00	0.3355
			10.02 ± 0.09	0.3255
		5.09 ± 0.12		1.1617

* The minimum value was not found and the errors were not calculated.

responds to the most accurate model and to the most probable values of the sought constants of reactions (6) and (7).

Data for criterial estimation of the results obtained in the processing of some titration curves are given in Table 1. With an excess of metal ions ($c_{\text{HTOq}} : c_{\text{M}} = 1 : 5$ and $1 : 3$), the stability constants of the complexes MTOq^+ ($\log \beta_1$) and $\text{M}(\text{TOq})_2$ ($\log \beta_2$) are simultaneously obtained and the function F takes a minimum value. The quantity $\Delta\alpha$ (α is the fraction of the complex) at these concentrations reaches 15–20%. When α changes insignificantly ($c_{\text{HTOq}} : c_{\text{M}} = 1 : 1$ and $5 : 1$), the

function is insensitive to stability constant. Under these conditions, the model that considers the formation of a complex by reaction (6) or (7) is most accurate. The $\log \beta_1$ value will be slightly overestimated because it includes part of the greatest constant $\log \beta_2$. The latter should be chosen as the most reliable constant.

The $\log \beta_1$ and $\log \beta_2$ values for different concentrations of HTOq, which passed the criterial selection, are given in Table 2 (errors are cited as standard deviations). The stability constants of the complexes do not depend, to within the measurement error, on the concentrations of the reagents, which indicates the absence of systematic errors. The average stability constants determined from four to five independent titrations are given below (298 K, $I = 0.01$, KCl):

$$\text{Zn } \log \beta_1 = 3.77 \pm 0.31 (8.10 \pm 0.30);$$

$$\log \beta_2 = 8.44 \pm 0.85 (16.18 \pm 0.20);$$

$$\text{Cd } \log \beta_1 = 3.63 \pm 0.52 (6.17 \pm 0.32);$$

$$\log \beta_2 = 8.38 \pm 0.37 (14.60 \pm 0.14).$$

The corresponding stability constants of complexes with HOq are enclosed in parentheses [10, 11]. The errors were calculated as a confidence interval for the corresponding t -test coefficients. Thus, the constants of complexation between HTOq and Zn^{2+} and Cd^{2+} ions

Table 2. $\log \beta$ values of the Zn^{2+} and Cd^{2+} complexes with HTOq in aqueous solution at 298 K

M	c_{HTOq} , mol/l	$\log \beta_1$	$\log \beta_2$
Zn^{2+}	0.2	3.86 ± 0.23	8.76 ± 0.43
	0.4	3.33 ± 0.12	8.13 ± 0.33
	0.6	3.64 ± 0.31	8.53 ± 0.47
Cd^{2+}	0.2	3.35 ± 0.15	8.79 ± 0.22
	0.4	3.25 ± 0.22	8.04 ± 0.18
	0.6	3.82 ± 0.26	8.31 ± 0.32

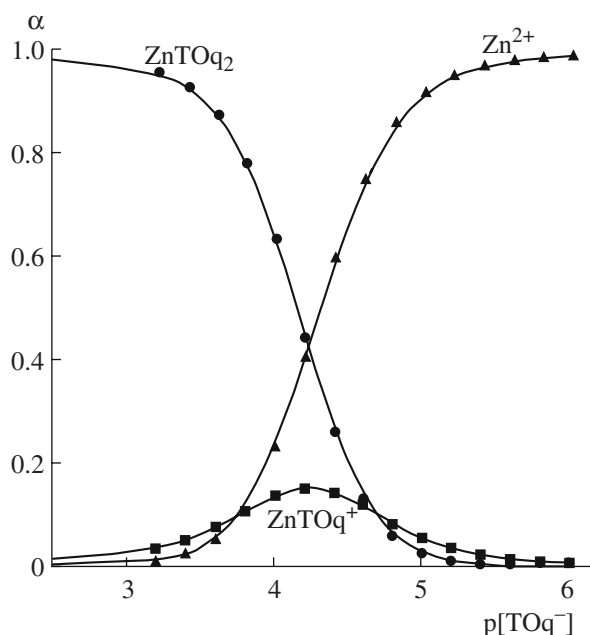


Fig. 3. Equilibrium diagram for Zn^{2+} complexes with HTOq in aqueous solution ($I = 0.01$, 293 K).

are equal to within the measurement error. The inequality $A_{\text{Cd}(\text{TOq})_n} > A_{\text{Zn}(\text{TOq})_n}$, which follows from Fig. 2, can probably be explained by the ratio of the molar absorption coefficients ($\epsilon_{\text{Cd}(\text{TOq})_n} > \epsilon_{\text{Zn}(\text{TOq})_n}$).

The equilibrium diagram for Zn^{2+} complexes with HTOq in aqueous solution is shown in Fig. 3. The solution contains both complexes at almost all equilibrium concentrations of TOq^- ; only at $[\text{TOq}^-] \geq 10^{-3}$ mol/l is the complex ZnTOq_2 dominant. However, potentiometric titration at such high concentrations of the ligand is impossible because of the poor solubility of the complexes with HOq and HTOq. The optimal conditions for potentiometric determination of the stability constants of hydroxyquinolinates are the use of five- to sixfold excess of the metal [10–12]. The fraction distribution diagram for the complexes in the HTOq– Cd^{2+} system at different pH values and different $c_{\text{HTOq}} : c_{\text{M}}$ ratios is shown in Fig. 4. At pH 7.5, the yields of the complexes in the presence of an excess of the metal (Fig. 4a) are one order of magnitude higher than in the presence of an excess of the ligand (Fig. 4b). This allows more reliable estimation of their stability constants.

To sum up, we found from potentiometric and spectrophotometric data that $\log \beta_{\text{Zn}(\text{TOq})_n}$ is approximately equal to $\log \beta_{\text{Cd}(\text{TOq})_n}$ and that $\epsilon_{\text{Cd}(\text{TOq})_n}$ is greater than $\epsilon_{\text{Zn}(\text{TOq})_n}$. A comparison with the stability constants of the corresponding complexes of 8-hydroxyquinoline reveals the inequality $\log \beta_{\text{M}(\text{TOq})_n} < \log \beta_{\text{MOq}_n}$, i.e.,

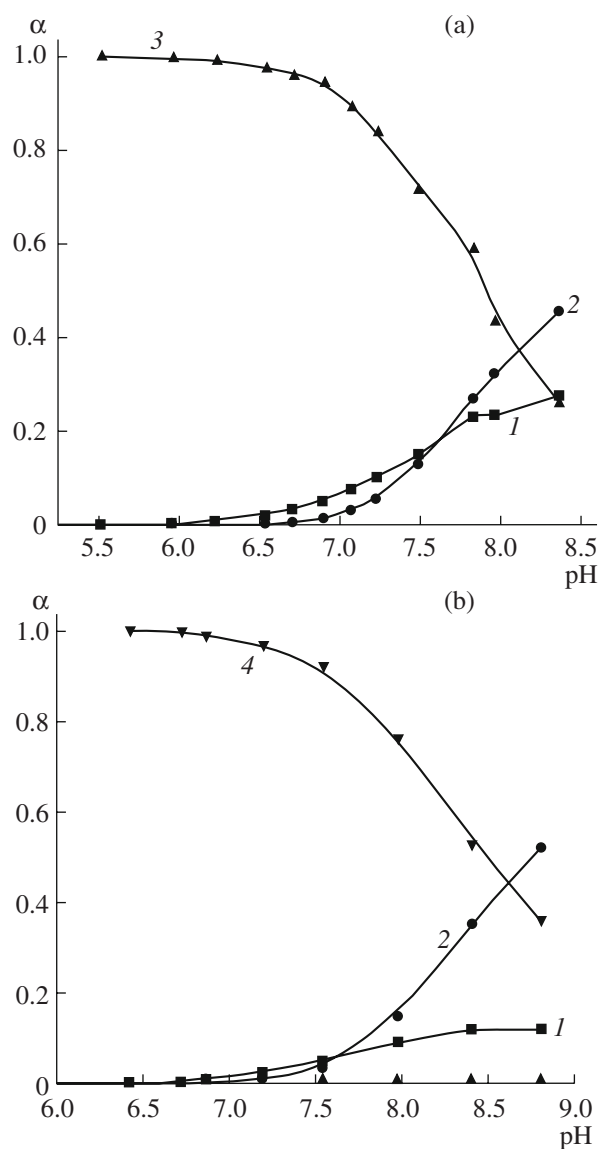


Fig. 4. Species distribution diagram for the HTOq– Cd^{2+} system at $c_{\text{HTOq}} : c_{\text{Cd}^{2+}} =$ (a) 1 : 5 and (b) 5 : 1 for different pH values: (1) CdTOq^+ , (2) CdTOq_2 , (3) Cd^{2+} , and (4) CdTOq^- .

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