Studies on the Polymerization of Acrolein Oxime. VIII. Formation of Poly(acrolein oxime)–Copper(II) Complexes and Absorption of Molecular Oxygen by the Complexes

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ABSTRACT: Acrolein oxime was polymerized under different conditions. Formation constants for poly(acrolein oxime)–copper(II) complexes were determined by applying the modified Bjerrum method. The polymers form stronger complexes than their monomeric analogues. The formation constants for polymer complexes are dependent on the oxime group content in the polymer used. An aqueous solution of polymer complexes can effectively absorb molecular oxygen. The mechanism of the absorption is considered to involve cyclic redox reaction of copper ions: a copper(II) ion is reduced by the coordinated poly(acrolein oxime) to a copper(I) ion and the resultant copper(I) ion is oxidized by oxygen to the copper(II) ion.
KEY WORDS   Poly(acrolein oxime)–Copper(II) Complex / Complexation Constants / Oxygen Absorption / Oxidation–Reduction /

Acrolein oxime (AOM) can be anionically polymerized on heating to give a polymer whose molecular weight ranges from 2000 to 3000. Poly(acrolein oxime) (PAOM) contains 1,2-addition, 1,4-addition, and two types of hydrogen transfer structures. Half of the overall structures is known to be the 1,2-addition-type of structural unit with a pendant oxime group[1]. In addition, AOM also undergoes polymerization in the presence of anionic and cationic catalysts. PAOM produced by butyllithium catalyst, compared with that obtained thermally, generally has a lower molecular weight (ca. 1000) and forms a similar proportion of the structural units.[2] On the other hand, PAOM with a low molecular weight (a few hundreds) and with a high content of oxime group could be obtained by hydrochloric acid catalyst.[3] PAOMs obtained under different conditions of polymerization differ from one another in physical properties such as solubility.

The complexation constant of PAOM with metal ions also seems to depend on the structure of the ligand. The complexation constants have been determined by Mutō et al.[4] based on the assumption that PAOM contains only structural units having the pendant oxime group. Since PAOM contains, in practice, a variety of structural units, the formation constant of the complex is measured using modified Bjerrum method[5] and considering the oxime group content.

Mixing of aqueous solutions of PAOM and copper(II) nitrate produces a complex which is capable of absorbing molecular oxygen. The absorption behavior is considered to differ from that of the solid complex. The present paper deals with the absorption of molecular oxgen by an aqueous solution of PAOM–copper(II) complexes.

EXPERIMENTAL

Materials

AOM and propionaldoxime(POM) were prepared by oximation of acrolein and propionaldehyde with hydroxylamine hydrochloride, respectively.[6] Polymers were prepared as follows: (1) A polymer (PAOM-I) was produced by thermal bulk polymerization at 60°C;[1] (2) a polymer (PAOM-II) was

produced by bulk polymerization at 30°C in the presence of butyllithium;[2] and (3) a polymer (PAOM-III) was obtained by hydrochloric acid-catalyzed polymerization at 0°C using dichloroethane as a solvent.[3]

Characterization

The number of carbon–carbon double bonds was calculated by determining the iodine value.[7] The oxime group in PAOM was determined by the Van Slyke method.[8] The molecular weight of PAOM was determined in a dimethylformamide solution at 70°C using a vapor-pressure osmometer (Hitachi Perkin-Elmer, model 115).

pH Titrations

Since PAOM is insoluble in water and soluble in acidic and basic solutions, back-tiration was performed with a Hitachi-Horiba H-5 pH meter at 20°C for constant ion strength: to an alkali solution of PAOM was added aqueous copper(II) nitrate and the solution was then titrated with nitric acid. Precipitation occurred at neutral pH value, and the precipitate dissolved again in the acidic region. When the precipitate was present, a constant pH value was attained only after a long time. All readings were taken after the pH had attained equilibrium; the pH values have been found to be identical whether the readings were made with the electrodes immersed only in the supernatant solution or in the gel phase.[9]

Manometric Measurements

The volumes of molecular oxygen absorbed by the aqueous solution of the complex were measured manometrically using a conventional Warburg apparatus.

Potential Measurements

The potential was referred to the saturated calomel electrode (SCE) using platinum wire as the cathode; the electrolyte was a solution of PAOM, copper(II) nitrate, and potassium nitrate, which was added to keep the ion strength constant.

RESULTS AND DISCUSSION

Complexation Constants of Cu(II) with PAOM

AOM was polymerized under different conditions. Table I shows the characterizations of the PAOM

Table I. Characteristics of PAOM

PAOM	% of C=C bond[a]	% of oxime group[b]	Molecular weight
PAOM-I	42.0	46.0	2100
PAOM-II	50.7	42.8	820
PAOM-III	14.6	73.8	556

[a] % of structural units having one carbon–carbon double bond per unit.
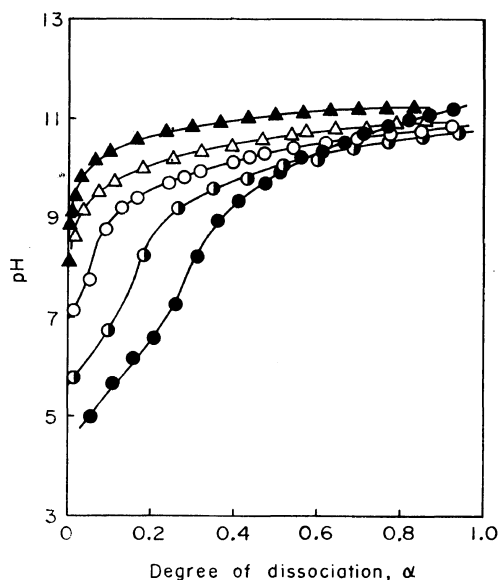[b] % of structural units having one pendant oxime group per unit.

Figure 1. pH titration of oximes: ○, [PAOM-I] = 1.04×10^{-2} mol dm^{-3}; ◑, [PAOM-II] = 1.00×10^{-2} mol dm^{-3}; ●, [PAOM-III] = 1.01×10^{-2} mol dm^{-3}; △: [AOM] = 1.02×10^{-2} mol dm^{-3}; ▲, [POM] = 1.09×10^{-2} mol dm^{-3}; $\mu = 0.1$ (KNO$_3$); temp, 20°C.

obtained. Figures 1 and 2 show the titration curves for three kinds of PAOM, AOM, and POM as a monomeric analogue, both in the presence and absence of copper(II) nitrate. The titration curve for PAOM-I is found to be analogous to that for the monomer, while PAOM-III gives an S-shaped curve. One possible explanation for these observations is that, the higher the oxime group content in PAOM is, the more favorable and stronger the nearest neighbor interaction among the closely situated oxime group becomes:
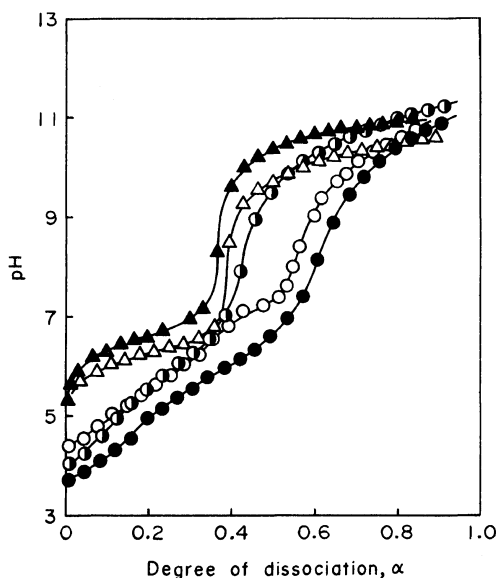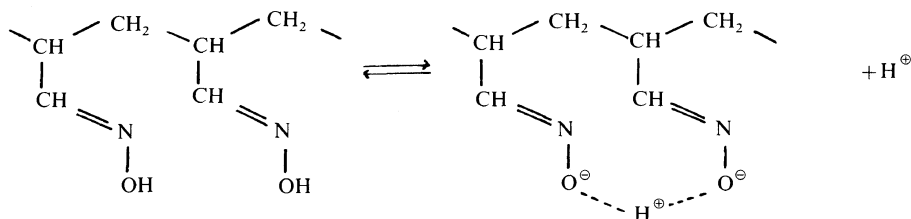
Figure 2. pH titration of oximes in the presence of copper(II) nitrate: $[Cu(NO_3)_2] = 1.69 \times 10^{-3}$ mol dm^{-3}; $\bigcirc$, [PAOM-I] $= 7.44 \times 10^{-3}$ mol dm^{-3}, $\hspace{-0.1em}\ominus\hspace{-0.1em}$, [PAOM-II] $= 7.15 \times 10^{-3}$ mol dm^{-3}, $\bullet$, [PAOM-III] $= 7.18 \times 10^{-3}$ mol dm^{-3}, $\triangle$, [AOM] $= 7.27 \times 10^{-3}$ mol dm^{-3}, $\blacktriangle$, [POM] $= 7.82 \times 10^{-3}$ mol dm^{-3}; $\mu = 0.1$ (KNO$_3$); temp, 20°C.
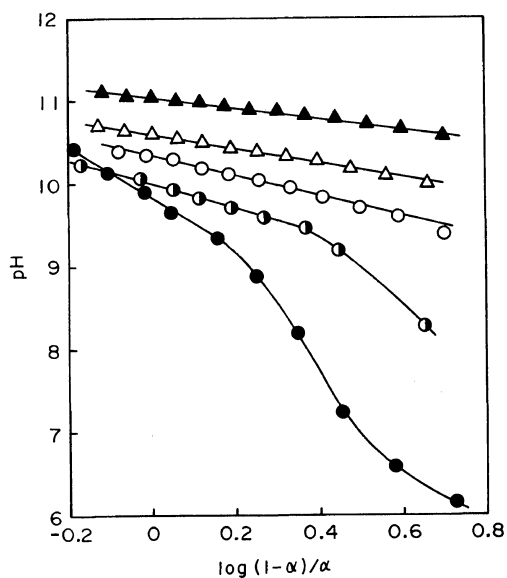
Figure 3. Henderson–Hasselbalch plots of oximes: $\bigcirc$, PAOM-I: $\hspace{-0.1em}\oplus\hspace{-0.1em}$, PAOM-II; $\bullet$, PAOM-III; $\triangle$, AOM; $\blacktriangle$, POM; $\mu = 0.1$ (KNO$_3$); temp, 20°C.

In the titration curves of PAOM in the presence of Cu(II) ions, a buffer region can be observed, which suggests that PAOM-Cu(II) complexes are formed.

The Henderson–Hasselbalch plots are given in Figures 3. Although the plots of pH $vs.\log[(1-\alpha)/\alpha]$, as expected from Figure 1, are linear over a wide range of the degree of dissociation for PAOM-I, AOM, and POM, remarkable deviations from straight lines are observed for PAOM-II and PAOM-III. A similar behavior has been observed in the case of poly(vinylamine hydrochloride).[10] Kimura et al. explained this behavior on the basis of nearest neighbor interactions among closely situated amino groups, and proposed a modified

Henderson–Hasselbalch equation. Unfortunately, since there were no modifications of the Henderson–Hasselbalch equation which were applicable to PAOM, the apparent ionization constant pK_a and the constant n had to be estimated from the linear portion of the plots. The values obtained are summarized in Table II.

Mutō et al.[4] have obtained p$K_a = 11.6$ and $n = 2.36$ for PAOM produced by thermal polymerization, based on the assumption that the polymer consists only of structural units having a pendant oxime group. The values obtained in the present work are different from their results. However, if only 1,2-addition is assumed to take place in our case, the agreement is within the experimental error. The value of pK_a and n for PAOM-I are close to those

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Table II. pK_a and n values for Henderson–Hasselbalch equation

Oxime	pK_a	n
PAOM-I	10.35	1.2
PAOM-II	10.00	1.2
PAOM-III	9.82	3.0
AOM	10.61	0.83
POM	11.07	0.71
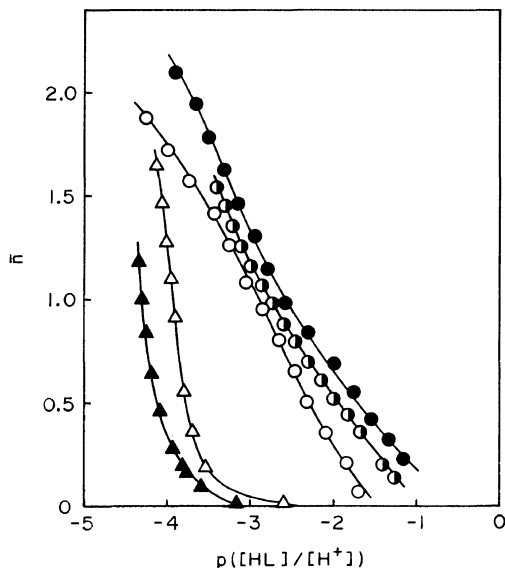
Figure 4. Modified Bjerrum plots for oxime–copper(II) system. The oxime symbols are ○, PAOM-I, ◑, PAOM-II, ●, PAOM-III, △, AOM, and ▲, POM. Temp, 20°C.

for AOM; this may be because the oxime group content is actually up to 50%, that is, a neighboring

oxime group would be rare and thus the nearest neighbor interaction would be very weak.

Figure 4 shows plots of $\bar{n}$ vs. $p([HA]/[H^+])$ for $0.01\ mol\ dm^{-3}$ oximes and $0.005\ mol\ dm^{-3}$ $Cu(NO_3)_2$ in the presence of $0.1\ mol\ dm^{-3}$ KNO_3. Complexation constants are estimated according to the treatment of Gregor et al.[5] The values obtain are summarized in Table III, in which data of Mutō et al. are also listed for comparison. Symbols shown in the table corresponding to the following reactions

$$HL \rightleftharpoons H^+ + L^+ \qquad K_a$$
$$HL + Cu^{2+} \rightleftharpoons CuL^+ + H^+ \qquad k_1$$
$$HL + CuL^+ \rightleftharpoons CuL_2 + H^+ \qquad k_2$$
$$Cu^{2+} + 2L^- \rightleftharpoons CuL_2 \qquad K'$$
$$K = k_1 \times k_2$$
$$\log K' = \log K + 2pK_a$$
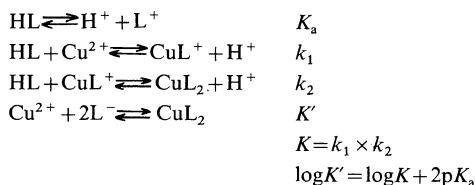
where HL and H^+ represent ligand and proton, respectively. Two metal salts, $Cu(NO_3)_2$ and $CuSo_4$, were used for AOM and POM, but complexation constants were independent of the paired anions. The table shows strikingly the enhancement of complexation in the case of polymer over that of the monomers, AOM and POM. In the case of PAOM, it is seen that changes in polymerization conditions has no effect on k_2 and K', but a slight effect on k_1. Roughly, the order of complexation of the ligands was

POM < AOM < PAOM-I < PAOM-II
< PAOM-III

The overall stability constant K' for PAOM-I is found to be two to three orders larger than that of Mutō et al. In our calculations, the oxime group

Table III. Complexation constants of copper(II) with oximes

Oxime	Metal salt	$\log k_1$	$\log k_2$	$\log K$	$\log K'$
PAOM-I	$Cu(NO_3)_2$	−2.33	−3.53	−5.86	14.84
PAOM-I[a]	''			−5.7	17.5
PAOM-II	''	−1.96	−3.58	−5.54	14.46
PAOM-III	''	−1.66	−3.53	−5.19	14.45
AOM	''	−3.78	−4.09	−7.87	13.35
AOM	$CuSO_4$	−3.85	−4.09	−7.94	13.28
POM	$Cu(NO_3)_2$	−4.10	−4.50	−8.60	13.54
POM	$CuSO_4$	−4.12	−4.46	−8.58	13.56

[a] Data of Mutō et al.[4]

content in PAOM-I was taken as 46%. If the polymer is assumed to consist only of structural units having the pendant oxime group, the K' value in the present work becomes similar to theirs.

In a polymer chelate with bivalent metals, neighboring groups along a chain are generally considered to bind the same metal ion. PAOM contains both chelating and nonchelating units, and the cheleting unit must come closer to increase the capability of complexation. This is supported by the fact that the complexation. constants for PAOM-III are greater than that for PAOM-II.

In spite of a similar content of oxime groups, the complexation constant of PAOM-II was slightly greater than that of PAOM-I. It appears that there is no difference in structures of the two PAOM except for molecular weight. It was, however, recognized that a butyl anion can make an attack upon an oxime group, i.e., the carbon–nitrogen double bond (3,4-addition) in the equimolar reaction of AOM and butyllithium, and that the subsequent elimination of lithium hydride results in the formation of ketoxime.[11] Therefore, there may be a slight difference in the structures of the two PAOM. Though an increase in the molecular weight results in an increased number of neighboring groups for a homopolymer, this would not be the case for a polymer containing various structural unlits. The relationship between molecular weight and complexation constant of ligand is ambiguous in the case of PAOM.

It was confirmed by the continuous variation method that a 2:1 complex was formed between AOM and copper(II) nitrate. In addition, the complex was found by elemental analysis to have the composition of 2 moles of AOM to one mole of Cu(II).[12] These findings are in agreement with the fact that the average number of ligands, $\bar{n}$, is maximum at about 2 (Figure 4), as will be described below. Though there are no data for analyzing the structure of a polymer complex, the behavior is anticipated to be similar to that of an AOM complex.

Absorption of Molecular Oxygen by Aqueous Solutions of Complexes

Polyoxime–metal complexes have been shown to be gas adsorbents in the solid state by Kim and Takizawa.[13] In the course of our study of the properties of PAOM–Cu(II)complexes, it was observed that an aqueous solution of these complexes can also absorb molecular oxygen. A similar obser-

vation was made in the case of AOM and POM.[12] In order to examine the capability of the absorption, three kinds of PAOM were studied. When aqueous solutions of PAOM and copper (II) nitrate are mixed together, the mixture becomes green and no percipitation occurs. Figure 5 shows the time course of oxygen consumption. The volumes depend on the
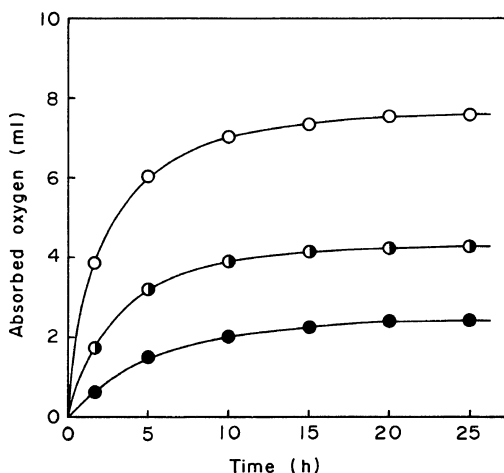

Figure 5. Absorption curves for the complex solutions at room temp: $[Cu^{2+}]=0.5$ mmol; ●, [PAOM-I]=1.0; ◐, [PAOM-II]=1.0; ○, [PAOM-III]=1.0 mmol; volume, 8 cm³.
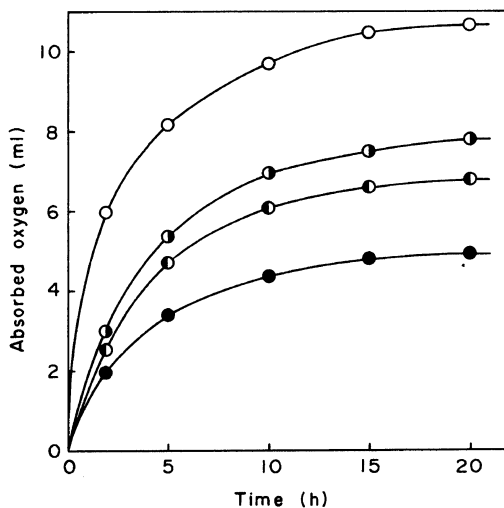

Figure 6. Absorption curves for the solution of PAOM-III–Cu(II) complex at room temp; $[Cu^{2+}]=0.534$ mmol. [PAOM-III]: ○, 1.608; ◐, 1.000; ◑, 0.804; ●, 0.530 mmol; volume, 8 cm³.
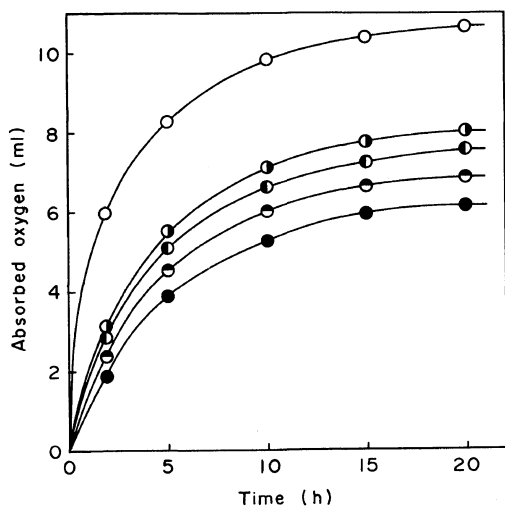
Figure 7. Absorption curves for the solution of PAOM-III–Cu(II) complex at room temp; [PAOM-III] = 1.61 mmol. [Cu^{2+}]: ○, 1.07; ⊘, 0.534; ◑, 0.267; ◐, 0.134; ◓, 0.020; ●, 0.0134 mmol; volume, 8 cm³.
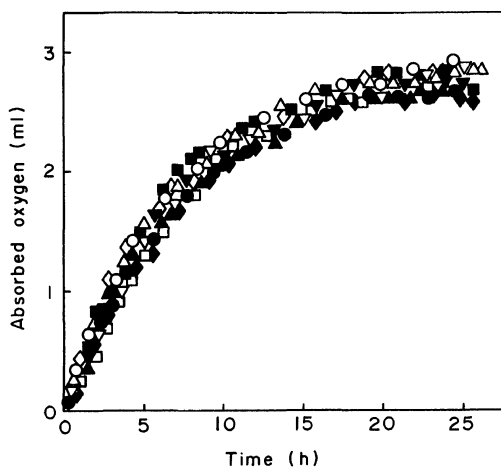

Figure 8. Resorption curves for the complex solutions at room temp: ○, ●, [PAOM-III] = 1.87, [Cu^{2+}] = 1.00; □, ■, [PAOM-III] = 0.94, [Cu^{2+}] = 1.00; △, ▲, [PAOM-III] = 0.94, [Cu^{2+}] = 0.5; ▽, ▼, [PAOM-III] = 0.47, [Cu^{2+}] = 1.00; ◇, ◆, [PAOM-III] = 0.47, [Cu^{2+}] = 0.50 mmol; resorption (○, □, △, ▽, ◇) and repeated resorption (●, ■, ▲, ▼, ◆); volume, 8 cm³.
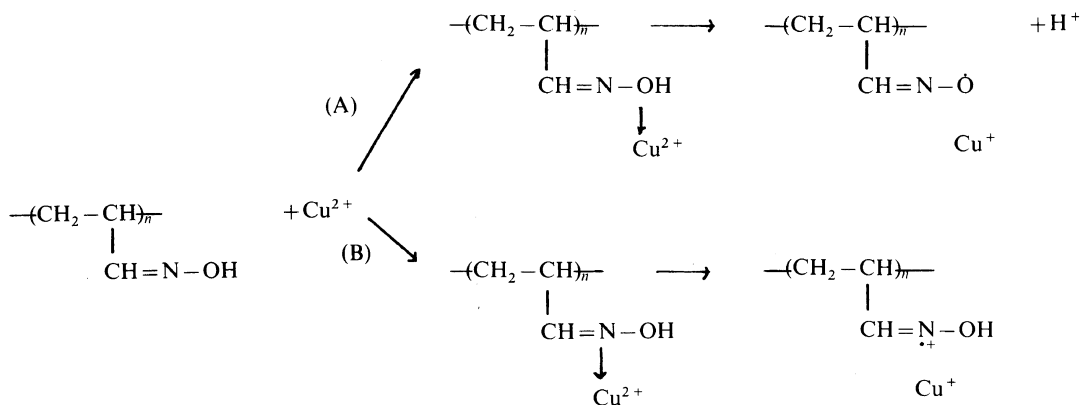
oxime group content in PAOM, and the PAOM-III complex, in which such content is a maximum, effectively absorbed oxygen. Because PAOM-II differs from PAOM-I in structure, as described above, in spite of the similar content of oxime groups, there is a difference in absorption capability between their copper complexes. The order of the capability is the same as that of the complexation constant.

Figures 6 and 7 indicate the dependence of the volumes of the absorbed oxgen on copper(II) ion and PAOM-III concentrations. The total volumes increase with time and level off within 20 h. In a definite concentration of PAOM-III (1.61 mmol), 1.07 and 0.54 mmol of copper(II) nitrate gave similar absorption curves, and the total volumes decrease slightly with decreasing concentration of copper(II) nitrate. However, the volume of the absorbed oxgen seems to be substantially independent of the concentration of metal salt present; a solution in which copper(II) nitrate had been reduced to one-eightieth of its original concentration, 1.07 to 0.034 mmol, could still absorb as much as 60% of its original volume. On the other hand, for a definite concentration of copper(II) nitrate, the volumes of oxygen absorbed depend on the concentration of PAOM-III present.

Figure 8 shows reabsorption curves for solutions of PAOM-III–Cu(II) complexes. The complex solutions first leveled off, then were desorbed for 3 h at room temperature under reduced pressure [3 mmHg (0.4kPa)]; absorption-desorption was repeated once more under similar conditions. The repeated resolved oxygen volumes are independent of concentration of PAOM-III and Cu(II) ions and are found to be approximately 2.7 cm³. This amount may be ascribed to the volume of a simple sorption, in other words, the volume of reversible absorption.

The total volumes of absorbed oxygen are summarized in Table IV. The molar ratios of absorbed oxygen to oxime group in PAOM are in the range of 0.26 to 0.34. Thus four moles of oxime group may react with one mole of molecular oxygen in the presence of copper ions.

From these results, the oxygen absorption may be explained on the basis of the oxidation-reduction of copper ions. When Cu(II) ions are reduced to Cu(II) ions, there are two possible paths.

$$-(CH_2-CH)_{\overline{m}} \longrightarrow -(CH_2-CH)_{\overline{m}} \quad +H^+$$
$$\begin{array}{ccc} | & & | \\ CH=N-OH & & CH=N-\dot{O} \\ & \downarrow & \\ & Cu^{2+} & Cu^+ \end{array}$$

(A)

$$-(CH_2-CH)_{\overline{m}} \quad +Cu^{2+}$$
$$\begin{array}{c} | \\ CH=N-OH \end{array}$$

(B)

$$-(CH_2-CH)_{\overline{m}} \longrightarrow -(CH_2-CH)_{\overline{m}}$$
$$\begin{array}{ccc} | & & | \\ CH=N-OH & & CH=\underset{\cdot+}{N}-OH \\ \downarrow & & \\ Cu^{2+} & & Cu^+ \end{array}$$

As will be described later, the reaction probably proceeds by path (B). On the other hand, the resultant Cu(I) ions are easily oxidized by oxygen to Cu(I) ions. Consequently, the cyclic redox reaction of copper ion is repeated until the oxime group is consumed. In other words, the total volumes of absorbed oxygen depend on the concentration of PAOM present.

$$Cu(II) \underset{O_2}{\overset{-CH=N-OH}{\rightleftharpoons}} Cu(I)$$
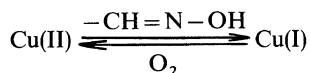
Potentiometric experiments were performed in order to prove the assumption mentioned above. The potential for the solution of copper(II) nitrate was found to be 0.376 V. When a definite amount of PAOM is added to the solution in nitrogen atmosphere, as shown in Figure 9, it tends to become lower with time, and rises again when the atmosphere is replaced with oxgen. Durig the period of potential increase, the solution can absorp oxygen, and when the oxygen absorption ceases the potential also levels off. This fact provides strong evidence in con-

Table IV. Absorption of molecular oxygen by PAOM-III–Cu(II) complexes in aqueous solution at room temperature

[PAOM-III][a] mmol	mmole of oxime group [A]	[Cu^{2+}] mmol	Total amount of absorbed oxygen [B] cm^3 (mmol)	Resorbed oxygen [C] cm^3 (mmol)	[B]−[C] [A]
1.04[b]	4.78×10^{-1}	9.94×10^{-2}	2.5 (0.10)		
1.00[c]	4.48×10^{-1}	9.94×10^{-2}	4.3 (0.18)		
1.01	7.45×10^{-1}	9.94×10^{-2}	7.6 (0.31)		
1.87	1.38	1.00	12.6 (0.52)	2.7 ± 0.5 (0.11 ± 0.02)	0.29 ± 0.02
9.40×10^{-1}	6.94×10^{-1}	1.00	7.7 (0.31)	2.7 ± 0.5 (0.11 ± 0.02)	0.28 ± 0.03
4.70×10^{-1}	3.47×10^{-1}	1.00	4.7 (0.20)	2.7 ± 0.3 (0.11 ± 0.01)	0.26 ± 0.03
4.70×10^{-1}	3.47×10^{-1}	5.00×10^{-1}	5.5 (0.23)	2.7 ± 0.3 (0.11 ± 0.01)	0.34 ± 0.03
1.61	1.19	1.07	10.6 (0.43)		
1.61	1.19	5.34×10^{-1}	10.6 (0.43)		
1.61	1.19	2.67×10^{-1}	8.0 (0.33)		
1.61	1.19	1.34×10^{-1}	7.5 (0.31)		
1.61	1.19	1.34×10^{-2}	6.2 (0.25)		
1.00	7.38×10^{-1}	5.34×10^{-1}	7.1 (0.29)	2.2　(0.09)	0.27
8.00×10^{-1}	5.90×10^{-1}	5.34×10^{-1}	6.7 (0.27)		

[a] Oxime group content of PAOM-III is 73.8%.

[b] PAOM-I was used. Its oxime content is 46.0%.
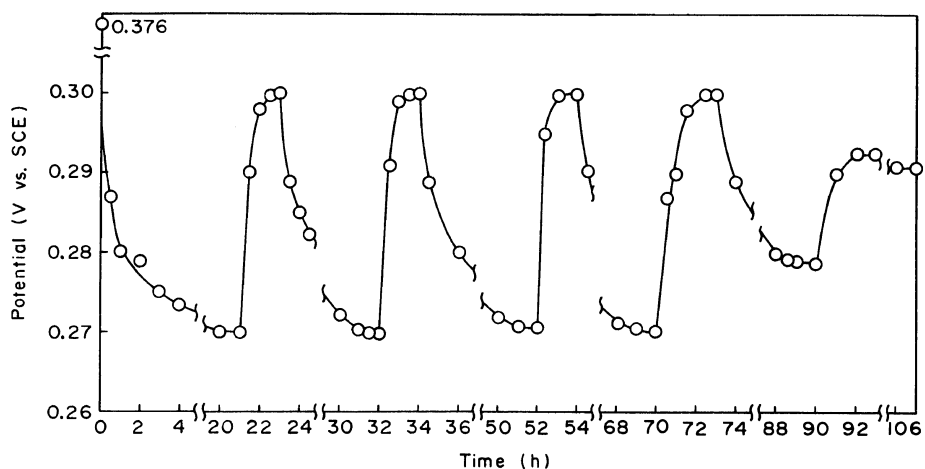
[c] PAOM-II was used. Its oxime content is 44.8%.

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Figure 9. Potential change for PAOM-III–Cu(II) complex system at room temp; [PAOM-III] = 5 mmol; [Cu^{2+}] = 2.5 mmol; μ = 0.5 (KNO$_3$).
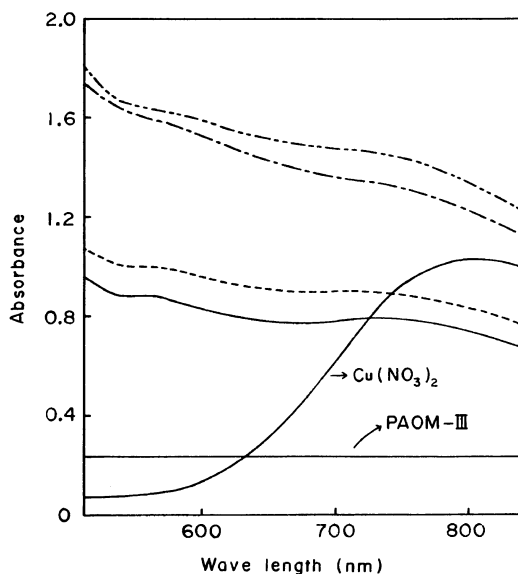

Figure 10. Change in absorption for PAOM-III–Cu(II) system in the atmosphere of nitrogen: after 0.3 (—·—·—), 2.5 (—·—), 6 (------), and 15 (———) h; [PAOM-III] = 0.8 mol dm^{-3}; [Cu(NO$_3$)$_2$] = 0.4 mol dm^{-3}.
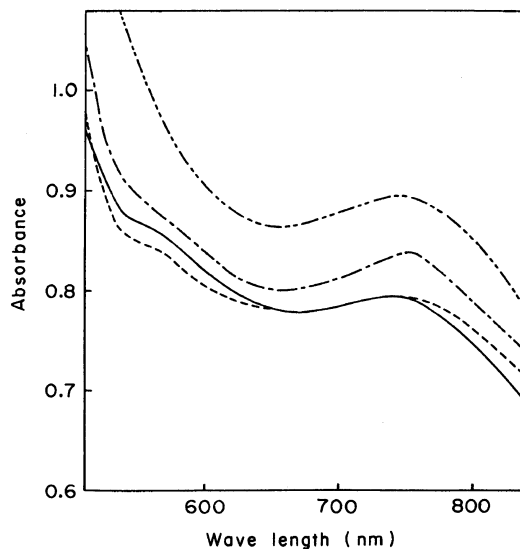
Figure 11. Change in absorption for PAOM-III–Cu(II) system in the atomosphere of oxygen: after 0 (———), 3 (------), 8 (—·—), and 24 (—·—·—) h; [PAOM-III] = 0.8 mol dm^{-3}; [Cu(NO$_3$)$_2$] = 0.4 mol dm^{-3}.

firmation of the oxidation-reduction of copper ions.

Copper(II) nitrate and copper(II) complexes show the absorption bands at *ca.* 750 and *ca.* 570 nm, respectively. In the atmosphere of nitrogen (Figure 10), the absorbance was found to decrease with time, but the shape of the curves remained un-changed. When the atmosphere was replaced with oxygen (Figure 11), the intensity at 750 nm became stronger with time, but the band at 570 nm, identified as an *d–d* transition, overlaps with a lower wave-length band, and the intensity did not change remarkably. These findings also support the occur-
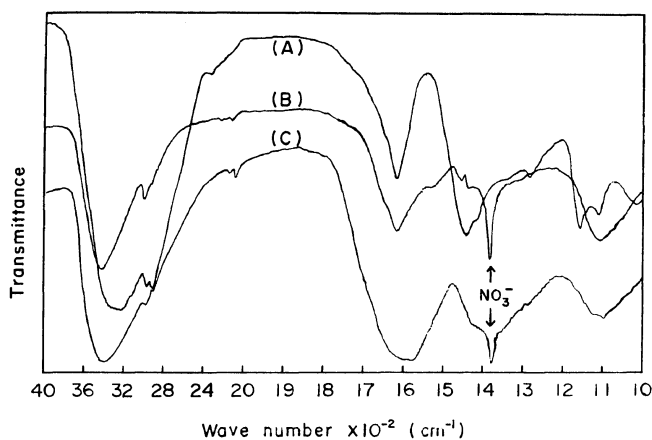
Figure 12. IR spectra of PAOM-III and its copper(II) complex: A, PAOM-III; B, PAOM-III–Cu(II) complex prepared in the presence of nitrogen; C, PAOM-III–Cu(II) complex absorbed oxygen.

rence of a redox reaction of copper ions.

Figure 12 shows IR spectra of PAOM-III and its copper(II) complexes (oxime/Cu(II) = 2/1 by mole). The complex solution was evaporated in nitrogen atmosphere and the IR spectrum of the precipitate was quickly measured in a KBr disc. The shift of the O–H stretching to a considerably lower frequency (3200 cm^{-1}), shown in spectrum (A), indicates the formation of hydrogen bonds of two types, O—H---N and O–H---O;[14] the lower frequency value (1620 cm^{-1}) of the C=N stretching suggests participation of nitrogen atoms in the hydrogen bonding. When Cu(II) ions are added to PAOM-III solution in the presence of nitrogen, the hydrogen bond of the O—H---N type is broken and the nitrogen atom in the oxime group coordinates again to the Cu(II) ions. Consequently, the band at 3220 cm^{-1} is shifted to 3440 cm^{-1} and the absorption due to the C=N stretching bocome broad but does not shift (Figure 12(B)). When the complex thoroughly absorbs oxygen, the absorptions due to the O–H stretching and the C=N streching become slightly broad with no shift and broad with a shift to 1570 cm^{-1}, respectively (Figure 12 (C)). This finding suggests that electron transfer from the nitrogen atoms in oxime groups helps to derive Cu(II) ions toward Cu(I) ions. The absorption due to the CH_2 deformation, which appears at 1450 cm^{-1}, diminishes in the IR spectra of the complex because of the disorder of structure. In addition, the absorption peak assigned to NO_3^- stretching vibration appears at 1380 cm^{-1}.

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