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The Effect of Adduct Formation on the Distribution of Bis(8-quinolinolo) Zinc(II) between Nonaqueous Solvents

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NOTE

The Effect of Adduct Formation on the Distribution of Bis(8-quinolinolo) Zinc(II) between Nonaqueous Solvents

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Abstract

This investigation concerns the formation of adducts between bis(8-quinolinolo) zinc(II) and several nitrogen bases, and the effect of adduct formation on the distribution of zinc between two nonaqueous solvents, nitromethane and 1-decanol. Pyridine and 4-isopropylpyridine formed adducts with the zinc-8-quinolinol chelate in nitromethane. The addition of the nitrogen bases enhanced the distribution of zinc into nitromethane coincident with the adduct formation. The influence of the addition of nitrogen base on the distribution of zinc indicated that dibutyl amine forms a 1 : 1 adduct with the zinc-8-quinolinol chelate in 1-decanol.

INTRODUCTION

Bis(8-quinolinolo) zinc(II) ($ZnOx_2$) forms adducts in a variety of solvents. Schweitzer et al. (*1*) made an extensive study of adduct formation in 10 different solvents and found that the adducts ranged from 2 molecules of water in nonpolar hexane to 2 molecules of solvent in 1-butanol. The species were identified by varying the pH and reagent concentration and observing the effect on the distribution ratios of the chelates between water and an inert solvent. Chou and Freiser (*2*) observed adduct formation with nitrogen bases by similar methods. In a previous study the authors used two immiscible organic solvents (nitromethane/1-decanol) to

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study the effect of small amounts of water on the distribution of several metal oxinates (*3*).

This study was undertaken to determine whether zinc oxinate would form adducts with several nitrogen bases in either nitromethane or 1-decanol, and, if so, what effect the adduct formation would have on the distribution of zinc between these two solvents. The formation of $ZnOx_2$ adducts with pyridine and 4-isopropylpyridine in nitromethane and the effect of the adduct formation on zinc distribution is described.

EXPERIMENTAL

Chemicals

The preparation of the zinc-8-quinolinol chelate has been previously described (*3*). The purity of the complex was verified by DTA and CHN analysis. 1-Decanol and nitromethane were purified by methods described elsewhere (*4*). Other chemicals were reagent grade.

Apparatus and Methods

UV-Visible Spectrophotometer. All spectrophotometric data were obtained with a Beckman Model DB recording spectrophotometer equipped with matched 1 cm silica cells.

Atomic Absorption Spectrophotometer. A Jarrell-Ash model 82–360 Ebert-mounted 0.5 m grating monochrometer equipped with Jarrell-Ash electronics, including a 90 H2 mechanical chopper, ac amplifier, Sargent Model S-72150 recorder, and a 1P28 photomultiplier detector, was used. The sampling system was a Beckman large bore turbulent flow burner. The spectral source was a Westinghouse Model WL 22811 zinc hollow-cathode.

Gas Chromatograph. A Micro Tek 2500R chromatograph equipped with a thermal conductivity detector was used for chromatographic measurements. A Sargent SR (1 mV) recorder and Disc Instruments, Inc., integrator were used to record the chromatograms and measure peak areas. Injections were made with a 10-μl Hamilton syringe equipped with a Chaney adapter.

Gas Chromatographic Columns. A 2 ft by 1/4 in. o.d. stainless steel column packed with 10% silicone gum rubber on Anakron AB was used for the determination of the distribution of the nitrogen bases between nitromethane and 1-decanol.

Procedure

The extraction procedures used for the distribution studies and the atomic absorption analysis procedures for the zinc have been described previously (*3*).

RESULTS AND DISCUSSION

Pyridine and 4-isopropylpyridine formed adducts in nitromethane but not in 1-decanol. Adduct formation was determined by the bathochromic shifts of the maximum absorbance band of zinc oxinate upon the addition of the nitrogen bases.

Adduct formation is represented as

$$Zn(Ox)_2 + xB \rightleftarrows Zn(Ox)_2 \cdot B_x \tag{1}$$

The equilibrium constant, K_f, for the reaction is

$$K_f = \frac{[ZnOx_2 \cdot B_x]}{[ZnOx_2][B]^x} \tag{2}$$

which, upon rearrangement, can be written as

$$\log \frac{[Zn(Ox)_2 \cdot B_x]}{[Zn(Ox)_2]} = x \log [B] + \log K_f \tag{3}$$

Equation (3) shows that a log-log plot of the concentration ratio of the two chelate species vs the concentration of added base should yield the number of base molecules in the adduct and the equilibrium constant of the reaction. The absorptivities of each species were determined at 378 and 400 nm. Calculation of adduct absorptivities were based on the assumption that the adduct, exclusively, was present in solution when the addition of excess base did not shift the absorption band.

Figure 1 is a log-log plot showing adduct formation over an approximate 10-fold range of base concentration. Adduct formation was insignificant at lower concentrations, and decomposition of $Zn(Ox)_2$ occurred at higher base concentrations.

The effects of the addition of varying amounts of pyridine and 4-isopropylpyridine on the distribution of $Zn(Ox)_2$ between nitromethane and 1-decanol are shown in Fig. 2. The total zinc concentration was 1.00×10^{-4} for each extraction. The zinc concentration in nitromethane increased with the addition of base. A comparison of Figs. 1 and 2 shows that the change in the distribution ratio due to the addition of each base coincides with adduct formation in nitromethane.

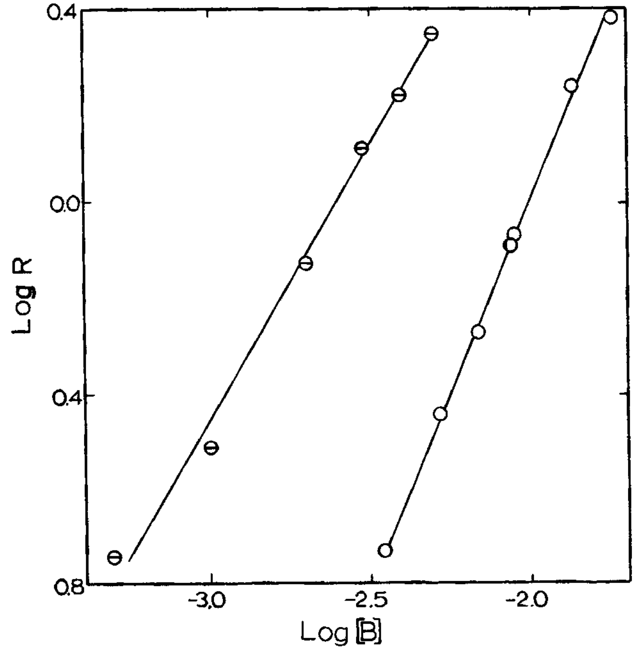

FIG. 1. Log-log plot of the ratio $[Zn(Ox)_2B_x]/Zn(Ox)_2$ vs base concentration. (○) Pyridine; (⊖) 4-isopropylpyridine.

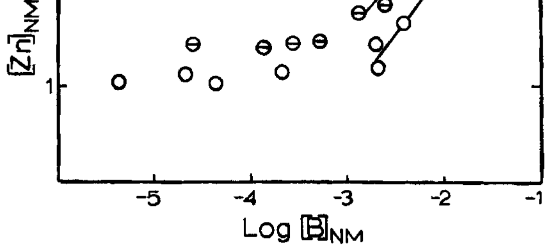

FIG. 2. Plot of zinc concentration vs the log of base concentration for the distribution of $Zn(Ox)_2$ between nitromethane (NM) and 1-decanol. (○) Pyridine; (⊖) 4-isopropylpyridine.

Regression analysis of the spectrophotometric data (Fig. 1) and extraction data (Fig. 2) resulted in the slopes listed in Table 1. Although the treatment of the extraction data is empirical, the change in zinc distribution between the two nonaqueous solvents appears to indicate the molecular ratio of base to $Zn(Ox)_2$. The direct spectrophotometirc determination of adduct formation and the change in the zinc distribution with added base indicate a higher base to chelate ratio for pyridine than for 4-isopropylpyridine.

The effect on zinc distribution of a stronger base, dibutylamine (DBA), is shown in Fig. 3. DBA was unique in that the free base is totally extracted into 1-decanol. Direct spectrophotometric determination of adduct

TABLE 1

Comparison of Spectrophotometric and Extraction Data

Base	Log R[a]/log B	$[Zn]_{NM}$[b] × 10^5/log B
Pyridine	1.64 ± 0.04	1.23 ± 0.09
4-Isopropylpyridine	1.12 ± 0.06	0.97 ± 0.09

[a] R is the ratio of molar concentrations of the $Zn(Ox)_2$-base adduct to $Zn(Ox)_2$ (Eq. 3).

[b] $[Zn]_{NM}$ is the equilibrium Zn concentration in nitromethane after extraction with 1-decanol.

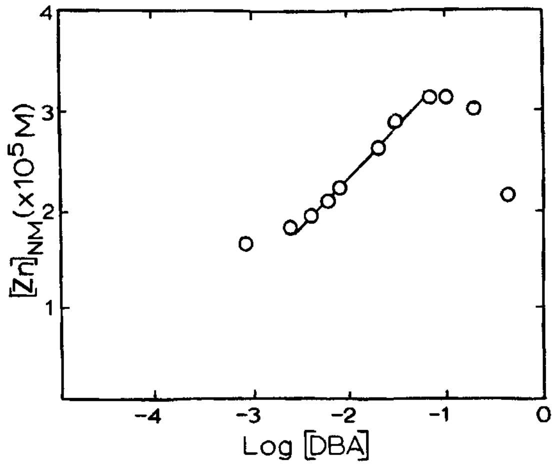

FIG. 3. Plot of zinc concentration vs log [DBA] for the distribution of $Zn(Ox)_2$ between nitromethane and 1-decanol.

formation in 1-decanol was not possible because of the background absorption of DBA. Figure 3 shows that DBA also enhances the extraction of zinc into nitromethane. Regression analysis over the linear range shown in Fig. 3 resulted in a slope of 1.06 ± 0.06, which indicates the formation of a 1 : 1 adduct in 1-decanol.

The enhancement of the distribution of zinc into nitromethane by each of the three nitrogen bases is due to the replacement of one 1-decanol molecule with one molecule of base. Prior to the addition of base, the zinc oxinate species in 1-decanol (D) or in nitromethane saturated with 1-decanol is $Zn(Ox)_2 \cdot D_2$.

The formation of an adduct,

$$Zn(Ox)_2 \cdot (D)_2 + B \rightleftarrows Zn(Ox)_2 \cdot D \cdot B + D$$

results in a species that partitions more favorably into nitromethane.

The influence of pyridine and 4-isopropylpyridine on the distribution of zinc coincides with spectrophotometric evidence of adduct formation in nitromethane. The effect of DBA on zinc distribution is indicative of adduct formation in a system that could not be observed spectrophotometrically.

Acknowledgment

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