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Effects of ionenes on structure and catalytic activity of cobaltphthalocyanine, 5^{a)}

The catalytic role of cobaltphthalocyanine aggregates

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SUMMARY:

The interaction of several ionenes with tetrasodium phthalocyaninatocobalttetrasulfonate (**1**) was investigated spectrophotometrically, both in the unreduced and reduced state. The 2,10- and 2,12-ionenes **2 d**, **e** appeared to induce monomerization of the phthalocyanine moiety, especially of the reduced form which is ascribed to hydrophobic effects. All other ionenes studied strongly induced aggregation of the cobalt complex. Kinetic thiol oxidation experiments revealed large differences between the macromolecular effects of the hydrophobic 2,10-ionene **2 d** and the hydrophilic ionenes. These phenomena are explained by the different catalytic activity of phthalocyanine in its monomeric and aggregated form.

Introduction

In recent years, the role of polymers in catalytic processes has gained considerable interest. Polymers have been used as catalysts, promoters and supports¹⁻³⁾ and have been studied as such in detail, because of the possibility they offer to combine functional groups or specific geometric configurations⁴⁾. Thus, it becomes possible to design "tailor-made" catalyst systems or e.g. to mimic enzymes.

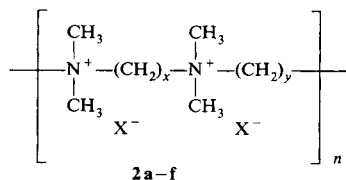
Several effects of polymers on catalytic reactions have been discussed in literature. Most important are concentration effects and structural effects³⁾. Concentration effects are essential in polyelectrolyte catalysis⁵⁾, where local substrate ion concentrations can be substantially increases as a result of electrostatic interaction. An important structural effect involves site-isolation^{1,2)}, which implies that the polymer coils prevent deactivating interaction between catalytic sites (e.g. dimerization).

Site-isolation has also been proposed⁶⁾ to be of importance in the process under study in our laboratory, viz. the polyamine-enhanced autoxidation of thiols in the presence of tetrasodium phthalocyaninatocobalttetrasulfonate (**1**). It was demonstrated^{6,7)} that the investigated rate-enhancing polymers, poly(vinylamine) and ionenes (poly(quaternary ammonium salts) (**2**)), efficiently suppress formation of the catalytically inactive oxygen-bridged dimers of **1**. Nevertheless, it was also shown^{7,8)} that the formation of oxygen-free dimers (or higher aggregates) is even promoted by these polymers. Therefore, the question arose whether monomeric sites are needed for the catalytic thiol conversion or dimers are actually the catalytically active species.

^{a)} Part 4: cf. ⁹⁾.

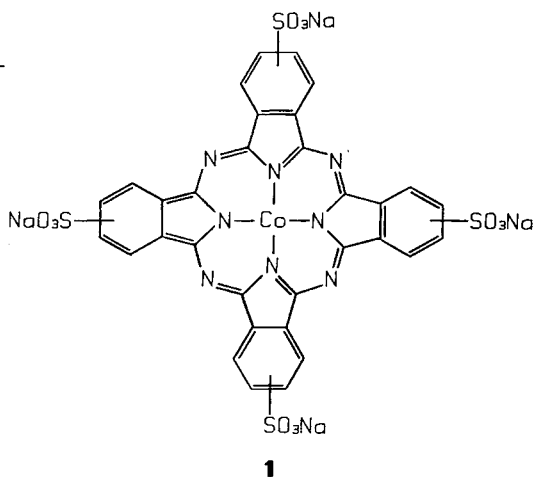
In order to answer this question, we have now studied a polymer system, closely resembling those already under investigation, in which only extremely small amounts of the catalyst are present in the dimeric form. This enabled us to compare the catalytic activity of monomers and dimers of **1** directly. The results of this study are presented here.

In addition, our investigations of the behaviour of the dimeric complex in the presence of thiol are discussed, especially with respect to the degree of aggregation of **1** under those conditions.



X = Br

	x	y
2a	2	4
b	2	6
c	2	8
d	2	10
e	2	12
f	6	6



Experimental part

Syntheses of ionenes: Ionenes **2a**, **2b** and **2d** were prepared according to the method reported by Brouwer et al.¹⁰⁾ Ionenes **2c**, **2e** and **2f** were synthesized analogously, using the starting materials *N,N,N',N'*-tetramethylenediamine (TMEDA) and 1,8-dibromooctane for **2c** (yield 83%), TMEDA and 1,12-dibromododecane for **2e** (yield 70%) and *N,N,N',N'*-tetramethyl-1,6-hexanediamine and 1,6-dibromohexane for **2f** (yield 92%). C,H,N-analyses revealed all samples were >95% pure. Since the ionenes are very hygroscopic, they may contain small amounts of water. Values for the number-average molecular weight \bar{M}_n were determined by titration with hydrochloric acid after terminating the products with amine groups¹¹⁾; the values obtained were: 7300 for **2a**, 9200 for **2b**, 10^4 for **2c**, **2d** and **2f** and $1,3 \cdot 10^4$ for **2e**. Polymer concentrations were expressed as concentration of ammonium groups ($[N^+]$ in mol/L).

Other reagents

Tetrasodium phthalocyaninatocobalttetrakisulfonate (1), kindly provided by Dr. *T. P. M. Beelen*, was synthesized according to an adaptation by Zwart¹²⁾ of the method described by Weber and Busch¹³⁾.

2-Mercaptoethanol (Fluka) was distilled prior to use and kept under nitrogen in a sealed ampoule.

All *other materials* used were of analytical purity and were used without further purification.

Spectrophotometry: Spectrophotometric measurements were performed on a Hewlett Packard 8451A diode array spectrophotometer using 1,000 cm quartz cuvettes. The cells were kept in a thermostat at $25,0 \pm 0,5^\circ\text{C}$.

*Catalytic activity measurements*¹¹⁾

All reactions were carried out in a modified Warburg apparatus at $25,0 \pm 0,5^\circ\text{C}$. The stirring speed was 2600 r.p.m. at which no diffusion limitation occurs for our catalytic system¹⁰⁾. Reaction rates were determined by measuring the oxygen uptake rate.

Measurements with 2,10-ionene were performed using a mass flow controller with a capacity of 10 mL/min, for all other experiments the capacity was 50 mL/min. Standard conditions: reaction volume 100 mL, 1 atm. O₂-pressure and concentration of 2-mercaptoethanol [RSH]₀ = 0,043 or 0,071 mol/L. The pH was adjusted at an initial value of 9,0–9,2 with NaOH.

Results and discussion

Ionene-induced aggregation/deaggregation of 1

In order to find a catalytically active polymer with the ability to isolate the monomeric cobalt complex, we investigated **1** in combination with a large variety of ionenes by using visible light spectroscopy. This technique is very suitable in discriminating between the monomeric and dimeric phthalocyanine complexes¹⁴⁾, because the absorption maxima of both compounds differ considerably: the monomer has its main absorption band at 662 nm whereas the dimer mainly absorbs at 628 nm (higher aggregates have a spectrum very similar to the dimers but the wavelength of the maximum λ_{max} is lowered to about 620 nm). Thus, the ratio of the absorbances at 628 and 662 nm, A_{628}/A_{662} , is a measure of the relative amount of dimerized (aggregated) cobalt species.

Upon addition of 2,6-, 2,8-, or 6,6-ionene to a solution of **1**, the amount of aggregates gradually increases until a ratio of $[\text{N}^+]:[\text{Co}] = 4:1$ is reached, where the positive charges on the ionene are just matching the negative charges of the phthalocyaninetetrasulfonate. Further addition of these ionenes up to $[\text{N}^+]/[\text{Co}] = 10^5$, has no effect on the position of the monomer-dimer equilibrium, since A_{628}/A_{662} remains constant. We therefore may conclude that these ionenes, like 2,4-ionene (as was described previously^{7,8)}), have no propensity to isolate the monomeric cobalt complex.

However, 2,10- and 2,12-ionene did show a site isolation effect at high $[\text{N}^+]/[\text{Co}]$ -ratios. This effect is illustrated in Fig. 1 for 2,10-ionene. It clearly demonstrates that at low ionene concentrations aggregation is enhanced analogously to the other ionene systems, but with a large excess of 2,10-ionene ($[\text{N}^+]/[\text{Co}] \geq 10^3$) the equilibrium is shifted back to the monomer side, as can be concluded from the decrease of A_{628}/A_{662} . At $[\text{N}^+]/[\text{Co}] = 10^5$ the monomer concentration is even higher than it was at the same cobalt concentration without any ionene present.

It must be noted that the distinct behaviour of 2,10- and 2,12-ionene, as compared to the other ionenes studied, cannot be explained by the difference in charge densities: although 6,6-ionene has the same charge density as 2,10-ionene, it does not show any

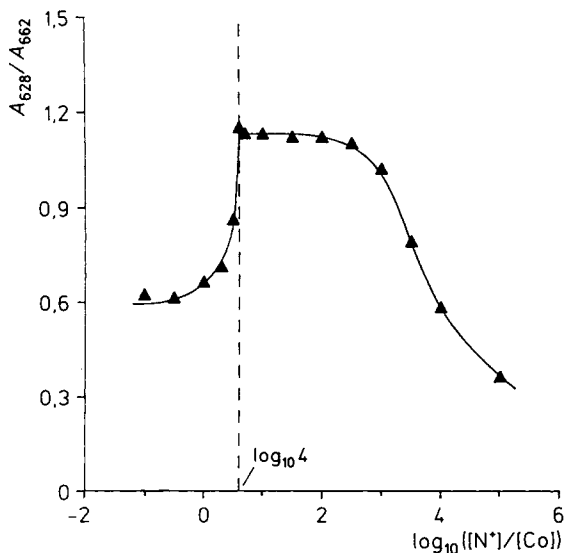


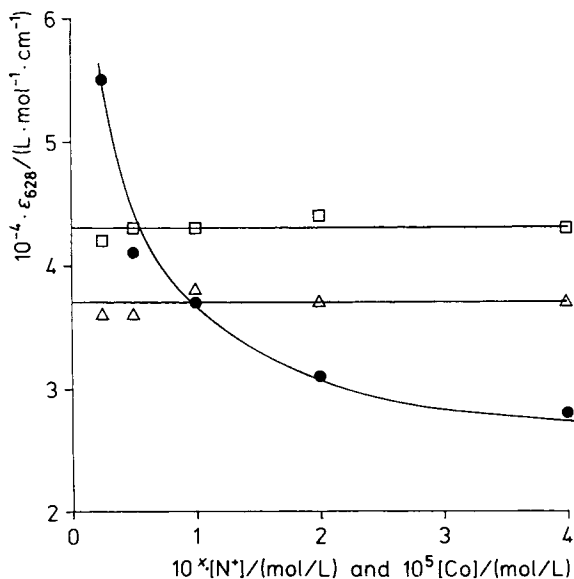
Fig. 1. Ratio of absorbances at 628 and 662 nm as a function of $[N^+]/[Co]$ for 2,10-ionene (**2d**). Aqueous solutions, $[Co] = 2 \cdot 10^{-6}$ mol/L

site isolation effect in the investigated concentration range. Apparently, the effect of site isolation is due to some other property of the 2,10- and 2,12-ionenes; most probably the hydrophobic character¹⁵⁾ of the C_{10} - and C_{12} -chain segments plays a role. Characterization of this hydrophobicity is part of our current investigations.

Hydrophobic effects may also underlie another phenomenon we observed. At a constant $[N^+]/[Co]$ -ratio of 2000, dilution of the catalyst solution caused an increase in the relative amount of dimeric complex: the molar absorbance at 628 nm increased while at 662 nm it decreased; for example, at $[N^+] = 8 \cdot 10^{-2}$ mol/L $A_{628}/A_{662} = 0,70$, whereas at $[N^+] = 5 \cdot 10^{-3}$ mol/L this ratio was found to be 0,93. Thus, in this respect the system behaves opposite to the polymer-free system. The same behaviour was found for 2,12-ionene.

We look upon this effect as an indication of the existence of micelle-like structures inducing the monomerisation¹⁶⁾ of the phthalocyanine. Upon dilution (at constant $[N^+]/[Co]$) the micelles will be broken down resulting in a molecular solution that will behave more like the other (hydrophilic) ionene systems. Therefore, further diluting a 2,10-ionene solution at low $[N^+]$ level should lead to identical results as were obtained for the other ionenes. Indeed, in all these cases, no change of molar absorbance with polymer concentration was observed, indicating a constant degree of aggregation. The constancy of the molar absorption coefficient at 628 nm for 6,6-ionene and for 2,10-ionene at $[N^+]/[Co] = 10$ (low $[N^+]$, i.e. no micellar structures) is presented in Fig. 2. By comparison, the changing molar absorption coefficient for the 2,10-ionene at $[N^+]/[Co] = 2000$ (high $[N^+]$, i.e. micellar structures) is shown in the same figure.

Fig. 2. Dependence of the molar absorption coefficient (ϵ_{628}) at 628 nm on catalyst concentration. Aqueous solutions of (\square): 6,6-ionene, $[N^+]/[Co] = 1000$, $x = 2$; (\bullet): 2,10-ionene, $[N^+]/[Co] = 1000$, $x = 2$; (\triangle): 2,10-ionene, $[N^+]/[Co] = 10$, $x = 4$



Effects of thiol on aggregates

The investigations described above, made clear that aggregation of **1** can be easily controlled by addition of certain ionenes and by choosing appropriate concentrations of the components.

To obtain insight in the role of the aggregates during the catalytic conversion of thiols, catalyst systems with different degrees of aggregation were now studied in the presence of 2-mercaptoethanol (under anaerobic conditions; it has been shown previously that oxygen addition does not affect the structure of the phthalocyanine in the presence of ionenes⁷⁾). These experiments were primarily focused on elucidating whether thiolate anions can break up the aggregates (by forming coordinative bonds with cobalt via its two axial positions and/or by changing the valency of the central cobalt ion).

First, an excess of 2,10-ionene was used, in order to determine the spectrum of the interaction product of the monomeric catalyst and the thiol. This spectrum is presented in Fig. 3 a and is typical of monomeric one-electron-reduced phthalocyaninatocobalt. It shows main absorption bands at 316 nm (Soret-band), 476 nm (metal-to-ligand charge transfer, MLCT) and 706 nm (Q-band) and shoulders around 440 and 650 nm, which is in very good agreement with the literature¹⁷⁻¹⁹⁾.

The same procedure using 2,4-ionene led to a different spectrum, shown in Fig. 3 b. Here, both the MLCT- and Q-bands have been shifted to shorter wavelengths, viz. 454 and 684 nm, and the fine structure has disappeared. Similar effects are observed for

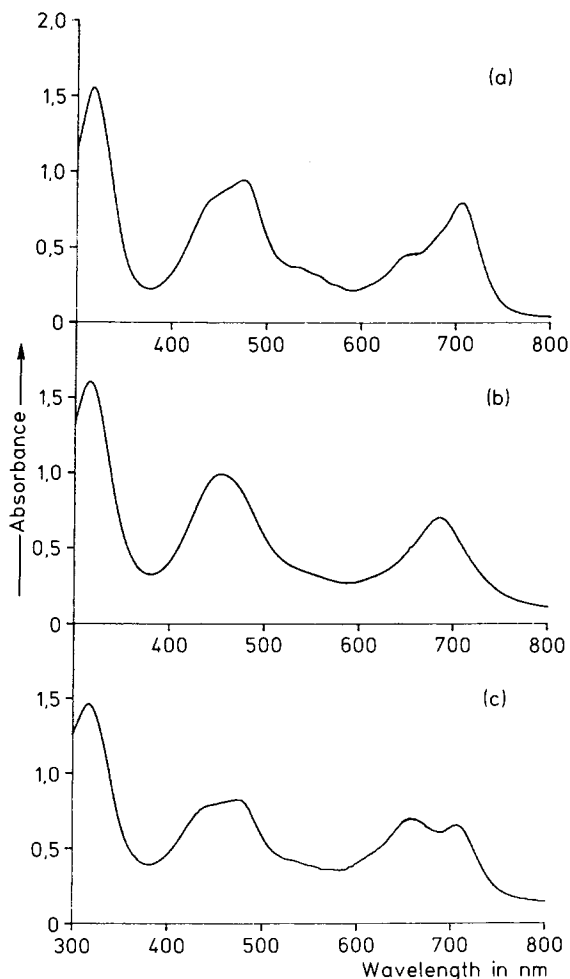


Fig. 3. Photometric spectra of **1** in water in the presence of thiol (RSH) and ionene under anaerobic conditions; $[\text{Co}] = 4 \cdot 10^{-5}$ mol/L, $[\text{RSH}] = 4,8 \cdot 10^{-2}$ mol/L. (a) monomeric $(\text{Co(I)Pc}(\text{NaSO}_3)_4)^-$, 2,10-ionene, $[\text{N}^+]/[\text{Co}] = 3000$, pH = 9; (b) aggregated $(\text{Co(I)Pc}(\text{NaSO}_3)_4)^-$, 2,4-ionene, $[\text{N}^+]/[\text{Co}] = 3000$, pH = 9; (c) mixture of monomeric and dimeric $(\text{Co(I)Pc}(\text{NaSO}_3)_4)^-$, 2,10-ionene, $[\text{N}^+]/[\text{Co}] = 6$, pH = 8

the Co(II) species upon its aggregation, which leads us to the assignment of the spectrum of Fig. 3b to aggregated^{a)} $[\text{Co(I)Pc}(\text{NaSO}_3)_4]_n^{n-}$, where Pc stands for the phthalocyanine moiety. This is in good agreement with the findings of Kozlyak et al.¹⁸⁾, who analogously claim to be able to control Co(II)- and Co(I)-phthalocyanine aggregation by the addition of cationic soaps (monomerization) or (poly)salts

^{a)} Nevin et al., who reduced the cobalt complex electrochemically, also observed the spectrum of Fig. 3b and ascribed it to the monomeric form. However, we think their assignment is not well-argued and the absence of aggregates under their conditions, viz. a high cobalt concentration ($5 \cdot 10^{-4}$ mol/L) and a very high ionic strength (0,9 mol/L), seems very unlikely²⁰⁾.

(aggregation). The similarity between their results with hexadecyltrimethylammonium bromide and ours with 2,10-ionene is striking and again indicative of hydrophobic effects playing a role in the 2,10-ionene systems.

The polymer-free catalyst was also studied in the presence of thiol. Its spectrum appeared to be very similar to that of the 2,4-ionene-containing system (Fig. 3b), indicating the presence of mainly the dimeric Co(I) species under these conditions. In the case of the polymer-free system, the equilibrium could be reversibly shifted to the side of the monomer resulting in a spectrum identical to Fig. 3a by heating the solution to 85 °C.

When the 2,4-ionene-containing system was heated to 85 °C, no dissociation of aggregates could be observed. Thus, 2,4-ionene stabilizes aggregates in the Co(I) form as well as in the Co(II) form. In addition, it was established that ionene enhances the degree of cobalt reduction, which could be deduced from the higher ratio of the intensities of the MLCT- and Q-bands, respectively, for the 2,4-ionene system as compared with the polymer-free system. Especially at low thiolate concentrations the difference was obvious. The 2,10-ionene also caused an increased reduction. This strongly supports our view¹⁰ that ionenes, due to their cationic charge, strongly increase the local concentration of thiolate anions (the reductive species).

Concentration effects on the degree of Co(I) aggregation

The reduced catalyst systems were further investigated in dependence of the $[N^+]/[Co]$ -ratio and of the concentration of thiolate anions, $[RS^-]$, which was varied by changing the pH or the thiol content of the solution.

For 2,10-ionene it was expected that at $4 < [N^+]/[Co] < 10^3$ the aggregated Co(I) species would be observed, in analogy to the results for the unreduced system (Fig. 1). Indeed, the presence of aggregates in this region could be demonstrated, although invariably monomeric species appeared to be present as well, as shown in Fig. 3c. Only below an $[N^+]/[Co]$ -ratio of 5 no monomeric species were observed. The degree of aggregation depended mainly on the concentration of thiolate anions RS^- : increasing $[RS^-]$ resulted in a decrease of the amount of aggregates present, even at $[N^+]/[Co]$ -ratios where Co(II) dimers were stable. Therefore, it is clear that thiolate ions act as axial ligands of the phthalocyaninatocobalt molecules, thus disrupting their dimeric structure.

Another factor that influenced aggregation was ionene concentration rather than $[N^+]/[Co]$ -ratio. At $[N^+] > \approx 10^{-4}$ mol/L the system was measurably deaggregating. We assume that this deaggregation is induced by micelle-formation.

At $[N^+]: [Co(I)Pc(SO_3)_4]^{5-}] = 5:1$ precipitation occurred due to charge compensation, however, the precipitate redissolved upon addition of more ionene. Similar behaviour was found for 2,4-ionene, but this system was more colloidal in character, as appeared from its high turbidity.

The 2,4-ionene was expected to enhance the degree of aggregation, reaching a maximum value at $[N^+]/[Co] = 5$ and remaining constant for higher ratios. However, at $[N^+]/[Co] = 5$ an additional effect (apart from colloid formation) took place,

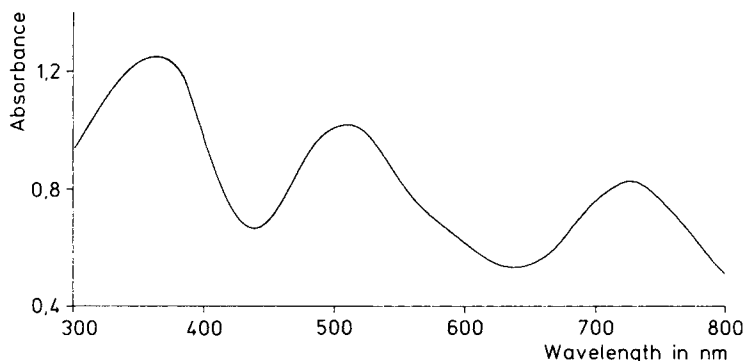


Fig. 4. Photometric spectrum of aqueous 1 in the presence of thiol (RSH) and 2,4-ionene at $[N^+]/[Co] = 5$; $[Co] = 4 \cdot 10^{-5}$ mol/L, $[RSH] = 4,8 \cdot 10^{-2}$ mol/L, pH = 9, equilibration time 1 h

illustrated by the spectrum in Fig. 4, which complicated the interpretation of our results. As can be seen, all absorption maxima were shifted to longer wavelengths. The process occurred at a very low rate and equilibrium was only reached after about 1 h, resulting in absorption maxima at 364, 506 and 736 nm. The spectrum is difficult to assign, especially the band at 364 nm, since values in this region have only been reported for oxidized forms^{21,22)} of the cobalt complex which are probably not formed in the presence of thiol, i. e. under reducing conditions. More likely, a doubly reduced species is formed, since an excess of thiol was being used. Indeed, when the applied concentration of thiolate anions was smaller than twice the cobalt concentration, the phenomenon was not observed. However, the spectrum we obtained differs considerably from the spectrum for $[Co(I)Pc^-(NaSO_3)_4]^{2-}$ reported by Nevin et al.²⁰⁾ The discrepancy may be due to the presence of different ligands. The presence of a species with mixed valence cannot be ruled out either, since delocalization of electrons over the aggregates may occur. In this respect, it is interesting to note that the compound exhibiting the spectrum of Fig. 4 was not formed in the non-aggregating 2,10-ionene system.

Upon further addition of 2,4-ionene the spectrum of aggregated Co(I) was restored and the Q-band was shifted to even shorter wavelength (about 650 nm), presumably indicating an even higher degree of aggregation. At large excesses of ionene ($[N^+]/[Co] > 100$) this band shifted back to 686 nm, but no evidence was found for the existence of monomeric Co(I) up to $[N^+]/[Co] = 10^4$, which was in agreement with our expectations.

Catalytic activity measurements: effect of varying $[N^+]/[Co]$

The catalytic activity of several ionenes was determined under standard conditions (see *Exptl. part* and Tab. 1). As can be seen from Tab. 1, the activity of 2,10-ionene was extremely low as compared with the other ionenes. The difference is too large to be

Tab. 1. Catalytic activities of ionenes **2a–d**, **f**^{a)}

Ionene	σ ^{b)}	Activity ^{c)}
2a	1,44	2 550
2b	1,15	2 040
2c	0,96	1 680
2f	0,82	1 420
2d ^{d)}	0,82	40

a) Conditions: pH = 9,0, initial thiol concentration $[\text{RSH}]_0 = 0,071 \text{ mol/L}$, $[\text{N}^+] = 10^{-3} \text{ mol/L}$, $[\text{Co}] = 2 \cdot 10^{-7} \text{ mol/L}$.

b) Charge density parameter¹⁰⁾.

c) Expressed in mol thiol per mol Co per s.

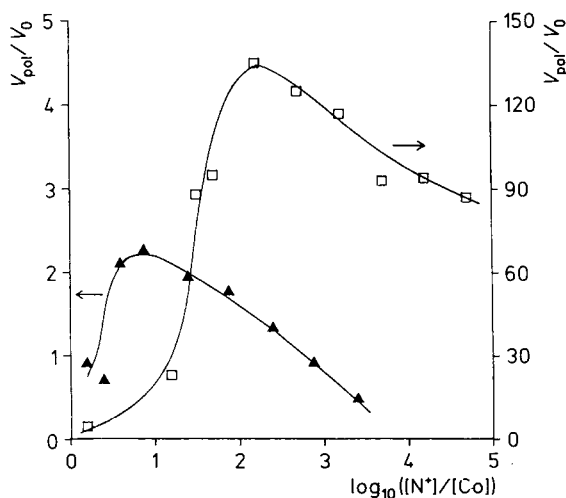
d) $[\text{Co}] = 4 \cdot 10^{-6}$ instead of $2 \cdot 10^{-7} \text{ mol/L}$, where the activity was too low to be measured.

explained by a charge density effect. On the other hand, we believe this strongly indicates that the dimeric cobalt complex is the catalytically active species, since all tested ionene systems contain predominantly dimers except the much less active 2,10-ionene system.

The results obtained by varying the $[\text{N}^+]/[\text{Co}]$ -ratio (see below) and the catalyst concentration (discussed in the next section) of 2,4- and 2,10-ionene systems provided more supporting evidence to our hypothesis.

In Fig. 5 thiol oxidation rates for the 2,4- and 2,10-ionene systems are depicted as a function of the $[\text{N}^+]/[\text{Co}]$ -ratio, with the rates expressed relative to the rate measured for the polymer-free catalyst. It is evident that, while the 2,4-ionene largely enhances the reaction rate (up to more than 120-fold), the 2,10-ionene exhibits an

Fig. 5. Effect of varying $[\text{N}^+]/[\text{Co}]$ on thiol oxidation rate (V_{pol}/V_0) of ionenesystems relative to the rate of the polymer-free catalyst; $V_0 = 30 \text{ mol RSH per mol Co per s}$, pH = 9,0–9,1, $[\text{RSH}]_0 = 0,071 \text{ mol/L}$. (\square) 2,4-Ionene, $[\text{Co}] = 2 \cdot 10^{-7} \text{ mol/L}$; (\blacktriangle) 2,10-ionene, $[\text{Co}] = 4 \cdot 10^{-6} \text{ mol/L}$



activity of the same order of magnitude as the polymer-free system. Both polymer catalysts show an optimum in activity, the 2,4-ionene at $[N^+]/[Co] \approx 200$ and the 2,10-ionene at $5 \leq [N^+]/[Co] \leq 10$. In our opinion, both curves can be explained on the basis of the ability of the ionenes to locally increase the concentration of thiolate anions and our hypothesis that dimers (aggregates) are the catalytically active sites.

According to the preceding section, aggregates will be present in both systems at $[N^+]/[Co(I)] < 5$. Since there is an excess of phthalocyanine in this region, the charge on the ionenes will be completely compensated and an enrichment of the catalyst domains with thiolate anions will not take place. The activities in this region should therefore be comparable to the activity of the polymer-free catalyst, which was indeed found.

Increasing the $[N^+]/[Co]$ -ratio will lead to an increase in local thiolate concentration $[RS^-]_{local}$, having a positive effect on the reaction rate. In the case of 2,10-ionene, however, this effect is partly undone by the rate lowering due to the dissociation of the aggregates. At relatively low $[N^+]/[Co]$, or more precisely, at low $[N^+]$ where presumably only a small number of micelles is present (vide supra), the thiolate concentration effect dominates over the deaggregation, and a (small) rate enhancement with respect to the polymer-free case is found. However, at high $[N^+]/[Co]$ deaggregation prevails and the relative reaction rate decreases below a value of 1.

For the 2,4-ionene no Co(I) deaggregation was observed and at $[N^+]/[Co] < 100$ aggregation even appeared to be enhanced (shift of λ_{max} from 684 to 650 nm), while also the stability of the aggregates was increased. Together with the increased local thiolate anion concentration, this apparently results in a highly efficient catalyst. Since thiolate enrichment may be expected to be of similar importance in the 2,4- and 2,10-ionene systems, it can be concluded that aggregation mainly determines the high activity of the 2,4-ionene catalyst.

Above $[N^+]/[Co] = 200$ also the activity of the 2,4-ionene was found to decrease again, which may be caused by the following two effects. First, using spectroscopy we demonstrated that the degree of Co(I) aggregation slightly decreases in this region, indicated by a shift of the Q-band to longer wavelength. If the reaction rate is related to the degree of catalyst aggregation, this explains at least partly the observed decrease of activity. In addition, it seems plausible that in this region also $[RS^-]_{local}$ is somewhat lowered; in other words, when large excesses of ionene are applied, many RS^- -rich domains will not contain the cobalt complex and thus be ineffective. In this way, the efficiency of the catalyst will decrease, as was indeed established. Nevertheless, it must be noted that even at $[N^+]/[Co]$ -ratios as high as $5 \cdot 10^4$ still 65% of the optimum activity is retained.

Dependence of catalytic activities on catalyst concentration

Fig. 6 shows the results of thiol oxidation rate measurements as a function of catalyst concentration, where $[N^+]/[Co]$ was kept constant. The 2,4-ionene displays a linear relationship, in full agreement with the Michaelis-Menten kinetic model that has been published earlier²³. It is also in accordance with our theory of aggregates being the

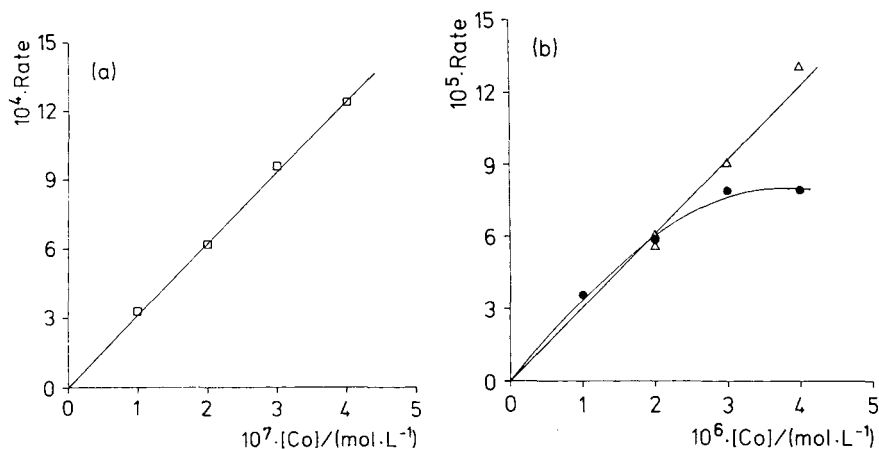


Fig. 6. Dependence of thiol oxidation rate (in mol RSH per L per s) on catalyst concentration; pH = 9,2, $[RSH]_0 = 0,043$ mol/L. (a) 2,4-Ionene, $[N^+]/[Co] = 2000$; (b) 2,10-ionene, $[N^+]/[Co] = 10$ (Δ) and $[N^+]/[Co] = 2000$ (\bullet)

active species, provided that the degree of aggregation over the concentration range studied is constant. In Fig. 2 it has been shown that this condition is indeed being fulfilled.

For the 2,10-ionene, it was demonstrated that at high $[N^+]$ the amount of aggregate is decreased (see preceding sections). Therefore, the activity is no longer proportional to the catalyst concentration when $[N^+]/[Co]$ is kept at a high value. On the other hand, when $[N^+]/[Co]$ is kept sufficiently low (in such a way that $[N^+] < 10^{-4}$ mol/L), no deviation of linearity is observed, as also can be seen in Fig. 6b.

All kinetic data are thus consistent with our theory. Moreover, additional evidence is presented in Fig. 7, in which the results of catalytic experiments in ethanol/water mixtures are presented. Addition of alcohols to a solution of **1** or its reduced form favours the formation of the monomeric species²⁴), whereas in the presence of 2,4-ionene the aggregates remain intact⁹). The curves of the activities versus ethanol content show a pattern that parallels the occurrence of the aggregates in these solvent mixtures: the polymer-free system exhibits a considerable loss of activity (about 75% at 25 vol.-% ethanol content), while the loss in the ionene system is only small (about 10% at 25 vol.-% ethanol). The minor activity decrease in the latter case may well be due to solvational effects.

We therefore propose that the catalytic species in the phthalocyanine-catalyzed thiol oxidation is the dimerized (or even higher aggregated) cobalt complex. This is in good agreement with the results of Beelen et al.²⁵), who observed a large rate increase when the (polymer-free) negatively charged catalyst complex **1** was combined with an equimolar amount of its positively charged tetra-ammonium counterpart, in which case the occurrence of dimers is evident. A summary of the occurrence of aggregates in the various systems described in this paper is presented in Tab. 2.

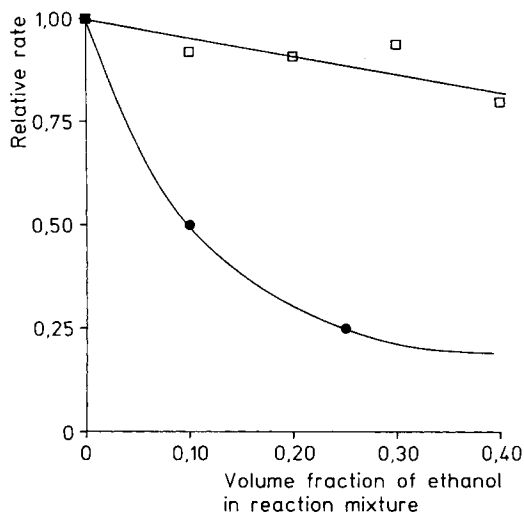


Fig. 7. Effect of ethanol on thiol oxidation rate. Rate expressed relative to the value in 100% water; $[Co] = 2 \cdot 10^{-7}$ mol/L, pH = 9,2–9,5, $[RSH]_0 = 0,14$ mol/L. Polymer-free system (●); with 2,4-ionene, $[N^+] = 10^{-3}$ mol/L (□)

Tab. 2. Occurrence of phthalocyanine aggregates in various systems; -- means no aggregates, - little aggregates, +/- aggregates and monomers in comparable amounts, + mainly aggregates, and ++ only aggregates present

	1					
	unreduced			reduced (+RSH)		
	water 25 °C	alcohol	high temp.	water 25 °C	alcohol	high temp.
Polymer-free	+/-	-	-	+	-	-
Amphiphilic ionene $c \ll cmc^a$	+	+/-	+	+/-	-	--
$c > cmc^a$	+/-	-	-	--	--	--
Polyelectrolyte-type ionene	++	++	++	++	++	++

^{a)} c = mass concentration; cmc = critical micelle concentration

Final remarks

The question remains, why aggregates would be catalytically more active than the monomeric complex.

In our opinion, mainly two effects are involved. In the first place, the ionene-containing aggregates were found to be very stable, e. g. against high temperatures and against complex formation with ligands like alcohols or oxygen⁷⁾. The latter can give rise to the so-called μ -peroxo complex that is known to deactivate the catalyst⁶⁾. Prevention of formation of this complex therefore enhances the reaction rate.

Furthermore, the redox properties of aggregates are presumably more favourable than those of the monomeric species. This was also suggested by Nevin et al.²⁶⁾, who demonstrated that binuclear and tetranuclear phthalocyanines reduce oxygen more efficiently than the mononuclear compound. They attributed this increased activity to the electronic coupling between the phthalocyanine rings.

- 1) W. T. Ford (ed.), *"Polymeric Reagents and Catalysts"*, ACS Symposium Series **308**, Am. Chem. Soc., Washington DC, 1986
- 2) P. Hodge, D. C. Sherrington (eds.), *"Polymer-supported Reactions in Organic Synthesis"*, J. Wiley and Sons, New York 1980
- 3) E. Tsuchida, H. Nishide, *Adv. Polym. Sci.*, **24**, 1 (1977)
- 4) G. Wulff, B. Heide, G. Hefmeier, *React. Polym., Ion Exch., Sorbents* **6**, 299 (1987)
- 5) N. Ise in: *"Polyelectrolytes and their applications"*, edited by A. Rembaum and E. Sélégny, D. Reidel, Dordrecht, The Netherlands 1975
- 6) J. H. Schutten, P. Piet, A. L. German, *Makromol. Chem.* **180**, 2341 (1979)
- 7) J. van Welzen, A. M. van Herk, A. L. German, *Makromol. Chem.* **188**, 1923 (1987)
- 8) J. van Welzen, A. M. van Herk, A. L. German, *Makromol. Chem.* **189**, 587 (1988)
- 9) A. M. van Herk, K. H. van Streun, J. van Welzen, A. L. German, *Br. Polym. J.*, **21**, 125 (1989)
- 10) W. M. Brouwer, P. Piet, A. L. German, *J. Mol. Catal.* **31**, 169 (1985)
- 11) K. H. van Streun, P. Piet, A. L. German, *Eur. Polym. J.* **23**, 941 (1987)
- 12) J. Zwart, H. C. van der Weide, N. Bröker, C. Rummens, G. C. A. Schuit, A. L. German, *J. Mol. Catal.* **3**, 151 (1977-78)
- 13) J. H. Weber, P. H. Busch, *Inorg. Chem.* **4**, 469 (1965)
- 14) L. C. Gruen, R. J. Blagrove, *Aust. J. Chem.* **26**, 319 (1973)
- 15) Micelle-like behaviour of ionenes has been reported recently: V. Soldi, N. de Magalhães Erismann, F. H. Quina, *J. Am. Chem. Soc.* **110**, 5137 (1988)
- 16) J. R. Darwent, I. McCubbin, G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **78**, 903 (1982)
- 17) L. D. Rollmann, R. T. Iwamoto, *J. Am. Chem. Soc.* **90**, 1455 (1968)
- 18) E. I. Kozlyak, A. S. Erokhin, A. K. Yatsimirskii, *Zh. Obshch. Khim.* **58**, 76 (1988)
- 19) E. I. Kozlyak, A. S. Erokhin, A. K. Yatsimirskii, I. V. Berezin, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **35**, 741 (1986)
- 20) W. A. Nevin, W. Liu, M. Melnik, A. B. P. Lever, *J. Electroanal. Chem.* **213**, 217 (1986)
- 21) W. Liu, M. R. Hempstead, W. A. Nevin, M. Melnik, A. B. P. Lever, C. C. Leznoff, *J. Chem. Soc., Dalton Trans.:* **1987**, 2511
- 22) J. F. Myers, G. W. Rayner Canham, A. B. P. Lever, *Inorg. Chem.* **14**, 461 (1975)
- 23) A. M. van Herk, A. H. J. Tulleman, J. van Welzen, A. L. German, *J. Mol. Catal.* **44**, 269 (1988)
- 24) Y.-C. Yang, J. R. Ward, R. P. Seiders, *Inorg. Chem.* **24**, 1765 (1985)
- 25) T. P. M. Beelen, to be published
- 26) W. A. Nevin, W. Liu, S. Greenberg, M. R. Hempstead, S. M. Marcuccio, M. Melnik, C. C. Leznoff, A. B. P. Lever, *Inorg. Chem.* **26**, 891 (1987)