

# Studies of 8-Quinolinethiol as Chelating Agents. III.<sup>1)</sup> Distribution Behavior of 8-Quinolinethiol between Chloroform and Aqueous Solutions

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**Synopsis.** The distribution behavior of 8-quinolinethiol between chloroform and aqueous solutions was examined and compared with that of 8-quinolinol. The distribution coefficient was  $K_{DR}=2140$  and macroscopic acid dissociation constants were  $pK_{a1}=2.05$  and  $pK_{a2}=8.39$ .

8-Quinolinethiol is a useful organic reagent for the chloroform extraction and photometric determination of heavy metals.<sup>2,3)</sup> Equilibrium constants for the extraction of the reagent itself are necessary to study the stoichiometric extraction of metals with 8-quinolinethiol. It is also interesting to compare the extraction behavior of 8-quinolinethiol with that of 8-quinolinol because it is assumed that 8-quinolinethiol exists predominantly as the zwitter ionic form in aqueous solutions,<sup>4)</sup> but that almost all 8-quinolinol exists as the neutral form.

## Experimental

**Reagents.** 8-Quinolinethiol was prepared by the method of Kealey and Freiser<sup>5)</sup> and its sodium salt by the method of Nakamura and Sekido.<sup>6)</sup> The sodium salt was purified by recrystallization three times from ethanol and dried *in vacuo*. 8-Quinolinol was also recrystallized three times from ethanol. The chloroform solution of 8-quinolinethiol was prepared as following. Into a 200 ml separatory funnel containing 10 ml of pH 4–5 buffer solution was added the required amount of sodium salt of 8-quinolinethiol under nitrogen gas, and then the resulting solution was shaken for 3 min with the aliquot of chloroform taken so as to obtain the required concentration of the reagent,  $2 \times 10^{-5}$  M (1 M = 1 mol dm<sup>-3</sup>).

**Apparatus.** Extraction was made with a Taiyo M-100N type incubator. UV and visible absorption spectra were taken with a Hitachi 124 type double beam spectrophotometer. A Hitachi-Horiba pH meter M-5 with a glass-calomel electrode pair was used.

**Procedures.** Into a 50 ml cylindrical tube containing 10 ml of  $2 \times 10^{-5}$  M 8-quinolinethiol chloroform solution was added 10 ml of the aqueous solution, which was adjusted to the desired pH by a buffer solution and to 0.1 ionic strength by the addition of sodium perchlorate. After shaking at 25 °C until the equilibrium was attained, two phases were separated with a centrifuge for 2 min, then 5 ml of the aqueous phase was pipetted out and its pH was measured. Concentrations of the reagent in the chloroform phase and/or the aqueous phase were spectrophotometrically obtained and distribution ratios were calculated.

## Results and Discussion

8-Quinolinethiol exists as both the neutral form, HR, and the zwitter ionic form, H<sup>+</sup>R<sup>-</sup>, in a solution. Therefore, acid dissociation phenomena of 8-quinolinethiol are represented by the following explanatory Scheme 1. The relationships between the various equilibrium constants in Scheme 1 and macroscopic acid dissociation constants, called  $K_{a1}$  and  $K_{a2}$ , are as follows:

$$K_{a1} = K_{aA} + K_{aB}, \quad (1)$$

$$\frac{1}{K_{a2}} = \frac{1}{K_{aC}} + \frac{1}{K_{aD}}, \quad (2)$$

$$K_t = \frac{[\text{Zwitter ion}]}{[\text{Neutral}]} = \frac{[\text{H}^+\text{R}^-]}{[\text{HR}]} = \frac{K_{aA}}{K_{aB}} = \frac{K_{aD}}{K_{aC}}. \quad (3)$$

As it is expected that the species existing in the organic phase is only HR, the distribution ratio of the reagent,  $D_R$ , is represented by Eq. 4:

$$D_R = \frac{[\text{HR}]_o}{[\text{H}_2\text{R}^+] + [\text{HR}] + [\text{H}^+\text{R}^-] + [\text{R}^-]}, \quad (4)$$

where the subscript *o* represents the concentration in the organic phase. The simplifications of Eq. 4 on the lower pH (<2) and the higher pH (>8) media and the appropriate substitutions give Eqs. 5 and 6 respectively:

$$D_R = \frac{[\text{HR}]_o}{[\text{H}_2\text{R}^+] + [\text{HR}] + [\text{H}^+\text{R}^-]} = \frac{K_{a1}K_{DR}}{(1 + K_t)\{[\text{H}^+] + K_{a1}\}}, \quad (5)$$

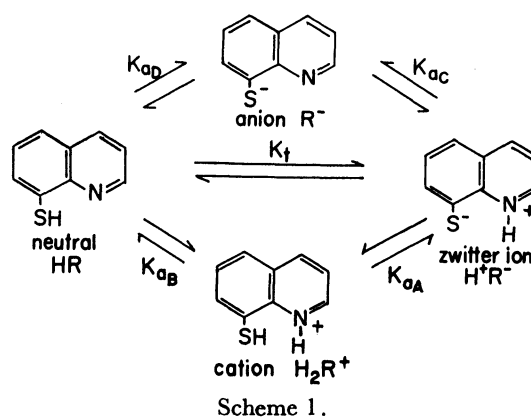
$$D_R = \frac{[\text{HR}]_o}{[\text{HR}] + [\text{H}^+\text{R}^-] + [\text{R}^-]} = \frac{[\text{H}^+]K_{DR}}{(1 + K_t)\{[\text{H}^+] + K_{a2}\}}, \quad (6)$$

where  $K_{DR}$  is the distribution coefficient of the reagent, defined as  $K_{DR} = [\text{HR}]_o / [\text{HR}]$ . Moreover, on the condition of  $[\text{H}^+] \gg K_{a1}$ , and  $[\text{H}^+] \ll K_{a2}$ , Eqs. 5 and 6 are simplified and expressed in logarithmic forms as Eqs. 7 and 8, respectively.

$$\log D_R = \log \frac{K_{DR}}{1 + K_t} - pK_{a1} + \text{pH} \quad (7)$$

$$\log D_R = \log \frac{K_{DR}}{1 + K_t} + pK_{a2} - \text{pH} \quad (8)$$

The plots of  $\log D_R$  for 8-quinolinethiol as a function of pH are shown in Fig. 1 with those for 8-quinolinol. A horizontal portion of maximum  $\log D_R$  for 8-quinolinethiol,  $\log D_{R\max} = 2.65$ , appears in the range of pH 4 to 7, which indicates that the reagent exists completely as HR and H<sup>+</sup>R<sup>-</sup>. As  $K_{DR}$  is related with  $D_{R\max}$  by Eq. 9,  $K_{DR} = 2140$  is obtained by substituting the values  $D_{R\max} = 10^{2.65} = 447$  and  $K_t = 3.83$  in Eq. 9. A linear



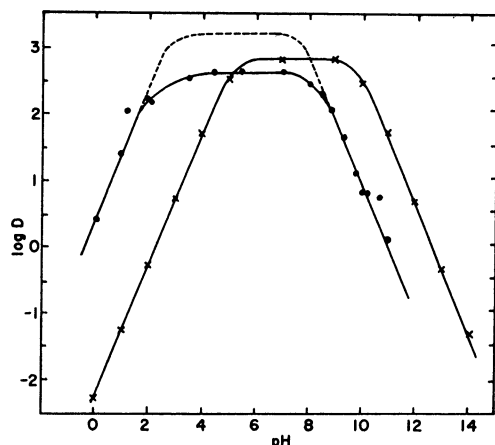


Fig. 1. Effects of pH on distribution of 8-quinolinethiol and 8-quinolinol between chloroform and aqueous solution.  
 —•—: 8-Quinolinethiol, —x—: 8-quinolinol, —: if all 8-quinolinethiol were the neutral form.

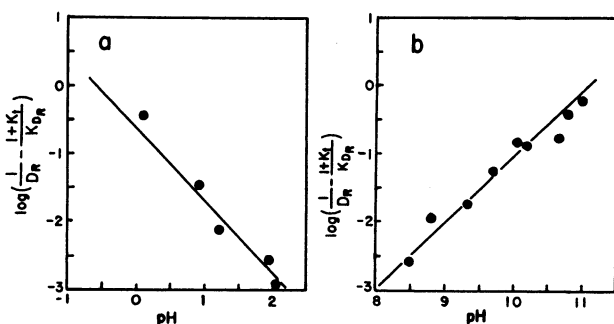


Fig. 2. Plots of  $\log \{(1/D_R) - (1 + K_t)/K_{DR}\}$  vs. pH.  
 (a) In acidic region and (b) in alkaline region.

$$K_{DR} = D_{R_{max}}(1 + K_t) \quad (9)$$

portion with the slope of +1 in the range of pH -0.5 to 1.5 and that with the slope of -1 in the range of pH 8.5 to 11 are found as expected from Eqs. 7 and 8, respectively, and  $pK_{a1}=2.05$  and  $pK_{a3}=8.39$  were obtained from the pH values at  $\log D_R=0$ . As was expected from the values of  $pK_{a1}=5.13$  and  $pK_{a3}=9.89$  for 8-quinolinol,<sup>6)</sup> 8-quinolinethiol is extracted into chloroform in the lower pH range than that which 8-quinolinol is extracted. Although  $K_{DR}(2140)$  for 8-quinolinethiol is much larger than  $K_{DR}(772)$  for 8-quinolinol, the horizontal portion of the maximum distribution ratio for 8-quinolinethiol is lower than that for 8-quinolinol, because about 78% of 8-quinolinethiol

TABLE 1. EQUILIBRIUM CONSTANTS FOR 8-QUINOLINETHIOL

	Present work	Previous work
$K_t$		3.8 <sup>a)</sup>
$pK_{a1}$	2.05	2.0 <sup>b)</sup>
$pK_{a2}$	2.15	2.10
$pK_{a3}$	2.73	2.68
$pK_{a4}$	8.39	8.36 <sup>c)</sup>
$pK_{a5}$	8.29	8.26 <sup>c)</sup>
$pK_{a6}$	7.72	7.68 <sup>c)</sup>

a) Ref. 3. b) Ref. 7. c) Ref. 8.

in aqueous solution exists as the zwitter ionic form, while almost all 8-quinolinol exists as the neutral form.<sup>4)</sup> If all of 8-quinolinethiol exists as the neutral form, the horizontal portion of the  $\log D$ -pH curves will be higher than that for 8-quinolinol, as shown on the broken line in Fig. 1. Equations 10 and 11 are derived from Eqs. 5 and 6, respectively.

$$\log \left( \frac{1}{D_R} - \frac{1 + K_t}{K_{DR}} \right) = -pH - \log K_{DR} + pK_{a3} \quad (10)$$

$$\log \left( \frac{1}{D_R} - \frac{1 + K_t}{K_{DR}} \right) = pH - \log K_{DR} - pK_{a6} \quad (11)$$

The plots of  $\log \{(1/D_R) - (1 + K_t)/K_{DR}\}$  vs. pH are shown in Figs. 2a and 2b. Two straight lines with slopes of -1 and 1 are given and  $pK_{a3}=2.73$  and  $pK_{a6}=7.72$  are obtained from the values of  $\log K_{DR}$  and of the pH on  $\log \{(1/D_R) - (1 + K_t)/K_{DR}\}=0$ . Thus, the values of  $pK_{a1}$ ,  $pK_{a2}$ ,  $pK_{a4}$ , and  $pK_{a5}$  are calculated by using Eqs. 1, 2, and 3, and these values are tabulated in Table 1 with values obtained by potentiometric and photometric methods. As shown in Table 1, these values are in fair accord with those reported previously.<sup>7,8)</sup> Such agreement confirms that 8-quinolinethiol exists predominantly as the zwitter ionic form in aqueous solutions.

## References

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