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Citation	北海道大學水産學部研究彙報, 35(1), 35-42
Issue Date	1984-03
Doc URL	https://hdl.handle.net/2115/23846
Type	departmental bulletin paper
File Information	35(1)_P35-42.pdf

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Bull. Fac. Fish. Hokkaido Univ.
35(1), 35-42. 1984.

Effect of a Quaternary Ammonium Base on the Distribution Equilibrium of 8-Hydroxyquinoline

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Abstract

Distribution equilibrium of 8-hydroxyquinoline (oxine, HA) between the aqueous and organic (1, 2-dichloroethane) phases was investigated in the presence of a quaternary ammonium base, so-called zephiramine ($Z^+ \cdot Cl^-$). In acidic solution, zephiramine has no effect on the distribution of oxine. In alkaline solution, the formation of the ion-association complex of oxinate ion (A^-) with zephiramine ion (Z^+), AZ, was observed. And, the complex was distributed between the aqueous and 1, 2-dichloroethane phases. Constants obtained were $pK_1=4.96$, $pK_2=10.01$, $\log D_{HA}=2.5$, $\log K_{AZ}=3.0$, $\log D_{AZ}=1.3$, $\log K_{ZCl}=2.7$, and $\log D_{ZCl}=0.89$, K and D being dissociation constant and distribution constant, respectively. The dissociation of oxine was apparently enhanced above pH 9.5. But, the enhancement of dissociation of ligand by a quaternary ammonium base is not reason for highly ligand-coordinated chelate formation.

Introduction

The author has discussed the behavior of a valence-saturated but coordination-unsaturated chelate which can be extracted into an inactive solvent in the presence of a quaternary ammonium base.[1-6] According to a series of their studies, the effects of a quaternary ammonium base on extraction systems have been grouped in the three categories: 1) Formation of an inactive solvent-soluble chelate by displacing the coordinated water molecule with the molecule of chelating agent.[1] 2) Formation of a highly ligand-coordinated anionic chelate which results in the formation of an ion-associated complex with the quaternary ammonium base existing in the solution.[1-4] 3) Formation of an inactive solvent-soluble chelate by displacing the water molecule with the quaternary ammonium base molecule itself.[5]

For the detailed discussion on the second category, it is necessary to elucidate the equilibrium of species of a ligand in the presence of a quaternary ammonium base. In this paper, the equilibrium of 8-hydroxyquinoline (oxine) was investigated in the presence of tetradecyldimethylbenzylammonium chloride, so-called zephiramine ($Z^+ \cdot Cl^-$).

The following symbols are used:

[ ]; concentration in the aqueous phase
$[\ ]_{org}$; concentration in the organic phase
HA ; oxine molecule
H_2A^+ ; oxinium ion
A^- ; oxinate ion

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Z^+ ; zephiramine ion
AZ ; ion-association complex of oxinate ion and zephiramine ion
K_1 ; dissociation constant of H_2A^+
K_2 ; dissociation constant of HA
K_{AZ} ; dissociation constant of AZ
D_{HA} ; distribution constant of HA
D_{AZ} ; distribution constant of AZ

Experimental

Reagents

Oxine solution. (a) 1.2×10^{-3} M; dissolve 0.174 g of 8-hydroxyquinoline in 5 m*l* of hot acetic acid and diluted to 1 *l* with water. (b) 3×10^{-4} M; dissolve 0.0435 g of the reagent in 1 *l* of 1, 2-dichloroethane.

Zephiramine solution, 2×10^{-2} M. Dissolve 7.36 g of tetradecyldimethylbenzylammonium chloride in 1 *l* of water.

Buffer solution. The pH of a solution was adjusted with acetate buffer (pH< 6.2), borate buffer (6.2<pH<12) or sodium hydroxide solution (pH>12).

General procedure

Determination of dissociation constants

Each 5 m*l* of 1.2×10^{-3}M oxine solution, a buffer solution and the zephiramine solution was placed in a test tube and diluted to 20 m*l* with water. The absorption spectrum of the solution was measured against water as a reference. The dissociation constants, K_1 and K_2, were determined from the change of absorption spectra caused by variation of pH. K_{AZ} was calculated from the change of absorption spectra with variation of zephiramine concentration.

Determination of distribution constants

Twenty m*l* of 3×10^{-4} M oxine-1, 2-dichloroethane solution and 20 m*l* of an aqueous solution containing buffer and zephiramine were shaken for a definite time in a separatory funnel. After each phase was filtered through a filter paper, the absorption spectra of the organic and the aqueous phases were measured against 1,2-dichloroethane and water as references, respectively. From the changes of the absorption spectra of the organic and the aqueous phases with variations of pH and zephiramine concentration, D_{HA} and D_{AZ} were determined.

Results and Discussion

Dissociation constants and distribution constants

Because of amphoteric nature of oxine, H_2A^+ is formed in an acidic solution and A^- in an alkaline solution. The dissociation constants are expressed as follows:

$$K_1=\frac{[HA]\,[H^+]}{[H_2A^+]} \tag{1}$$

$$K_2=\frac{[A^-]\,[H^+]}{[HA]} \tag{2}$$

In acidic solution, the isosbestic point at 335 nm indicated the equilibrium was between HA and H_2A^+ (Table 1). The spectra did not change with the addition of

zephiramine whose concentrations were zero, 1×10^{-5} M, 1×10^{-4} M, and 1×10^{-3} M. Thus, the author concludes that zephiramine has no effect on the dissociation of oxine in acidic solution. As listed in Table 1, the increase of absorbance at 360 nm (H_2A) and the decrease at 310 nm (HA) indicate the transition of oxine from HA to H_2A^+. K_1 is determined by plotting log ($[HA]/[H_2A^+]$) against log $[H^+]$. The results agree with the published data[7-12] (Table 2).

When oxine was distributed between the aqueous phase and 1, 2-dichloroethane, no changes in the absorption spectra were observed in either of the phases with the addition of zephiramine. Consequently, the author concludes that zephiramine has no effect on the distribution of HA. D_{HA} is expressed by

$$D_{HA}=\frac{[HA]_{org}}{[HA]} \tag{3}$$

Introduction of equation (1) into equation (3) gives:

Table 1. Spectrophotometric data on 8-hydroxyquinoline* for the determination of K_1 andK_2.

pH	Absorbance			
	310 nm	321 nm	335 nm	360 nm
1.72	0.459	—	0.370	0.485
3.40	0.465	—	0.370	0.480
3.71	0.468	—	0.370	0.450
4.20	0.499	—	0.370	0.414
5.05	0.605	—	0.370	0.259
6.12	0.711	—	0.370	0.085
7.40	0.740	0.624	—	0.050
9.10	0.696	0.624	—	0.189
9.93	0.595	0.624	—	0.400
10.30	0.539	0.624	—	0.521
11.31	0.440	0.624	—	0.786
13.00	0.430	0.624	—	0.810

* $[HA]=3\times10^{-4}$ M.

Table 2. Values of the dissociation constants and the distribution constants.

pK_1	pK_2	log D_{HA}	log K_{AZ}	log D_{AZ}	log K_{ZCl}	log D_{ZCl}	Ref.
4.5	9.7						7
5.09	9.82	2.86					8
4.93	9.71						9
4.88	9.89						10
4.910	9.814						11
5.004	9.658	2.66					12
4.96	10.01	2.5	3.0	1.3	2.7*	0.89*	This work

* Ref. 5.

Table 3. Spectrophotometric data on 8-hydroxyquinoline* for the determination of D_{HA}.

pH	Absorbance	
	360 nm of aqueous phase	310 nm of organic phase
0.1 N HCl	0.510	0.000
1.51	0.432	0.080
2.00	0.343	0.250
2.50	0.240	0.400
2.90	0.175	0.510
3.00	0.154	0.536
4.95	0.020	0.745
7.01	0.020	0.745

* $[HA]=3\times10^{-4}$ M.

$$K_1 \cdot D_{HA}=\frac{[HA]_{org}[H^+]}{[H_2A^+]} \quad (4)$$

$[HA]_{org}$ and $[H_2A^+]$ were determined by absorbances at 310 nm in the organic phase and 360 nm in the aqueous phase (Table 3), and D_{HA} is calculated (Table 2).

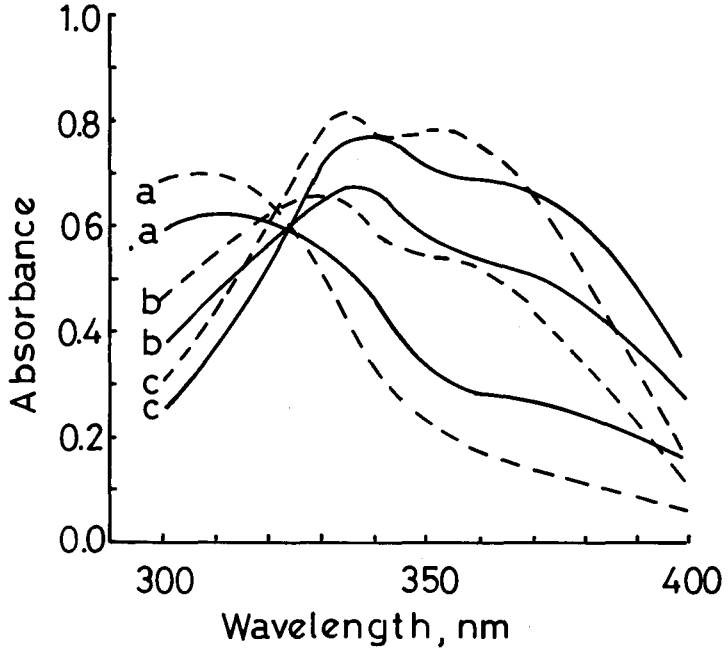


Fig. 1. Absorption spectra in alkaline solution in the absence and presence of zephiramine. ····· $[Z]=0$ and —— $[Z]=1\times10^{-3}$ M; pH=(a) 9.10, (b) 10.30 and (c) 12.01; $[HA]=3\times10^{-4}$ M.

In alkaline solution, the increase of absorbance at 360 nm indicates the formation of A^- from HA with increase of pH in the absence of zephiramine (Table 1). K_2 is determined by plotting log ($[A^-]/[HA]$) against log $[H^+]$.

With the addition of zephiramine, no changes of the absorption spectra were observed in acidic solution, but changes of the absorption spectra occurred in an alkaline solution (Fig. 1). The shift of the absorption maximum to a longer wavelength indicates an interaction between A^- and zephiramine. Variations of absorbances depending on the concentration of zephiramine were investigated at pH 13 (Table 4). When the pH is over 12, total oxine concentration is assumed to equal oxinate ion concentration, and an isosbestic point at 370 nm suggests the following equilibrium (Fig. 1-c):

$$A^- + Z^+ \Longleftrightarrow AZ, \qquad K_{AZ} = \frac{[A^-]\,[Z^+]}{[AZ]} \tag{5}$$

In the presence of zephiramine over 4×10^{-3} M, all of the oxinate ion is supposed to combine with zephiramine. Molar absorption coefficients of the ion-association complex and oxinate ion are 2.2×10^3 and 2.7×10^3 at 360 nm, respectively. K_{AZ} is calculated by plotting log ($[A^-]/[AZ]$) against log $[Z^+]$ by using the spectrophotometric data. As shown in Fig. 2, the ion-association complex, AZ, is distributed between the two phases. The distribution constant of AZ is given by

$$D_{AZ} = \frac{[AZ]_{org}}{[AZ]} \tag{6}$$

At pH 14, the present species are A^-, AZ and Z^+ in both phases. Therefore, introduction of equation (5) into equation (6) gives:

Table 4. Spectrophotometric data at pH 13 for the determination of K_{AZ}.

HA 10^{-4} M	Z 10^{-3} M	Absorbance	
		360 nm	370 nm
0.6	0	0.168	0.142
0.6	1	0.141	0.142
1.2	0	0.333	0.290
1.2	1	0.299	0.290
1.8	0	0.485	0.410
1.8	1	0.429	0.410
2.4	0	0.645	0.564
2.4	1	0.575	0.564
3.0	0	0.795	0.700
3.0	0.1	0.790	0.700
3.0	0.5	0.755	0.700
3.0	1	0.714	0.700
3.0	3	0.676	0.700
3.0	4	0.672	0.700
3.0	5	0.672	0.700

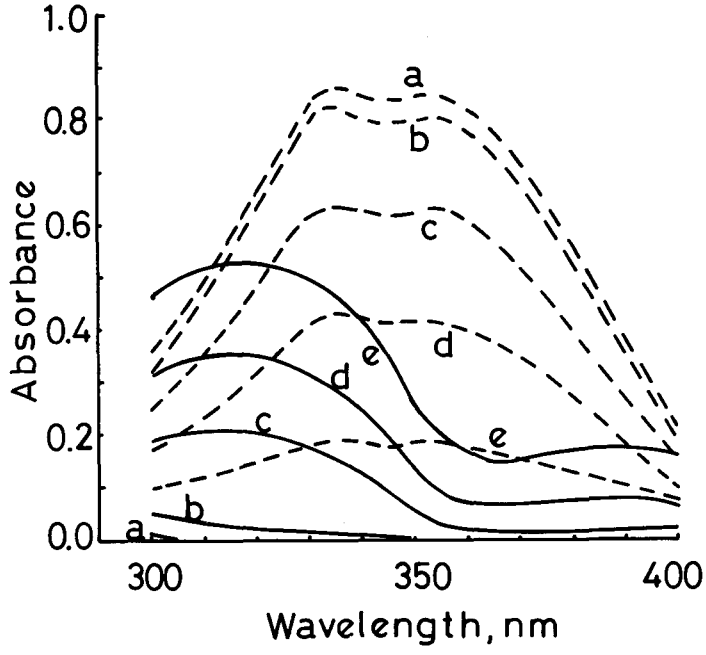


Fig. 2. Absorption spectra at pH 14 in the aqueous and the organic phases. ------ Aqueous phase and —— organic phase; [Z]=(a) 0, (b) 1×10^{-5} M, (c) 1×10^{-4} M, (d) 2×10^{-4} M, and (e) 5×10^{-4} M and 1×10^{-3} M; [HA]=3×10^{-4} M.

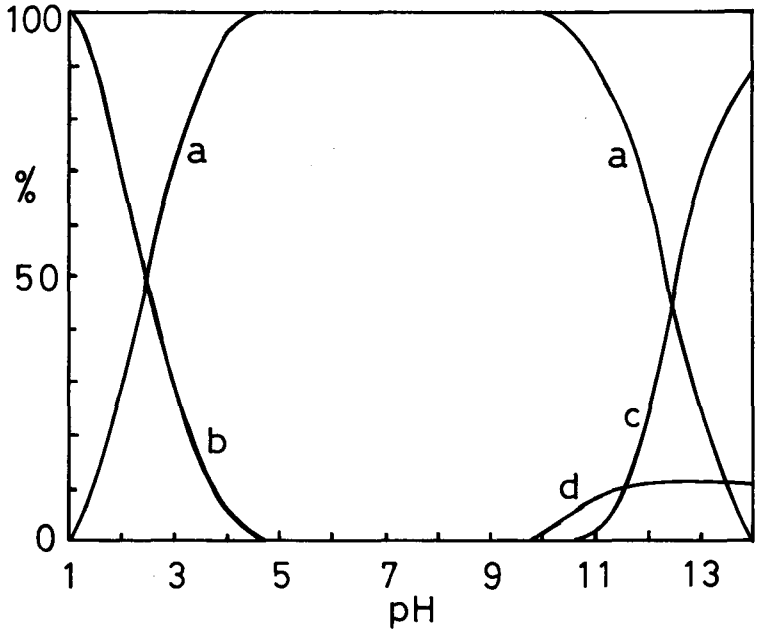


Fig. 3. Distribution of 8-hydroxyquinoline in the presence of zephiramine. [HA]=1×10^{-2} M, and [Z]=1×10^{-3} M; (a) $[HA]_{org}$, (b) $[H_2A^+]_{aq}$, (c) $[A^-]_{aq}$, and (d) $[AZ]_{org}$.

$$\frac{D_{AZ}}{K_{AZ}} = \frac{[AZ]_{org}}{[A^-][Z^+]} \tag{7}$$

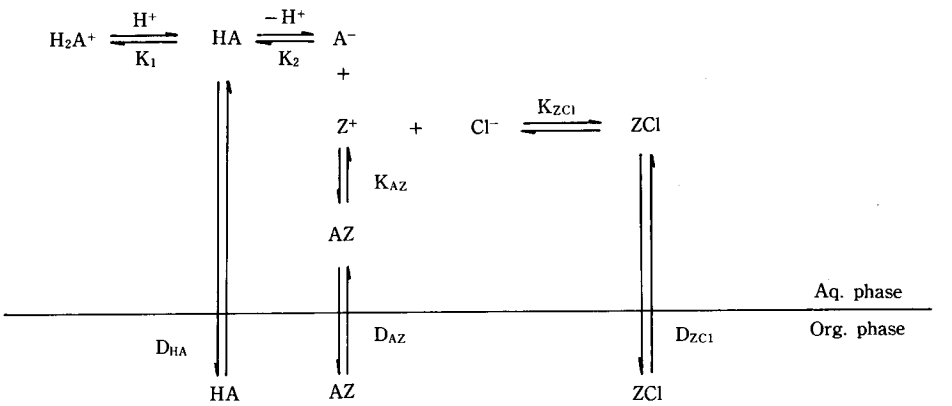
The equation (7) is rewritten by using $[A^-]$ and total concentrations of oxine and zephiramine as follows:

$$\frac{D_{AZ}}{K_{AZ}} = \frac{[HA]_T - [A^-]}{[A^-]([Z]_T + [A^-] - [HA]_T)} \tag{8}$$

D_{AZ} is determined by using total concentrations of zephiramine and oxine, oxinate ion concentration obtained spectrophotometrically and the value of K_{AZ} obtained above (Table 2).

Formation of a highly ligand-coordinated complex

The scheme of distribution of oxine in the presence of zephiramine is as follows:



The equilibrium diagram is shown in Fig. 3. By formation of AZ, the dissociation of HA to A^- is apparently enhanced above pH 9.5. Nishida[13] and Kohara[14] stated that the cause for formation of a highly ligand-coordinated complex is the enhancement of dissociation of chelating agent by a quaternary ammonium base. But their studies can not explain the extraction of oxinates, because the highly ligand-coordinated oxinate is formed and extracted below pH 9.5.[2,4] The author proposes that the enhancement of dissociation of ligand by a quaternary ammonium base is not a reason for highly ligand-coordinated chelate formation. As to the last category of extraction systems, the authors have reported[5,6] that zephiramine adducts to the valence-saturated but coordination-unsaturated chelate by partial or full replacement of the coordinated water molecules or their protons with zephiramine. It may be concluded that this peculiar effect of a quaternary ammonium base makes the formation of highly ligand-coordinated metal chelate, easy. If the adduct force of zephiramine on the ordinary chelate is stronger than that of a ligand, the highly ligand-coordinated chelate is not formed, and the opposite case, the highly ligand-coordinated chelate is formed.

Acknowledgements

I would like to thank emeritus Prof. M. Nishimura for his advice and discussions.

I am also very grateful to Dr. S. Tsunogai and the members of the Laboratory of Analytical Chemistry of this faculty for their valuable discussions.

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