Thermal and Spectrophotometric Studies of 8-Mercaptoquinoline-5-sulfonic Acid and Its Sodium Salt

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(Received November 9, 1972)

Thermal and spectrophotometric studies of 8-mercaptoquinoline-5-sulfonic acid and its sodium salt synthesized by an improved method are reported. In order to determine the best formula for the weighing of organic reagent, the thermal stabilities of 8-mercaptoquinoline-5-sulfonic acid and its sodium salt and the amount of water of crystallization were examined with a thermal balance. It was found that the disodium dihydrate was of the best form. The ultraviolet and visible absorption spectra in aqueous-ethanol solution were measured, the tautomeric constant K_t between neutral and zwitterion forms being estimated and acid dissociation constants obtained spectrophotometrically. The absorption spectra and the equilibrium constants of the reagents were compared with those of 8-mercaptoquinoline, 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulfonic acid.

Analytical application of 8-mercaptoquinoline, a typical organic reagent containing nitrogen and sulfur ligand atoms, has recently been studied by many analytical chemists. Stoichiometric studies of 8-mercaptoquinoline have been reported by a few investigators,[1–3] but they are not as extensive and systematic as those of 8-hydroxyquinoline and its metal chelates. This may be attributed to the difficulty of finding a favorable organic solvent capable of dissolution of many kinds of metal 8-mercaptoquinoline chelates.

Introduction of a sulfonic acid group at 5-position of the quinoline nucleus makes its metal chelates soluble in water. Thus it is possible to study stoichiometrically the various metal 8-mercaptoquinoline-5-sulfonic acid chelates as water soluble metal 8-mercaptoquinoline chelates.

The present paper deals with the thermal and spectrophotometric studies of 8-mercaptoquinoline-5-sulfonic acid and its sodium salt synthesized by an improved method. Their thermal stabilities, air oxidation, acid dissociation constants and ultraviolet and visible absorption spectra are compared with those of 8-mercaptoquinoline, 8-hydroxyquinoline, and 8-hydroxyquinoline-5-sulfonic acid.

Experimental

Materials. 8-Mercaptoquinoline-5-sulfonic acid and its derivatives have been synthesized by Vogt and Hein[4] and Bankovskis *et al.*[5] In order to raise the yield of the reagents, an improved synthesis from 8-hydroxyquinoline was attempted.

8-Hydroxyquinoline-5-sulfonic Acid: The methods by Coll and Coll[6] and Matsumura[7] were adopted for the synthesis from 8-hydroxyquinoline. Yield: 90%.

8-Aminoquinoline-5-sulfonic Acid: The synthesis of 8-aminoquinoline from 8-hydroxyquinoline by Vorozhtzov and Kogan[8] was utilized. 8-Hydroxyquinoline-5-sulfonic acid (45 g, 0.20 mol), ammonium sulfite (70 g, 0.52 mol), 28% ammonia (50 ml, 0.36 mol) and 100 ml of water are charged in an autoclave and heated at 150—160 °C, for 6—7 hr. under 10—15 atm. The gray green precipitate formed was dissolved with water, insoluble residues being filtered off. When the filtrate was concentrated to 300 ml followed by addition of 36% hydrochloric acid (50 ml, 0.58 mol), yellow to orange precipitate was formed. This was filtered and washed with water. One litre of water was added to the crude 8-aminoquinoline-5-sulfonic acid (10 g). A small amount of active carbon was added to the solution and heated for 30 min. After filtration, the filtrate was concentrated to 500 ml. On cooling, pure 8-aminoquinoline-5-sulfonic acid (*ca.* 6 g) was obtained.

Found: C, 44.55; H, 3.99; N, 11.32%. Calcd for $C_9H_{10}N_2O_4$: C, 44.62; H, 4.16; N, 11.56%. 8-Aminoquinoline-5-sulfonic acid was obtained by recrystallization from water as a mixture of yellow needle crystal and orange cube crystal. Both exist as monohydrate at room temperature, their anhydride being obtained by drying at 100—110 °C. Decomposition temperature is 220 °C.

8-Mercaptoquinoline-5-sulfonic Acid Disodium Salt Trihydrate: The synthesis of 8-mercaptoquinoline from 8-aminoquinoline by Kealey and Freiser[9] was utilized. 8-Aminoquinoline-5-sulfonic acid monohydrate (4.84 g, 0.02 mol) once at least recrystallized, was added to 150 ml of 24% hydrobromic acid solution (0.65 mol) and heated for dissolution. After complete dissolution, the solution was rapidly cooled in an ice-bath to deposit the fine crystal. To the resulting suspension, was added 10% sodium nitrous acid solution dropwise in an ice-bath until potassium iodide-starch paper turned blue. Excess sodium nitrous acid was decomposed by addition of 2 M sulfamic acid solution. The diazotized solution was gradually added to a solution of thiourea (1.7 g, 0.022 mol) dissolved in 50 ml of water at 30—40 °C, the solution then being heated at 90 °C for a short time. The reacting solution changed to red and a white precipitate was formed. To the resulting solution containing the precipitate was added hypophosphorous acid (2—5 equivalent amounts of 8-aminoquinoline-5-sulfonic acid) and heated to dissolve the precipitate. After the solution was filtered, the filtrate was cooled in an ice-bath and 100 g of solid sodium hydroxide

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[8] N. N. Vorozhtzov and I. M. Kogan, *Ber.*, **65**, 142 (1932).

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was gradually added with sufficient stirring under nitrogen gas. 8-Mercaptoquinoline-5-sulfonic acid disodium salt trihydrate formed as a yellow precipitate. After being filtered, the precipitate was washed twice with 90% ethanol. It was then dried for 1—2 hr under reduced pressure by means of a water-jet pump.
Yield: 80—90%. The crude product of 5—6 g was throughly dissolved in 50 ml of water and then 150 ml of ethanol was added. A yellow cube crystal was formed. After filtration, the precipitate was washed twice with 10 ml of ethanol and dried for 1—2 hr under reduced pressure by means of water-jet pump and then kept in a desiccator with silica gel under nitrogen.
Yield: 60—65%. Yellow cube crystals.

Found: C, 31.68; H, 3.19; N, 3.97%. Calcd for $C_9H_5NO_3S_2Na_2$: C, 31.86; H, 3.27; N, 4.13%.

8-Mercaptoquinoline-5-sulfonic Acid: To 8-mercaptoquinoline-5-sulfonic acid disodium salt trihydrate (3.3 g, 0.01 mol) dissolved in 45 ml of water was added 2.5 ml of 35% hydrochloric acid solution and 2.5 ml of 50% hypophosphorous acid, and the resulting red solution was heated for 1—2 hr on a water-bath and allowed to stand overnight. Faint yellow to faint brown silk thread-like 8-mercaptoquinoline-5-sulfonic acid was formed from the deep red solution. After the precipitate was filtered, it was washed twice with 3—4 ml ethanol and dried for 1—2 hr under reduced pressure, and kept in a desiccator with silica gel under nitrogen. The crude product was recrystallized from water containing hypophosphorous acid.
Yield: 63%.

8,8′-Diquinolyldisulfide-5,5′-disulfonic Acid Trihydrate: To 8-mercaptoquinoline-5-sulfonic acid disodium salt trihydrate (3.43 g, 0.01 mol) dissolved in 50 ml of water was added 2 ml of 35% hydrochloric acid and then 3% hydrogen peroxide solution until the red color disappeared completely. The resulting solution was allowed to stand overnight. Faint yellow cube crystal was formed.
Yield: 70%.

Found: C, 40.15; H, 3.42; N, 5.49%. Calcd for $C_{18}H_{18}N_2O_9S_4$: C, 40.44; H, 3.39; N, 5.24%.

Apparatus. Ultraviolet and visible absorption spectra were measured with a Hitachi 124 type spectrophotometer with 1 cm quartz cells. A Horiba Model P pH meter with glass and calomel electrodes was standardized against aqueous buffer (pH 4.01 and 6.86). Thermogravimetric curves were obtained with a Cho Thermobalance apparatus.

Thermogravimetric Measurement. About 100 mg of sample powder was weighed out into a holder for thermobalance and the temperature was elevated at a rate of 5 °C/min. The weight and temperature were read at regular time intervals.

Spectrophotometric Measurement. All the solutions were deaerated by bubbling with nitrogen. The absorption spectra were measured at 20±1 °C under nitrogen atmosphere. The solutions were buffered with perchloric acid, sodium hydroxide, acetic acid and disodium hydrogen phosphate and were adjusted with sodium perchlorate to maintain the ionic strength at 0.1 except for the solution with pH below 1.0.

Determination of Acid Dissociation Constants. All the acid dissociation constants for 8-mercaptoquinoline-5-sulfonic acid were determined spectrophotometrically. The macroscopic acid dissociation constants K_a at the ionic strength 0.1 and at 20±1 °C were determined by the equation

$$pK_{a_1} = \log (d_b - d)/(d - d_a) + pH \qquad (1)$$

where d is the absorbance at 454 or 278 nm at the particular pH, d_b the absorbance in 1.00×10^{-3} M perchloric acid and d_a the absorbance in 5 M perchloric acid. The values of pK_{a_1} obtained for each pH were averaged. pK_{a_2} was determined in a similar way. pK_a' was estimated roughly by a graphical method. The values of the microscopic acid dissociation constants K_{a_A}, K_{a_B}, K_{a_C}, and K_{a_D} were obtained by the following equation and the values of K_{a_1}, K_{a_2} and the tautomeric constant K_t.

$$K_t = [\text{zwitterion}]/[\text{neutral}] = K_{a_D}/K_{a_C} \qquad (2)$$

$$K_{a_1} = K_{a_A} + K_{a_B} \qquad (3)$$

$$1/K_{a_2} = 1/K_{a_C} + 1/K_{a_D} \qquad (4)$$

Determination of Tautomeric Constant. The tautomeric constant K_t was roughly estimated by two methods. 1) On the assumption that both extinction coefficients for 8-methylmercaptoquinoline-5-sulfonic acid and the neutral form of 8-mercaptoquinoline-5-sulfonic acid are the same at a corresponding wavelength, the ratio of the extinction coefficient at 339 nm of 8-methylmercaptoquinoline-5-sulfonic acid to the apparent extinction coefficient of 8-mercaptoquinoline-5-sulfonic acid in aqueous solution at 322 nm gives the fraction of the neutral form of 8-mercaptoquinoline. 7980 was taken[4] as the molar extinction coefficient at 339 nm for 8-methylmercaptoquinoline-5-sulfonic acid. 2) It is possible to estimate the expected absorbance at 322 nm for 100% neutral form of 8-mercaptoquinoline-5-sulfonic acid by using the data that the ratios of the increment of the absorbance at 322 nm to the decrement of the absorbance of the absorption maxima around 450 nm in various v/v% ethanol solution are approximately 1.6. The ratio of the absorbance in aqueous solution at 322 nm to the expected absorbance as 100% neutral form at the same wavelength gives the fraction of the neutral form of 8-mercaptoquinoline-5-sulfonic acid.

Results and Discussion

Thermal Stability. In order to find the best formula for gravimetry of the reagent, the thermal stability of 8-mercaptoquinoline-5-sulfonic acid and its sodium salt and the amount of water of crystallization were examined with a thermal balance. The thermogravimetric curves are given in Fig. 1 and the results in Table 1. We see that 8-mercapto and 8-hydroxyquinoline-5-sulfonic acids are less stable than the corresponding sodium salts and that 8-mercaptoquinoline-

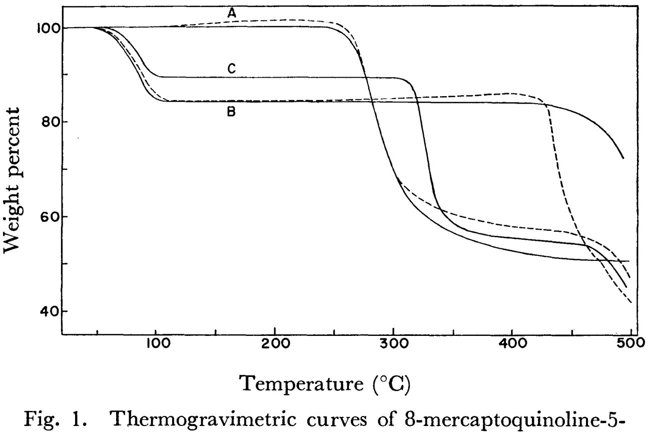

Fig. 1. Thermogravimetric curves of 8-mercaptoquinoline-5-sulfonic acid and its disodium salt.
A: 8-mercaptoquinoline-5-sulfonic acid
B: 8-mercaptoquinoline-5-sulfonic acid disodium salt trihydrate
C: 8,8′-Diquinolyldisulfide-5,5′-disulfonic acid trihydrate
——: in nitrogen gas, ------: in air.

TABLE 1. THERMOGRAVIMETRIC RESULTS FOR 8-MERCAPTO AND 8-HYDROXYQUINOLINE -5-SULFONIC ACID AND THEIR DERIVATIVES

Reagent	Dehydration		Decomposition begins at
	Temperature	Weight loss%	
8-Mercaptoquinoline-5-sulfonic acid disodium salt trihydrate	50—105°C	Found: 15.90% Calcd for $C_9H_5NO_3S_2Na_2\cdot 3H_2O$: $3H_2O$, 15.93%	415°C
8-Mercaptoquinoline-5-sulfonic acid			240°C
8,8′-Diquinolyldisulfide-5,5′-disulfonic acid trihydrate	60— 95°C	Found: 10.10% Calcd for $C_{18}H_{12}N_2O_6S_4\cdot 3H_2O$: $3H_2O$, 10.11%	300°C
8-Hydroxyquinoline-5-sulfonic acid disodium salt 3.5 hydrate	40— 78°C	Found: 14.00% Calcd for $C_9H_5NO_4SNa_2\cdot 5H_2O$: $2.5H_2O$ 14.42%	355°C
	78—110°C	Found: 6.04% Calcd for $C_9H_5NO_4SNa_2\cdot 3.5H_2O$: H_2O, 5.77%	
8-Hydroxyquinoline-5-sulfonic acid dihydrate	70—105°C	Found: 7.23% Calcd for $C_9H_7NO_4S\cdot 2H_2O$: H_2O, 6.90%	270°C
	105—147°C	Found: 6.42% Calcd for $C_9H_7NO_4S\cdot 2H_2O$: H_2O, 6.90%	

5-sulfonic acid and its sodium salt are more stable than the corresponding 8-hydroxy compounds. 8-Mercaptoquinoline-5-sulfonic acid sodium salt anhydride is so hygroscopic that it rapidly increases about 11.8% in wt. when exposed to air for 1 hr. It may be concluded that the form of 8-mercaptoquinoline-5-sulfonic acid disodium dihydrate is the best for weighing. In the thermogravimetric curves in air for 8-mercaptoquinoline-5-sulfonic acid and its disodium salt (dashed lines of curves A and B, respectively), the former increases in weight by 1.0—1.2% in the temperature range 120—240 °C, the latter by 1.8—2.1% in the range 240—408 °C. A similar phenomenon was found with the sodium salts of 8-mercaptoquinoline[10] and 8-selenoquinoline.[11] It is assumed that the sodium salt of 8-mercaptoquinoline-5-sulfonic acid is oxidized by air.

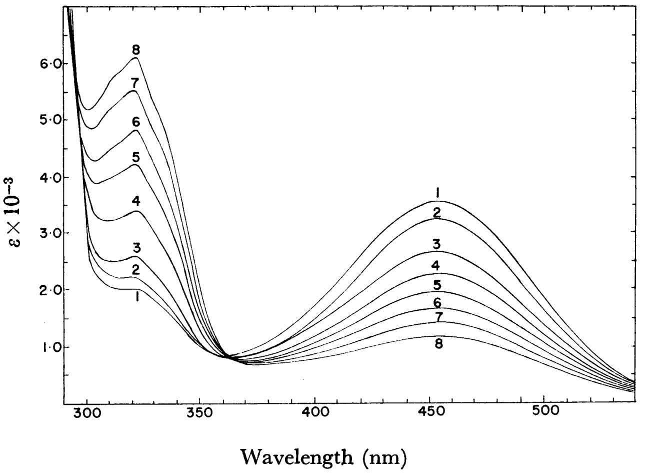

Fig. 2. Time dependence of the spectra of 1.00×10⁻⁴M 8-mercaptoquinoline-5-sulfonic acid solution in 1.00×10⁻³M perchloric acid at 35 °C.
Standing time: 1: 0 hr., 2: 1 hr, 3: 5 hr, 4: 10 hr, 5: 15 hr, 6: 20 hr, 7: 25 hr, 8: 30 hr.

Ultraviolet and Visible Absorption Spectra of the Reagent. Ultraviolet and visible spectra of 8-mercaptoquinoline-5-sulfonic acid were measured in order to know the stability of the reagent in aqueous solution against oxidation, species existing in various pH, acid dissociation constant, and tautomeric constant.

Oxidation in Aqueous Solution: When 8-mercaptoquinoline-5-sulfonic acid in aqueous solution is allowed

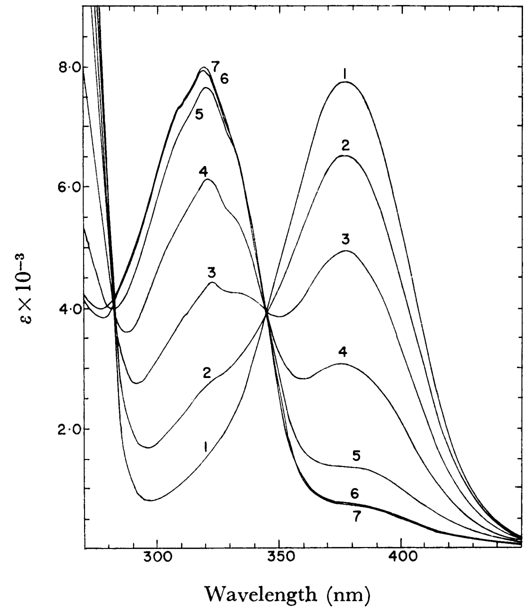

Fig. 3. Time dependence of the spectra of 1.00×10⁻⁴M 8-mercaptoquinoline-5-sulfonic acid solution at pH 10.02 and at 35 °C.
Standing time: 1: 0 hr, 2: 2 hr, 3: 4 hr, 4: 6 hr, 5: 8 hr, 6: 10 hr, 7: 12 hr.

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[10] Y. Mido and E. Sekido, This Bulletin, **44**, 2127 (1971).

[11] E. Sekido and I. Fujiwara, *Talanta*, **19**, 647 (1972).

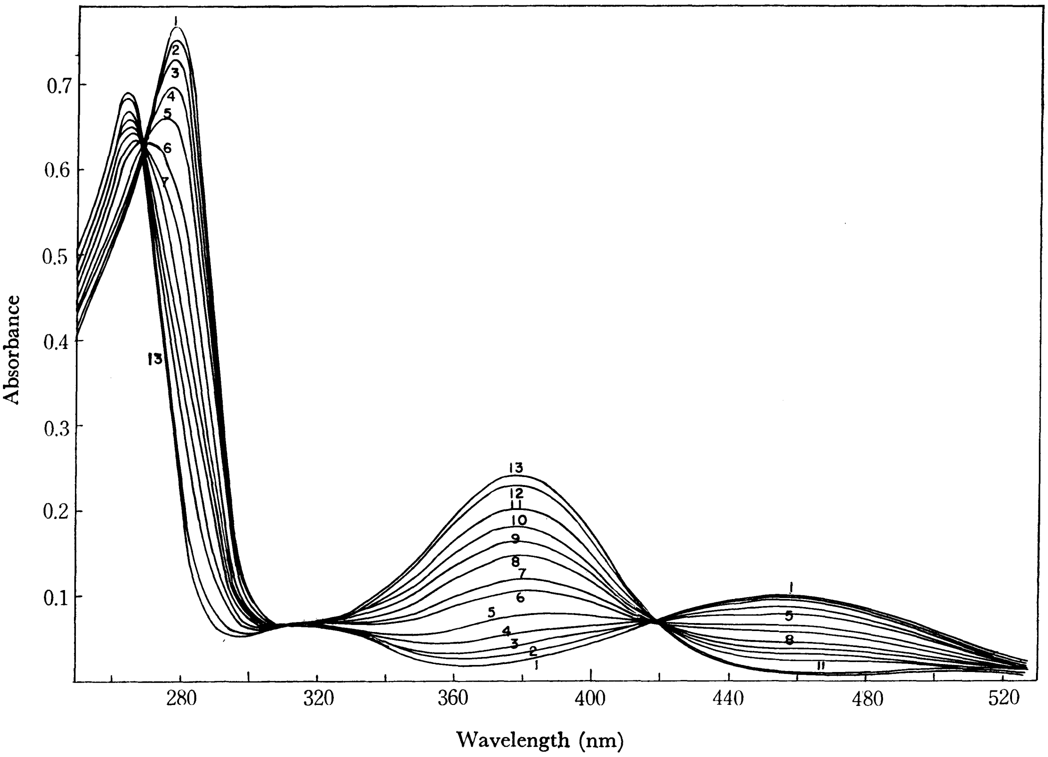


Fig. 4. Absorption spectra of 8-mercaptoquinoline-5-sulfonic acid at various acid concentration of perchloric acid and at $\mu = 1.00$.
Concentration of the reagent: 3.00×10^{-5}M. Concentration of perchloric acid: 1: 1.00×10^{-3}M, 2: 1.00×10^{-2}M, 3: 2.00×10^{-2}M, 4: 3.00×10^{-2}M, 5: 5.00×10^{-2}M, 6: 8.00×10^{-2}M, 7: 1.00×10^{-1}M, 8: 2.00×10^{-1}M, 9: 3.00×10^{-1}M, 10: 5.00×10^{-1}M, 11: 1.00M.

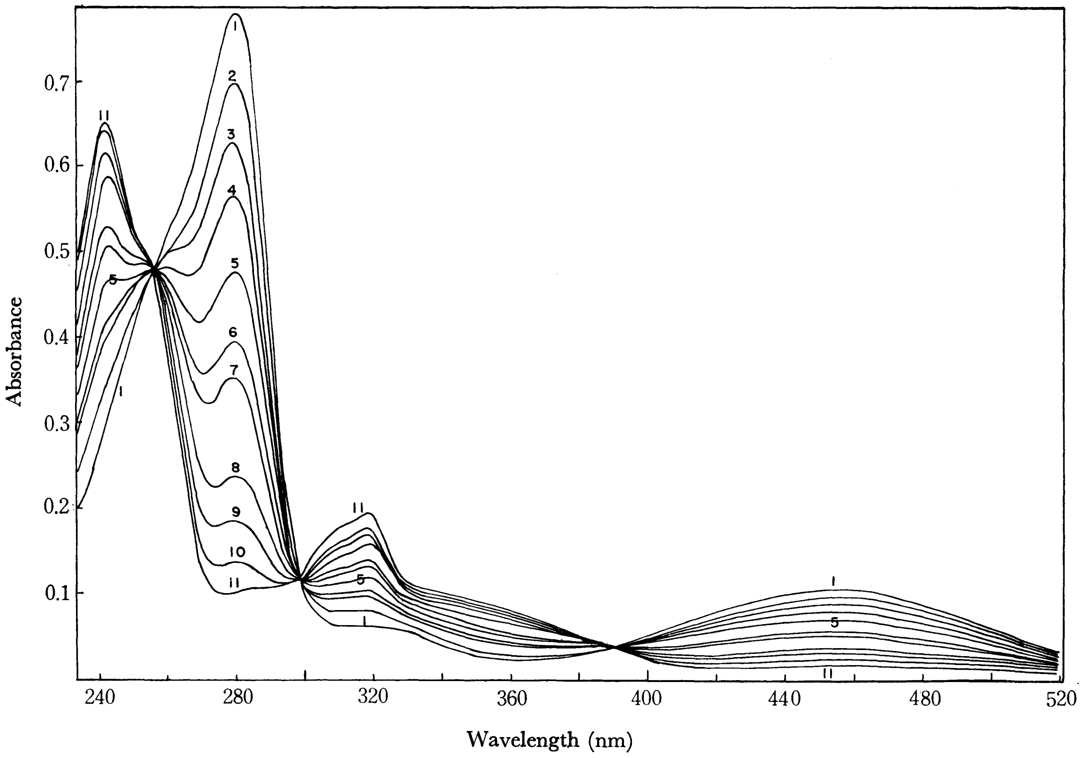
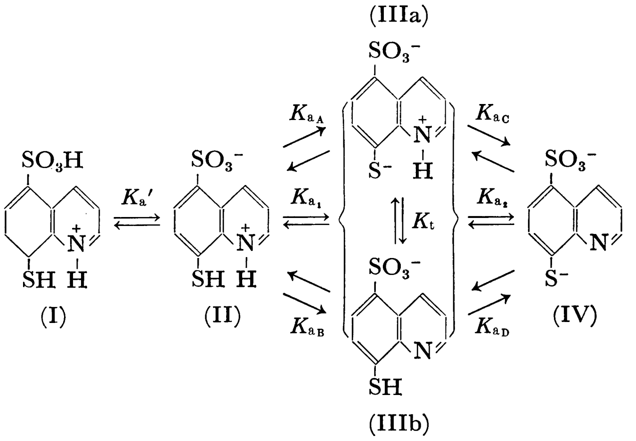


Fig. 5. Absorption spectra of 8-mercaptoquinoline-5-sulfonic acid in various pH solution at $\mu = 0.10$.
Concentration of the reagent: 3.00×10^{-5}M. pH: 1: 2.73, 2: 4.82, 3: 6.18, 4: 6.75, 5: 7.10, 6: 7.26, 7: 7.46, 8: 7.56, 9: 7.74, 10: 8.02, 11: 8.42, 12: 9.00, 13: 11.03.

to stand in air, it is gradually oxidized giving rise to the formation of 8,8′-diquinolyldisulfide-5,5′-disulfonic acid. Changes in the ultraviolet and visible absorption spectra by air oxidation at pH 3.0 and 10.0 were examined at 35 °C at which temperature oxidation is more accelerated than that at room temperature. The results are shown in Figs. 2 and 3, respectively. The intensities of the absorption maxima at 454 and 279 nm for pH 3.0 and at 378 nm for pH 10.0 decrease with time, while those at 322 and 243 nm for pH 3.0 and at 378 nm for pH 10.0 increase with time. The time required to oxidize half the amount of reagent at 35 °C is about 12 hr for pH 3.0 and about 5 hr for pH 10. The reagent is more rapidly oxidized with increase in pH. It is assumed that electron donation, or the oxidation of the $-S^-$ group of the anion (IV) existing in a high pH solution, accelerated to a greater extent than in the other species (I), (II), (III_a), and (III_b) of the reagent.

Ultraviolet and Visible Absorption Spectra of 8-Mercaptoquinoline-5-sulfonic Acid in Aqueous Solution: The ultraviolet and visible absorption spectra of 1.00×10^{-4} M 8-mercaptoquinoline-5-sulfonic acid at various concentrations of perchloric acid from 1.00×10^{-3} to 10.0 M and those in the pH range 3.0—12.0 are shown in Figs. 4 and 5, respectively. The relationship between the absorption maxima of 8-mercaptoquinoline-5-sulfonic acid and pH is shown in Fig. 6. The intensities of absorption at 454 and 279 nm decrease with the concentration of perchloric acid and disappear above 3.0 M. The absorption maximum at 322 nm in the solution of pH 3.0 shifts slightly toward 318 nm with acid concentration. The intensity increases and a weak absorption appears around 360 nm as a shoulder of the absorption at 318 nm. The weak absorption of 311 nm hardly recognized as an absorption at pH 3.0 appears as a shoulder of the absorption of 318 nm. The isosbestic points appear at 389 and 298 nm in the pH range 5.0—0, but the absorption bands in perchloric acid with concentration above 3 M deviate from these points. The absorption bands at 454 and 279 nm which exhibit the constant maximum absorbance in the pH range 3.0—5.0 decrease with alkaline concentration. Those at 378 and 265 nm increase. Isosbestic points exist at 419, 323, and 270 nm. (Fig. 5).

The ultraviolet and visible absorption spectra for 8-mercaptoquinoline-5-sulfonic acid in various pH solutions are similar to those for 8-mercaptoquinoline[2,3] except for the change in absorption at 318 nm below pH 0. Thus the changes in absorption spectra correspond to those of the structures I↔II↔III↔IV as follows:



From the changes of absorbance at 454 nm in the acidic and alkaline sides we obtained the values $pK_{a_1} = 0.90 \pm 0.03$ and $pK_{a_2} = 7.50 \pm 0.04$, respectively. Similarly from the changes of absorbance at 278 nm, $pK_{a_1} = 0.90 \pm 0.01$ and $pK_{a_2} = 7.48 \pm 0.09$ were obtained in good accordance with above.

The following results are found for the absorption band at 318 nm. 1) The absorption curves of the reagent in perchloric acid with concentration above 1.00 M deviate from the isosbestic points at 389 and 298 nm. 2) The plot of the absorbance *vs.* pH at

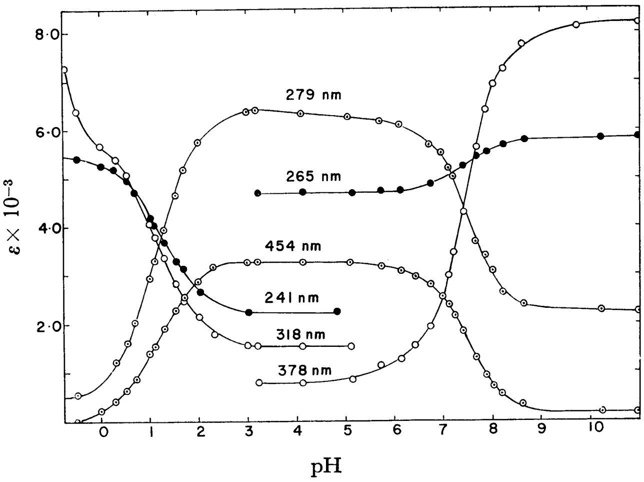


Fig. 6. Relationship between the molar absorptivities at the absorption maxima of 8-mercaptoquinoline-5-sulfonic acid and pH.

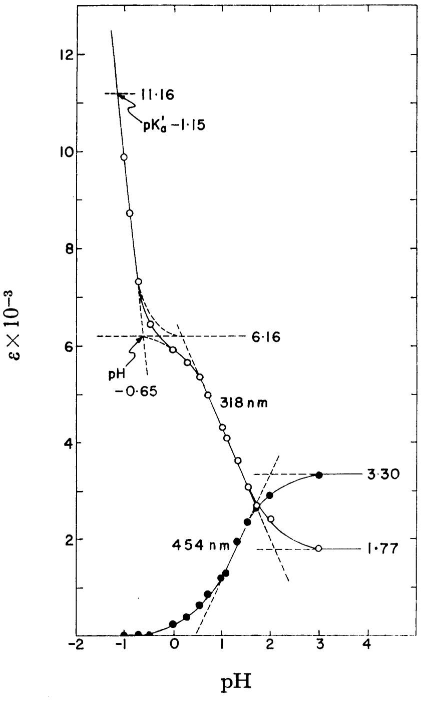


Fig. 7. Graphical determination of pK_a'.

Table 2. Relationship between absorbance of 8-mercaptoquinoline-5-sulfonic acid and concentration of perchloric acid

Concentration of perchloric acid (M)	Absorbance at 454 nm	Absorbance at 318 nm		$\frac{A_{318}-0.177}{0.330-A_{454}}$
1.00×10^{-3}	0.330	0.177		
1.00×10^{-2}	0.292	0.237		
2.00×10^{-2}	0.261	0.267		
3.00×10^{-2}	0.232	0.305		
5.00×10^{-2}	0.195	0.359		1.35
8.00×10^{-2}	0.155	0.403		1.29
1.00×10^{-1}	0.140	0.429		1.33
2.00×10^{-1}	0.087	0.495		1.31
3.00×10^{-1}	0.065	0.532		1.34
5.00×10^{-1}	0.041	0.562		1.33
1.00	0.023	0.590		1.35
			Mean	1.33 ± 0.04
3.00	0.002	0.640		1.41
5.00	0	0.731		1.61
8.00	0	0.870		2.10
10.00	0	0.987		2.45

318 nm has a point of inflexion around pH 0 (Fig. 7). 3) The ratio of the increase in absorbance at 318 nm to its decrease at 454 nm becomes greater in perchloric acid with concentration above 1 M (Table 2). These results are obtained also in the case of hydrochloric acid. This indicates that species (I) may be formed in a strong acid solution. The value of pK_a' for the equilibrium $I \rightleftharpoons II + H^+$ is estimated as follows. The absorbances at 454 and 318 nm of the 1.0×10^{-4} M reagent in various concentrations of perchloric acid solution in the range 1.00×10^{-3}—10.0 M were measured. The ionic strength at 1.0 was maintained in the range 1.00×10^{-3}—1 M perchloric acid. The results are given in Table 2, and the plots of absorbances at 454 and 318 nm *vs.* pH in Fig. 7. $pK_{a_1}=1.14\pm0.02$ ($\mu=1.0$) was obtained from the values of absorbance at 454 nm and Eq. (1). If species (I) is not formed in a strong acid solution, the upper limit of the absorbance at 318 nm will be estimated as $d_a=0.330\times1.33\pm0.177=0.616$. Using $d_a=0.616$ and $d_b=0.177$, $pK_{a_1}=1.13\pm0.02$ ($\mu=1.0$) could be obtained. This is in good accordance with 1.14 ± 0.02 mentioned above. The plot of the absorbance at 318 nm *vs.* pH below -0.5 is found to be linear with a slope -1 (Fig. 7). Thus the value of pK_a' was roughly estimated to be -1 (dotted line, Fig. 7).

Ultraviolet and Visible Absorption Spectra of 8-Mercaptoquinoline-5-sulfonic Acid in Ethanol-Water Media: The absorption spectra of 8-mercaptoquinoline-5-sulfonic acid in aqueous-ethanol mixtures containing 1.00×10^{-3} M of perchloric acid are sohwn in Fig. 8. The wavelength of the absorption maxima and the molar extinction coefficients of the species in several kind of aqueous-ethanol mixtures are given in Table 3. The

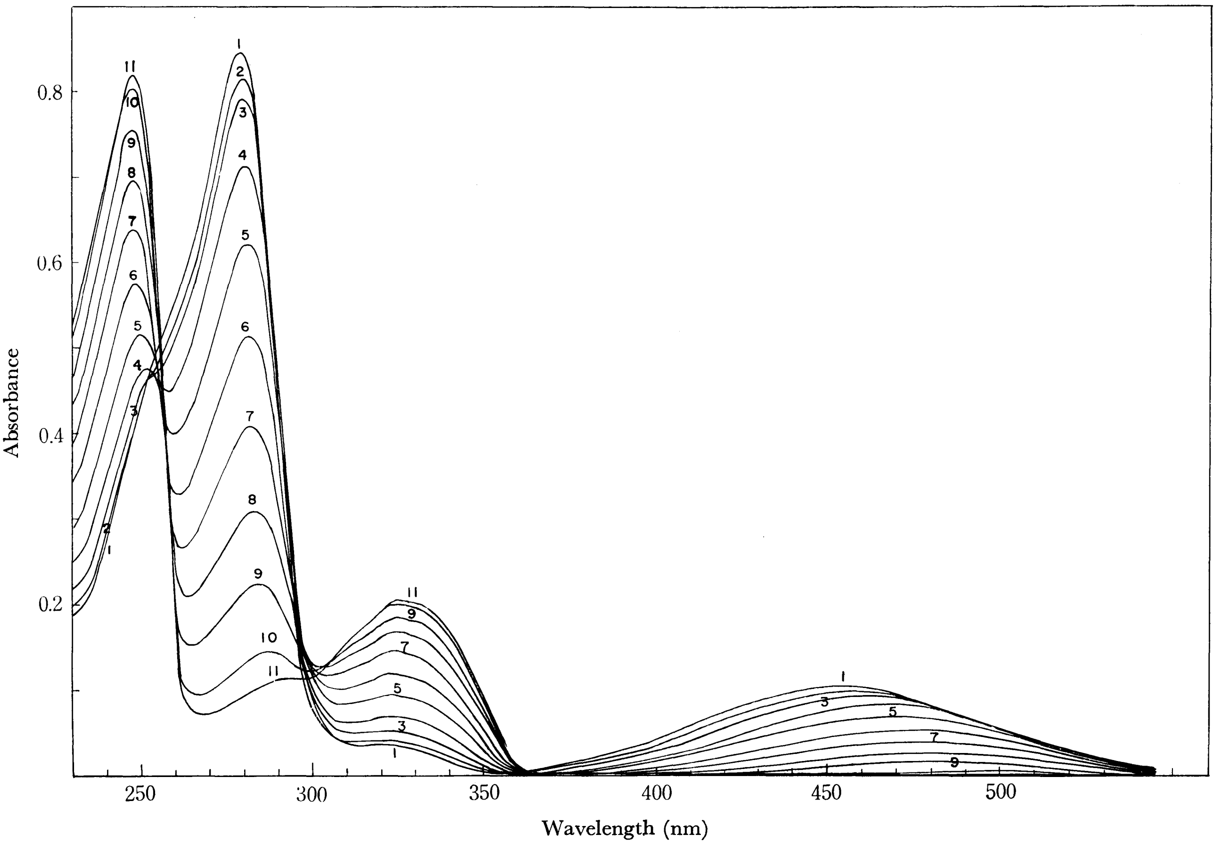


Fig. 8. Absorption spectra of 8-mercaptoquinoline-5-sulfonic acid in aqueous ethanol containing 1.00×10^{-3}M of perchloric acid at $\mu=0.005$.
Concentration of the reagent: 3.33×10^{-3}M. Concentration of ethanol (v/v%): 1: 0%, 2: 10%, 3: 20%, 4: 30%, 5: 40%, 6: 50%, 7: 60%, 8: 70%, 9: 80%, 10: 90%, 11: 95%.

TABLE 3. EFFECT OF THE CONCENTRATION OF ETHANOL ON ABSORPTION MAXIMA (nm) AND MOLRA ABSORPTIVITY ($l\cdot mol^{-1}\cdot cm^{-1}$) OF 8-MERCAPTOQUINOLINE-5-SULFONIC ACID

Concn of ethanol % (v/v)	Cation (II) in 1.02 M $HClO_4$							
	$\lambda^{a)}$	ε	λ	ε	λ	ε	$\lambda^{a)}$	ε
0	241	2.13×10^4	(311)	4.67×10^3	318	5.45×10^3	(340)	3.00×10^3
30	241	2.20×10^4	(310)	4.77×10^3	318	5.28×10^3	(340)	3.00×10^3
60	242	2.23×10^4	(310)	5.00×10^3	319	5.20×10^3	(340(	3.12×10^3
80	241	2.21×10^4	(310)	5.17×10^3	319	5.20×10^3	(340)	3.24×10^3
90								

Zwitterion (IIIa) in 1.00×10^{-3} M $HClO_4$				Neutral (IIIb) in 1.00×10^{-3} M $HClO_4$				Anion (IV) in 1.09×10^{-2} M NaOH			
λ	ε	λ	ε	$\lambda^{a)}$	ε	λ	ε	λ	ε	λ	ε
279	2.53×10^4	454	3.26×10^3	(255)	1.50×10^4	322	1.42×10^3	265	2.32×10^4	378	8.47×10^3
281	2.14×10^4	466	2.64×10^3	252	1.43×10^4	324	2.48×10^3	266	2.41×10^4	382	8.47×10^3
282	1.23×10^4	478	1.34×10^3	247	1.92×10^4	324	4.91×10^3	267	2.48×10^4	387	8.47×10^3
285	6.67×10^3	488	$6.3\ \times10^2$	247	2.25×10^4	324	6.14×10^3	268	2.53×10^4	389	8.47×10^3
288	4.32×10^3	494	$2.0\ \times10^2$	247	2.41×10^4	325	6.58×10^3	268	2.53×10^4	391	8.47×10^3

a) Figures in parentheses indicates shoulder.

TABLE 4. EQUILIBRIUM CONSTANTS OF 8-MERCAPTOQUINOLINE-5-SULFONIC ACID AND 8-MERCAPTOQUINOLINE IN AQUEOUS SOLUTION

Compunds	pK_a'	pK_{a_1}	pK_{a_2}	K_t	pK_{a_A}	pK_{a_B}	pK_{a_C}	pK_{a_D}
8-MQ-5-$SO_3H^{a)}$	−1.15	0.91±0.03	7.50±0.04	$5.6^{c)}$	0.98	1.73	7.43	6.68
				$3.9^{d)}$	1.01	1.59	7.40	6.81
8-$MQ^{b)}$		2.0 ±0.1$^{e)}$	8.36±0.1$^{f)}$	$3.8^{g)}$	2.10	2.68	8.26	7.68

a) 8-MQ-5-SO_3H: 8-Mercaptoquinoline-5-sulfonic acid.
b) 8-MQ: 8-Mercaptoquinoline.
c) by method 1.
d) by method 2.
e) Ref. 12.
f) Ref. 13.
g) Ref. 2.

absorption maximum in aqueous solution shifts to longer wavelength with the increase of ethanol content, its intensity decreasing significantly. Thus in 95% ethanol solution the absorption maximum shifts from 454 nm in aqueous solution to 498 nm in 95% ethanol and the apparent extinction coefficient decreases from 3.26×10^3 to 1.8×10^2. On the other hand, the absorption maximum at 322 nm in aqueous solution shifts slightly to longer wavelength 325 nm in 95% ethanol, but the apparent extinction coefficient increases from 1.42×10^3 to 6.58×10^3. In the range 300—200 nm, the absorption maximum at 279 nm decreases with the increase of ethanol content and that at 255 nm increases. It is assumed that zwitterion form IIIa is transferred into neutral form IIIb with the increase of ethanol content which causes the lowering of the dielectric constant of the solution. The absorption bands having peaks at 454 and 279 nm correspond to the zwitterion form and those at 323 and 255 nm to the neutral form. The absorption maxima of both the cation and the neutarl having –SH group are slightly shifted, but those at the longer wavelengths of both the zwitterion and anion having $-S^-$ group are significantly shifted to longer wavelength with the increase of the ethanol content (Table 3). This is remarkable for the zwitterion. Increase of the water content may stabilize the ground state to a greater extent for zwitterion (IIIa) or anion (IV) and the absorption maximum will shift to the blue side. Thus these absorption bands might be assigned to the charge transfer absorption in which $-S^-$ group takes part.

Equilibrium Constants of 8-Mercaptoquinoline-5-sulfonic Acid in Aqueous Solution. The tautomeric constant K_t=[zwitterion]/[neutral] was calculated to be 5.6 by method (1), and 3.9 by method (2). It was found that 80—85% of the reagent exists as the zwitterion and 20—15% as the neutral form in aqueous solution. Table 4 shows the equilibrium constants of 8-mercaptoquinoline-5-sulfonic acid and 8-mercaptoquinoline. The values of pK_{a_1} and pK_{a_2} for 8-mercaptoquinoline-5-sulfonic acid are lower than the corresponding ones for 8-mercaptoquinoline. This can be attributed to the electron with drawing power of the sulfonic acid group substituted at 5-position of the quinoline nucleus. The difference for pK_{a_1} (1.09) is larger than that for pK_{a_2} (0.86). The somewhat larger decrease of pK_{a_1} seems to be due to the fact that the value of K_t 3.9—5.6 for 8-mercaptoquinoline-5-sulfonic acid is somewhat larger than that for 8-mercaptoquinoline, 3.8.

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