

# Investigation of 8-mercaptoquinoline (thiooxine) and its derivatives

## 107. Absorption spectra, ionization constants and distribution of 5,8-dimercaptoquinoline between organic solvents and water

\*YA. ASHAKS, \*S. RAPIOVÁ, \*M. ZIKMUND, and \*YU. BANKOVSKII

\**Institute of Inorganic Chemistry, Academy of Sciences of the Latvian SSR,  
226 934 Riga*

\**Institute of Inorganic Chemistry, Slovak Academy of Sciences,  
842 36 Bratislava*

Received 12 January 1981

Accepted for publication 3 September 1981

Absorption spectra of 5,8-dimercaptoquinoline in water and organic solvents have been studied. Ionization constants ( $pK_1 = 1.74$ ;  $pK_2 = 4.64$ ;  $pK_3 = 9.41$ ) at ionic strength  $0.1 \text{ mol dm}^{-3}$  and temperature  $20^\circ\text{C}$  and also distribution constants of the reagent in two-phase systems chloroform—water ( $pK_D = 2460$ ), benzene—water ( $pK_D = 930$ ), and isooctane—water ( $pK_D = 33$ ) have been determined.

Изучены спектры поглощения 5,8-димеркаптохинолина в воде и в органических растворителях. При ионной силе 0.1 и температуре  $20^\circ\text{C}$  определены константы ионизации ( $pK_1 = 1.74$ ;  $pK_2 = 4.64$ ;  $pK_3 = 9.41$ ) а также константы распределения реагента в двухфазных системах хлороформ—вода ( $pK_D = 2460$ ), бензол—вода ( $pK_D = 930$ ) и изоктан—вода ( $pK_D = 33$ ).

5,8-Dimercaptoquinoline has been studied with the aim to elucidate the ability of different mercapto groups to interact with metal ions; the effect of mercapto group in the 5th position on physicochemical properties of inner complex compounds has been investigated.

### Experimental

The synthesis of the reagent was described in [1]. 5,8-Dimercaptoquinoline is an anhydrous dark blue crystalline substance, in distinction to the 8-mercaptoquinoline which precipitates from aqueous solution in the form of a dark red dihydrate. 5,8-Dimercaptoquinoline was gradually oxidized in the air to 5,8-polyquinolylpolydisulfide. A stable hydrobromide that can be stored was obtained and this was used in the present study.

Hydrogen bromide salt of 5,8-dimercaptoquinoline was dissolved in  $10 \text{ cm}^3$  of ethanol on heating and  $1 \text{ cm}^3$  of the obtained solution was diluted with buffer solution to  $100 \text{ cm}^3$ . Thus.

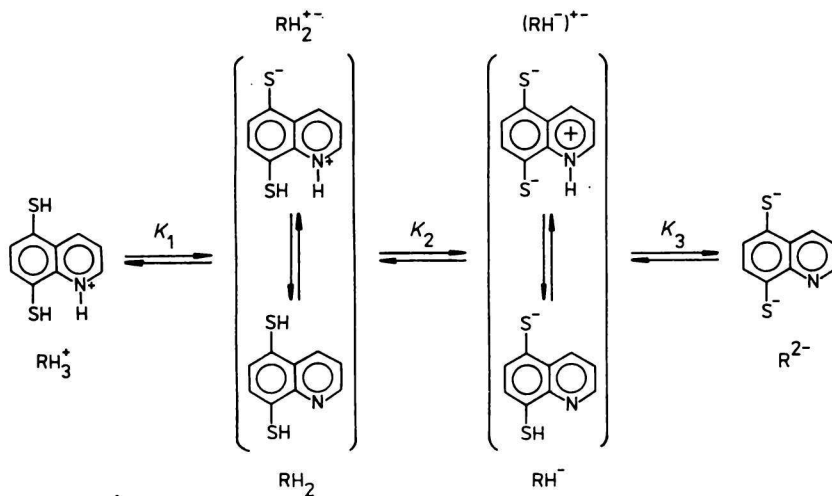
aqueous solutions of 5,8-dimercaptoquinoline contained 1% of ethanol. In order to take absorption spectra in organic solvents, free 5,8-dimercaptoquinoline was used.

The absorption spectra were obtained with an automatic Specord UV VIS spectrophotometer, the optical measurements were performed with a SF-16 spectrophotometer. Hydrogen ion concentration was measured using pH-meter type M-25 (Radiometer) with calomel electrode K 401 and glass electrode G202B calibrated to the accuracy of  $\pm 0.02$  pH.

## Results and discussion

### Absorption spectra

The equilibria between various forms of 5,8-dimercaptoquinoline in aqueous solutions are shown in Scheme 1.



Scheme 1

The absorption spectra of 5,8-dimercaptoquinoline in aqueous solutions at different hydrogen ion concentration are shown in Fig. 1. The curve 1 characterizes the protonated form of the reagent ( $RH_3^+$ ). The curve 2 characterizes the neutral form of the reagent, absorption maxima at 280 and 482 nm correspond to the zwitterionic form ( $RH_2^{+-}$ ), but overlapped maximum in the region of 320–350 nm corresponds to the thiolic form ( $RH_2$ ) of the reagent. The curve 3 characterizes the reagent with ionized mercapto group in the 5th position (the ionization constant of the mercapto group in the molecule of 5-mercaptoquinoline is by 1.5 degrees larger

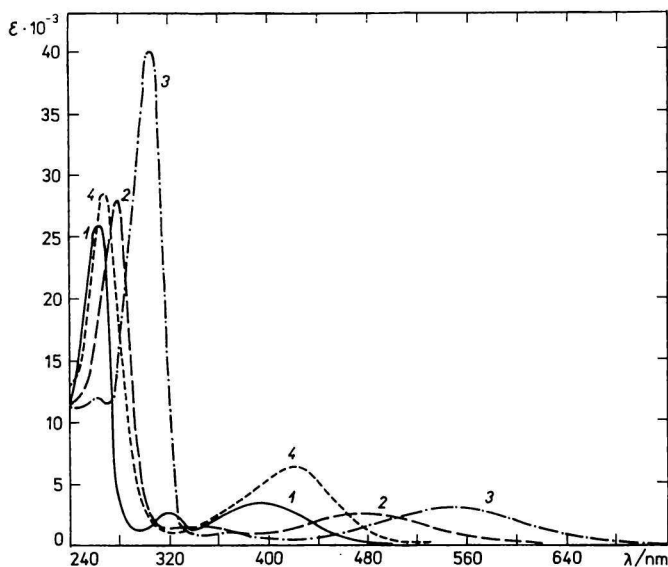


Fig. 1. Absorption spectra of different forms of 5,8-dimercaptoquinoline in aqueous solution.

1. Dimercaptoquinolinium ion  $\text{RH}_3^+$  (3 M-HCl); 2. zwitterionic form of 5,8-dimercaptoquinoline  $\text{RH}_2^{+-}$  (pH 3.2); 3. zwitterionic form of 5,8-dimercaptoquinoline  $(\text{RH}^-)^{+-}$  (pH 7.0); 4. 5,8-dimercaptoquinoline with both mercapto groups ionized  $\text{R}^{2-}$  (pH 13.0).

than that in the molecule of 8-mercaptoquinoline, therefore it can be assumed that also in the molecule of 5,8-dimercaptoquinoline the mercapto group is ionized first in the 5th position), the absorption maxima at 305 and 550 nm correspond to the zwitterionic form  $(\text{RH}^-)^{+-}$ , those at 263 and 373 nm — to the thiolic form  $(\text{RH}^-)$  of the reagent. The curve 4 characterizes the 5,8-dimercaptoquinoline ( $\text{R}^{2-}$ ) with both mercapto groups ionized.

The dependence of the formation of zwitterionic forms of 5,8-dimercaptoquinoline on hydrogen ion concentration is shown in Fig. 2. The zwitterionic forms  $\text{RH}_2^{+-}$  and  $(\text{RH}^-)^{+-}$  are formed in the pH range from 3.0 to 3.6 and from 5.8 to 7.8, respectively.

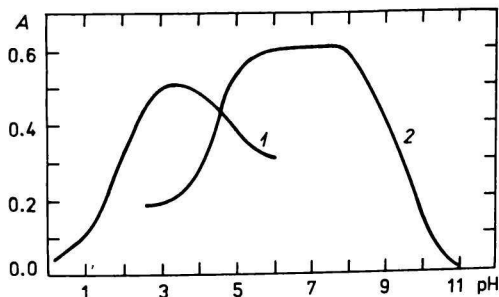


Fig. 2. Dependence of the formation of zwitterionic form of 5,8-dimercaptoquinoline on hydrogen ion concentration.

1. Zwitterionic form  $\text{RH}_2^{+-}$ ; 2. zwitterionic form  $(\text{RH}^-)^{+-}$ .

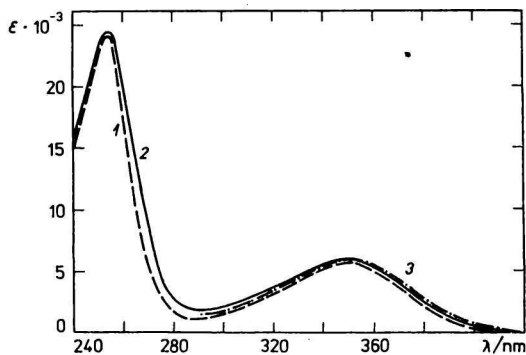


Fig. 3. Absorption spectra of 5,8-dimercaptoquinoline in organic solvents.  
1. Isooctane; 2. chloroform; 3. benzene.

Table 1

Maxima and molar absorption coefficients of 5,8-dimercaptoquinoline in various media

Medium	Form of the reagent	$\lambda_{\max}/\text{nm}$	$\frac{\epsilon_{\max}}{\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$
3 M-HCl	$\text{RH}_3^+$	264	26 000
		323	2 600
		395	3 500
pH 3.2	$\text{RH}_2^{+} + \text{RH}_2$	280	28 000
		482	2 500
pH 7.0	$(\text{RH}^-)^{+-} + \text{RH}$	263	12 000
		305	40 000
		373	1 150
		550	3 050
0.1 M-NaOH	$\text{R}^{2-}$	269	28 500
		420	6 300
Chloroform	$\text{RH}_2$	254	24 400
		348	6 000
Benzene	$\text{RH}_2$	350	5 850
Isooctane	$\text{RH}_2$	253	24 000
		349	5 800

In slightly polar and nonpolar organic solvents (chloroform, benzene, isooctane) 5,8-dimercaptoquinoline exists in a thiolic form ( $\text{RH}_2$ ) the absorption spectra of which (Fig. 3) show maxima at 253—254 and 348—350 nm. In Table 1 the maxima and the molar absorption coefficients of 5,8-dimercaptoquinoline in various media are listed.

### Solubility in water and organic solvents

In order to determine the solubility in water, the solution of 5,8-dimercaptoquinoline in hydrochloric acid is adjusted to pH 3.2 or 7.0 using the solution of sodium acetate or tetraborate (at these pH values the higher yield of the zwitterionic forms  $\text{RH}_2^{+-}$  and  $(\text{RH}^-)^{+-}$  was observed). After the sample was allowed to stand for 10 min at 20°C, the precipitate of 5,8-dimercaptoquinoline was filtered off, the absorbance of the solution was measured at 482 or 550 nm and, using molar absorption coefficients of the respective zwitterionic forms (Table 1), the concentration of the reagent in the solution was calculated.

In order to determine solubility of 5,8-dimercaptoquinoline in organic solvents the reagent was shaken for 30 min in the solvent, the excess of the reagent was filtered off, the absorbance of the solution was measured and the concentration of the reagent in the solution was calculated, using molar absorption coefficient of the thiolic form (Table 2).

Table 2

Solubility of 5,8-dimercaptoquinoline in water and in organic solvents

Solvent	Solubility $S \cdot 10^3 / \text{mol dm}^{-3}$
Water (pH 3.2)	1.2
Water (pH 7.0)	4.6
Chloroform	4200
Benzene	3200
Isooctane	48

### Ionization constants

According to the above-given scheme of equilibrium, the ionization constants of 5,8-dimercaptoquinoline  $K_1$ ,  $K_2$ , and  $K_3$  are cumulative constants. They do not characterize individual equilibria but their sum.

The ionization constants were determined spectrophotometrically according to the method described in [2], at ionic strength  $0.1 \text{ mol dm}^{-3}$ , temperature 20°C with the accuracy of  $\pm 0.02$  units of  $\text{p}K$ .

Based on ten measurements the following average values were determined:  $\text{p}K_1 = 1.74$ ;  $\text{p}K_2 = 4.64$ ;  $\text{p}K_3 = 9.41$ .

*Extraction with organic solvents*

The dependence of extraction of 5,8-dimercaptoquinoline with organic solvents on hydrogen ion concentration is shown in Fig. 4. 5,8-Dimercaptoquinoline is extracted with chloroform best of all in the interval 1.5 M-HCl—pH 6.3; with benzene in the interval 1 M-HCl—pH 5.7, and with isooctane in the interval pH 1.2—pH 4.8. It is typical that the mean value of the intervals of extraction of 5,8-dimercaptoquinoline with organic solvents is about pH 3, *i.e.* the same pH value at which the zwitterionic form  $\text{RH}_2^{+-}$  and the thiolic form  $\text{RH}_2$  of the reagent are formed in higher yield. The thiolic form of the reagent is extracted with organic

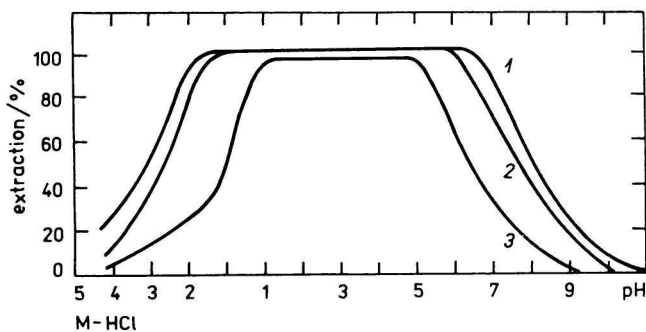


Fig. 4. Dependence of extraction of 5,8-dimercaptoquinoline with organic solvents on hydrogen ion concentration in aqueous phase.

1. Chloroform; 2. benzene; 3. isooctane.

solvents and as the extraction of this form proceeds, the equilibrium is shifted and the zwitterionic form  $\text{RH}_2^{+-}$  changes into the thiolic form. The forms of 5,8-dimercaptoquinoline with a ionized mercapto group in the 5th position  $(\text{RH}^-)^{+-}$  and  $\text{RH}^-$  cannot be extracted with slightly polar organic solvents. Consequently, the extraction of 5,8-dimercaptoquinoline in the pH region of formation of these forms (pH 5.8—7.8) decreases. Neither the protonated form  $(\text{RH}_3^+)$  nor the form of the reagent  $(\text{R}^{2-})$  with both mercapto groups ionized can be extracted with slightly polar organic solvents.

Using a two-phase ionization constant, the distribution constant of 5,8-dimercaptoquinoline between organic solvents and water has been determined [3]. The results are listed in Table 3.

Table 3

Two-phase ionization constants and distribution constants of 5,8-dimercaptoquinoline between organic solvents and water at ionic strength  $0.1 \text{ mol dm}^{-3}$  and  $20^\circ\text{C}$

Two-phase system	$pK'_2$	$K_D$
Chloroform—water	8.03	2460
Benzene—water	7.61	930
Isooctane—water	6.16	33

The data in Table 3 show that on application of a polar or aromatic solvent (chloroform or benzene) the distribution constant of 5,8-dimercaptoquinoline is considerably higher than that obtained on application of an aliphatic solvent (isooctane).

### References

1. Ashaks, Ya. V. and Bankovskii, Yu. A., *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 1972, 592.
2. Albert, A. and Serjeant, E. P., *Konstanty ionizatsii kislot i osnovanii.* (Ionization Constants of Acids and Bases.) Pp. 68—69. Izd. Khimiya, Moscow, 1964.
3. Bankovskii, Yu. A., *Khimiya vnutrikompleksnykh soedinenii merkaptokhinolina i ego proizvodnykh.* (Chemistry of the Chelate Complexes of Mercaptoquinoline and Its Derivatives.) Pp. 96—101. Izd. Zinatne, Riga, 1978.