Metallosurfactants of Cu(II) and Fe(III) Complexes as Catalysts for the Destruction of Paraoxon

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ABSTRACT: Two micellized Cu(II) and Fe(III) ion complexes of octadecyl diethylene tri-1-amide are used as nucleophilic reagents in the cleavage of the phosphate ester paraoxon. These complexes form metallomicelles, which coordinate with the paraoxon phosphorous (chemically similar to the nerve agent sarin). Association colloids (e.g., micelles, microemulsions, or vesicles) increase the rate of the nucleophilic reaction. Hence, it is reasonable to examine the hydrolysis process of paraoxon in aqueous metallomicelles. As micelles form and incorporate reactants, the rate constant should change; therefore, the rate constant should be affected by the critical micelle concentrations (CMC) of Cu(II) and Fe(III) complexes. The concentrations tested were the CMC value, two values lower, and two values higher. The CMC was found to be the most reactive concentration. The kinetic data (half-life times) for paraoxon degradation were 6.1 and 28.8 min in the presence of the Cu(II) and the Fe(III) metallomicelle complex, respectively. The stability constants of the metal complexes showed large values that denoted significant stability for both complexes.

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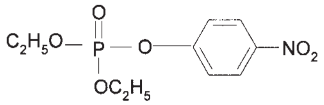
KEY WORDS: Catalytic destruction, metallosurfactants, paraoxon, stability constant.

Metallomicelles have been reported to catalyze the hydrolysis of phosphate esters because of their enzyme-like efficiency (1,2). Transition metal ions play a key role in the hydrolytic activity of a variety of enzymes, and great effort has been devoted to designing metallocomplexes containing nucleophilic groups capable of the activity of the added nucleophilic species (3–6).

The critical feature of the catalytic process is the formation of a ternary complex involving a ligand surfactant, a metal ion, and the phosphorous compound in which the metal cation activates the hydroxyl nucleophile in a pseudo-intermolecular process (7–9).

Previous investigations of metallosurfactants have used the phospholytic hydrolysis of some pesticides such as paraoxon (Scheme 1) as models or simulants of the chemical warfare agent sarin (10–16). These metallosurfactants have included Cu(II) (7,10); Zn(II) (3,7–9); Ni(II) (3,7–9,17); Ru(II) (18,19); and metallomicelle layers of Cu(II), Fe(III) (20), Co(II), and Cr(III) (21). The latter complexes were recently studied for the hydrolysis of malathion and paraoxon. Along these lines, efforts have been continued to synthesize two novel metallosurfactant complexes formed from octadecyl diethylene, tri-1-amide, and the metal ions of Cu(II) or Fe(III), to be investigated as estrolytic agents toward paraoxon.



o,o-Diethyl *p*-nitrophenyl phosphate (paraoxon)

SCHEME 1

EXPERIMENTAL PROCEDURES

Melting points were uncorrected. Infrared spectra were recorded *via* a Fourier transform infrared (FTIR) ATI Mattson Genesis FTIR^{TM} spectrophotometer. Microelemental analysis was performed with a Vario EL, Elementar instrument (National Research Center, Cairo, Egypt). Surface tension measurements (20) were performed with a du Noüy ring tensiometer (type 8451; Krüss, Hamburg, Germany). Kinetic traces were recorded with a Model 6505 ultraviolet/visible spectrophotometer (Jenway, Dunmow, Essex, England). Mass spectroscopy was carried out using an HP Model MS-5988 mass spectrometer (Palo Alto, CA).

Chemicals. Diethylene triamine and oleic acid were obtained from Ridel-deHaën Co. (Seelze, Germany). Paraoxon was from Greyhound Chromatography & Allied Chemicals (Birkenhead, Merseyside, United Kingdom). Anhydrous cupric chloride and anhydrous ferric chloride were from Aldrich Chemical Co. Ltd. (Milwaukee, WI).

*Synthesis of ligand **I**.* Equimolecular proportions of diethylene triamine and oleic acid were heated at 150°C in a three-necked flask with continuous stirring until the theoretical amount of water was collected (22). The resulting product was recrystallized from ethanol to give the proper octadecyl diethylene tri-1-amide (**I**) as a yellowish paste in 85–90% yield.

General procedure for the synthesis of complexes. Stoichiometric amounts of ligand **I** and the metal chloride of Cu(II) or Fe(III) were dissolved in an ethanol solution. The mixture was heated

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Abbreviations: CMC, critical micelle concentration; FTIR, Fourier transform infrared.

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at 80–90°C for 1 h and then cooled slowly to room temperature. Recrystallization was carried out, and the complex obtained was washed first with an ethanol/ether mixture (1:10) and then with ether (21,22). The resulting crystals were dried to give the proper complex, (**A**) for Cu(II) as deep blue crystals or (**B**) for Fe(III) as brown crystals, in 90–95% or 70–75% yield, respectively.

Stability constant determinations of complexes ***A*** *and* ***B***. The continuous variation method is a simple and widely used method for spectrophotometric determination of the metal stability constant (23). Stock solutions of 0.01 M ligand **I** and anhydrous $FeCl_3$ in dimethyl formamide were prepared. The ligand solution was dropped into a 10-mL volumetric flask to which a $CuCl_2$ or $FeCl_3$ solution (9–1 mL) was added. The absorbance of the solutions was measured at 275 and 290 nm for the Cu(II) and the Fe(III) complex, respectively.

Kinetic hydrolysis of paraoxon. All reactions were carried out in a phosphate buffer system prepared using 200 mL of 0.1 M $Na_2HPO_4 \cdot 12H_2O$ and 1.0 mL of 0.1 N HCl and adjusted to pH 8. Kinetic measurements were taken spectrophotometrically at 25°C. The reaction was initiated by adding 0.0015, 0.004, 0.0065, 0.008, and 0.01% of paraoxon in purified benzene (stock solution 0.1%) to 0.015, 0.04, 0.065, 0.08, and 0.1% of complex **A**, or 0.008% of paraoxon to 0.08% of complex **B**. The rates of hydrolysis were followed by monitoring the release of *p*-nitrophenolate in the presence of Na_2CO_3 at 400 nm as the reaction proceeded (7,14–17).

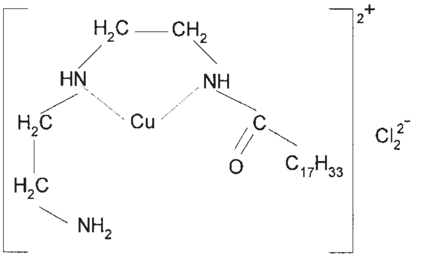
RESULTS AND DISCUSSION

Synthesis and complexation of ligand ***I***. The chemical structure of ligand **I** and its complexes, **A** and **B**, may be denoted as shown in Scheme 2.

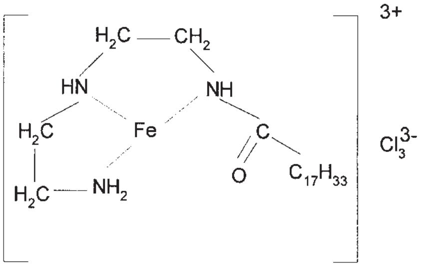
The structural elucidation of the products was confirmed as follows: (i) Microelemental analyses of the ligand and its complexes are shown in Table 1. (ii) Infrared spectra of the prepared compounds are shown in Table 2. (iii) The mass spectrum of compound **A** is given in Figure 1 along with its fragmentation patterns.

$H_2NCH_2CH_2N(H)CH_2CH_2N(H)COC_{17}H_{33}$

(**I**)



(**A**) Octadecyl diethylene 1,4 diamine 7-amide cuprate chloride



(**B**) Octadecyl diethylene 1,4-diamine 7-amide ferrate chloride

SCHEME 2

Stability constant determination for complexes ***A*** *and* ***B***. Spectrophotometric investigations of the Cu and Fe complexes were performed to identify the formation and composition of the most stable complex possible in solution. However, the solution mixture of Cu(II) or Fe(III) and ligand **I**, at pH 8, was found to exhibit strong absorption bands at 275 and at 290 for the Cu(II) and Fe(III) complexes, respectively. This is presumably characteristic of the complexes. The corresponding results were represented graphically as a plot of the mole fraction of ligand **I** in the mixture vs. absorbance, and gave a triangular-shaped curve (23). The values of the stability constant, K_{stab}, for complexes **A** and **B** were 0.64×10^6 and 0.41×10^6, respectively. The higher the value of K_{stab}, the stronger and more stable was the complex formed. Moreover, the experiment using the continuous variation method indicated the presence of a 1:1 ligand/metal ion complex (23).

Surface tension measurement. Complexes **A** and **B** were long-chain chelates of Cu(II) and Fe(III), which formed metallomicelles when dissolved in water. The critical micelle concentrations (CMC; mol/L) of complexes **A** and **B** were 2.3×10^{-3} and 1.5×10^{-3}, respectively. The concentrations used in the hydrolysis process are recorded in Table 3.

Destruction of paraoxon. The appropriate kinetic data are presented in Table 3 and in Figures 2 and 3.

TABLE 1
Microelemental Analyses of Ligand I and Complexes A and B

	C (%)		H (%)		N (%)		Cl (%)		Cu, Fe (%)	
Compound	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
I	71.94	71.01	12.26	12.11	11.44	11.96				
A	52.64	52.98	8.97	8.81	8.37	8.51	14.16	14.22	12.67	12.77
B	49.89	50.12	8.50	8.87	7.94	8.21	20.12	20.44	10.55	11.01

TABLE 2
Infrared Absorption Frequencies for Characteristic Bands of Ligand I and Complexes A and B

	Band							
Compound	$-CH_3$	$-CH_2$	$N-CH_2-$	$-NH_2$	–NH	–CONH–	Cu–N	Fe–N
I	1450	2950–1880	2800	3450–3340	1870	1650		
A	1456	2932–2852	2780	3556	1937	1652	446	
B	1456	3003–2931	2840	3381	1868	1636		409

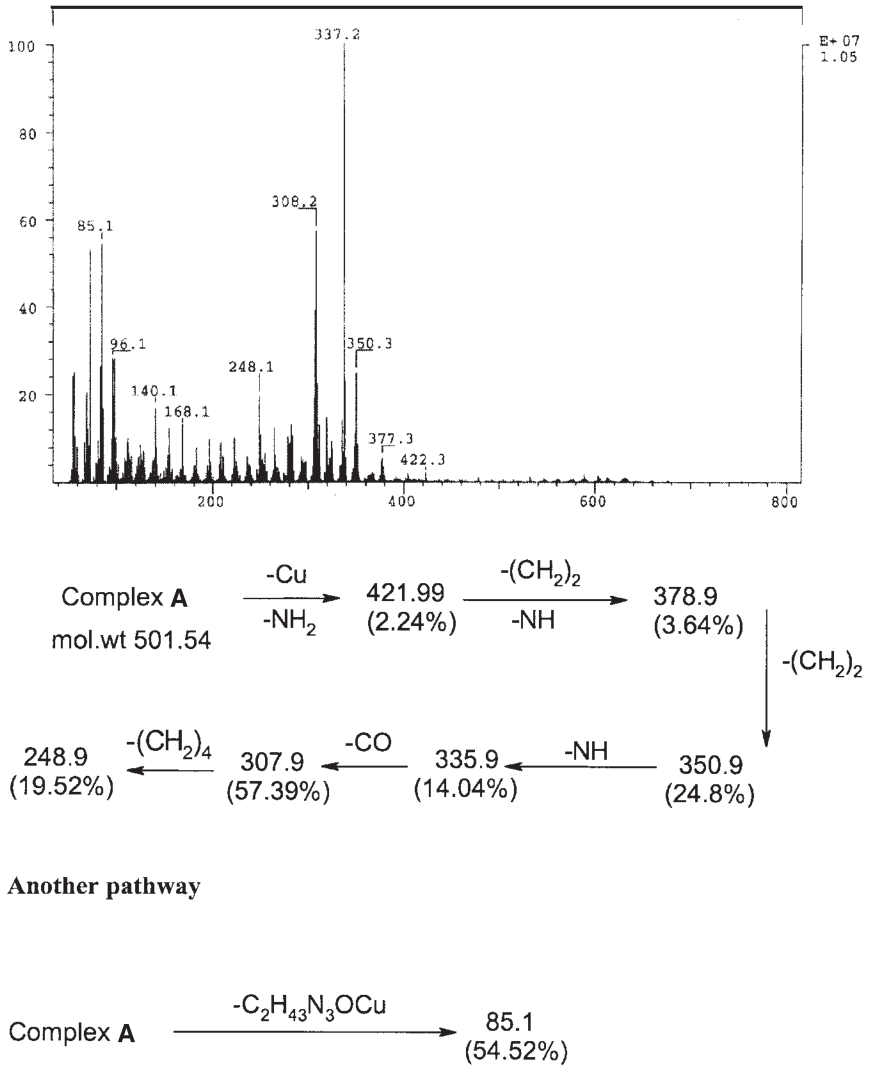


FIG. 1. Mass spectrum and fragmentation patterns of complex A.

The kinetic data in Table 3 show that the observed rate constant, K_{obs}, was that at the CMC value for the metallomicellar system of Cu(II). This was likely associated with micellization. However, one should consider that because of their amphiphilic character, they aggregate in water-forming metallomicelles having a Stern region filled with cupric ions (1).

Metallomicelles are well known to accelerate the hydrolysis rate of the phosphate ester, where they increase the pH at the water–aggregate interface in which the reaction occurs (2). The electrostatic interaction between the cationic centers in the metallosurfactants aggregates, and P=O in paraoxon might activate the intermolecular nucleophilic attack of metal-bound OH on the phosphorous atom, depending on the addition–elimination mechanism, either by stabilizing a pentacoordinate phosphorus oxy anion or by enhancing the leaving group ability of the (surfactant) *p*-nitrophenolate fragment (2). The final absorbance observed for *p*-nitrophenolate occurred by separation from the paraoxon,

TABLE 3
Kinetic Data of the Destruction Process

Complex	Conc. × 10^{-3} (mol/L)	K_{obs} × 10^{-4} $(s^{-1})^a$	$t_{0.5}$ (min)
A	0.5	2	57.8
	1.4	3	38.5
	2.3	19	6.1
	2.9	2	57.8
	3.6	12	9.6
B	1.5	4	28.9

[a] K_{obs}, observed rate constant.

which is soluble in benzene, as a hydrolysis fragment soluble in water.

The observed rate constant for the Fe(III) complex was slower than that for the Cu(II) complex. The hydrolysis process involved nucleophilic attack of the metal-bound OH (OH formed from a water molecule that had lost a proton after binding to the metal at pH 8). Since Cu(II) ions are less electropositive than Fe(III) ions, the former showed stronger hydration (24).

Previous research (21) demonstrated that a micellar Fe(III) complex showed higher hydrolytic acceleration than a Cu(II) complex toward malathion because of the ability of the former to better coordinate with the thionate sulfur.

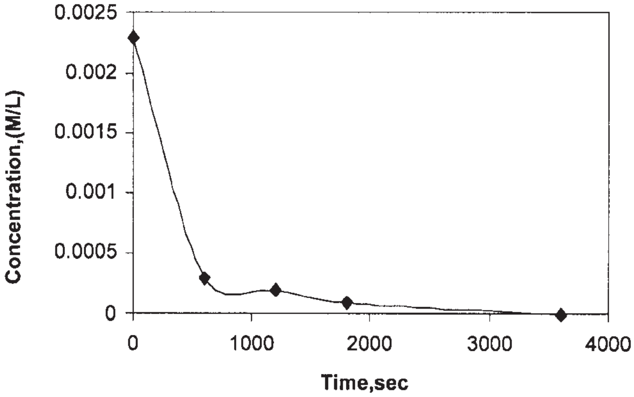


FIG. 2. Transformation of paraoxon by complex **A**.

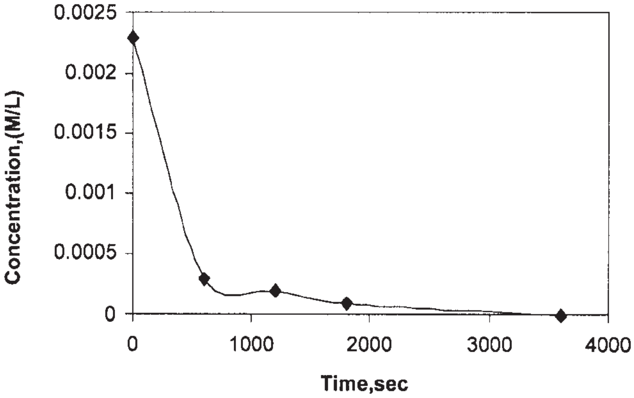


FIG. 3. Transformation of paraoxon by complex **B**.

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