Effects of solvents on the cobalt phthalocyanine-catalyzed oxidation of hydrophobic thiols

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Abstract

The use of organic solvents in the oxidation of 1-dodecanethiol, catalyzed by cobalt(II) phthalocyanine-tetrasodiumsulfonate ($CoPc(NaSO_3)_4$)/2,4-ionene, drastically influences the reaction mechanism. Without an organic solvent the reaction proceeds at the thiol–water phase boundary, where the ionene interacts with the negatively charged 1-dodecanethiol droplets. The degree of complexation between the 2,4-ionene and the thiolate anions diminishes when apolar solvents, like toluene, are added. This leads to a tremendous shift of the N^+/Co ratio, which is a measure of the optimal ionene/$CoPc(NaSO_3)_4$ ratio, from 1250 to 15. Only the maximal catalytic activity is dependent on the amount of apolar solvent used over the whole range of solvent compositions. It is proposed that the reaction proceeds at the phase boundary, but the degree of complexation between the quaternary ammonium groups of the ionene and the thiolate anions decreases with addition of an apolar solvent. The low optimal N^+/Co ratio of about 15 is apparently sufficient for both binding the ionene to the droplet surface as well as for stabilizing the active dimeric form of the catalyst. When water-insoluble more polar solvents such as 1-octanol are used, the opposite phenomenon is observed: the optimal 2,4-ionene concentration rises. In the latter situation the 2,4-ionene is still able of interacting strongly with the thiolate anions present at the interface of the droplets.

1. Introduction

Polycations exhibit large effects on the cobalt phthalocyanine-catalyzed autoxidation of thiols to disulfides [1–4]. It has been demonstrated before that addition of poly(quaternary ammonium)salts, the so-called ionenes, to the cobalt(II) phthalocyanine-tetrasodiumsulfonate – ($CoPc(NaSO_3)_4$) (Fig. 1) catalyzed autoxidation of mercaptoethanol leads to a drastic rate

enhancement. In case of addition of 2,4-ionene (Fig. 2) a 40-fold rate increase in the mercaptoethanol oxidation rate was observed [1,2].

In the presence of these polycations, the formation of the catalytically inactive dioxygen bridged μ-peroxo complex is strongly suppressed and simultaneously aggregates of $CoPc(NaSO_3)_4$ are formed [5]. Furthermore, the presence of polycations leads to higher local concentrations of the thiolate anions near the catalytically active sites in the polyelectrolyte domain (substrate enrichment). These three effects collectively con-

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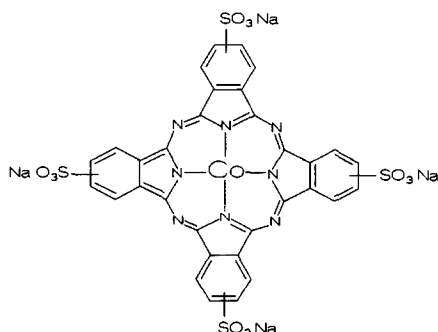
Fig. 1. Structure of CoPc(NaSO$_3$)$_4$.

$$2\ RSH\ +\ O_2\ \xrightarrow{\ OH^-,\ CoPc\ }\ RSSR\ +\ H_2O_2$$

Scheme 1.

H_2O_2 could be a problem, because H_2O_2 may cause breakdown of the CoPc(NaSO$_3$)$_4$ complex [12]. In addition, it was mentioned that during the precipitation of the insoluble disulfide entrainment of the catalyst occurred [9]. This could lead to a loss of activity in the case of continuous operation. Addition of solvents, in which substrate as well as product are soluble, will probably reduce the drawbacks and will lead to an enhancement of the reaction rate. Generally, organic solvents were used before because of the insolubility of the thiol in water [8,13–15].

In this paper, the influence of different solvents on the catalytic oxidation of 1-dodecanethiol will be described. First, in order to study the effect of deactivation which is probably caused by co-precipitation of the disulfide and the catalytic complex, the reaction rate in consecutive runs are examined with and without an organic solvent. It appeared that addition of an apolar solvent, in which 1-dodecanethiol dissolves, had such a drastic influence on the optimal reaction conditions that further attention was focused on gaining a better understanding of the reaction mechanism. Contrasting effects, obtained with water-insoluble more polar solvents, have also been considered.

tribute to an increase in the catalytic activity induced by polycations [2,4].

Also, considerable attention has been paid to the influence of polymers on the more complex mechanism of the hydrophobic thiol autoxidation [6–11]. The hydrophilic 2,4-ionene showed a large effect on the CoPc(NaSO$_3$)$_4$-catalyzed oxidation of water-insoluble 1-dodecanethiol (DM) (Scheme 1) [9]. Further enhancement of the reaction rate could be achieved by coupling a hydrophobic moiety to the ionene chain. Well-defined amphiphilic polystyrene–ionene diblock copolymers showed better co-catalytic properties in cobalt phthalocyanine-catalyzed DM oxidations than 2,4-ionene, as a result of hydrophobic interactions with the hydrophobic thiol [11]. Recently, it was shown that the addition of monodisperse ionene oligomers, with four quaternary ammonium groups and with butylbromide endgroups, caused a tremendous rate increase in the DM oxidation by a factor of 100 as compared with the polymer-free system [10].

However, some disadvantages of the dodecanethiol oxidation have been reported with CoPc(NaSO$_3$)$_4$/2,4-ionene in water as catalyst [9]. First, it appeared that H$_2$O$_2$, formed at the thiol–water interface, is directly transported to the bulk of the aqueous phase. The non-catalytic consecutive reaction step of H$_2$O$_2$ reacting with RSH is therefore impossible. Second, accumulation of
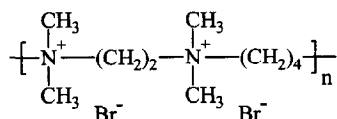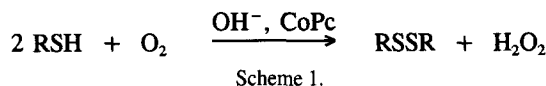
2. Experimental section

2.1. Materials

CoPc(NaSO$_3$)$_4$ was kindly provided by Dr. T.P.M. Beelen (Eindhoven University of Technology) and had been prepared by a slight adaption of the original method described by Weber and Busch [16,17]. 2,4-Ionene was synthesized according to the method described by Rembaum et al. [1,2,18].

2.2. Catalytic activity measurements

The catalytic thiol autoxidations were carried out batchwise as reported previously, in an all-

Fig. 2. Structure of 2,4-ionene.

glass double-walled Warburg apparatus (250 ml), equipped with a powerful mechanical glass stirrer (the stirring speed was 2600 rpm) and thermostated at $25.0 \pm 0.1°C$ [9,19]. First, the catalyst solution consisting of the polymer, organic solvent, base and doubly distilled water, was added to the reactor. Then, the reaction vessel was degassed, followed by saturation of the solution with oxygen. After repeating this procedure twice, the mixture was stirred vigorously for 5 minutes. Using 1-dodecanethiol (dodecylmercaptan, DM) (Janssen Chimica, 98%), the reaction was started by introducing a concentrated $CoPc(NaSO_3)_4$ solution to the oxygen-saturated reactor, already containing dodecanethiol, polymer and base. Prior to use, DM was vacuum distilled, stored in the dark and kept under argon in sealed flasks at 5°C. Reaction rates were monitored by measuring the oxygen uptake.

The total reaction volume, i.e. water and organic solvents, was always 0.1 dm^3. Unless stated otherwise the 1-dodecanethiol concentration was 2.1×10^{-2} mol·dm^{-3} (= 0.5 vol.%). In all experiments the hydroxide anion concentration was kept constant at 0.1 mol·dm^{-3}, based on the total reaction volume. Toluene (Merck, p.a.), n-hexane (Merck, p.a.), n-dodecane (Janssen Chimica, 99 + %), cyclohexane (Merck, p.a), 1-octanol (Janssen Chimica, 99%), 1-decanol (Janssen Chimica, 99%) and 1-dodecanol (Janssen Chimica, 98%) were used without any further purification.

2.3. Characterization

The H_2O_2 concentration was determined spectrophotometrically using $TiCl_3$–H_2O_2 as reagent [20]. H_2O_2 contents of the reaction mixtures were measured after complete thiol conversion. 1-Dodecanethiol concentrations were determined by gas chromatography (GC) on a Hewlett Packard 5890 II, equipped with an apolar capillary column (5 m, 530 μm HPI). 1-Dodecanol was used as internal standard. A Malvern autosizer IIc was used to measure droplet size distributions. The surface tension properties of DM in water

were performed with a Sensa Dyne bubble tensiometer and with a Krüss tensiometer K10T (ring method). The latter method was also used to determine the interfacial tension between an organic phase, consisting of 1-dodecanethiol and/or toluene, and water.

3. Results and discussion

During the $CoPc(NaSO_3)_4$-catalyzed oxidation of 1-dodecanethiol the water-insoluble didodecyldisulfide is formed. This disulfide precipitates in water and is assumed to be able to capture the cobalt complex and the ionene [9]. We investigated the influence of the addition of toluene, in which both the substrate and the disulfide are soluble. This could prevent any possible deactivation. In Fig. 3 the oxidation rates are presented in consecutive runs, with and without toluene. It should be remarked that we cannot use the normal reaction procedure for DM oxidations. This leads, in case of DM oxidations in water, to lower activities when the reactions are started by addition of DM instead of cobalt catalyst [9].

No significant deactivation can be observed after several runs. The disulfide formed precipitates, but is apparently not able to co-precipitate the catalyst complex. However, in a toluene–water mixture, with a lower ionene concentration, a decrease in reaction rate can be observed. Nevertheless, higher catalytic activities are observed as
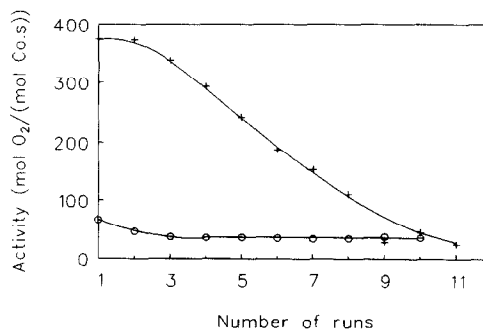
Fig. 3. The 1-dodecanethiol oxidation rate in successive runs. $[CoPc(NaSO_3)_4] = 8 \times 10^{-7}$ mol·dm^{-3}, $[OH^-] = 0.1$ mol·dm^{-3}, $[DM] = 2.1 \times 10^{-2}$ mol·dm^{-3}, 2,4-ionene ($\bar{M}_n = 15000$ g·mol^{-1}). (+) Toluene/water, vol.%/vol.% = 5/94.5, $[N^+] = 10^{-5}$ mol·dm^{-3}; (○) no toluene, $[N^+] = 10^{-3}$ mol·dm^{-3}.
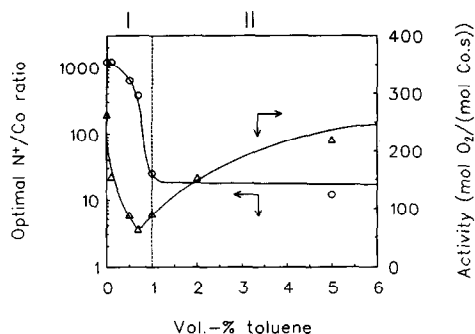
Fig. 4. Maximal 1-dodecanethiol oxidation rates and their corresponding optimal N^+/Co ratios as a function of the toluene concentration in toluene/water mixtures. $[CoPc(NaSO_3)_4] = 8 \times 10^{-7}$ mol·dm^{-3}, $[DM] = 2.1 \times 10^{-2}$ mol·dm^{-3}, 2,4-ionene ($\bar{M}_n = 5000$ g·mol^{-1}).

compared with the toluene-free system, even after several runs.

Furthermore, it appeared that less ionene was needed in order to obtain high oxidation rates. In order to study the drastic influence of toluene on the optimal catalytic conditions, the effect of the amount of toluene in toluene/water mixtures on the optimal N^+/Co ratio, which is a measure of the optimal 2,4-ionene/CoPc(NaSO_3)_4 ratio, and on their corresponding maximal catalytic activities of the dodecanethiol oxidation was examined (Fig. 4 and 5). It can be seen that addition of a relatively small amount of toluene results in a tremendous shift of the optimal N^+/Co ratio from 1250 to 15.

The optimal N^+/Co ratio decreases sharply upon addition of toluene to the reaction mixture. Adding more than 1 vol.% of toluene (up to 90 vol.%) did not further affect the optimal N^+/Co ratio: at 1 vol.% of toluene, where the toluene/DM vol.%/vol.% ratio is 2, the optimal N^+/Co ratio remains constant at a value of about 15. By contrast, the maximal thiol oxidation rate changes continuously over the whole range and three maxima can be observed. Five different regions can be distinguished in Fig. 5, where the reaction rate decreases or increases upon addition of more toluene to the reaction mixture. If the toluene fraction is greater than 1 vol.%, no precipitation of disulfide is observed during the measurements: the disulfide formed dissolves in the toluene.

Before explaining the tremendous drop in the optimal N^+/Co ratio, it is necessary to look in detail at the reaction mechanism without toluene. Van Welzen proposed the dodecanethiol oxidation in water proceeds at the phase boundary [9]. At the interface between the negatively charged thiol droplets and water, the ionene will bind to the thiol. In this boundary layer, $CoPc(NaSO_3)_4$ bound to the 2,4-ionene, will catalyze the thiol oxidation.

Several observations led to this proposal [9]. First, the reactions are started by addition of $CoPc(NaSO_3)_4$ instead of DM. Otherwise, a retardation was observed and lower reaction rates were measured, because the system requires some time to reach equilibrium conditions. The fact that the reaction proceeds at this thiol–water contact surface was explained by the dependence of the dodecanethiol oxidation rate on the N^+/Co ratio. On increasing the ionene concentration, the 2,4-ionene will bind to the thiol droplets. In the maximum the thiol droplets are optimally covered with ionene. Addition of more ionene, $CoPc(NaSO_3)_4$ will bind to the 2,4-ionene in the continuous phase and as a consequence the oxidation rate decreases. Furthermore, the reaction rate was largely dependent on the impeller speed.

Nevertheless, an emulsion-like system can be observed during the catalytic experiments. The question arises whether 1-dodecanethiol ($pK_a = \pm 10.8$) [21] in water at alkaline conditions (pH = 13) is able to form micelles. Therefore, we determined the surface tension properties
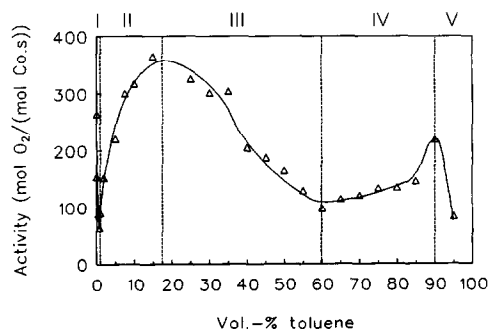

Fig. 5. Maximal 1-dodecanethiol oxidation rates at optimal N^+/Co ratios as a function of the toluene concentration in toluene/water mixtures. $[CoPc(NaSO_3)_4] = 8 \times 10^{-7}$ mol·dm^{-3}, $[DM] = 2.1 \times 10^{-2}$ mol·dm^{-3}, 2,4-ionene ($\bar{M}_n = 5000$ g·mol^{-1}).
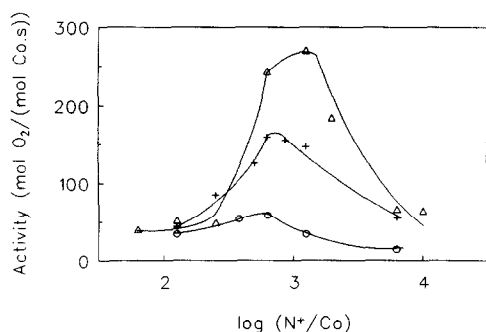
Fig. 6. Effects of the N^+ concentration on the 1-dodecanethiol oxidation rate at different DM concentrations. $[CoPc(NaSO_3)_4] = 8 \times 10^{-7}$ mol·dm^{-3}, 2,4-ionene ($\bar{M}_n = 6600$ g·mol^{-1}). $[DM] = 4.2 \times 10^{-3}$ mol·dm^{-3} (O), 1.05×10^{-2} mol·dm^{-3} (+), 2.1×10^{-2} mol·dm^{-3} (△).

of DM in water at pH = 13 with two independent techniques. No decrease in surface tension upon increasing concentration of DM could be observed with either of the two methods. However, the thiol–water interfacial tension is influenced by the pH, indicating surface-active properties of DM. Going from a pH of 7 to 13, the interfacial tension decreases from 37 mN/m to 7 mN/m. Therefore, it can be assumed that most probably no micelles are present during the catalytic oxidations.

In addition, the DM droplet surface area was varied by using different DM concentrations (Fig. 6). Reducing the DM concentration, i.e. the total droplet surface area is diminished, it can be seen that the optimal N^+ concentration is shifted to lower values and that the oxidation rate decreases simultaneously. Opposite results were observed when larger DM concentrations were applied.

On the basis of all the above mentioned arguments, it can be stated that the mechanism of the dodecanethiol oxidation catalyzed by $CoPc(NaSO_3)_4$/2,4-ionene in water proceeds at the thiol–water interface. The high optimal N^+ concentrations are a result of complexation between the negatively charged thiol droplets and the positively charged 2,4-ionene.

As remarked earlier, 1-dodecanethiol showed surface-active properties, therefore it should be possible to measure the mean droplet size. However, a stirring speed of 2600 rpm makes a simple determination of the droplet size distribution impossible. Despite an emulsion-like system, the

DM droplets are not sufficiently colloidally stable. Immediately after stopping the impeller, a large part of the thiol droplets coalesces and phase separation is observed. After phase separation, acidification and extraction of the aqueous phase, the DM concentration in the aqueous phase was measured by GC. It appeared that about 40% of the amount of DM (0.5 vol.% of DM is added) was present in the water phase. The DM must be present in droplets in the aqueous phase, because of the extremely low solubility of 1-dodecanethiol in water (3×10^{-5} mol·dm^{-3} at 50°C) [22]. These droplets appeared to have a volume average diameter of 10 μm.

Before returning to the influence of toluene on the dodecanethiol oxidation mechanism, we have to keep in mind that an organic solvent has no influence on the aggregation behaviour of $CoPc(NaSO_3)_4$ in the presence of ionene [2,23–25]. Hence, other explanations for the effect of toluene on the optimal catalytic conditions of the oxidation of DM have to be sought.

Therefore, we first examined the effects of the type of organic solvent added. It appeared that apolar solvents, like n-hexane, n-dodecane and cyclohexane showed analogous characteristics, both with regard to the optimal N^+/Co ratios as well as to the maximal oxidation rates, as toluene. On the other hand, with addition of water-insoluble more polar solvents, such as 1-octanol, 1-decanol or 1-dodecanol, a completely different type of behaviour was noted (Fig. 7). Instead of
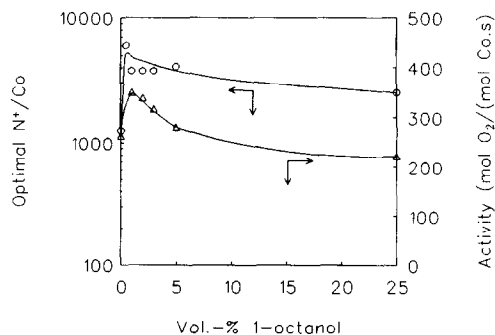

Fig. 7. Maximal 1-dodecanethiol oxidation rates and the corresponding optimal N^+/Co ratios as a function of the 1-octanol concentration in 1-octanol/water mixtures. $[CoPc(NaSO_3)_4] = 8 \times 10^{-7}$ mol·dm^{-3}, $[DM] = 2.1 \times 10^{-2}$ mol·dm^{-3}, 2,4-ionene ($\bar{M}_n = 15500$ g·mol^{-1}).
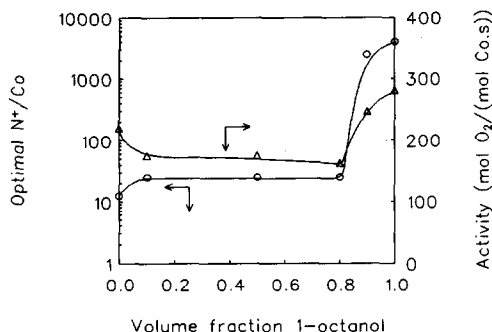
Fig. 8. Maximal 1-dodecanethiol oxidation rates and the corresponding optimal N^+/Co ratios as a function of the volume fraction 1-octanol in the organic phase in a toluene/1-octanol/water mixture. (Total volume percentage toluene and 1-octanol is kept constant at 5 vol.-%). $[CoPc(NaSO_3)_4] = 8 \times 10^{-7}$ mol·dm^{-3}, $[DM] = 2.1 \times 10^{-2}$ mol·dm^{-3}, 2,4-ionene ($\bar{M}_n = 4900$ g·mol^{-1}).

a radical decrease of the optimal N^+/Co ratio, an increase is observed. Also, the maximal activities are rather unaffected in contrast with those found with toluene. 1-Octanol, which has a similar water solubility as toluene, has a polarity similar to that of 1-dodecanethiol. Therefore, the behaviour with 1-octanol is not unexpected. At the droplet surface the polar heads of the alcohols are mixed with those of DM. Conceivably, the concentration of thiolate anions at the interface increases, because the polar alcohol groups are able of shielding the negatively charged thiol heads. This leads to an enhancement in the amount of N^+ interacting with the droplets.

The drastic shift in optimal N^+/Co ratio could be a result of a drastic increase in droplet size upon addition of toluene. In order to gain insight into this, the DM oxidation in a mixture of 1-octanol,
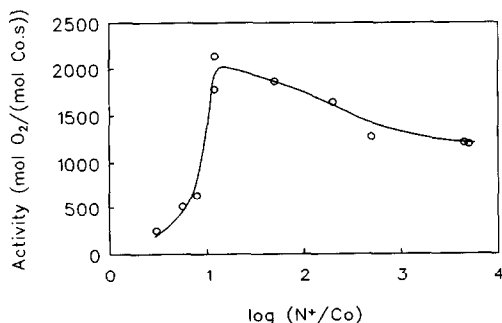

Fig. 9. The effect of the N^+/Co ratio on the 1-dodecanethiol oxidation rate in a methanol/water (80/20, vol.%/vol.%) mixture. $[CoPc(NaSO_3)_4] = 10^{-7}$ mol·dm^{-3}, $[DM] = 2.1 \times 10^{-2}$ mol·dm^{-3}, 2,4-ionene ($\bar{M}_n = 15000$ g·mol^{-1}).

toluene and water was studied (Fig. 8). From 1 vol.% of octanol onwards in Fig. 8, the droplet size will not vary much over the whole range. However, the optimal N^+/Co ratio radically drops at a small toluene fraction, thus, it is unlikely that the optimal N^+/Co is determined by differences in droplet sizes. Another important observation is that in a 1-octanol/toluene mixture the catalytic properties are dominated by the apolar solvent toluene: even at high octanol concentrations the optimal N^+/Co ratio is still relatively low and the effect on the catalytic activity is rather limited.

Also, the interfacial tension, which is an important parameter for the droplet size, between an organic phase, consisting of toluene and dodecanethiol (4/1, v/v) and water at pH = 13 (9 mN/m), did not differ from the interfacial tension measured between DM and water. Nevertheless, we tried to determine the droplet size distribution. It appeared that in the presence of 5 vol.% of toluene, 10% of the amount of DM added (= 0.5 vol.%) still was present in the aqueous phase in droplets after phase separation. The volume average droplet diameter was comparable with that measured without toluene. If 25 vol.% of toluene is added only 1% of the amount of DM is present in the aqueous phase. Thus, it can be concluded that the droplet size is not the determining factor in the drastic fall of the optimal N^+/Co ratio upon addition of an apolar solvent.

In addition, the molecular weight of polymeric 2,4-ionenes appeared to have no effect on the optimal N^+/Co ratio in region I–V. The application of different types of ionenes, like 2,6-, 2,10- and oleyl-3,3-ionene [9], resulted in a similar decrease of the optimal N^+ concentration. In the presence of toluene, variation of the pH only led to a decrease of the maximum catalytic activity. From region II onwards, no influence could be observed whether the reaction was started by addition of $CoPc(NaSO_3)_4$ or DM. The H_2O_2 concentration after complete reaction in all five regions indicated that no consecutive reaction between H_2O_2 and DM occurred as in homogeneous oxidations.

When the DM oxidation is homogeneously performed in a methanol/water mixture (Fig. 9), a relatively low optimal N^+/Co ratio can be observed. This is in agreement with the mercaptoethanol autoxidations [26], because the reaction proceeds according to a completely different mechanism.

On the basis of all the results, a reaction model can be proposed, where the dodecanethiol oxidation in toluene–water mixtures proceeds at the phase boundary. The low optimal N^+/Co ratio suggests that the primary function of the ionene has become the formation of the catalytically active dimers of $CoPc(NaSO_3)_4$. Already from a N^+/Co ratio of 4, dimeric catalyst species are formed and further addition of 2,4-ionene has no effect on the dimerization of $CoPc(NaSO_3)_4$ [2,5,26]. Apparently, only a small part of the polycation seems to be necessary for interaction with the droplets.

Now we are able to clarify the different regions (Figs. 4 and 5). In region I, the N^+/Co ratio drops because of a decrease of the degree of complexation between the quaternary ammonium groups of the ionene and the thiolate anions. The decrease in activity is most probably a result of a decrease in total surface area. The dodecanethiol–toluene droplets are less colloidally stable as compared with dodecanethiol droplets. This leads to coalescence of the droplets, resulting in larger droplet diameters.

From region II onwards the total surface area increases because of the increase in toluene concentration and, thus, the reaction rate rises. The main function of 2,4-ionene is the stabilization of the catalytically active dimeric form of the catalyst. Only a small part of the 2,4-ionene interacts with the thiolate anions at the outside of the droplets. When increasing the toluene concentration further a larger fraction of DM will be present inside the toluene droplets, which will lead to a depletion of the DM concentration at the outside of the droplets (region III).

At a toluene/water ratio of 1 the system turns from a toluene in water dispersion into a water in toluene dispersion. For reasons similar to those

for region II, the activity in region IV increases, because the reaction interface between toluene and water increases. In the last region V, the pH has increased to pH values of 14 and higher. These high ionic strengths result in lower DM oxidation rates.

4. Conclusions

Addition of water-insoluble apolar solvents to the $CoPc(NaSO_3)_4$/2,4-ionene-catalyzed oxidation of the hydrophobic 1-dodecanethiol has an enormous effect on the reaction mechanism. Without an apolar solvent there is a high degree of complexation between the thiolate anions and the 2,4-ionene, which leads to a high optimal N^+/Co ratio. However, in the presence of small amounts of toluene the optimal N^+/Co ratio decreases drastically from 1250 to 15. Introducing more solvent to the system appeared to have no effect on the polycation/catalyst ratio. The maximal oxidation rates vary over the whole solvent composition range and are determined by differences in droplet sizes. Presumably, only a small part of the 2,4-ionene interacts with the thiolate anions on the outside of the droplets and the main function of the ionene is the formation of the active dimeric catalyst species.

Contrasting results are realized when more polar solvents are added. If octanol is present the optimal N^+ concentration rises. Apparently, without apolar solvents 2,4-ionene strongly interacts with the negatively charged droplets.

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