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Effects of complexation of oppositely charged water-soluble cobaltphthalocyanines on the catalytic mercaptoethanol autoxidation

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Abstract

In order to elucidate the different promoting effects polycations have on the cobalt(II)phthalocyanine catalyzed autoxidation of 2-mercaptoethanol, the properties of mixtures of oppositely charged water-soluble cobalt(II)phthalocyanines were studied. The contribution of polycation induced dimerization of the catalyst was investigated by means of combinations of cobalt(II)phthalocyanine-tetra(trimethylammonium) iodide ($\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$) and cobalt(II)phthalocyanine-tetrasodium sulphonate ($\text{CoPc}(\text{NaSO}_3)_4$). A mixture of equimolar amounts of both phthalocyanines shows an increase in reaction rate for the 2-mercaptoethanol autoxidation as compared with an equal amount of one of the catalyst species separately. The highest activities are achieved when the positive charges of the positive phthalocyanine just match the charges of the negative $\text{CoPc}(\text{NaSO}_3)_4$. A mixture of cobalt(II)phthalocyanine-octacarboxylic acid ($\text{CoPc}(\text{COOH})_8$) and $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ exhibits its maximum activity at a ratio of 1:2, indicating the formation of a trimeric catalyst species. Visible light spectroscopy showed that these effects can be ascribed to the formation of aggregates of the phthalocyanines. Addition of a poly(quaternary ammonium) salt, a so-called ionene, to a stoichiometric complex of oppositely charged phthalocyanines results in an increase in the catalytic activity due to substrate enrichment. The activities of an ionene containing equimolar $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{NaSO}_3)_4$ system were never as high as those achieved for a conventional $\text{CoPc}(\text{NaSO}_3)_4/2,4$ -ionene system, probably as a result of the strong bonding between the two oppositely charged molecules, which prevents a break-up of the dimeric species. Conclusively, in order to achieve a high catalytic activity it is favourable to enhance the formation of aggregates of $\text{CoPc}(\text{NaSO}_3)_4$, which probably will break up after the first reaction step.

Key words: autoxidation; carboxylic acids; cobalt; phthalocyanine complexes; tetra(trimethylammonium) iodide ligand; tetrasodium sulphonate ligand; thiols

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Introduction

The effects polymers exert on the cobalt (II)phthalocyanine-tetrasodium sulphonate ($\text{CoPc}(\text{NaSO}_3)_4$) (Fig. 1) catalyzed autoxidation of thiols to disulphides are receiving much attention [1-6]. In our study on polymeric promoting effects we have found that several cationic polymers in homogeneous solution or in immobilized systems have large promoting effects on the $\text{CoPc}(\text{NaSO}_3)_4$ catalyzed thiol autoxidation [7-9].

The best co-catalysts proved to be poly (quaternary ammonium) salts, the so-called ionenes (Fig. 2) [10]. In the case of the addition of 2,4-ionene the highest rate enhancement is observed, i.e. by a factor 50, as compared with the polymer-free system [7]. In the presence of these polycations, the formation of the catalytically inactive dioxygen bridged μ -peroxo complex is strongly suppressed (1): the absorbance peak at 674 nm in the visible light spectrum disappears [11]. Furthermore, the presence of the ionenes leads to substrate enrichment in the polyelectrolyte domain (2), because the reactive species, i.e.

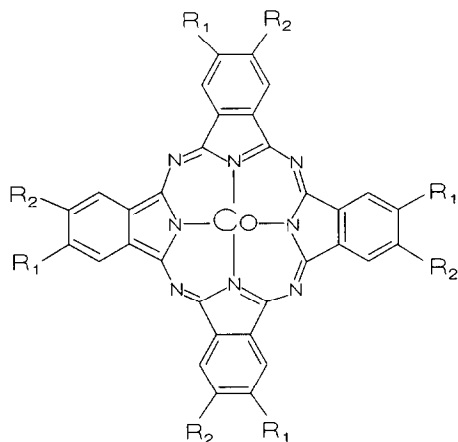


Fig. 1. Structure of $\text{CoPc}(\text{NaSO}_3)_4$, $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and $\text{CoPc}(\text{COOH})_8$.

	R ₁	R ₂
$\text{CoPc}(\text{NaSO}_3)_4$	SO_3Na	H
$\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$	$\text{N}(\text{CH}_3)_3\text{I}$	H
$\text{CoPc}(\text{COOH})_8$	COOH	COOH

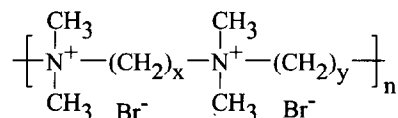


Fig. 2. Structure of x,y -ionene.

the thiolate anion, and the catalyst are both negatively charged. Additionally, Visible light spectroscopy shows that after addition of 2,4-ionene to a $\text{CoPc}(\text{NaSO}_3)_4$ solution the dimeric form (628 nm) is drastically favoured over the monomeric form (662 nm) (3). These dimers or aggregates of $\text{CoPc}(\text{NaSO}_3)_4$ are assumed to be more active than the monomeric species [11], resulting in a tremendous increase in the reaction rate.

These three effects, induced by polycations, collectively contribute to an increase in the catalytic activity. This article is a first attempt to elucidate which effect has the largest contribution to the observed rate enhancement. Therefore, we investigated the spectroscopic and catalytic properties of two mixtures of oppositely charged water-soluble cobalt(II)phthalocyanines, which offers us the possibility to study primarily the influence of dimerization of the catalyst in detail. In these cases, substrate enrichment due to a positively charged polymer domain does not occur. First, a combination of cobalt(II)phthalocyanine-tetra(trimethylammonium) iodide ($\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$) (Fig. 1) containing four positive charges and $\text{CoPc}(\text{NaSO}_3)_4$ with four negative charges, was studied by visible light spectroscopy and catalytic activity measurements. Subsequently, a mixture consisting of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and the eightfold negatively charged cobalt(II)phthalocyanine-octacarboxylic acid ($\text{CoPc}(\text{COOH})_8$) (Fig. 1) was investigated.

In addition, the effects of introducing simple salts and two negatively charged polymers, i.e. poly(styrene sodium sulphonate) (PNaSS) and poly(acrylic acid) (PAA), on the spectroscopic behaviour of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ was studied. Furthermore, we examined the effect of the addition of 2,4-ionene to the mixed phthalocyanine complexes and compared the catalytic activities with those observed for the conventional $\text{CoPc}(\text{NaSO}_3)_4/2,4$ -ionene system. Finally, a reaction mechanism will be proposed based on the new insights.

Experimental

Materials

$\text{CoPc}(\text{NaSO}_3)_4$ was prepared according to a slight adaption by Zwart et al. [12] of the method described by Weber and Busch [13]. $\text{CoPc}(\text{COOH})_8$ was kindly provided by Prof. H. Shirai (Shinshu University, Ueda, Japan). $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ was prepared starting from 150 mg cobalt(II) phthalocyanine-tetraamine, which was dissolved in 40 ml *N,N*-dimethylformamide (DMF), followed by the addition of 0.8 ml 2,6-dimethylpyridine, 7.2 ml DMF and 20 ml methyl iodide. After 2 days, the reaction mixture was poured into 300 ml dimethyl ether. The precipitate was filtered off and washed with 200 ml dimethyl ether. Then the product was dissolved in 500 ml H_2O and after 1 h at 90°C, the solution was filtered and the water was removed. The purifi-

cation procedure consisted further of dissolving the phthalocyanine in 100 ml DMF, which was poured into 200 ml dimethyl ether, followed by washing twice with 100 ml dimethyl ether. After filtration the product was dried in vacuum at 60°C.

Poly(styrene sodium sulphonate) ($\bar{M}_w = 70$ kg/mol) (Janssen Chimica) and poly(acrylic acid) ($\bar{M}_w = 500$ –1000 kg/mol) (Fluka) were used without further purification. 2,4-Ionene ($\bar{M}_n = 22$ kg/mol) was prepared according to the method described by Rembaum et al. [14].

Visible light spectroscopy

All VIS spectra were recorded on a Hewlett-Packard diode array Model 8451 A spectrophotometer at 25°C, using a 1-cm cell.

Catalytic activity measurements

The catalytic thiol autoxidations were carried out batchwise as reported previously [15], in an all-glass double-walled Warburg apparatus, equipped with a powerful mechanical glass stirrer (the stirring speed was 2600 rpm) and thermostated at $25.0 \pm 0.5^\circ\text{C}$. The catalyst solution consisting of the cobalt(II)phthalocyanine derivatives and polymers, was added to the reactor, followed by adjusting the pH by the addition of a concentrated KOH solution. The total reaction volume was 100 ml. The reaction was started by addition of 2-mercaptoethanol (ME). ME (98%, Janssen Chimica) was distilled prior to use, stored in the dark and kept under argon atmosphere in sealed flasks. Reaction rate was measured by monitoring the oxygen uptake with a digital mass flow controller (Inacom, Veenendaal), keeping the oxygen pressure constant at 100 ± 0.05 kPa. The initial reaction rate (experimental error $\pm 5\%$) was measured immediately after ME was added. The pH was monitored by a pHM 62 pH meter equipped with a GK 2401 B pH electrode (Radiometer).

Results and discussion

Visible light spectroscopy

The three polycation promoting effects, i.e. aggregation of the $\text{CoPc}(\text{NaSO}_3)_4$ catalyst combined with the disappearance of the catalytically inactive dioxygen bridged μ -peroxo complex and substrate enrichment in the presence of 2,4-ionene, result in a tremendous increase in the oxidation rate of 2-mercaptoethanol [7]. In order to elucidate which of the three 2,4-ionene induced promoting effects has the largest contribution, mixtures of oppositely charged water-soluble phthalocyanines can be utilized perfectly to study the effect of dimerization of the catalyst in the absence of ionene. As a consequence we investigated the spectroscopic behaviour of combinations of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and $\text{CoPc}(\text{NaSO}_3)_4$ in order to prove the existence of the dimeric form. Due to the fact that there is a lack of information about the

spectral properties of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$, it was necessary to study the spectroscopic behaviour of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ first.

Absorption spectra of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ at different pH values are depicted in Fig. 3. A broad absorption band in the visible light spectrum, consisting of a dimer peak at 626 nm and a monomer peak at 664 nm (Q-bands) can be observed. At high pH (i.e. > 12) the oxygen bridged μ -peroxo complex at 670 nm is formed. The addition of a simple salt, in this case KCl, affects the absorption spectrum, by simultaneously suppressing μ -peroxo complex formation and favouring the non-oxygen bridged dimeric form over the monomeric form at high ionic strengths (Fig. 3). Introducing simple salts to the positively charged phthalocyanine results in dimerization, which is caused by neutralization of the repulsive electrostatic forces of the peripheral quaternary ammonium groups by Cl^- , equivalent to Na^+ in the case of $\text{CoPc}(\text{NaSO}_3)_4$ [16]. As in the case of Na^+ , the induced aggregation of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ could be observed only at high salt concentrations.

It has been demonstrated before that positively charged polymers show similar or even a more effective behaviour, as compared with simple salts, in enhancing aggregation of $\text{CoPc}(\text{NaSO}_3)_4$ [11] and negative porphyrins [17]. Therefore, similar shielding effects should be expected in the case of addition of a negatively charged polymer, in fact a polysalt, to a $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ solution. Addition of different amounts of poly(styrene sodium sulphonate) (PNaSS) to an aqueous $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ solution only little affects the visible light absorbance spectrum and a small decrease of the μ -peroxo peak can be observed. Even at high concentrations PNaSS is not as effective as simple

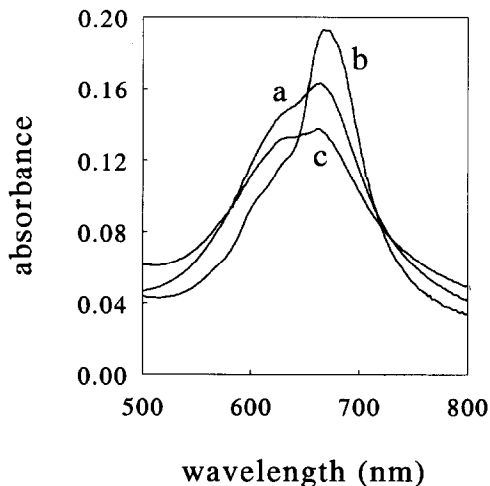


Fig. 3. Absorption spectra of aqueous solutions of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ at different pH and effect of KCl addition. (a) pH=9 (buffer, $I=0.1$ M), (b) pH=13 ($I=0.1$ M), (c) $M_{\text{KCl}}=0.30$ M; ($\text{Cl}^-/\text{CoPc}^{4+}=20000$) at pH=12 (buffer); $[\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4]=1.5 \times 10^{-6}$ mol·dm $^{-3}$.

salts in stabilizing the aggregates, probably as result of the less flexible backbone and the position of the negative charge in the bulky styrene side-groups.

In contrast poly(acrylic acid) (PAA), having a more flexible chain, induces aggregation of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ more effectively. Increasing the $\text{COO}^-/\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ ratio results in favouring the dimer absorbance band (626 nm) over the monomer band (664 nm). When the $\text{COO}^-/\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ ratio exceeds about 4, the ratio of the two absorbances remains constant (Fig. 4) almost similar to the 2,4-ionene/ $\text{CoPc}(\text{NaSO}_3)_4$ system [11]. Further aggregation, which was observed for $\text{CoPc}(\text{NaSO}_3)_4$ at high ionene concentrations, could not be detected in the PAA/ $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ system.

It has been reported [18,19] that positively charged phthalocyanines, like copper and cobalt N,N',N'',N''' -tetramethyltetra-2,3-pyridinoporphyrazin derivatives did not aggregate in aqueous solution due to the fact that positive charges are located in the ring. After addition of salts, probably a less complete shielding of the positive charges is possible due to delocalization of the positive charge over the porphyrin ring. Obviously, in our case the positive charges of the ammonium groups of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ are not delocalized in the conjugated π -system and are similar to positively charged porphyrins where the positive charges were localized at a substituent pyridinium group [20,21], resulting in the formation of aggregates for both systems. Thus, upon addition of salt or PAA, the counterions can perfectly match the localized positive charges of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$.

Combinations of oppositely charged phthalocyanines should give us the opportunity to study their aggregation behaviour in the absence of polymers. Looking at the visible light spectroscopy results of mixtures of $\text{CoPc}(\text{NaSO}_3)_4$

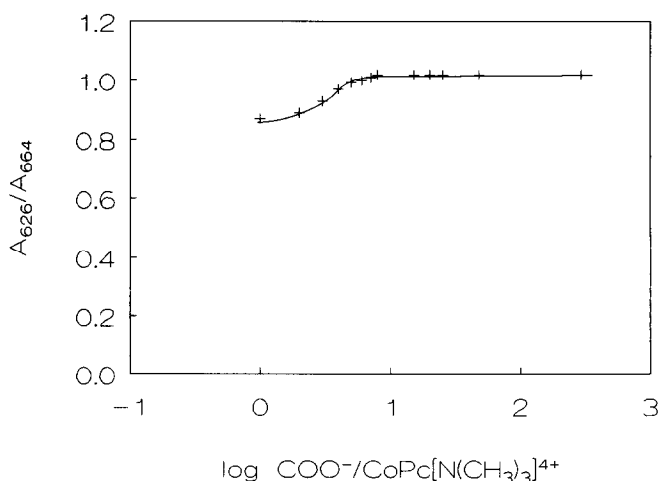


Fig. 4. Ratio of absorbances at 626 nm and 664 nm as a function of the COO^-/Co ratio for a $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{PAA}$ system. $[\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4] = 5 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$, $\text{pH} = 12$ (buffer, $I = 0.1 \text{ M}$).

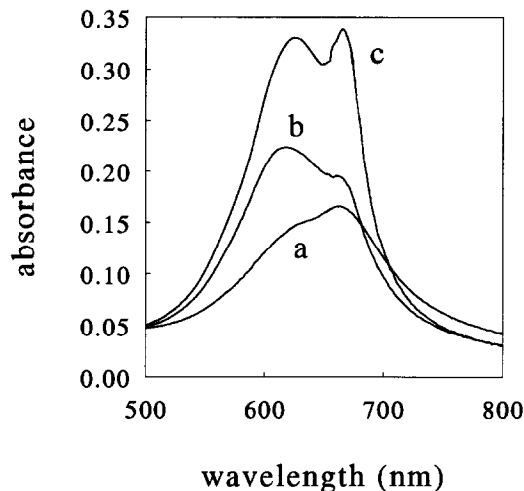


Fig. 5. Absorption spectra of mixtures of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and $\text{CoPc}(\text{NaSO}_3)_4$, keeping the total CoPc concentration constant. pH=9 (buffer, $I=0.1$ M). (a) $[\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4]=1.5 \times 10^{-5}$ M, (b) $[\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4]=1.0 \times 10^{-5}$ M $[\text{CoPc}(\text{NaSO}_3)_4]=0.5 \times 10^{-5}$ M, (c) $[\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4]=0.75 \times 10^{-5}$ M $[\text{CoPc}(\text{NaSO}_3)_4]=0.75 \times 10^{-5}$ M.

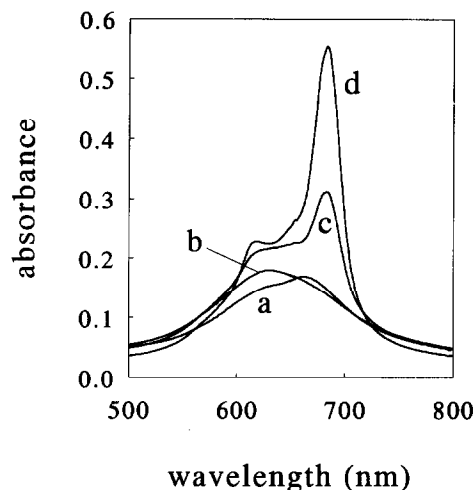


Fig. 6. Absorption spectra of mixtures of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and $\text{CoPc}(\text{COOH})_8$, keeping the total CoPc concentration constant. pH=9 (buffer, $I=0.1$ M). (a) $[\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4]=1.5 \times 10^{-5}$ M, (b) $[\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4]=1.25 \times 10^{-5}$ M $[\text{CoPc}(\text{COOH})_8]=0.25 \times 10^{-5}$ M, (c) $[\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4]=1.0 \times 10^{-5}$ M $[\text{CoPc}(\text{COOH})_8]=0.5 \times 10^{-5}$ M, (d) $[\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4]=0.75 \times 10^{-5}$ M $[\text{CoPc}(\text{COOH})_8]=0.75 \times 10^{-5}$ M.

and $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$, keeping the total amount of phthalocyanine constant, it can be seen that upon raising the $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ concentration the dimer/monomer ratio increases (Fig. 5). Obviously, hetero-dimeric complexes of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and $\text{CoPc}(\text{NaSO}_3)_4$ are formed, which remained stable even after increasing the pH to 13, i.e. no formation of μ -peroxo complexes

(see Fig. 3) could be observed. In contrast to $\text{CoPc}(\text{NaSO}_3)_4$ dimers, the so-called homo-dimers, in the hetero-dimers the opposite charges of the phthalocyanines are additive to the Van der Waals attraction resulting in considerable stabilization. Neither precipitation was observed, so the hetero-dimeric complexes remain water-soluble.

Aggregation phenomena are also detectable in the case of mixtures of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and the eightfold negatively charged $\text{CoPc}(\text{COOH})_8$ (Fig. 6). Responsible for the high absorbance at 684 nm is not the μ -peroxo complex formation of $\text{CoPc}(\text{COOH})_8$, but the presence of monomeric species, because $\text{CoPc}(\text{COOH})_8$ is unable to form μ -peroxo complexes [22]. In Fig. 6 is shown that upon increasing the $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ concentration the dimer/monomer ratio increases. The spectra of several mixtures of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and $\text{CoPc}(\text{COOH})_8$ clearly indicate that aggregation of the two phthalocyanines occurs.

Catalytic activity measurements

In order to determine the effects of dimeric cobaltphthalocyanine complexes on the catalytic activity we varied the concentration ratios of the two phthalocyanine combinations. In Fig. 7 the mercaptoethanol oxidation rates of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{NaSO}_3)_4$ mixtures are depicted as a function of the mole-fraction of $\text{CoPc}(\text{NaSO}_3)_4$, keeping the total amount of cobaltphthalocyanine constant. It clearly shows that at a $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{NaSO}_3)_4$ ratio of 1 the highest reaction rate is reached, which is about three times higher than the activity measured for the same amount $\text{CoPc}(\text{NaSO}_3)_4$. At this ratio the opposite charges of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ are

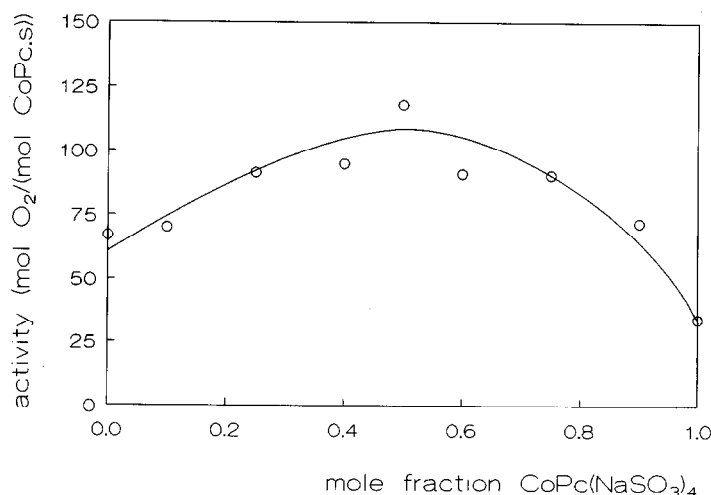


Fig. 7. The ME oxidation rate as function of the mole fraction of $\text{CoPc}(\text{NaSO}_3)_4$ in $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{NaSO}_3)_4$ mixtures. $[\text{CoPc}]_{\text{total}} = 4 \times 10^{-7}$ M, pH=9, $[\text{ME}] = 7.1 \times 10^{-2}$ M, $T = 25^\circ\text{C}$.

just matching the negative charges of $\text{CoPc}(\text{NaSO}_3)_4$, thus it may be concluded that dimeric complexes are responsible for the higher catalytic activity.

Moreover, it can be seen that the reaction rate of $\text{CoPc}(\text{NaSO}_3)_4$ is lower as compared with $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$, which is a result of electrostatic repulsion between the thiolate anion and the negative charges of $\text{CoPc}(\text{NaSO}_3)_4$. In order to compare the activity of the dimeric catalyst species with the activity of a $\text{CoPc}(\text{NaSO}_3)_4$ monomer, one must realize that a polymer-free $\text{CoPc}(\text{NaSO}_3)_4$ system, in fact, can consist of monomers, dimers and μ -peroxo complexes. However, Wöhrle et al. [23] showed that the activity of an aqueous $\text{CoPc}(\text{NaSO}_3)_4$ solution exhibits similar activity to the cobaltphthalocyanine monomers covalently bonded to a silica surface. Therefore, it is a good model for a $\text{CoPc}(\text{NaSO}_3)_4$ monomer in the catalytic system. Apparently, in an ionene-free $\text{CoPc}(\text{NaSO}_3)_4$ solution the presence of the catalytically inactive μ -peroxo complexes is compensated by the active dimeric cobalt species. Thus, the higher activity of the hetero-dimer compared with that of a $\text{CoPc}(\text{NaSO}_3)_4$ monomer is presumably caused by suppression of the inactive μ -peroxo complex. The absence of the μ -peroxo complex was also demonstrated in Fig. 5: the spectrum of the hetero-dimer could not be influenced even after raising the pH to 13.

The dependence of the mercaptoethanol oxidation rate on mixtures of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and $\text{CoPc}(\text{COOH})_8$ is depicted in Fig. 8. The results show the appearance of stoichiometric complexation of the $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{COOH})_8$ complex at a ratio of 2, where the highest activities are observed. At this point the eight negative charges of $\text{CoPc}(\text{COOH})_8$ are matched by the eight positive charges of two $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ molecules. Obviously,

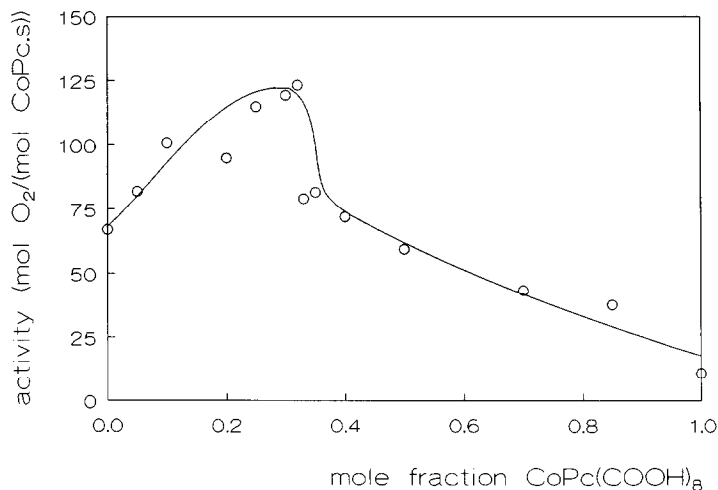


Fig. 8. The ME oxidation rate as function of the mole fraction of $\text{CoPc}(\text{COOH})_8$ in $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{COOH})_8$ mixtures. $[\text{CoPc}]_{\text{total}} = 4 \times 10^{-7} \text{ M}$, $\text{pH} = 9$, $[\text{ME}] = 7.1 \times 10^{-2} \text{ M}$, $T = 25^\circ \text{C}$.

trimeric complexes are responsible for this rate enhancement. The higher oxidation rate of $\text{CoPc}(\text{NaSO}_3)_4$ compared with that of $\text{CoPc}(\text{COOH})_8$ can be explained by the higher electrostatic repulsion between the phthalocyanine and the thiolate anion in the latter system.

The influence of substrate enrichment was investigated by studying the effects of polyelectrolytes on the activity of mixtures containing the different cobalt(II)phthalocyanines. First, the effects of introducing PNaSS and PAA on the oxidation rate of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ were studied. As presented in Table 1, it is demonstrated that after addition of PNaSS, the catalytic activity decreases as a result of the electrostatic repulsion between the negatively charged polymer domain and the thiolate anions. By contrast, the reaction rate for the $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{PAA}$ system (Table 1) remains constant or even a small increase can be observed, due to two complementary effects. The reaction rate is again reduced by the above mentioned substrate repulsion, but this effect is compensated by the formation of the catalytically very active $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ dimers on the flexible PAA.

Likewise, we investigated the influence of the addition of ionene to a reaction mixture containing oppositely charged phthalocyanines. Primarily, we studied the effect of addition of 2,4-ionene to an equimolar solution of $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and $\text{CoPc}(\text{NaSO}_3)_4$. After varying the procedure of addition, we were able to conclude that the bonding between $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and $\text{CoPc}(\text{NaSO}_3)_4$ is stronger than between $\text{CoPc}(\text{NaSO}_3)_4$ and 2,4-ionene, because similar activities were observed irrespective of the order of addition of the three compounds. In Table 2 the activities are presented for $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{NaSO}_3)_4$ mixtures with and without 2,4-ionene. Keeping the total cobaltphthalocyanine concentration constant, one sees that addition of 2,4-ionene raises the absolute activity of the dimeric $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{NaSO}_3)_4$ complex, but the reaction rates were much

TABLE 1

Dependence of ME oxidation^a rate for several PNaSS/ $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ and PAA/ $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ solutions

X/ $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$	Activity (mol O ₂ /(mol $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4 \cdot \text{s}$))	
	X = SO ₃ ⁻	X = COO ⁻
0	67	67
3	47	73
5	42	70
10	40	82
150	35	86
1000	37	95

^aConditions: $[\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4] = 4 \times 10^{-7} \text{ M}$, pH=9, $[\text{ME}] = 7.1 \times 10^{-2} \text{ M}$, T=25 °C.

TABLE 2

Effect of 2,4-ionene on the ME oxidation^a rates of different mixtures of CoPc[N(CH₃)₃I]₄ with CoPc(NaSO₃)₄ or CoPc(COOH)₈

CoPc[N(CH ₃) ₃ I] ₄ (10 ⁻⁷ M)	CoPc(NaSO ₃) ₄ (10 ⁻⁷ M)	CoPc(COOH) ₈ (10 ⁻⁷ M)	Activity mol (O ₂ / (mol CoPc·s))	Activity, 2,4- ionene added (mol O ₂ /(mol CoPc·s))
-	4	-	34	1100
2	2	-	118	314
4	-	-	67	65
-	-	4	10	25
2	-	2	56	109
2.67	-	1.33	121	165

^aConditions: pH=9, [ME]=7.1×10⁻² M, N⁺/Co=50, T=25°C.

lower than those with the conventional CoPc(NaSO₃)₄/2,4-ionene system. This difference in catalytic activities will be discussed later.

Addition of 2,4-ionene to several CoPc[N(CH₃)₃I]₄/CoPc(COOH)₈ mixtures leads to rate enhancement for all three investigated systems (Table 2) when compared with the ionene-free system. A similar rate increase by a factor 2 can be noticed for both the CoPc(COOH)₈ and the dimeric CoPc[N(CH₃)₃I]₄/CoPc(COOH)₈ complex. As reported elsewhere, this rate increase for a CoPc(COOH)₈/2,4-ionene system as compared with the polymer-free system, is only caused by substrate enrichment [22]. From the fact that a similar rate enhancement is observed for both the ionene containing dimeric CoPc[N(CH₃)₃I]₄/CoPc(COOH)₈ complex and the dimeric CoPc[N(CH₃)₃I]₄/CoPc(NaSO₃)₄ complex, we are able to conclude that both dimeric complexes are fully contained within the polyelectrolyte domain, and addition of 2,4-ionene only results in substrate enrichment.

Only for the trimeric CoPc[N(CH₃)₃I]₄/CoPc(COOH)₈ complex is a lower rate increase observed in the presence of 2,4-ionene. The reason for this difference in relative rate enhancement is the difference in electrostatic interactions with the positively charged polymer domain. Presumably, in the case of trimeric complexes all negative charges are shielded by the positively charged phthalocyanines, which leads to a situation in which it is very likely that a large part of the trimeric species is not present in the polycation domain. In the case of the dimeric CoPc[N(CH₃)₃I]₄/CoPc(NaSO₃)₄ complex there is also a shielding of the negative charges, but since there is only one positively charged phthalocyanine molecule involved in this shielding, one side of the negatively charged phthalocyanine will be accessible to electrostatic interaction with the positive polymer.

The enhanced catalytic activity of the dimeric CoPc[N(CH₃)₃I]₄/CoPc(NaSO₃)₄ complex as compared with the activity of a monomeric

CoPc(NaSO₃)₄ species by only a factor 3, would imply an overestimation of the importance of the polymer-induced dimerization, which, so far, has been assumed to be responsible for the largest promoting contribution in a CoPc(NaSO₃)₄/2,4-ionene system [7].

It is only justified to compare the activity of a dimeric CoPc[N(CH₃)₃I]₄/CoPc(NaSO₃)₄ complex with a CoPc(NaSO₃)₄ dimer if the electronic structure of both dimeric species is identical. First, the interaction between two phthalocyanines molecules can be ascribed merely to Van der Waals interactions [24-26]. Secondly, the peripheral groups have no significant influence on the electron distribution within the porphyrin ligand [27]. Only a slight difference in molecular orbitals might occur if the inter-ring distance between the phthalocyanines in the hetero-dimer is shorter than that in the homo-dimer, due to the extra electrostatic interaction. A different electronic structure should be reflected in discrepancies in the visible light spectrum between the hetero-dimeric and homo-dimeric species. When comparing the spectra of CoPc[N(CH₃)₃I]₄/CoPc(NaSO₃)₄ dimers (Fig. 5) with those of 2,4-ionene induced CoPc(NaSO₃)₄ dimers [11] no significant wavelength shifts can be observed. The above mentioned results make it reasonable that the catalytic activities of both dimeric species are comparable.

The question remains why the 2,4-ionene containing CoPc(NaSO₃)₄/CoPc[N(CH₃)₃I]₄ system is less active than the conventional CoPc(NaSO₃)₄/2,4-ionene system. The contribution of the three polycation promoting effects appeared to be dependent on the polymer/catalyst ratio [7]. If we look in more detail at the catalytic activity as a function of the 2,4-ionene/CoPc(NaSO₃)₄ ratio, expressed as the N⁺/Co ratio, the activity increases at higher ionene concentrations. At a N⁺/Co ratio of 4 higher activities, as compared with the polymer-free system, are achieved due to suppression of the μ-peroxo complex and the simultaneous formation of CoPc(NaSO₃)₄ dimers [7]. From that point on, the rate increase was ascribed to substrate enrichment and mainly to enhanced aggregation of the catalyst, i.e. higher aggregates of dimeric CoPc(NaSO₃)₄ species [11]. The optimal catalytic conditions, where the highest oxidation rates are observed, are reached at a N⁺/Co ratio of 50 [28].

Recently, we have shown that this optimal N⁺/Co ratio is a function of the molecular weight of 2,4-ionene [28]. Using monodisperse oligomeric 2,4-ionenes it was found that the optimal N⁺/Co ratio for a CoPc(NaSO₃)₄/2,4-ionene system decreases when the chain length of the ionene increases till a constant value was reached at eight N⁺ per chain. A similar dependence on the molecular weight of the 2,4-ionene was also found for the catalyst CoPc(COOH)₈, which is incapable of forming 2,4-ionene-induced aggregates [22]. Hence, it was possible to study exclusively the ionene-induced effect of substrate enrichment. The results showed that similar optimal N⁺/Co ratios were realized for both 2,4-ionene containing CoPc(COOH)₈ and CoPc(NaSO₃)₄ systems [22]. So we may conclude that the value for the optimal N⁺/Co ratio is predominantly determined by substrate enrichment.

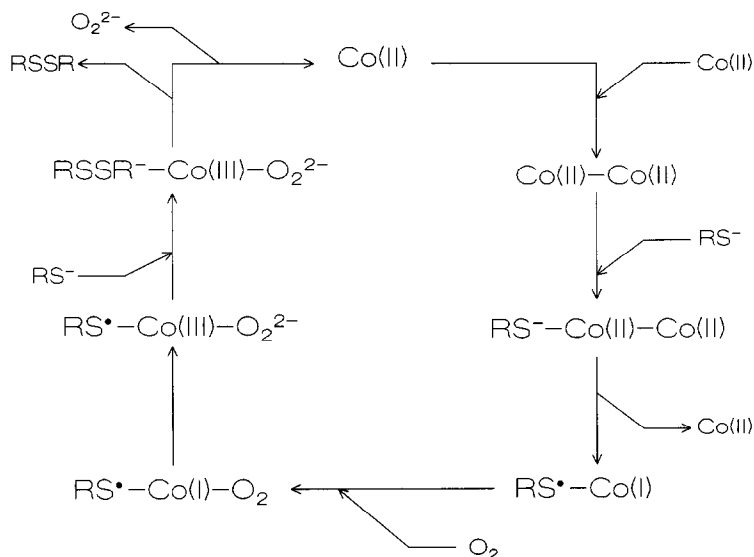
Therefore, the difference in catalytic activity between homo-dimers and hetero-dimers in the presence of ionene can not be ascribed solely to the formation of higher $\text{CoPc}(\text{NaSO}_3)_4$ aggregates.

An alternative explanation can be found in the fact that there is a difference between the intrinsic catalytic activities of a dimeric $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{NaSO}_3)_4$ species and a dimeric $\text{CoPc}(\text{NaSO}_3)_4$ species. It is known for clamshell binuclear phthalocyanine complexes that these exhibit better redox properties as compared with monomeric species [29,30]. The same authors also suggested that in these covalently bonded binuclear phthalocyanine systems with a flexible linkage between the phthalocyanine rings which normally show cofacial dimerization, addition of a coordinating species, followed by reduction or oxidation, leads to a decrease in the coupling effects. These observations were explained by a possible dissociation of the dimeric species [31–35].

Additionally, Pasternack observed a similar break-up of homo-dimeric porphyrins after ligation [36]. The ligation step to the porphyrin dimer appeared faster than the break-up into a monomer and a ligated monomer. After breaking up, a very fast consecutive ligation of both the monomer and ligated monomer occurred.

Considering these data, we suggest in our case that the 2,4-ionene induced formation of dimers of $\text{CoPc}(\text{NaSO}_3)_4$ improves the first step of addition of the thiolate anion, followed by oxidation of the thiolate and simultaneous reduction of $\text{Co}(\text{II})$ to $\text{Co}(\text{I})$. This step is followed by break-up of the dimeric species, which also provides two extra catalytic sites. All effects result in a higher catalytic activity of a $\text{CoPc}(\text{NaSO}_3)_4$ dimer as compared with a $\text{CoPc}(\text{NaSO}_3)_4$ monomer. In the case of the $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{NaSO}_3)_4$ dimers it is very unlikely that these dimers will break up after the first reaction step due to the strong electrostatic interaction, as was demonstrated by the catalytic experiments in which the procedure of the addition was varied. However, attempts [7] failed to derive evidence about the existence of a $\text{Co}(\text{I})\text{-RS}^*$ species formed after break-up of $\text{CoPc}(\text{NaSO}_3)_4$ dimers. On the other hand, it has not been established yet whether the dimeric species persists during the catalytic cycle. It has been demonstrated that aggregation is only little affected by addition of a second coordinating species: only at high thiolate anion concentrations will the dimer dissociate [7].

Other arguments supporting the mechanism of break-up of $\text{CoPc}(\text{NaSO}_3)_4$ dimers after ligation can be based on earlier described experiments for a $\text{CoPc}(\text{NaSO}_3)_4$ system with poly(vinyl amine) (PVAm) as polymeric promoter [37,38]. UV-VIS spectroscopy showed that the amount of dimers decreased upon raising the PVAm concentration, while enhanced catalytic activities were found. This effect is probably the result of the fact that a monomeric $\text{CoPc}(\text{NaSO}_3)_4$ molecule is capable of interacting electrostatically with the quaternary ammonium groups as well as of coordinating with a nitrogen atom from PVAm. Such a situation is very similar to the supposed structure of a



Scheme 1. Reaction mechanism of the homogeneous $\text{CoPc}(\text{NaSO}_3)_4/2,4\text{-ionene}$ catalyzed thiol oxidation. Co denotes the $\text{CoPc}(\text{NaSO}_3)_4$ complex.

$\text{CoPc}(\text{NaSO}_3)_4$ dimer, where a nitrogen atom from one $\text{CoPc}(\text{NaSO}_3)_4$ molecule is axially positioned above the metal centre of the other phthalocyanine ring. Probably, a coordinative interaction of the $\text{CoPc}(\text{NaSO}_3)_4$ molecule with the NH_2 group of PVAm has a similar effect on the thiol ligation as compared with a dimeric $\text{CoPc}(\text{NaSO}_3)_4$ species.

Resuming, an adaptation of the reaction mechanism for a $\text{CoPc}(\text{NaSO}_3)_4/2,4\text{-ionene}$ system, based on the reductive cycle of Zwart [39] and further developed by Van Herk et al. [40], is presented in Scheme 1. The catalyst is predominantly present in its dimeric form and leads to a faster ligation of thiolate anions, the subsequent reduction of $\text{Co}(\text{II})$ to $\text{Co}(\text{I})$, and the simultaneous oxidation of the thiolate anion to a thiol radical. After this step, the dimer breaks up and ligation of molecular oxygen occurs. Oxygen is reduced to peroxide by the oxidation of $\text{Co}(\text{I})$ to $\text{Co}(\text{III})$. Ligation of a second thiolate anion, followed by reduction of $\text{Co}(\text{III})$ leads to a release of the axially bonded reaction products. The free $\text{Co}(\text{II})$ phthalocyanine will now form a new dimer with a second phthalocyanine.

In order to prove above mentioned mechanism we are presently synthesizing a water-soluble covalently linked dimeric cobaltphthalocyanine species, which can function as a realistic model for a $\text{CoPc}(\text{NaSO}_3)_4$ dimeric species, capable of breaking up after the first addition step.

Conclusions

The visible light spectroscopy experiments clearly showed interaction between oppositely charged phthalocyanines, resulting in aggregated species for

both the $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{NaSO}_3)_4$ combination as well as $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{COOH})_8$ mixtures. Stoichiometric dimeric and trimeric catalyst complexes exhibited the highest catalytic activities measured so far for any phthalocyanine catalyzed mercaptoethanol autoxidation in the absence of polycations. The addition of 2,4-ionene to these complexes leads to a further reaction rate increase, purely due to substrate enrichment of thiolate anions near the active sites. The difference in catalytic activities between an ionene containing $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{NaSO}_3)_4$ system and the conventional $\text{CoPc}(\text{NaSO}_3)_4/2,4\text{-ionene}$ system can probably be ascribed to a faster ligation of thiolate anions and the subsequent break-up of the dimeric species.

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