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AUTOXIDATION OF THIOLS WITH COBALT(II) PHTHALOCYANINE-TETRA(SODIUM SULFONATE), ATTACHED TO POLY(VINYLAMINE) PART 5. EFFECT OF SURFACTANT AND THIOL VARIATION

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Summary

The autoxidation of various thiols, *viz.* 2-mercaptoethanol (ME), 3-mercaptopropane-1,2-diol (MP), mercaptoacetic acid (MA) and dodecyl-mercaptan (DM) with cobalt(II) phthalocyanine-tetra(sodium sulfonate) ($\text{CoPc}(\text{NaSO}_3)_4$) as a catalyst in the absence and presence of the basic poly(vinylamine) has been studied.

Differences among the oxidation rates of the various thiols are discussed qualitatively in terms of pK_{SH} , charge, water solubility and size of the substrates.

The effect of anionic, nonionic and cationic surfactant on the oxidation rate of these thiols has been investigated. In the absence of polymer the effect of various types of surfactant was small for the hydrophilic ME, MP and MA. However, for DM a micellar catalytic effect of cationic surfactant was observed, whereas anionic surfactant retarded the reaction.

When $\text{CoPc}(\text{NaSO}_3)_4$ was used in the presence of poly(vinylamine), large differences were observed between the effects of various types of surfactant on the oxidation rate of ME. Nonionic surfactant did not affect the high reaction rate, whereas cationic and anionic surfactants appeared to diminish the rate considerably, even at far below the critical micelle concentration.

These effects are discussed in terms of interactions between the polymer catalyst and surfactant. Furthermore, similarities and differences between polymeric catalysis and micellar catalysis in thiol oxidation are shown.

Introduction

The oxidation of thiols to disulfides is an important process in oil-sweetening and in biological systems. Among the catalysts known for this autoxidation [1], cobalt phthalocyanines in alkali appeared to be very efficient [2]. Attachment of the water-soluble cobalt phthalocyanine-

tetra(sodium sulfonate) ($\text{CoPc}(\text{NaSO}_3)_4$, see Fig. 1) to the basic poly(vinylamine) (PVAm) resulted in a 30 - 50-fold enhancement of the oxidation rate of 2-mercaptoethanol (ME) in water compared with the $\text{CoPc}(\text{NaSO}_3)_4/\text{OH}^-$ system [3]. The promoting power of the PVAm could be ascribed to prevention of binucleation of the $\text{CoPc}(\text{NaSO}_3)_4$ catalyst on the one hand, and enrichment of both the weakly acidic substrate and the $\text{CoPc}(\text{NaSO}_3)_4$ in the basic coils on the other. In several papers, the effect of pH [4, 5], molecular weight [6], polymer chain charge [7], ionic strength and substrate concentration [8] on reaction rate have been reported. In all these investigations ME was used as substrate, serving as a model for other thiols. In the present paper we extend our investigation to some other thiols, *i.e.* 3-mercaptopropane-1,2-diol (MP), mercaptoacetic acid (MA) and dodecylmercaptan (DM), the latter being sparingly soluble in water. The catalytic activity of both the conventional system ($\text{CoPc}(\text{NaSO}_3)_4/\text{OH}^-$) and the polymeric system ($\text{CoPc}(\text{NaSO}_3)_4/\text{PVAm}$) in the conversion of these thiols has been tested.

Furthermore, for both catalyst systems the effect of surfactants on the reaction rate has been studied, since the conversion of odorous thiols (they can be nose-detected in ppb) in surfactant-containing reaction systems is an important issue in industry, and one which provides a challenge in particular for chemists working in the field of polymeric and micellar catalysis.

Some of the results concerning the effect of surfactants on polyelectrolyte catalysis may be valid for other polyelectrolyte catalyst systems, provided only electrostatic interactions play a role in the catalysis.

Experimental

Hexadecyltrimethylammonium bromide (CTAB, Fluka, purum), sodium dodecylsulfate (SDS, Fluka, purissimum) and poly(oxyethylene)-

Fig. 1. Chemical structure of $\text{CoPc}(\text{NaSO}_3)_4$.

30-nonylphenol (Antarox CO-880, GAF, abbrev.: A-CO-880) were used as supplied.

Aqueous solutions of poly(vinylamine hydrochloride) (3% w/v; Poly-science Inc., Warrington FL, U.S.A.; $\bar{M}_n = 5 \times 10^4 \text{ g mol}^{-1}$ from viscosity experiments in water containing 0.01 N NaOH and 0.1 M NaCl [9]) were eluted through an Amberlite IRA 401 anion exchange column to remove the chloride. The PVAm solutions thus obtained were stored under nitrogen to prevent absorption of CO_2 .

2-Mercaptoethanol and dodecylmercaptan were distilled; the 3-mercaptopropane-1,2-diol and mercaptoacetic acid were used as supplied. Their purity (>99%) was determined iodometrically prior to use. $\text{CoPc}(\text{NaSO}_3)_4$ (kindly provided by Dr. T. P. M. Beelen) had been synthesised by a method analogous to that of Weber and Busch [10] as described by Zwart *et al.* [11].

Initial reaction rates were determined by monitoring the oxygen consumption during the first minute of reaction. The measurements were carried out at 25 °C as described previously [8].

The polymeric catalyst was prepared by mixing aqueous solutions of PVAm and $\text{CoPc}(\text{NaSO}_3)_4$, resulting in a polymer-organometal complex. The mixture was degassed twice and saturated with oxygen over a period of 20 min while stirring vigorously. The reaction was started by adding the substrate to the reaction vessel by means of a syringe. In the micellar catalyst system the substrate was added after degassing and saturating the soap mixture with oxygen. The reaction was started 30 s hereafter by adding the $\text{CoPc}(\text{NaSO}_3)_4$ catalyst, thus obtaining best reproducibility.

The turbidity τ during turbidimetric titration of the polymeric catalyst with SDS in the presence of ME was obtained from transmission measurements: $\tau = (\log I_0/I)/b$ where I_0 and I are the intensities of the incident and transmitted light, respectively, and b is the optical path length of the cell used. A Carl Zeiss PMQ II spectrophotometer operating at 600 nm wavelength was used with 1 cm cells.

Viscosity measurements on filtered solutions were carried out at 25.0 °C in a Hewlett Packard automatic solution viscometer of the Ubbelohde type. Measurements were conducted 20 min after addition of the thiol, since small time effects were observed.

Results and discussion

The $\text{CoPc}(\text{NaSO}_3)_4/\text{OH}^-$ catalyst system

Effect of thiol variation

Several papers have dealt with $\text{CoPc}(\text{NaSO}_3)_4$ in alkaline medium as a catalyst for the autoxidation of ME [3, 11, 12]. The alkali was needed to enhance the dissociation of the weakly acidic thiol, producing thiol anions, the latter generally being regarded as the reactive species.

In order to gain insight into the differences among the reactivities of the various thiols, as well as to compare this catalyst system with those containing surfactant or polymer, the reaction rate at optimal pH was measured for ME, MP, MA and DM. The results are listed in Table 1, columns 3 and 4. The negative logarithm of the dissociation constants of the sulfhydryl group of these thiols is listed in column 2. Obviously the pH optimum increases with increasing pK_{SH} , which corroborates the assumption that the thiol anions play a dominant role in the reaction mechanism. Moreover, for the almost equally acidic substrates ME and MP practically equal pH optima and reaction rates are observed. The oxidation rate of MA is considerably lower and only slightly dependent on pH. Probably the pH-dependent dissociation of the carboxylic acid group will contribute to this behaviour, since at lower pH the low thiol anion concentration and at higher pH the high ionic charge (-2) will hinder a fast autoxidation. A similar rate difference has been observed in the vitamin B₁₂ (Vit B₁₂) catalysed oxidation of ME and MA [16].

The oxidation rate of DM is low in comparison with the other thiols, probably due to lower water solubility and the large size of the substrate.

Effect of surfactant

The effect of surfactant on the thiol oxidation was investigated at the pH optimum. An anionic, a nonionic and a cationic surfactant were used, *viz.* sodium dodecyl sulfate (SDS), poly(oxyethylene)-30-nonylphenol (A-CO-880) and hexadecyltrimethylammonium bromide (CTAB) at 0.01 M. In Table 1, columns 5 - 7, the relative rates v_r compared with the surfactant-free system (column 4) are listed. For the water-soluble ME, MP and MA a slight decrement in reaction rate mostly occurs, irrespective of surfactant type in comparison with the corresponding surfactant-free reaction systems. However, for the DM-containing system an anionic surfactant retards the reaction; a nonionic surfactant acts rather indifferently, whereas a cationic surfactant causes a large enhancement. The latter observations are indicative of the occurrence of a so-called micellar catalysis in the oxidation of DM. The micellar catalytic action was first explained by Hartley [17] using simple electrostatic considerations: anionic micelles will retard reaction rates involving anions, whereas cationic micelles will cause the opposite effect. However, since for the present thiols a micellar effect is only observed for the long chain thiol DM, it seems that here interactions other than electrostatic, *i.e.* hydrophobic interactions, also play a role.

The influence of thiol and surfactant concentration as well as the effect of ionic additives on the oxidation rate of DM by micellar catalysis will be the subject of the next subsection.

Micellar catalysis in the oxidation of dodecylmercaptan

The effect of thiol concentration on the cationic micelle-catalysed oxidation rate of DM appears to be of the saturation type, and can be described with the Michaelis-Menten concept [18]. This means that the rate-determining reaction step takes place subsequent to substrate-catalyst complex formation:

TABLE 1

Polymeric and micellar effects on the $\text{CoPc}(\text{NaSO}_3)_4$ -catalysed oxidation of thiols

Thiol	pK_{SH}	$\text{CoPc}(\text{NaSO}_3)_4/\text{OH}^-^a$			v_t A-CO-880 ^f nonionic	v_t SDS ^f anionic	v_t CTAB ^f cationic	$\text{CoPc}(\text{NaSO}_3)_4/\text{PVAm}^a$	
		Optimal pH	v without surfactant ($\text{ml } \mu\text{mol}^{-1} \text{min}^{-1}$)					optimal pH	v_t^g
2-mercaptoethanol (ME)	9.6 ^b	10	38		0.4	0.9	0.3	8	28
3-mercaptopropane-1,2-diol (MP)	9.7 ^c	10	40		0.7	1.1	0.3	8	14
mercaptopoacetic acid (MA)	10.4 ^b	10 - 11 ^e	21		0.8	0.8	0.8	9 ^e	5
dodecylmercaptan (DM)	11 ^d	13	4		0.6	0.0	23	—	0

^a Duplicate measurements. Thiol concentration: $c_{\text{RSH}} = 0.19 \text{ M}$. Initial rates determined at pH optimum. v_t is expressed relative to the rate in the corresponding surfactant-free $\text{CoPc}(\text{NaSO}_3)_4/\text{OH}^-$ systems. Rate expressed in $\text{ml O}_2/\mu\text{mol CoPc}(\text{NaSO}_3)_4$, min.

^b Ref. 13.

^c Ref. 14.

^d Estimation by ref. 15.

^e Reaction rate is only slightly dependent on the pH.

^f Surfactant concentrations: $c_{\text{surf}} = 0.01 \text{ M}$. SDS = sodium dodecylsulfate; A-CO-880 = poly(oxyethylene)-30-nonylphenol; CTAB = cetyltrimethylammonium bromide.

^g Polymer concentration (repeating units): $c_N = 1.5 \times 10^{-3} \text{ M}$.

Fig. 2. Lineweaver-Burk plot for the oxidation of DM, catalysed by cationic micelles (CTAB) at pH = 13. $c_{\text{CoPc}(\text{NaSO}_3)_4} = 3.8 \times 10^{-7}$ M and $c_{\text{CTAB}} = 3.8 \times 10^{-3}$ M.

Fig. 3. Effect of surfactant concentration on the initial oxidation rate, v , of DM (polymer absent). (●) CTAB, (○) SDS, (■) A-CO-880. $c_{\text{CoPc}(\text{NaSO}_3)_4} = 3.8 \times 10^{-7}$ M; $c_{\text{DM}} = 0.04$ M; pH = 13.

Accordingly, linear plots of reciprocal initial reaction rate *versus* reciprocal substrate concentration are obtained (so-called Lineweaver-Burk plots):

$$\frac{1}{v} = \frac{1}{k_2[\text{E}_0]} + \frac{K_m}{k_2[\text{E}_0]} \frac{1}{[\text{S}]}$$

where v = the initial reaction rate, $[\text{E}_0]$ = the total catalyst concentration, E = unbound catalyst, P = product(s), $[\text{S}]$ = initial substrate concentration and $K_m = (k_{-1} + k_2)/k_1$ with $K_s = k_1/k_{-1}$ ($\approx K_m^{-1}$ for $k_2 \ll k_{-1}$).

In Fig. 2 the Lineweaver-Burk plot is shown for the DM oxidation and in Table 2 the turnover number k_2 and the Michaelis constant K_m are listed. These values will be discussed in relation with those obtained in the system $\text{CoPc}(\text{NaSO}_3)_4/\text{PVAm}$ in the next section.

In Fig. 3 the oxidation rate of DM is shown as a function of surfactant concentration. DM concentration is 4×10^{-2} M. Nonionic and anionic surfactants retard reaction rate. The rate-enhancing effect of CTAB, in comparison with the surfactant-free system $\text{CoPc}(\text{NaSO}_3)_4/\text{OH}^-$, exhibits a maximum at $c_{\text{CTAB}} = 4 \times 10^{-3}$ M. A maximum often has been observed in micellar catalysis [19], and was explained by solubilization of reactive anions in cationic micelles, thus making them less active. In the present case it is possible that at this surfactant concentration part of the catalytically

TABLE 2

Reaction constants in the oxidation of various thiols

Thiol	pH	$10^{-2} k_2$ (s^{-1})	K_m ($mol\ dm^{-3}$)
2-mercaptoethanol (ME) ^a	7.4	31 ± 4	0.11 ± 0.01
3-mercaptopropane-1,2-diol (MP) ^a	7.4	20 ± 3	0.05 ± 0.01
dodecylmercaptan (DM) ^b	13	3.9 ± 0.5	0.06 ± 0.01

^aIn polymeric system: $CoPc(NaSO_3)_4/PVAm$; $c_{CoPc(NaSO_3)_4} = 1.9 \times 10^{-7}$ M, $c_N = 1.5 \times 10^{-3}$ M, $T = 25.0^\circ C$.

^bIn micellar system: $CoPc(NaSO_3)_4/CTAB$; $c_{CoPc(NaSO_3)_4} = 3.8 \times 10^{-7}$ M, $c_{CTAB} = 3.8 \times 10^{-3}$ M, $T = 25.0^\circ C$.

Fig. 4. Effect of ionic additives on the initial oxidation rate of DM in a cationic micellar (CTAB) catalyst system at pH = 13. ($\square$) NaCl, ($\blacksquare$) Na benzoate, ($\bullet$) SDS (also shown in the inset). Reaction conditions as given in Fig. 3; $c_{CTAB} = 3.8 \times 10^{-3}$ M.

active anions, $CoPc(SO_3)_4^{4-}$, are solubilized in the cationic micelles, thus accounting for the decrease in rate at CTAB concentrations larger than 4×10^{-3} M (Fig. 3 ($\bullet$)).

The effect of ionic additives, *viz.* NaCl, Na benzoate and SDS, on the oxidation rate of DM is shown in Fig. 4. CTAB concentration was 3.8×10^{-3} M. It is obvious that NaCl, a salt with a small anion, hardly affects the reaction rate. The more hydrophobic benzoate ion has more influence, and the effect of SDS is dramatic. The latter substance may be assumed to be entirely mixed up with CTAB in the micelles. The inset in Fig. 4 shows that a complete loss of catalytic activity occurs at equal molar amounts of SDS and CTAB, *viz.* 3.8×10^{-3} M. The micelles may then be assumed to have zero net charge, and catalytic activity is no longer detected.

From Fig. 4 it becomes clear that small polar anions have little effect, and large hydrophobic anions have a large retarding effect on the micellar oxidation rate, thus emphasizing that both hydrophobic and electrostatic effects play a role in micellar catalytic activity. The importance of electrostatic as well as hydrophobic interactions in micellar catalysis was earlier stressed by other investigators [19, 20].

In contrast to the small effect observed here of NaCl on reaction rate in the micellar catalytic system, addition of NaCl to the polymeric catalytic system caused a considerable decrease in rate [8], emphasizing the importance of solely electrostatic interactions between substrate and catalyst in pure polyelectrolyte catalysis, where hydrophobic functionalities are absent.

The CoPc(NaSO₃)₄/PVAm catalyst system

Effect of thiol variation

Complexation of CoPc(NaSO₃)₄ with aqueous basic PVAm yields a catalyst exhibiting a much higher activity and considerably lower pH optimum than the polymer-free CoPc(NaSO₃)₄ system (Table 1, columns 8 and 9). The occurrence of an optimum at lower pH can be qualitatively explained by the high concentration of basic groups within the polymeric coils at intermediate pH values in the bulk. For ME, the pH-dependency of the oxidation rate has been investigated and discussed in more detail previously [4].

It is striking that, using the polymeric catalyst system, different oxidation rates are found for ME and MP, whereas no significant difference was found in the case of the polymer-free catalyst system (see Table 1).

In previous investigations on polymeric catalytic systems, it was shown that the Michaelis-Menten concept could be applied to describe the effect of ME concentration on reaction rate [6-8]. This concept also appears to be applicable to the oxidation of MP with the polymeric catalyst. In Fig. 5 Lineweaver-Burk plots are shown for both ME (★) and MP (●) at pH = 7.4. In Table 2 the values of k_2 and K_m are listed. Different values of k_2 and K_m are observed for the substrates ME and MP. It seems that the complex formation constant K_s ($\approx K_m^{-1}$) is larger for MP, but the apparent intrinsic activity of the catalytic sites is lower. Since both substrates possess practically identical dissociation constants, the observed differences in k_2 and K_m must originate from differences in size.

For DM, oxidized in the micellar catalyst system, the value of K_m is in the same range as that for ME and MP in the polymeric catalyst system (see Table 2). It may therefore be inferred that the equilibrium for substrate-catalyst formation is not greatly affected by the environment of CoPc-(SO₃)₄⁴⁻ (whether polymeric or micellar). The turnover number k_2 found for DM in the micellar system is lower than k_2 observed for ME and MP in the polymeric catalyst system. These differences must be ascribed to differences in reactivity of the substrates, since also in the surfactant- and polymer-free catalyst system, CoPc(NaSO₃)₄/OH⁻, the oxidation rate of DM was ten times lower than that of ME and MP.

Fig. 5. Lineweaver-Burk plots for the polymer-catalysed oxidation of ME (★) and MP (●) at pH = 7.4. $c_{\text{CoPC(NaSO}_3)_4} = 1.9 \times 10^{-7} \text{ M}$; $c_N = 1.5 \times 10^{-3} \text{ M}$.

MA shows rather low oxidation activity in the polymeric catalyst system, probably due to (1) competition between carboxylate and thiolate for a site on the catalyst and (2) electrostatic attraction between the negatively-charged reaction product (due to the COO^- moieties) and the positively-charged polymeric catalyst.

With DM as a substrate, no detectable catalytic activity is observed in the polymeric catalyst system. After stirring a PVAm solution containing DM, flocculation phenomena are observed. Probably DM, being rather hydrophobic, will be rejected by the water phase and interact relatively strongly within the polymeric region. Therefore, DM may not be converted under these conditions.

Effect of surfactant

In order to elucidate the effect of surfactants on the behaviour of polyelectrolyte catalysts in thiol oxidation, the oxidation rate of ME in the polymeric catalyst system was measured upon the addition of increasing amounts of SDS, A-CO-880 and CTAB.

In Fig. 6 (□) the initial oxidation rate of ME is plotted *versus* the logarithm of the SDS concentration. Polymer concentration (repeating units) is $1.5 \times 10^{-3} \text{ M}$. Initially, reaction rate is slightly enhanced, a maximum occurring at $\text{SDS}/N = 0.2$; adding more anionic surfactant causes a sharp decrease in reaction rate, with an inflection point at $\text{SDS}/N = 0.8$. Beyond this point reaction rate is very low. This tremendous effect of anionic surfactant on reaction rate occurs far below the critical micelle concentration (*cmc*) of SDS ($\text{cmc}_{\text{SDS}} = 8 \times 10^{-3} \text{ M}$ [21]). The decrease in rate is accompanied by the occurrence of turbidity of the reaction solution.

In separate experiments, the polymeric catalyst solution in the presence of ME was titrated turbidimetrically with SDS ((●) in Fig. 6). A maximum in turbidity was observed at $\text{SDS}/N = 0.8$. Addition of more SDS lead to complete transparency of the solution, but catalytic activity, as shown in Fig. 6 (□), further decreased, though slowly.

Fig. 6. Effect of SDS concentration on the initial oxidation rate, v , of ME (polymer-catalysed) ($\square$) and on the turbidity, τ , of the reaction solution ($\bullet$). $c_{\text{CoPc}(\text{NaSO}_3)_4} = 1.9 \times 10^{-7} \text{ M}$; $c_{\text{N}} = 1.5 \times 10^{-3} \text{ M}$; $c_{\text{ME}} = 0.19 \text{ M}$; $\text{pH} = 7.6$.

The increased turbidity is caused by flocculation [22] of the polymeric catalyst upon addition of SDS, and can be explained by adsorption of SDS onto the positively-charged polymer. Addition of excess SDS resolubilizes the polymer-surfactant complex (see Scheme 1) and the polymer solution

Scheme 1. Interaction of anionic SDS with positively-charged PVAm.

again becomes transparent. Similar adsorption phenomena were observed for the interaction of ionic surfactants with oppositely-charged polymers [23, 24] or latices [25], although phase separation and resolubilization of the flocculated complexes were not always reported. Analogous to colloid titrations of cationic polymers with anionic ones (see for example [26]) the surfactant-polymer interactions cited above seem to occur stoichiometrically on the basis of charge.

Application of this concept to the present observations makes it plausible that (1) the catalyst is 80% charged (on the basis of repeating units), and (2) the inflection point in Fig. 6. ($\square$), where the reaction rate becomes negligible, occurs at zero net charge of the polymer-surfactant complex. The latter result (2) is in complete agreement with our recent findings concerning the relation between the net polymer charge and reaction rate in copolymers of vinylamine and vinyl alcohol [7]. In addition, the

hydrophobic mantle, formed by SDS (Scheme 1), will expel ionic substrate out of the polymer domain.

The value found here for the polymer charge (80%) at pH = 7.6 is higher than that found earlier from potentiometric titrations, *viz.* 40% [6]. Probably due to an effective screening by the dodecylsulfate counter-ions, PVAm behaves like a stronger polyelectrolyte, and a higher degree of protonation is tolerated. This may also account for the initial slight increase of reaction rate at low SDS/N ratios, where the rate-enhancing electrostatic effect still dominates the rate-retarding effect of the diffuse hydrophobic mantle. The same discrepancy was observed in poly(ethylenimine). From colloid and potentiometric titrations the polymer charge at pH = 6.5 was found to be 65% and 32%, respectively [26].

During the preparation of this paper, preliminary results were published by Visser *et al.* concerning the enhancement of the catalytic activity of imidazole-containing polymers of isocyanides in the hydrolysis of activated esters upon the addition of cationic surfactant [27]. At the relevant pH values the polymer was negatively charged. Similar phenomena of precipitation and resolubilization of the polymer-surfactant complex were found, as well as an increase in chain charge when adding the surfactant. The increase in reaction rate was partially attributed to the hydrophobic mantle enhancing the local (hydrophobic) substrate concentration in the vicinity of the catalytic polymeric functions.

From these observations it may be inferred that in polyelectrolyte-surfactant complexes the hydrophobic surfactant mantle may enhance or retard reaction rate, depending on the hydrophobicity of the substrate.

In view of these findings with SDS adsorbed on PVAm, it is conceivable that DM also strongly adsorbs on the polymer, which accounts for the observed flocculation of PVAm in the presence of DM, as mentioned in the preceding section.

In Fig. 7 the effect of the nonionic surfactant A-CO-880 on the oxidation rate of ME is shown, clearly indicating that catalytic activity is maintained. Obviously this charged polymeric catalyst is indifferent toward non-ionic surfactant.

The effect of the cationic CTAB on the oxidation rate of ME is shown in Fig. 8 (□). Polymer concentration is 1.5×10^{-3} M. A decline in reaction rate is observed starting at very low concentrations of surfactant ($c_{\text{CTAB}} \ll \text{cmc}_{\text{CTAB}} = 9 \times 10^{-4}$ M [28]). Since the charges of surfactant and polymer have the same sign, direct polymer-surfactant interactions such as adsorption are less probable. However, monitoring the specific viscosity of the polymeric catalyst solution in the presence of CTAB (Fig. 8 (●)), and of KBr as a reference (Fig. 8 (○)), clearly shows that at low concentrations CTAB has a marked effect on viscosity, whereas a simple 1:1 electrolyte (KBr) exhibits no drastic effect. Obviously, CTAB has a greater charge-shielding effect than KBr. The great sensitivity of catalytic activity to small amounts of CTAB may be due to direct interactions with the $\text{CoPc}(\text{SO}_3)_4^{4-}$ moiety.

Fig. 7. Effect of A-CO-880 concentration on the initial oxidation rate, v , of ME (polymer-catalysed) (□). Other reaction conditions as in Fig. 6.

Fig. 8. Effect of CTAB concentration on the initial oxidation rate, v , of ME (polymer-catalysed) (□) and the specific viscosity of the polymer-containing reaction solution, η_{sp} , (●). As a reference, the effect on η_{sp} of a simple 1:1 electrolyte (KBr) is shown (○). Other reaction conditions as in Fig. 6.

General discussion

As follows from the observations above, thiols can be oxidized until odorless with high rates using polyelectrolyte or micellar catalysts. In order to select the proper catalyst system for the appropriate substrate, it may be useful to divide the thiol substrates into polar and hydrophobic groups. Table 3 shows the catalytic activity expected for these types of substrates in the

TABLE 3

Schematic representation of the activity of various catalytic systems for polar and hydrophobic thiols

Thiol type	CoPc(NaSO ₃) ₄ /OH ⁻				CoPc(NaSO ₃) ₄ /PVAm			
	no surf.	anionic	nonionic	cationic	no surf.	anionic ^a	nonionic ^a	cationic ^a
polar	0	0	0	0	+	—	+	—
hydrophobic	0	—	—	+	—	—	—	—

^a $c_{\text{surf}} < c_{\text{polymer}}$; + = large enhancement of reaction rate, 0 = no significant change of reaction rate, — = retardation of reaction rate, all in comparison with the surfactant- and polymer-free system CoPc(NaSO₃)₄/OH⁻.

various catalyst systems. The hydrophobic substrates are best oxidized in a cationic micellar system, whereas the polar thiols are oxidized very rapidly with a positively-charged polymeric catalyst (see also Scheme 2). In the

Scheme 2. Schematic representation of thiols in polymeric and micellar catalysis.

latter catalyst system, nonionic surfactant will not affect reaction rate even when present in large concentrations. Other types of surfactant will diminish the rate, especially at higher surfactant concentrations due to surfactant interactions with the polymeric catalyst.

Several catalytic effects have been reported in this paper, and though in most cases sound explanations for these observations could be presented, some of them are preliminary and require further investigation, *viz.*:

(1) the origin of the maximum in the plot of DM oxidation rate *versus* CTAB concentration (Fig. 3);

(2) the rate-retarding effect of cationic surfactant on the cationic polymeric catalyst activity (Fig. 8). Does it originate from surfactant interaction with the CoPc(SO₃)₄⁴⁻ moiety?

(3) the precise cause of relatively low DM conversion rates in polymer- and micelle-free, aqueous $\text{CoPc}(\text{NaSO}_3)_4$ solutions; which effect dominates rate: the low water solubility, its large size or the high $\text{p}K_a$?

(4) the low oxidation rate of MA in the polymeric system. Is it mainly caused by (i) competition between the COO^- and RS^- moieties for coordination with the phthalocyanine, (ii) a slow product release from the polymeric domain, due to electrostatic attraction or by (iii) an enhancement of ionic strength due to the double negative charge of the product?

Unfortunately, these points could not as yet be elucidated. Thus far, in thiol oxidation catalysis most attention has been paid to the (polymeric) catalysis of polar thiols. However, in many industrial systems the oxidation of more hydrophobic thiols is relevant, and therefore more attention must be paid to catalyst systems capable of oxidizing these substrates. Micellar systems, where both electrostatic and hydrophobic interactions play a role, will be most promising for this purpose.

Conclusions

— Good water soluble thiols can be oxidized at high rates when $\text{CoPc}(\text{NaSO}_3)_4$ is used as a catalyst in the presence of the basic PVAm. For the sparingly water-soluble amphipolar DM, no catalytic effect was observed in this catalyst system.

— The oxidation rate of DM is greatly enhanced when $\text{CoPc}(\text{NaSO}_3)_4$ is used in alkaline medium in the presence of cationic micelles. Anionic micelles retard the reaction rate, and nonionic micelles retard to a lesser extent. The oxidation rate of the good water soluble thiols is, however, only slightly affected by addition of surfactants.

— In the cationic polyelectrolyte catalysis of ME, anionic surfactant retards the reaction rate due to adsorption at the polymer chain, thus decreasing the net charge on the polymer and increasing hydrophobicity in the neighbourhood of the catalytic sites. Nonionic surfactant does not affect catalytic activity, while cationic surfactant diminishes reaction rate, possibly due to interaction with $\text{CoPc}(\text{NaSO}_3)_4$.

— In the present polymeric catalyst system electrostatic interactions dominate, whereas in the micellar catalyst system hydrophobic interactions between substrate and micelle also play an important role.

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