

Effects of ionenes on structure and catalytic activity of cobaltphthalocyanine. 1. Visible light spectroscopic investigations

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Effects of ionenes on structure and catalytic activity of cobaltphthalocyanine, 1

Visible light spectroscopic investigations

Joke van Welzen, Alex M. van Herk, Anton L. German*

Laboratory of Polymer Chemistry, Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, The Netherlands

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SUMMARY:

The structural behaviour of cobalt(II)phthalocyanine-tetrasodium sulfonate ($\text{CoPc}(\text{NaSO}_3)_4$) (1), a catalyst used in thiol oxidation, was investigated in the presence of ionenes (poly(quaternary ammonium salts), (2)) using visible light spectroscopy. It was observed that ionenes, which have been shown to promote the catalytic activity, strongly enhance the aggregation of the cobalt complex. No cobalt site isolation occurred up to $\text{N}^+/\text{Co} = 10^5$. Furthermore, a stoichiometric $\text{CoPc}(\text{NaSO}_3)_4$ /ionene complex appeared to be formed with an N^+/Co -ratio of 4:1. This ratio was found to hold for ionenes with \bar{M}_n varying from 6100 to 22000 and charge densities from 0,8 to 1,5. As the charge density was increased, the observed $\text{CoPc}(\text{NaSO}_3)_4$ spectrum was more affected. Experiments with oxygen in alkaline solution revealed that the complex was resistant toward oxygen adduct formation in the presence of ionenes. This phenomenon is discussed in relation to the catalytic activity of the system.

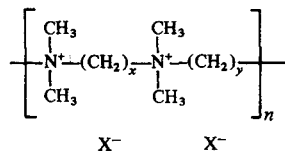
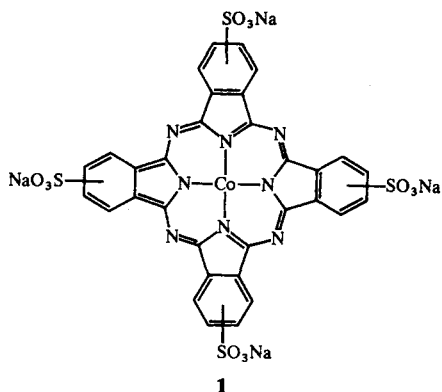
Introduction

A well known catalyst for the oxidative conversion of thiols into the corresponding disulfides is cobalt(II)phthalocyanine-tetrasodium sulfonate¹⁾, $\text{CoPc}(\text{NaSO}_3)_4$, (1). It is being used industrially in the so-called Merox oil sweetening process.



In particular, investigations by Schutten et al.^{2,3)} and Brouwer et al.⁴⁻⁶⁾ have shown that addition of basic polymers, such as poly(vinylamine) (PVAm), strongly promotes the catalytic activity (about 40-fold). According to these authors, the rate enhancement is caused by three major effects: (1) a local increase (within the polymer coil domain) of the concentration of the thiolate anion, that is involved in the rate determining step⁴⁾; (2) a local increase of the $\text{CoPc}(\text{NaSO}_3)_4$ concentration by coordinative bonding^{2,5)}; (3) the isolation of the catalytic sites, resulting in prevention of the formation of oxygen bridged dimeric cobalt species, which are believed to be inactive as a catalyst³⁾.

Our present work is aimed at elucidating the role of the polymer in more detail. As a model system we are currently investigating $\text{CoPc}(\text{NaSO}_3)_4$ in the presence of ionenes (poly(quaternary ammonium salts), (2)). These polymers are preferred over PVAm since their cationic charge, required for increasing the local thiolate anion



2 (X = Br, OH, etc.)

2a: x = 2; y = 4

2b: x = 2; y = 6

2c: x = 2; y = 10

concentration, is independent of pH. As a consequence, the catalytic activity is less influenced by pH than in the case of PVAm.

Furthermore, the maximum activity is even somewhat higher for ionenes and their catalytic activity decreases less in successive thiol oxidation runs⁶. This also makes the behaviour of the ionenes an interesting object of study.

An important difference between PVAm and ionenes is the lack of groups allowing coordinative interaction in the latter. This implies that the interaction of the ionene polymers with the cobalt complex must be purely electrostatic, whereas PVAm can additionally form dative bonds through its amine groups².

Therefore, our attention was primarily focused on the structure of the CoPc(NaSO₃)₄/ionene system, of which a study is presented in this paper.

Experimental part

Syntheses: CoPc(NaSO₃)₄ (**1**), synthesized as described by Zwart et al.⁷, was kindly provided by Dr. T. P. M. Beelen. The ionenes **2a**–**c** (with x = 2 and y = 4, 6, or 10) were prepared according to the method reported by Brouwer et al.⁶. The reagents were obtained from Fluka AG (purum) and used without further purification.

\bar{M}_n -variation: The molecular mass of the 2,4-ionene **2a** was varied either by limiting the polymerization time (down to 6 h) or by non-stoichiometric combination of the reagents. After modification of the bromide endgroups with a large excess of *N,N,N',N'*-tetramethylethylenediamine, \bar{M}_n was determined by endgroup titration under nitrogen atmosphere, using an excess of HCl, and NaOH as the titrant⁸. The experiments described here, were carried out using ionenes with \bar{M}_n values of 1 800, 2 200, 3 400, 6 100, 13 000, 16 000 and 22 000.

Ionene concentration: The concentration of ionene solutions was expressed as the concentration of ammonium groups ([N⁺]), i. e. twice the concentration of repeating units.

Visible light spectroscopy: Spectroscopic measurements were performed with a Hewlett Packard 8451 A diode array spectrophotometer, equipped with a high intensity deuterium lamp. A cuvette of l = 1,000 cm length was used, thermostatted at 25,0 ± 0,5 °C. Whenever it was necessary, the measured phthalocyanine absorbances were corrected for absorption by ionenes. From the absorbance values, apparent absorptivities ($\epsilon_{\lambda}^{\text{app}}$) were calculated according to

$$\epsilon_{\lambda}^{\text{app}} = \frac{\text{Absorbance (at } \lambda)}{[\text{Co}] \cdot l} \quad (2)$$

Results and discussion

Salt/polysalt effects

It is well known that $\text{CoPc}(\text{NaSO}_3)_4$ in neutral aqueous solution exhibits two absorption maxima in the visible region, due to partial dimerisation⁹⁾ according to



with dimerisation constant $K_D = [D]/[M]^2$.

The dimeric complex D, presumably formed by overlap of the extended π -electron systems, shows a maximum at 628 nm, whereas the monomer M has its maximum at 662 nm. Formation of oxygen-bridged dimers¹⁰⁾ ($\lambda_{\text{max}} = 674$ nm) does not occur under those conditions, unless the pH of the solution is raised.

Upon addition of simple salts, like KCl, the absorptivity at 628 nm increases¹⁰⁾. This means K_D is increased, probably as a result of partial neutralisation (shielding effect) of the repulsive electrostatic forces caused by sulfonate anions.

Larger amounts of salt cause loss of the isosbestic points and a shift of the dimer absorption maximum to lower wavelengths (620–622 nm). This shift is thought to be the result of the formation of polynuclear $\text{CoPc}(\text{NaSO}_3)_4$ aggregates, as was demonstrated for the copper analogue by Kratky and Oelschlaeger¹¹⁾.

Similar effects should be expected in the case of ionene addition, since ionenes are in fact polysalts. Moreover, charged polymers in general are known to enhance association of oppositely charged dye molecules¹²⁾.

Indeed, this behaviour was observed for the $\text{CoPc}(\text{NaSO}_3)_4$ /ionene system (see Fig. 1). Even a very dilute ionene solution (10^{-5} mol/l in N^+ , 10^{-6} mol/l in Co) showed the spectrum typical of $\text{CoPc}(\text{NaSO}_3)_4$ oligomers. On these grounds it can be concluded that the positive effect of ionenes on the $\text{CoPc}(\text{NaSO}_3)_4$ aggregation process is high.

Effects of varying the N^+ /Co-ratio

In order to obtain more detailed information about the effects of ionenes on the cobalt complex structure, visible light spectroscopic measurements were carried out over a wide range of N^+ /Co-ratios, using different ionenes. The results for 2,4-ionene **2a** ($\bar{M}_n = 22000$) are given in Figs. 1 to 3. In a qualitative way, all other ionenes tested showed the same behaviour. Analogous measurements were performed with NaBr instead of ionenes (Fig. 4). The essential features of the figures are discussed below.

Looking at Fig. 3, three regions can be distinguished: one where N^+ /Co < 4 (I), one where N^+ /Co > 100 (III) and the intermediate region (II).

In region I, as N^+ /Co increases from 0 to 4, it appears that $\epsilon_{628}^{\text{app}}/\epsilon_{662}^{\text{app}}$, which is a measure of the relative amount of aggregated cobalt species, gradually increases. This is obviously due to dimerisation (oligomerisation), as described in the previous section.

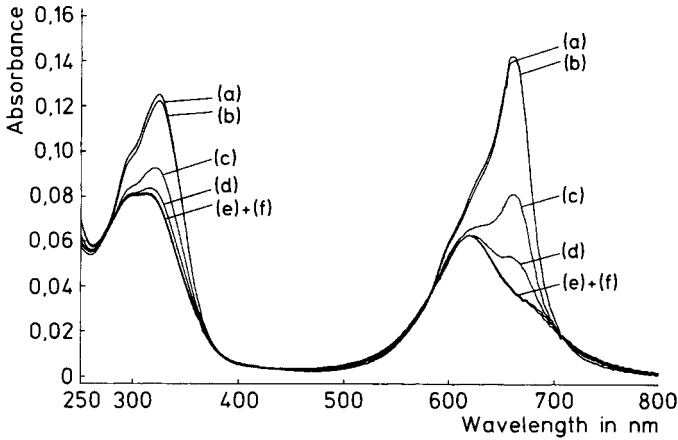


Fig. 1. Visible spectra of neutral aqueous solutions of $\text{CoPc}(\text{NaSO}_3)_4$ ($2 \cdot 10^{-6}$ mol/l) in the presence of various amounts of 2,4-ionene ($\bar{M}_n = 22000$). (a): $\text{N}^+/\text{Co} = 0$, (b): $\text{N}^+/\text{Co} = 0,1$, (c): $\text{N}^+/\text{Co} = 3$, (d): $\text{N}^+/\text{Co} = 4$, (e): $\text{N}^+/\text{Co} = 5$, (f): $\text{N}^+/\text{Co} = 100$

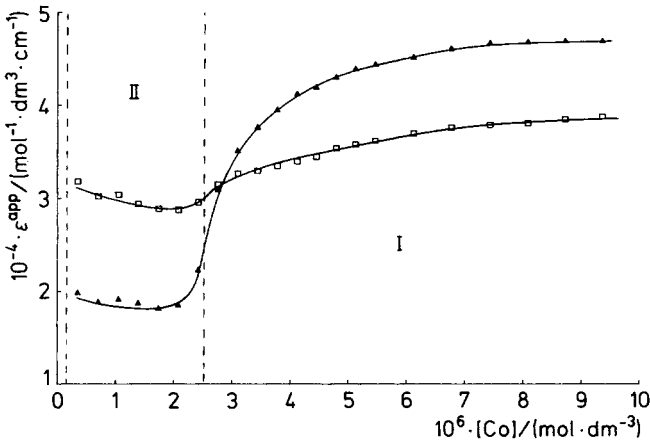


Fig. 2. Apparent absorptivities ϵ^{app} of $\text{CoPc}(\text{NaSO}_3)_4/2,4\text{-ionene}$ solutions versus $[\text{Co}]$; (\square): $\lambda = 628$ nm, (\blacktriangle): $\lambda = 662$ nm; $[\text{N}^+]$ was kept constant at 10^{-5} mol/l, \bar{M}_n of the ionene was 22000

Simultaneously, both $\epsilon_{628}^{\text{app}}$ and $\epsilon_{662}^{\text{app}}$ are gradually decreasing, probably as a result of strong interaction of $\text{CoPc}(\text{SO}_3)_4^{4-}$ with the highly positively charged ionene, thus lowering the molar absorptivities of both M and D. This concept is supported by our observation that the decrease of $\epsilon_{628}^{\text{app}}$ and $\epsilon_{662}^{\text{app}}$ becomes less pronounced as the charge density of the ionene decreases (by taking 2,6- or 2,10-ionene instead of 2,4-ionene).

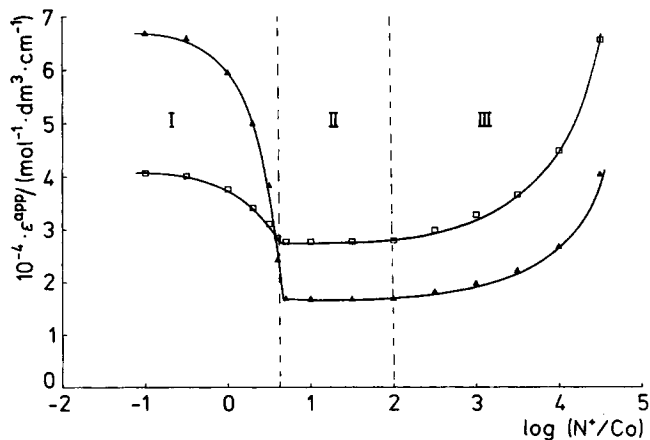


Fig. 3a.

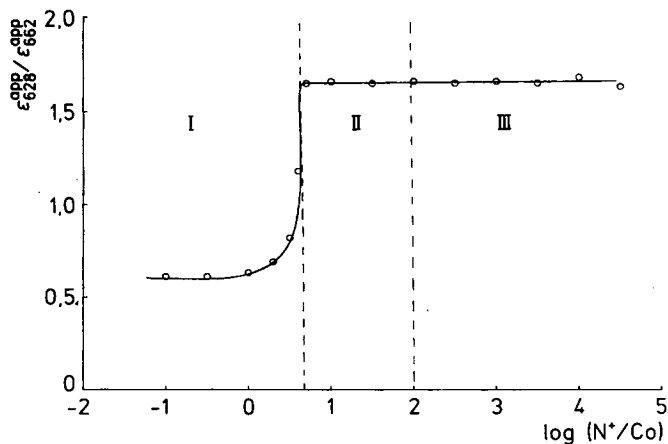


Fig. 3b.

Fig. 3a. Dependence of the apparent absorptivities ϵ^{app} at 628 nm (\square) and 662 nm (\blacktriangle) on the N^+/Co -ratio

Fig. 3b. $\epsilon_{628}^{\text{app}}/\epsilon_{662}^{\text{app}}$ as a function of the N^+/Co -ratio. $[\text{Co}]$ was kept constant at $2 \cdot 10^{-6}$ mol/l, the ionene used was 2,4-ionene ($\bar{M}_n = 22000$)

The value of $\epsilon_{628}^{\text{app}}/\epsilon_{662}^{\text{app}}$ at constant N^+/Co -ratio is dependent on charge density too, as can be seen from Tab. 1, where values at $N^+/\text{Co} = 4$ are presented. From these data it can be concluded that the electronic structure of the cobalt complex is more affected as the ionene charge density becomes larger. It is interesting to note that for the catalytic activity of the complex the same trend was found⁶.

At $N^+/\text{Co} = 4$ a discontinuity appears in the $\epsilon_{628}^{\text{app}}$ -, the $\epsilon_{662}^{\text{app}}$ - and the $\epsilon_{628}^{\text{app}}/\epsilon_{662}^{\text{app}}$ -plots. Beyond this point, up to $N^+/\text{Co} = \text{approx. } 100$ (region II), all three quantities

Tab. 1. Effect of polymer charge density on the spectroscopic behaviour of $\text{CoPc}(\text{NaSO}_3)_4/\text{ionene}^{\text{a)}$

Ionene	Charge ^{b)} density	$\epsilon_{628}^{\text{app}} \cdot 10^{-4}$	$\epsilon_{662}^{\text{app}} \cdot 10^{-4}$	$\epsilon_{628}^{\text{app}} / \epsilon_{662}^{\text{app}}$
		$l \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$	$l \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$	
2a (2,4)	1,45	2,80	1,70	1,6
2b (2,6)	1,15	2,91	1,98	1,4
2c (2,10)	0,82	2,98	2,61	1,1
NaBr ^{c)}	—	4,23	6,22	0,7

a) ϵ^{app} -values at $\text{N}^+/\text{Co} = 4$, $[\text{Co}] = 2 \cdot 10^{-6} \text{ mol/l}$; all ϵ^{app} -values $\pm 0,05 \cdot 10^4 l \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$; $\bar{M}_n = 22000$.

b) Taken from ref. 6).

c) System without ionene; $\text{N}^+/\text{Co} = 4$, $[\text{Co}] = 2 \cdot 10^{-6} \text{ mol/l}$.

remain constant. This strongly suggests the formation of an ionene/ $\text{CoPc}(\text{NaSO}_3)_4$ complex with *fixed* stoichiometry (4:1). Adding more ionene only results in an increase of the concentration of cobalt-free ionene without the existing complex being affected.

When NaBr was used instead of ionene (Fig. 4), the plots of the apparent absorptivities versus the Na^+/Co -ratio did not show any discontinuity associated with the formation of strongly interacting complexes. The only effects observed were increasing aggregation of the cobalt complex due to increasing salt concentration and, at very high concentration, coordination of bromide ions (see below).

The fixed stoichiometry of 4:1 was found to hold for 2,4-ionenes **2a** with $\bar{M}_n > 6100$, as well as for 2,6- and 2,10-ionenes **2b** and **2c** (both with $\bar{M}_n > 10000$). The 2,4-ionenes with low molecular mass (see experimental part), which were also investigated, gave rise to lower values, down to 2:1 for $\bar{M}_n = 1800$, presumably as a result of loss of coil structure for the small oligomer chains. Thus, it is clear that there is a strong tendency toward 4:1 N^+/Co complexation, provided the ionene contains a sufficient number of ammonium groups.

It should be noted that at a ratio of 4:1 8 positive charges on the ionene are just matching the opposite charge on the dimeric cobalt complex. This suggests that the high electrostatic potential of the polymer plays a dominant role in the interaction between the polymer and $\text{CoPc}(\text{NaSO}_3)_4$. Assuming this is true, it can be expected that other negatively charged molecules also show a tendency to form strong complexes with ionenes at the ratio where the charges are matching. We therefore studied combinations of ionenes with the model compounds $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$. It was found that at a mole ratio of $x:1$ ($\text{N}^+:\text{Fe}(\text{CN})_6^{x-}$) a precipitate was formed¹³⁾, indicating that the electrostatic potential is indeed an important factor in the interaction between ionene and metal complexes.

Regarding region III, it appears that a large excess of ionene ($\text{N}^+/\text{Co} > 100$) causes the absorptivities to increase again. However, as can be seen from the constancy of $\epsilon_{628}^{\text{app}}/\epsilon_{662}^{\text{app}}$ in this region, the cobalt complex remains in the aggregated

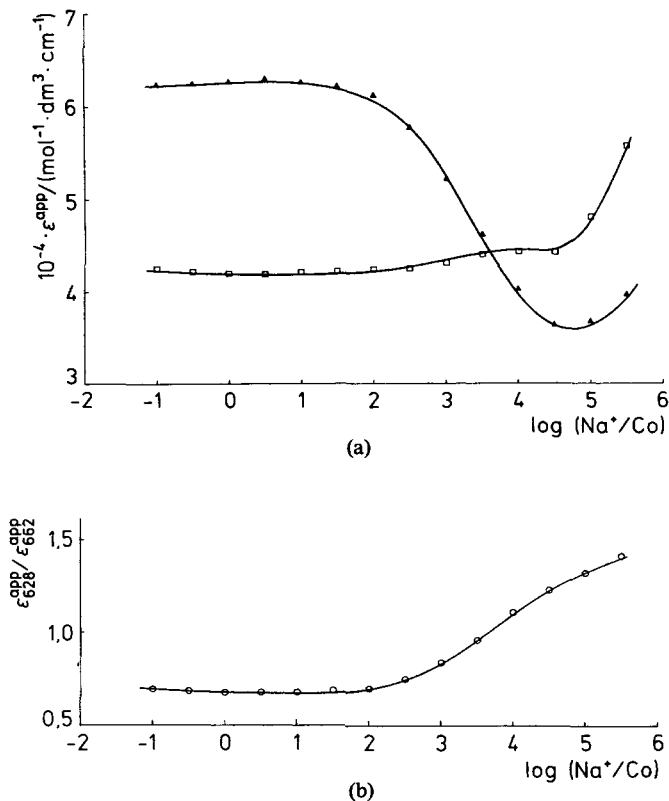


Fig. 4. Effect of varying the Na^+/Co -ratio for (a) the apparent absorptivities ϵ^{app} at 628 nm (\square) and 662 nm (\blacktriangle) and (b) $\epsilon_{628}^{\text{app}}/\epsilon_{662}^{\text{app}}$. $[\text{Co}]$ was kept constant at $2 \cdot 10^{-6}$ mol/l

form. This is very surprising, since site isolation was expected to occur. However, no evidence of an increased occurrence of the monomeric species was found, except in the case of 2,10-ionene **2c**, where a decrease of $\epsilon_{628}^{\text{app}}/\epsilon_{662}^{\text{app}}$ at $\text{N}^+/\text{Co} > 1000$ was recorded.

A possible explanation of the absorptivity enhancements in region III is that the bromide ions, which are present as counterions of the ionene, coordinate to the axial positions of the cobalt complex¹⁴. We tried to obtain supportive evidence to this hypothesis by measuring the spectral change of a $\text{CoPc}(\text{NaSO}_3)_4$ /ionene solution with $\text{N}^+/\text{Co} = 10$ upon the addition of KBr. Indeed, we found an absorptivity increase, which strongly supports our concept of coordinative interaction (see also Fig. 4).

Effects of oxygen

Both for the polymer-free¹⁵⁾ as well as for the PVAm-bound⁵⁾ catalyst it has been argued that the formation of oxygen-bridged $\text{CoPc}(\text{NaSO}_3)_4$ dimers, induced by alkali addition, inactivates the catalyst. Therefore, it was assumed that an important function of the polymer would be the cobalt site isolation. From the foregoing, however, it is evident that in our case no site isolation occurs, at least not under normal reaction conditions (in our laboratory usually $[\text{Co}] = 2 \cdot 10^{-7}$ mol/l and $[\text{N}^+] = 10^{-3}$ mol/l).

Nevertheless, as we established spectrophotometrically (Fig. 5), formation of the oxygen adduct appears to be suppressed by ionenes. Only in very basic solutions (pH > 13) the corresponding absorbance maximum at 670 nm was observed, but even then the adduct could easily be removed from the solution by bubbling through nitrogen for about 15 min.

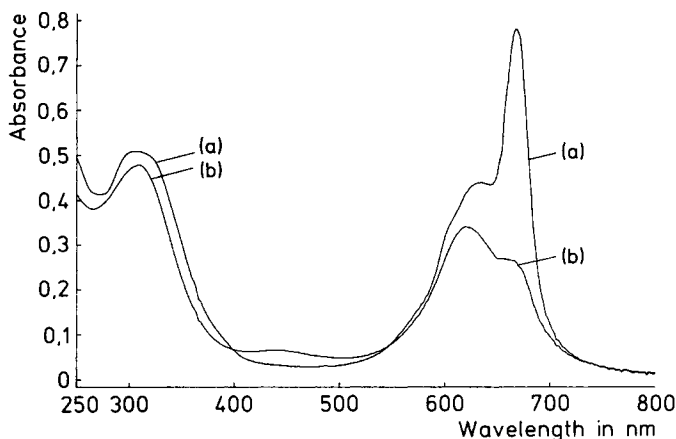


Fig. 5. Spectra of 10^{-5} mol/l $\text{CoPc}(\text{NaSO}_3)_4$ solutions at pH = 12,5 under oxygen atmosphere; (a): without additives, (b): in the presence of 2,4-ionene, $[\text{N}^+] = 10^{-3}$ mol/l; $\bar{M}_n = 22000$

Substantially different results were obtained in the absence of ionenes, using simple salts instead. In that case, even in a solution at pH 11, the oxygen adduct was found to be formed and, in addition, the adduct appeared to be much more stable (at pH = 13, after 2 h of bubbling through nitrogen, the peak at 670 nm had still not completely disappeared)¹⁶⁾.

Since we observed that simple salts do not give rise to stoichiometric complexation with $\text{CoPc}(\text{NaSO}_3)_4$, whereas ionenes do, it seems likely that the difference in behaviour toward oxygen reflects the difference in interaction with the cobalt complex. Presumably, the stronger interaction of ionenes with $\text{CoPc}(\text{NaSO}_3)_4$ makes oxygen adduct formation unfavourable.

This seems to be in contradiction with the very high thiol oxidation activities reported for the ionene systems⁶⁾ (with turnover numbers of approx. 3000 s^{-1}), since

obviously oxygen is needed during the catalytic cycle. However, both facts can be in agreement, provided that the redox reaction step involving oxygen, takes place by a so-called outersphere mechanism. Such a mechanism, viz. oxidation of the cobalt centre *mediated* by the abstraction of an electron from the phthalocyanine *ring* and thus without direct metal-oxidant interaction, was recently suggested by Geiger et al.¹⁷⁾ for $\text{CoPc}(\text{NaSO}_3)_4$ oxidized by Ce^{4+} , Cl_2^- or Br_2^- . One-electron oxidation of the ring by oxygen was mentioned by Ogata et al.¹⁸⁾, who studied CoPc in organic solvents.

Conclusions

From our investigations the following can be concluded:

- ionenes, like ordinary salts, largely enhance aggregation of $\text{CoPc}(\text{NaSO}_3)_4$ in aqueous solution,
- between ionene and cobalt species there exists a very strong interaction resulting in the formation of a complex with fixed stoichiometry (preferentially $\text{N}^+ : \text{Co} = 4 : 1$),
- the interaction becomes stronger with increasing charge density on the polymer (Tab. 1), and thus runs parallel with increasing reaction rates,
- in the presence of ionene the formation of catalytically inactive oxygen-bridged cobalt complexes is effectively suppressed.

It must be emphasized that both the stoichiometric complexation and the resistance against oxygen adduct formation have not been found for simple salts, indicating that these effects are essentially polymeric in character. Whether this is due only to the high electrostatic potential of the polymer or also to a special chemical microenvironment, created within the polymer coil domain, will be the subject of further investigations, which will comprise viscometric and spectroscopic studies of model systems.

The effect of thiol on the catalyst complex structure will also be studied in the near future. In particular, it is required to find out whether the cobalt dimers (oligomers) are the catalytically active sites, or a monomeric species, which might be formed upon addition of the thiol.

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