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Abstract

Full Text

Chemistry

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PROTONATION AND ACID DISSOCIATION OF 8-MERCAPTOQUINOLINE IN AQUEOUS SOLUTIONS

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The sulfur-containing analog of 8-hydroxyquinoline–8-mercaptoquinoline (thiooxine) ([1,2]), is recommended as a reagent for the determination of microquantities of a number of elements ([3–8]). Thiooxine can also be used for the purification of substances from microimpurities by extraction of thiooxinates at different acidities. The behavior of thiooxine in aqueous solutions and the constant of its acid dissociation remain unstudied, which makes it difficult to quantitatively characterize the process of formation and extraction of metal thiooxinates.

It may be assumed that in aqueous thiooxine solutions, depending on the acidity, there exists an equilibrium analogous to that in solutions of 8-hydroxyquinoline ([9]):

$$\text{(II)} \rightleftharpoons \text{(I)} \rightleftharpoons \text{(III)}$$

where the left equilibrium is marked H^+, the right equilibrium is marked OH^-, and the last structure may also be represented by an alternative resonance form.

That is, besides the molecular form of 8-mercaptoquinoline, the solution contains mercaptoquinolinium ions and mercaptoquinolinate ions.

The aim of the present work was to establish the ranges of hydrogen-ion concentrations within which the corresponding forms of thiooxine predominantly exist, and to determine the constants of acid dissociation and protonation. The stated problem was solved by studying absorption spectra with changing hydrogen-ion concentration in solution.

The thiooxine used in the work, in the form of the dihydrate $C_9H_7NS \cdot 2H_2O$, was obtained from the sodium salt after careful purification by the method described in the literature ([10]). Preparation of a titrated thiooxine solution from the dihydrate is impossible, since it can exist only in the moist state. Therefore, a series of thiooxine solutions of identical concentrations was prepared by introducing into a 50-ml volumetric flask a constant amount of thiooxine

Fig. 1. Absorption curves of an 8-mercaptoquinoline solution at various pH values. 1–0.57; 2–1.98; 3–3.36; 4–3.98; 5–8.87.

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Fig. 2

Figure 2: Fig. 2

solution in $2N$ HCl and bringing the volume to the mark with a buffer mixture of the required pH. The substances used for preparing the buffer solutions were purified: hydrochloric acid and ammonia were distilled, and sodium acetate was purified from impurities–

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metal impurities by extraction of thiooxinates with chloroform. A definite acidity in the pH range 0-11 was created with hydrochloric acid, acetate-hydrochloric acid, and acetate-ammonia buffer solutions. A constant ionic strength was maintained in all solutions; the experiments were carried out at a temperature of $20 \pm 1^{\circ}$. The acidity of the solutions was monitored by measurement on an LP-58 pH meter with a glass electrode. Measurements of the light absorption of thiooxine solutions were performed on an SF-4 spectrophotometer with a deuterium lamp in quartz cuvettes, $l = 1$ cm.

Fig. 2. Absorption curves of a solution of 8-mercaptoquinoline at different pH values.
1–5.31; 2–6.70; 3–7.89; 4–8.33; 5–8.40; 6–8.85; 7–9.76.

The data used to construct the absorption curves in Figs. 1, 2, and 3 were obtained by photometry of solutions in which the concentration of thiooxine was lower than in the series of experiments used to calculate the acid-dissociation or protonation constant. This is due to the fact that the molar absorption coefficients at the maxima of thiooxine in the far ultraviolet (240-280 $m\mu$) are much larger than those in the nearer ultraviolet or visible region.

Depending on the concentration of hydrogen ions, five groups of maxima are clearly manifested in the absorption spectra of thiooxine solutions (Fig. 1). At pH < 2, only two maxima are observed: at wavelengths of 240 and 315 $m\mu$. When the pH changes from 1 to 3, the maximum at 315 $m\mu$ is attenuated (Fig. 3), and the maximum at 240 $m\mu$ disappears completely. At the same time, absorption bands arise at 250, 275, and 440 $m\mu$. In the pH range 3-7, the height of these maxima reaches its maximum value. In the region pH > 7, the maxima at 250 and 275 $m\mu$ disappear and an absorption band appears at 260 $m\mu$, reaching its maximum value at pH ~ 9. At the same time, a decrease

Fig. 3

Figure 3: Fig. 3

in the maximum at 440 $m\mu$ is observed, along with the appearance and increase of an absorption band corresponding to a wavelength of 365 $m\mu$.

Fig. 3. Dependence of the absorption of 8-mercaptoquinoline solutions on pH at wavelengths: 1–315; 2–365; 3–440 $m\mu$.

In the acidic region, isosbestic points should be noted at 250, 295, and 378 $m\mu$, corresponding to the indicated changes in the absorption spectra. In the region pH > 7, isosbestic points are found at wavelengths of 268 and 408 $m\mu$.

The results obtained make it possible to interpret with confidence the shifts of equilibria in aqueous solutions of thiooxine. The absorption bands at 240 and 315 $m\mu$ are observed only in acidic solutions and are characteristic of the thiol protonated form (II) of 8-mercaptoquinoline. The region of predominant existence of this form is served by solutions whose pH value is less than 3.

The absorption maxima at 250, 275, and 440 $m\mu$, appearing in the pH range 3-7, correspond to the molecular, undissociated form (I) of 8-mercaptoquinoline. At pH > 7, dissociation occurs with cleavage of hydrogen from the sulfhydryl group and formation of the thione form (III) of 8-mercaptoquinoline, which is accompanied by the appearance of absorption bands at 260 and 365 $m\mu$.

Confirmation of the validity of such a judgment is provided by changes in the absorption spectra of aqueous solutions of quinoline, isoquinoline, and 8-hydroxyquinoline that occur with changes in the concentration of hydrogen ions. In acidic solutions, as in thiooxine, maxima are observed in the region 240-280 mμ, with high molar coefficients and characteristic of the quinoline nucleus. In addition, absorption bands caused by protonation of the heterocyclic nitrogen are observed: for quinoline at 315 mμ, isoquinoline at 330 mμ, and 8-hydroxyquinoline at 310-315 and 360 mμ. In the alkaline region maxima are observed in the region 240-260 mμ, and for 8-hydroxyquinoline also at 330-340 mμ.

The protonation constant of 8-mercaptoquinoline was calculated by the method of N. P. Komar' ([11]), from measurement data at wavelengths of 440 and 315 mμ. The acid dissociation constant was calculated by the method of isobestic points ([12,13]) and by the method of N. P. Komar' from measurement data at wavelengths of 365 and 440 mμ. The results of the calculation are given in Table 1.

Table 1

Values of pK for protonation and acid dissociation of 8-mercaptoquinoline

Protonation, calculation method$\lambda =$ 315 mμ	Acid dissociation, method of isobestic points$\lambda =$ 365 mμ	Acid dissociation, method of isobestic points$\lambda =$ 440 mμ	Acid dissociation, calculation method$\lambda =$ 365 mμ	Acid dissociation, calculation method$\lambda =$ 440 mμ
2.11 ± 0.01	8.4 ± 0.4	8.6 ± 0.4	7.9 ± 0.4	8.0 ± 0.5

The good agreement of the pK values for protonation and acid dissociation, calculated by different methods at different wavelengths, makes it possible to regard them as reliable. The value of the protonation pK obtained by us (2.11) agrees with the results of Albert and Barlin ([14]), who carried out measurements at a wavelength of 280 mμ (pK 2.05).

Stone and Friedman ([9]) give for 8-hydroxyquinoline a pK value of 10.4, and Phillips and Merritt ([15]), 9.7. When the –OH group is replaced by the –SH group, a greater strengthening of the acidic properties would have been expected than that determined by us. The not very considerable increase in the acidity of 8-mercaptoquinoline in comparison with 8-hydroxyquinoline is explained by the fact that, owing to the lower affinity of the proton for the sulfur atom, an additional bond of the proton with the nitrogen atom of the heterocycle arises. This phenomenon also leads to a certain decrease in the acidic properties of 8-mercaptoquinoline.

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Note: Figure translations are in progress. See original paper for figures.