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Effects of ionenes on structure and catalytic activity of cobaltphthalocyanine, 3^{a)}

Interaction of 2,4-ionene with cobaltphthalocyanine and model compounds

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SUMMARY:

In order to obtain detailed information about the interaction between the constituents of the cobaltphthalocyanine-tetrasodium sulfonate/ionene system, a catalyst used in thiol autoxidation, 2,4-ionene was studied in combination with $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_6^{3-}$, congo red, and several metal(II)phthalocyanines. In all cases, stoichiometric complexation was observed, at a ratio where the positive charges on the polymer were just matching those of the anionic species. The hexacyanoferrate complexes were found to be less stable than the dye complexes, due to the formation of dye aggregates in the latter systems. These aggregates appear to enhance the electrostatic interaction with the polymer to such an extent that even irreversible ionomeric "crosslinking" may occur. The results are discussed in relation to the catalytic activity of the polymeric catalyst.

Introduction

In 1985 it was found by Brouwer et al.¹⁾ that ionenes (poly(quaternary ammonium salts) (1)), in combination with cobaltphthalocyanine-tetrasodium sulfonate ($\text{CoPc}(\text{NaSO}_3)_4$ (2)), show a very high catalytic activity toward the autoxidation of thiols. Because of the favourable properties of ionenes, such as the well-defined, pH-independent cationic charge and the easily controllable charge density, these polymers are very suitable as model compounds in detailed polymer catalytic research.

1 (X = Br, OH, etc.)

^{a)} Part 2: cf. ²⁾.

2

CR (3)

The main objective in polymer catalysis is to identify the specific polymeric effects responsible for reaction rate enhancement. Therefore, the mechanism in the absence and presence of the polymer has to be elucidated, which requires both kinetic and structural investigations. With respect to the $\text{CoPc}(\text{NaSO}_3)_4$ /ionene system, our first results along these lines have been published recently^{2,3}.

The kinetic work²⁾ revealed that the process can be described by a two-substrate Michaelis Menten model, the thiolate anion being the one substrate and dioxygen the other. The spectroscopic investigations³⁾ demonstrated that ionenes form stable stoichiometric complexes with $\text{CoPc}(\text{SO}_3)_4^{4-}$, that are resistant against oxygen-adduct formation in the absence of thiol. Since complexation occurs at an $\text{N}^+:\text{Co}$ ratio of 4:1, i.e. where the positive charges on the ionene are just matching the negative charges on the cobalt species, it was suggested that electrostatic interaction plays a dominant role in complexation.

To obtain more insight in this type of interactions, the effects of ionenes on $\text{CoPc}(\text{NaSO}_3)_4$ have now been studied in relation to their effects on model compounds. The results of this study, which comprises viscometric, spectrophotometric and turbidimetric measurements, are presented in this paper.

Experimental part

Reagents: $\text{MTPc}(\text{NaSO}_3)_4$, with $\text{Mt}=\text{Co}$, Cu , Fe , Mn , and VO , were synthesized as described by Zwart et al.⁴⁾ and kindly provided by Dr. T. P. M. Beelen. The 2,4-ionene was prepared according to the method reported by Brouwer et al.¹⁾. The reagents were obtained from Fluka AG (purum) and used without further purification. M_n of the ionene was 6300, as determined by titration with hydrochloric acid after terminating the product with amine groups⁵⁾.

The model compounds $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (p. a.), $\text{K}_3\text{Fe}(\text{CN})_6$ (p. a.), and congo red (CR(3)) (95%) were purchased from Merck and used without further purification. During all experiments doubly distilled water was used.

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

Viscometry: Measurements were carried out at $25,00 \pm 0,05^\circ\text{C}$ in an Ubbelohde viscometer. The solutions were filtered before use. All values reported were obtained by averaging the results of four repetitive measurements. The pH of the solution was not controlled but was found to be approximately neutral in all cases. Apparent reduced viscosities ($\eta_{\text{red}}^{\text{app}}$) are presented, as defined by Eq. (1):

$$\eta_{\text{red}}^{\text{app}} = (\eta - \eta_i) / (\eta_i c_i) \quad (1)$$

with η = viscosity of solution, η_i = viscosity of 10^{-2} mol/l ionene solution, and c_i = ionene concentration of the solution ($=10^{-2}$ mol/l).

Spectrophotometry and turbidimetry: Spectrophotometric and turbidimetric measurements were performed on a Hewlett Packard 8451^A diode array spectrophotometer using 1,000 cm quartz cuvettes. The cells were thermostatted at $25,0 \pm 0,5^\circ\text{C}$. The turbidity τ was obtained from light absorption measurements, using the relationship:

$$\tau = \frac{\log_{10} (I_0 / I)}{b} \quad (2)$$

where I_0 , I = intensity of incident, transmitted light, respectively, and b = optical path length (in cm).

Turbidity measurements were carried out at a wavelength of 800 nm. In the case of the $\text{CoPc}(\text{NaSO}_3)_4$ /ionene and the congo red/ionene systems, the values were corrected for minor dye absorbance at 800 nm.

Results and discussion

Viscometry

Viscometry is a useful technique to study interactions between polymers and additives, like salts or metal complexes, because interactions usually are accompanied by changes in polymer coil dimensions. Therefore, viscometry was applied to our catalyst system, to obtain additional proof of the proposed $\text{CoPc}(\text{SO}_3)_4^{4-}$ /ionene complex formation.

Furthermore, the ionene was examined in combination with $\text{Fe}(\text{CN})_6^{4-}$, an entity that can only interact electrostatically. This would enable us to determine whether the catalyst complexation can be completely explained in terms of electrostatic interactions or whether other secondary binding forces are involved. The results are shown in Fig. 1.

As can be seen, in both systems the apparent reduced viscosity strongly decreases as the metal content is raised. This effect was expected to occur, since the added anions

Fig. 1. Apparent reduced viscosity η_{red}^{app} in water as a function of metal complex/ionene ratio (X/N^+), with $X = \text{Fe}(\text{CN})_6^{4-}$ (▲) and $X = \text{CoPc}(\text{SO}_3)_4^{4-}$ (○). $[N^+] = 10^{-2}$ mol/l, temp. = $25,00 \pm 0,05^\circ\text{C}$

will shield off the positive charges on the polymer chains, resulting in contraction of the polymer coils. The same effect was also mentioned by Brouwer et al.⁶⁾, who studied analogous systems with poly(vinylamine) instead of ionene.

In their experiments, the results for the model compound practically coincided with those obtained for the catalyst, indicating similar interactions between each of the two metal complexes and the polymer. However, our measurements of the ionene system reveal that $\text{CoPc}(\text{SO}_3)_4^{4-}$ gives rise to a much stronger viscosity decrease than $\text{Fe}(\text{CN})_6^{4-}$, especially for $\text{Co}/N^+ > 0,02$. According to Brouwer⁶⁾, this additional viscosity decrease can be explained by assuming the occurrence of intra- or intermolecular chelate formation. Since ionenes contain no groups allowing coordinative interaction, this chelation should, in the present case, be interpreted as the formation of ionomeric "crosslinks" between the cationic polymer chains by means of bridging cobalt complex anions. Such an effect becomes even more likely, when considering the ability of the phthalocyanine to form dimers and higher aggregates⁷⁾ that carry multiple negative charges, thus facilitating this type of "crosslinking". Because the hexacyanoferrate anion does not show aggregation, interchain interactions are expected to occur much less in that case.

In our previous spectroscopic work³⁾ it has been demonstrated that optimum $\text{CoPc}(\text{NaSO}_3)_4$ /ionene complexation, occurring at $\text{Co}/N^+ = 0,25$, is accompanied by maximum aggregation. Thus, if our hypothesis is true, the viscosity should decrease upon addition of $\text{CoPc}(\text{NaSO}_3)_4$ until this ratio is reached and should then remain constant. Unfortunately, this experiment, that would verify our hypothesis, could not be carried out, because some precipitation of the complex occurred at the concentrations needed (i.e. $[\text{Co}] \geq 10^{-3}$ mol/l and $[N^+] = 10^{-2}$ mol/l). For this reason, spectrophotometry and turbidimetry were chosen to provide further supporting evidence to our theory.

Spectrophotometry: aggregation effects

From the spectroscopic investigations described in ref.³⁾, it was concluded that ionenes strongly enhance the aggregation of $\text{CoPc}(\text{NaSO}_3)_4$ ⁸⁾. Recently, we have found that the same is true for other phthalocyanines, viz. copper-, manganese-, iron(II)-, and vanadylphthalocyanine-tetrasodium sulfonates. In all these cases, addition of ionene caused a shift of the Q-band absorptions to shorter wavelengths, indicating a decrease in the amount of monomer complex present and an increase in dimer (oligomer) content. Therefore, it can be stated that ionenes enhance phthalocyanine aggregation independent of the central metal ion.

In order to find out if ionenes generally induce oligomerization of compounds with aggregation ability, ionene was also investigated in combination with congo red (CR). This dye is known to associate strongly in aqueous solution⁹⁾ and was therefore expected to behave similar to the cobalt catalyst, although its structure is completely different (cf. formula 3).

In Fig. 2 the spectra are shown recorded for congo red solutions containing different amounts of ionene. It clearly shows that the addition of ionene to the dye causes a decrease of absorbance over the total wavelength range, which indicates that interaction between polymer and dye takes place. The peak at 498 nm, which is associated with the presence of monomeric dye species, decreases more strongly than the absorption maximum of the dimers (oligomers) at 344 nm. Thus again, it can be concluded that the ionene enhances aggregate formation.

The congo red spectrum gradually changes upon ionene addition until a ratio of $\text{N}^+ : \text{CR} = 2:1$ is reached, where the charges on the polyelectrolyte are just matching those on the dye. Further addition of ionene has no effect on the spectrum (see Fig. 2, lines (d) and (e): the spectrum of the solution with $\text{N}^+/\text{CR} = 100$ coincides with the one for $\text{N}^+/\text{CR} = 2$), which strongly indicates the formation of a stoichiometric polymer/dye complex. Completely analogous results have been reported earlier for

Fig. 2. Spectra of congo red (CR)/ionene aqueous solutions: $\text{N}^+/\text{CR} = 0$ (a), 0,5 (b), 1 (c), 2 (d), and 100 (e). $[\text{CR}]$ was kept constant at 10^{-5} mol/l, pH = 7

Fig. 3. Spectra of $\text{CuPc}(\text{NaSO}_3)_4$ in 50/50 (v/v) DMF/water in the absence (a) and in the presence of ionene (b). $[\text{Cu}] = 8 \cdot 10^{-6}$ mol/l, $[\text{N}^+] = 10^{-2}$ mol/l

the cobalt catalyst system³⁾ and were also found for the other metalphthalocyanines. In these cases, complexation occurred at $\text{N}^+ : \text{Mt} = 4:1$ ($\text{Mt} = \text{Co}, \text{Cu}, \text{Mn}, \text{Fe},$ and VO), in accordance with the matching charges on the components. Apparently, stoichiometric complexation is not restricted to the catalyst system, but generally occurs when ionene is combined with anionically charged compounds with a propensity for aggregation.

It should be mentioned here that all aggregated complexes appeared to be highly stable. In polymer-free systems, the phthalocyanine aggregates are known to dissociate into monomeric species upon addition of e.g. *N,N*-dimethylformamide (DMF)¹⁰⁾, but when this solvent was added to a solution also containing ionene, the aggregates remained. This effect is illustrated in Fig. 3, depicting spectra obtained for $\text{CuPc}(\text{NaSO}_3)_4$ in a 50/50 (v/v) DMF/water mixture, in the absence (a) and presence (b) of 2,4-ionene. Spectrum (a) shows the characteristics of the purely monomeric complex, spectrum (b) corresponds with the dimer (oligomer) form.

Turbidimetry

Polymer-metal complexes, as concerned here, which are primarily based on electrostatic interaction, are often electroneutral. As a consequence, such complexes are usually less soluble in polar solvents like water, resulting in precipitation or formation of colloidal systems. Turbidity measurements can therefore be a powerful tool in tracing this type of complexation, provided that the concentrations of the compounds are chosen within the appropriate range.

Indeed, the formation of the catalyst complex could easily be demonstrated in this way, as can be seen in Fig. 4. This figure shows that optimum turbidity is reached at the complexing ratio of $\text{N}^+/\text{Co} = 4$, which is in excellent agreement with the results of earlier experiments³⁾. Furthermore, it is obvious that the complex is highly stable: once it has been formed, disturbing the stoichiometry by adding either component

Fig. 4. Dependence of turbidity τ on the $N^+/\text{CoPc}(\text{SO}_3)_4^{4-}$ ratio in water; ($\square$): $[N^+]$ was kept constant at 10^{-3} mol/l, $[\text{Co}]$ was increased; ($\blacktriangle$): $[\text{Co}]$ was kept constant at $2 \cdot 10^{-4}$ mol/l, $[N^+]$ was increased

has no effect on the turbidity, indicating that no resolubilization occurs. This implies that when a *solution* of the catalyst system is needed, one should mix the components carefully and in the right order, i. e. the compound desired in excess must be taken as the one, to which the other is added dropwise (otherwise a precipitate may be formed irreversibly). Of course, this precaution is not necessary at low concentrations, where the complex is completely soluble.

Analogous results were obtained for the congo red/ionene system, as demonstrated in Fig. 5. In this case, the stable complex, which could not be resolubilized either, was formed at a ratio of $N^+/\text{CR} = 2$, again in accordance with the matching of opposite charges.

Fig. 5. Turbidity τ vs. $N^+/\text{congo red (CR)}$ ratio in water; ($\square$): $[\text{CR}]$ was kept constant at 10^{-3} mol/l, $[N^+]$ was increased; ($\blacktriangle$): $[N^+]$ was kept constant at 10^{-3} mol/l, $[\text{CR}]$ was increased

Fig. 6. Effect of varying the $N^+ / \text{Fe}(\text{CN})_6^{x-}$ ratio on the turbidity τ of the aqueous solution; (□): $x = 4$, (▲): $x = 3$. $[\text{Fe}(\text{CN})_6^{x-}]$ was kept constant at 10^{-3} mol/l, $[N^+]$ was varied

Finally, the model compounds $\text{Fe}(\text{CN})_6^{x-}$ (with $x = 3$ and 4) were examined turbidimetrically. The results, depicted in Fig. 6, indicate that these compounds can also form stoichiometric complexes with ionenes. Also in this case, the charges are matching, since optimum turbidity is observed at $N^+ / \text{Fe}(\text{CN})_6^{x-} = 3$ and 4 for $x = 3$ and 4, respectively. Nevertheless, an important difference to the dye systems remains: unlike the catalyst and the congo red species, these model complexes resolubilize easily upon addition of either constituent, as appears from the symmetry of the curves. This behaviour unambiguously indicates that these complexes are less stable than those of the dye systems, suggesting a less strong interaction between the $\text{Fe}(\text{CN})_6^{x-}$ anions and the polyelectrolyte.

We postulate that this difference is a consequence of the fact that the hexacyanoferrates can only be present in their monomeric form, whereas the dye compounds form dimers and higher aggregates. In the previous section, this aggregation was demonstrated spectrophotometrically and it was shown even to be enhanced by the presence of ionene. In turn, turbidimetry shows that aggregate formation enhances the electrostatic interaction between ionene and anions. Considering reported aggregation numbers of 45 for congo red¹¹⁾ and up to 20 for $\text{CuPc}(\text{NaSO}_3)_4$ ¹²⁾ (both in polymer-free, salt containing solutions), implying entities carrying charges of -80 to -90 , this interaction enhancement seems plausible. These unusually high charges should indeed lead to very stable complexes. Also the formation of ionomeric "crosslinks" between polymer chains is most likely to occur, which is consistent with our viscometric results.

Catalyst structure versus activity

The structure of the catalyst complex now has to be related to the mechanism of the thiol oxidation process. In our opinion, the high stability of the aggregated complex as well as the large extent of aggregation are important features in this respect.

From the shift of the Q-band in the VIS-spectrum to shorter wavelengths upon ionene-induced aggregation, it can be concluded that the aggregated molecules adopt a stacked configuration⁹). This implies that the axial coordination positions of cobalt are not readily accessible. Therefore, if axial coordination of substrate to cobalt is needed during the catalytic cycle, the aggregates should be broken up. Because of the high stability of the aggregates, this additional reaction step, not taken into account in previous studies, may have a limiting effect on the overall reaction rate. The high stability also becomes manifest in the formation of the (catalytically inactive) dinuclear dioxygen-bridged cobalt complex, which easily occurs in polymer-free systems¹³), whereas it was shown to be strongly suppressed in ionene containing solutions³). However, considering the reaction of cobalt with thiol, rate limitation as a result of aggregate dissociation seems very unlikely, since for the ionene containing aggregated catalyst much higher thiol turnover numbers were found¹¹) (as high as 3300 s⁻¹) than for the only slightly aggregated polymer-free system (83 s⁻¹ for a solution containing tetramethylammonium hydroxide¹¹).

Another possibility is that the aggregates persist during the catalytic cycle and that electron transfer processes involving the cobalt ion are mediated by the phthalocyanine ring system. These outersphere redox reactions have been suggested previously^{3,14}) and are presumably facilitated by the enhanced delocalization of the π -electrons over the large aggregates¹⁵).

Thus, it will be worthwhile to study the behaviour of the catalyst complex in the presence of thiol, especially with regard to the degree of aggregation and the redox properties, which will be the subject of further investigations.

Conclusions

From turbidimetric and spectrophotometric investigations it has been shown that 2,4-ionene can form complexes with negatively charged compounds. The stoichiometry of these complexes corresponds to the ratio at which positive and negative charges are just matching. Thus, it can be concluded that complexation is achieved by electrostatic interaction.

However, to stabilize the complexes, some additional binding forces appear to be needed. In ionene/dye systems, e.g. containing phthalocyanine or congo red, these forces appear to be intermolecular interactions between dye molecules by π -overlap, resulting in aggregated species. Aggregation has been studied spectrophotometrically and was shown to be enhanced by ionene. It involves concentration of negative charges (increase of charge density), thus leading to a stronger interaction with the ionene. Viscometric results even suggest the formation of ionomeric "crosslinks" in the ionenes, as a consequence of this aggregation effect.

On these grounds, we propose interaction structures schematically given in Fig. 7. Non-aggregating compounds are believed to exhibit predominantly intrachain or reversible interchain interactions with ionene (Fig. 7(a)), whereas systems containing the catalyst or congo red may show also irreversible interchain interactions ("crosslinks") (b).

Fig. 7. Schematic representation of proposed interaction structures of $\text{Fe}(\text{CN})_6^{4-}$ /ionene (a) and $\text{CoPc}(\text{SO}_3)_4^{4-}$ /ionene (b) complexes

Presumably the aggregated structure of the catalyst complex has a large influence on its reactivity. Therefore, it seems interesting to study the effects of ligands on the stability of the aggregates.

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