

# Effect of metal phthalocyanine complex aggregation on the catalytic and photocatalytic oxidation of sulfur containing compounds

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## Abstract

Water soluble zinc (II) 2,9,16,23-phthalocyanine tetrasulfonic acid [ZnPc(SO<sub>3</sub>H)<sub>4</sub>], zinc (II) 2,9,16,23-phthalocyanine tetracarboxylic acid [ZnPc(COOH)<sub>4</sub>] and sterically hindered bulky zinc(II) 2,9,16,23-tetrakis(8-quinolineoxy-5-sulfonicacid)-phthalocyanine [ZnPc(QnSO<sub>3</sub>H)<sub>4</sub>] complexes have been studied as photocatalysts for oxidation of 2-mercaptoethanol and sodium thiosulfate. The ZnPc(QnSO<sub>3</sub>H)<sub>4</sub> complex exhibited the highest photocatalytic activity due to its low aggregation degree in aqueous medium. In the presence of tetrabutylammonium chloride, quinoline and ethanol additives the monomerization degree of the ZnPc(SO<sub>3</sub>H)<sub>4</sub> and ZnPc(COOH)<sub>4</sub> complexes is increased, their photocatalytic activity being close to that of ZnPc(QnSO<sub>3</sub>H)<sub>4</sub>. Because of high aggregation degree of ZnPc(SO<sub>3</sub>H)<sub>4</sub> and ZnPc(COOH)<sub>4</sub> in viscous medium, the quantum yields of singlet dioxygen generation and the photocatalytic oxidation rates of the sulfur-containing compounds are decreased. The photocatalytic activity of ZnPc(QnSO<sub>3</sub>H)<sub>4</sub> is slightly changed in viscous medium and in the presence of additives. The low aggregation degree of this complex allowed to establish enhanced and lowered rates of photocatalytic oxidation of 2-mercaptoethanol and sodium thiosulfate, respectively, on increasing medium viscosity. The effect of medium viscosity on ZnPc(QnSO<sub>3</sub>H)<sub>4</sub> photocatalyzed oxidation of the two substrates is discussed. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Photocatalysis; Oxidation; Phthalocyanine complexes; Mercaptans; Thiosulphates; Solvent effect

## 1. Introduction

Sulfur-containing compounds, such as mercaptans, alkali sulfides, alkali sulfites, and alkali thiosulfates are by-products of industrial processes and pollutants of waste and natural waters [1,2]. The complete oxidation of sulfur-containing compounds, before discharging them into

waterways, has been suggested as a possible solution of the environmental pollution problem. Phthalocyanine and porphyrin complexes are effective catalysts and photocatalysts for thiol and hydrosulfide oxidation by dioxygen [1–9]. The activation of dioxygen and the possibility of its participation in a catalytic or photocatalytic process is dependent on the electronic structure of the phthalocyanine complexes and the central metal atom [6,7,10]. Phthalocyanine complexes containing metal ions with unfilled d orbitals, like Co<sup>2+</sup>, can reversibly coordinate

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and activate dioxygen in the dark [2–11] which is the basis of the redox mechanism of catalytic oxidation of sulfur-containing compounds [5]. These catalysts have found wide application in the catalytic oxidation of mercaptans in oil fractions [2,12]. The oxidation of thiols and alkali sulfides catalyzed by cobalt phthalocyanine complexes (CoPc) is not complete, the end products being disulfides, sulfur and thiosulfates, respectively [3–9]. Recently it has been established [6–9] that metal-free phthalocyanine complexes and those containing a central metal ion with filled electron shells or d orbitals exhibit high photocatalytic activity in the complete oxidation of sulfur-containing compounds. On interaction between dioxygen and the long-living triplet state of these complexes, a chemically more reactive singlet dioxygen  $^1\text{O}_2(^1\Delta_g)$  is formed which further interacts with compounds

containing sulfur of various oxidation state. An additional photon-induced electron transfer between mercaptans and excited phthalocyanine molecules may also occur, but the influence of this process on the photocatalytic oxidation rate of the sulfur-containing compounds is negligible [7].

The catalyst effectiveness is substantially affected by aggregation of the phthalocyanine complexes [6,7,9] which is specific of this type of molecules [13]. In photoinitiated processes, upon formation of dimers as a result of bimolecular triplet annihilation, the excited triplet electron state of the complexes is quenched, the quantum yield of  $^1\text{O}_2(^1\Delta_g)$  being decreased [6,7,9,14]. It has been shown [6,7,9] that upon self-association in solution the photocatalytic activity of the phthalocyanine complexes is decreased by 5–10 times.

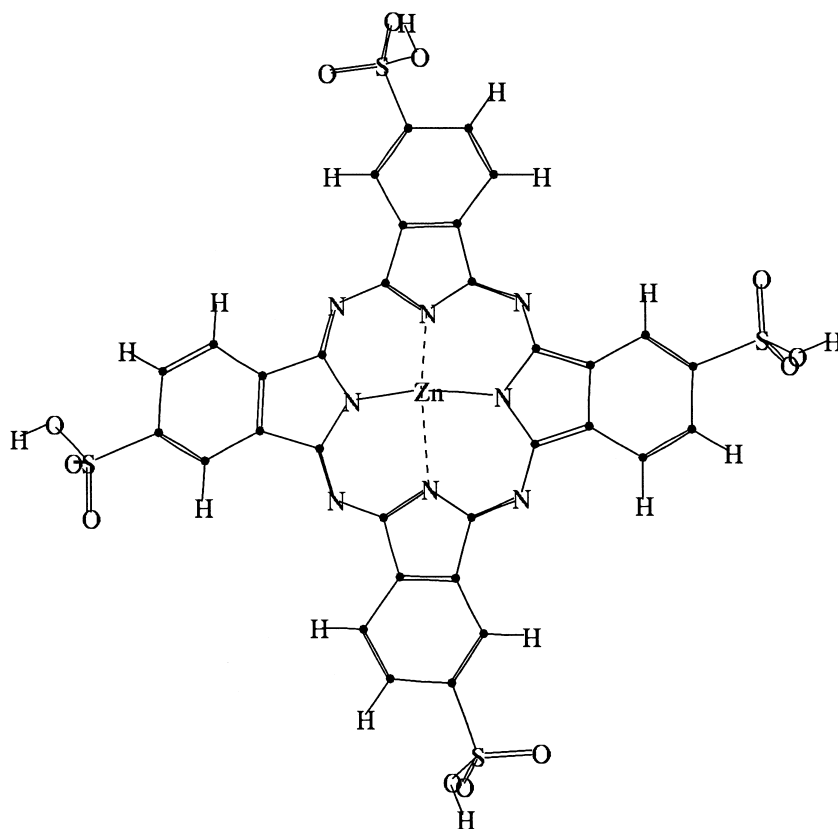


Fig. 1. Molecular structure of zinc (II) 2,9,16,23-phthalocyanine tetrasulfonic acid.

This study deals with the effect of medium and of the steric structure of the phthalocyanine complexes on their aggregation with the purpose to find suitable conditions for the investigated catalysts to demonstrate high activity in the reactions of 2-mercaptoethanol (MEA) and sodium thiosulfate oxidation.

## 2. Experimental

Cobalt (II) 2,9,16,23-phthalocyanine tetrasulfonic acid [ $\text{CoPc}(\text{SO}_3\text{H})_4$ ], cobalt 2,9,16,23-phthalocyanine tetrasulfonic acid [ $\text{ZnPc}(\text{SO}_3\text{H})_4$ ], and zinc (II) 2,9,16,23-phthalocyanine tetracarboxylic acid [ $\text{ZnPc}(\text{COOH})_4$ ] were prepared and purified according to methods described in the literature [15,16]. Zinc(II) 2,9,16,23-tetrakis(8-quinolineoxy-5-sulfonic

acid)-phthalocyanine [ $\text{ZnPc}(\text{QnSO}_3\text{H})_4$ ] was synthesized by methods for preparation of phenoxy-substituted phthalocyanine complexes [7,17], as follows. 4-Nitrophthalic nitrile (8.7 g, 50 mmol) and excess of 8-hydroxyquinoline-5-sulfonic acid monohydrate (18.2 g, 75 mmol) were dissolved in 100 ml of dry methyl sulfoxide under inert gas. Dry potassium carbonate (27.2 g, 200 mmol) was added. The same amount of potassium carbonate was admitted after 6 h stirring at room temperature. After 12 h the mixture was added to 500 ml 1 M hydrochloric acid. The isolated product (11 g, 70% yield) was recrystallized from ethanol. IR (KBr): 1284 and 1260  $\text{cm}^{-1}$  (Ar–O–Ar). 4-(8-Quinolineoxy)-phthalonitrile (4.5 g, 12 mmol) was mixed with zinc(II) acetate dihydrate (2.0 g, 7 mmol) and further heated at 473 K for 6 h to yield  $\text{ZnPc}(\text{QnSO}_3\text{H})_4$  [7,17]. The reaction

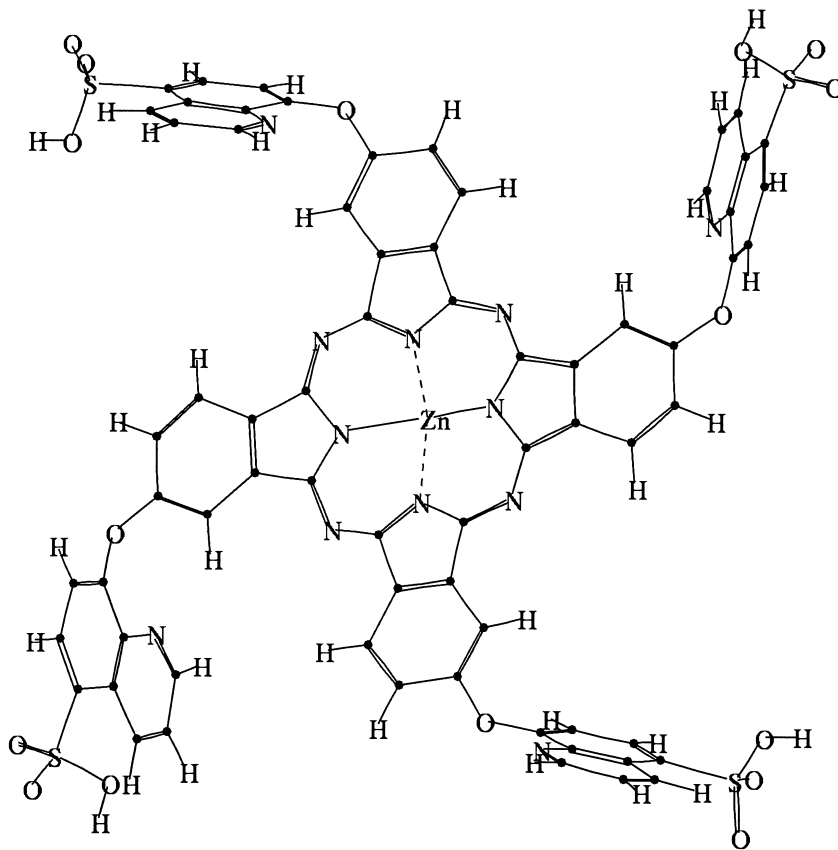


Fig. 2. Molecular structure of zinc(II) 2,9,16,23-tetrakis(8-quinolineoxy-5-sulfonic acid)-phthalocyanine.

product was consecutively treated with 1,2-dichloroethane and acetone in a Soxhlet apparatus. Finally, a dark green product was isolated. Yield 2.8 g (60%). IR (KBr): 1265 and 1238  $\text{cm}^{-1}$  (Ar–O–Ar). Anal. calcd. for  $\text{C}_{68}\text{H}_{36}\text{N}_{12}\text{O}_{16}\text{S}_4\text{Zn}$ : C 55.51, H 2.49, N 11.43, S 8.71; found: C 53.92, H 2.57, N 11.53, S 8.21.

The structures of  $\text{ZnPc}(\text{SO}_3\text{H})_4$  and sterically hindered  $\text{ZnPc}(\text{QnSO}_3\text{H})_4$  complexes are shown in Figs. 1 and 2 were obtained after geometric optimization by means of GAMESS program package using a standard parameterization for AM1 [18].

The viscosity of pure and mixed solvents was determined by means of glass capillary vis-

cometers. Viscosity in centipoise ( $\eta$ ) was calculated for solvent density at 293 K (Table 1).

Absorption spectra of the phthalocyanine complexes were registered on a Hewlett-Packard 89500 UV–VIS spectrophotometer (Fig. 3). Monomer phthalocyanine complex concentrations (Table 1) were determined through UV–VIS absorption spectroscopy by using the following equation [19,20]:

$$\left(\frac{\varepsilon_M - \varepsilon_i}{C^{i0}}\right)^{1/2} = (2K_D \Delta\varepsilon)^{1/2} - (2K_D/\Delta\varepsilon)^{1/2}(\varepsilon_M - \varepsilon_i), \quad (1)$$

where  $\Delta\varepsilon = \varepsilon_M - \varepsilon_D/2$ .  $\varepsilon_M$ ,  $\varepsilon_D$  and  $\varepsilon_i$  are molar absorbances of the monomer, dimer and

Table 1

Photooxidation of 2-mercaptoethanol (10 mmol) and  $\text{Na}_2\text{S}_2\text{O}_3$  (30 mmol) in aqueous solution at pH = 9.24, catalyzed by water-soluble phthalocyanine complexes (1.7  $\mu\text{mol}$ )

No.	Complex	Modifying additive	$[\text{MPC}]_{\text{mon}}$ $\mu\text{mol} \pm 10\%$	$\eta$ (cp) $\pm 2\%$	MEA $r$ ( $\text{min}^{-1}$ ) $\pm 7\%$	$\text{Na}_2\text{S}_2\text{O}_3$ $r$ ( $\text{min}^{-1}$ ) $\pm 7\%$
1	$\text{CoPc}(\text{SO}_4\text{H})_4$	–		0.89	81	–
2	$\text{CoPc}(\text{COOH})_4$	–		0.89	105	–
3	$\text{ZnPc}(\text{SO}_3\text{H})_4$	–	0.70	0.89	29	3.9
4	$\text{ZnPc}(\text{COOH})_4$	–	0.63	0.89	21	0.8
5	$\text{ZnPc}(\text{QnSO}_3\text{H})_4$	–	0.99	0.89	152	6.4
6	$\text{ZnPc}(\text{COOH})_4$	Qun <sup>a</sup>	0.80	0.89	79	1.8
7	$\text{ZnPc}(\text{COOH})_4$	TBAC <sup>b</sup>	1.39	0.94	177	3.5
8	$\text{ZnPc}(\text{COOH})_4$	TBAC <sup>c</sup>	1.15	0.92	80	2.6
9	$\text{ZnPc}(\text{COOH})_4$	EtOH <sup>d</sup>	1.54	0.95	154	3.1
10	$\text{ZnPc}(\text{QnSO}_3\text{H})_4$	EtOH <sup>d</sup>	1.54	0.95	170	6.8
11	$\text{ZnPc}(\text{COOH})_4$	Etgl <sup>e</sup>	0.85	1.5	26	0.9
12	$\text{ZnPc}(\text{COOH})_4$	Gl <sup>f</sup>	0.79	2.2	19.5	0.8
13	$\text{ZnPc}(\text{COOH})_4$	Gl <sup>f</sup>	0.66	4.7	13.7	0.7
14	$\text{ZnPc}(\text{COOH})_4$	Gl <sup>f</sup>	0.52	7.5	10.7	0.6
15	$\text{ZnPc}(\text{COOH})_4$	Gl <sup>f</sup>	0.43	10.4	9.5	0.5
16	$\text{ZnPc}(\text{COOH})_4$	Gl <sup>f</sup>	0.35	15.7	8.2	0.4
17	$\text{ZnPc}(\text{COOH})_4$	Gl <sup>f</sup>	0.31	19.0	7.9	0.4
18	$\text{ZnPc}(\text{COOH})_4$	Gl <sup>f</sup>	0.31	23.5	8.0	0.3
19	$\text{ZnPc}(\text{COOH})_4$	Gl <sup>f</sup> -TBAC <sup>b</sup>	0.94	23.5	65	1.1
20	$\text{ZnPc}(\text{QnSO}_3\text{H})_4$	Gl <sup>f</sup>	1.14	2.2	160	6.4
21	$\text{ZnPc}(\text{QnSO}_3\text{H})_4$	Gl <sup>f</sup>	1.07	4.7	166	5.6
22	$\text{ZnPc}(\text{QnSO}_3\text{H})_4$	Gl <sup>f</sup>	1.01	7.5	171	5.0
23	$\text{ZnPc}(\text{QnSO}_3\text{H})_4$	Gl <sup>f</sup>	0.96	10.4	174	4.8
24	$\text{ZnPc}(\text{QnSO}_3\text{H})_4$	Gl <sup>f</sup>	0.92	15.7	177	4.6
25	$\text{ZnPc}(\text{QnSO}_3\text{H})_4$	Gl <sup>f</sup>	0.92	19.0	178	4.5

<sup>a</sup>20  $\mu\text{mol}$ .

<sup>b</sup>1 mmol.

<sup>c</sup>0.3 mmol.

<sup>d</sup> $\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}$  (1:1).

<sup>e</sup>Water-dissolved ethylene glycol.

<sup>f</sup>Water-dissolved glycerol.

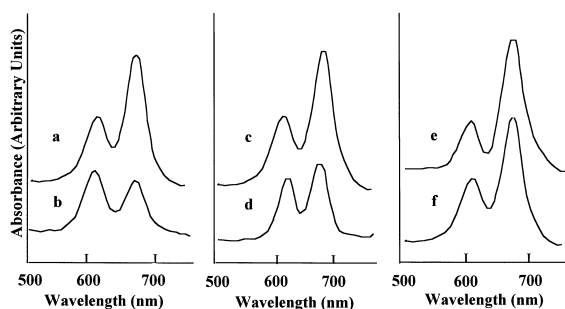


Fig. 3. UV-Vis spectra of: (a)  $\text{ZnPc}(\text{COONa})_4$ ; (c)  $\text{ZnPc}(\text{SO}_3\text{Na})_4$ ; (e)  $\text{ZnPc}(\text{QnSO}_3\text{H})_4$  dissolved in  $\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}$  (1:1) and (b)  $\text{ZnPc}(\text{COONa})_4$ ; (d)  $\text{ZnPc}(\text{SO}_3\text{Na})_4$ ; (f)  $\text{ZnPc}(\text{QnSO}_3\text{H})_4$  dissolved in  $\text{H}_2\text{O}$ .

phthalocyanine complex in the  $i$ th solution,  $C^{i0}$  is the total concentration of the complex in the  $i$ th solution, and  $K_D$  is a dimerization constant. The molar extinction coefficients ( $\text{l mol}^{-1} \text{cm}^{-1}$ ) for  $\text{ZnPc}(\text{COOH})_4$ ,  $\text{ZnPc}(\text{SO}_3\text{H})_4$  and  $\text{ZnPc}(\text{QnSO}_3\text{H})_4$ , determined in water-ethanol (1:1), were 48 200, 72 400 and 67 900, respectively.

The rates of 2-mercaptoethanol or sodium thiosulfate catalytic and photocatalytic oxidation were evaluated through the consumption of dioxygen which was measured by a gas burette. The oxidation process was performed at 293 K,  $\text{pH} = 9$  and atmospheric pressure in a static reactor by exposure to a halogen lamp (12 V, 50 W), the illumination being  $38 \text{ mW}/\text{cm}^2$ . Products of the catalytic oxidation of sulfur-containing compounds were characterized by methods described elsewhere [6,7].

### 3. Results and discussion

It is known that the effectiveness of phthalocyanine complexes as catalysts and photocatalysts for oxidation of sulfur-containing compounds is decreased on self-association [3,5–10,17,21]. The self-association with charged phthalocyanine complexes and the nature of the intermolecular interactions that lead to this process are widely discussed in the literature [6,7,9,13]. The presence of monomer-dimer

equilibrium of the phthalocyanine complexes in solution is confirmed by the existence of specific electron transitions in the Q band ( $\lambda = 600\text{--}800 \text{ nm}$ ) [6,7,22–24]. In agreement with previous assignment [25], the absorption transitions at 670–680 and 630 nm (Fig. 3) are attributed to monomeric and dimeric species, respectively.

UV-VIS spectra ( $\lambda = 670\text{--}680 \text{ nm}$ ) of  $\text{ZnPc}(\text{QnSO}_3\text{H})_4$ ,  $\text{ZnPc}(\text{SO}_3\text{H})_4$  and  $\text{ZnPc}(\text{COOH})_4$  in aqueous medium (Fig. 3b,d,f) and monomer concentrations estimated according to Eq. (1) (Table 1) show that the dimerization process proceeds to the highest extent with  $\text{ZnPc}(\text{COOH})_4$ . By reason of better solvation ability in aqueous medium [6,10,13,17,21], sulfonated phthalocyanine complexes oligomerize to a lower extent than those containing carboxylic groups. Among the three investigated complexes in aqueous medium, the monomer concentration of  $\text{ZnPc}(\text{QnSO}_3\text{H})_4$  was the highest one (Table 1). By contrast with  $\text{ZnPc}(\text{SO}_3\text{H})_4$  and  $\text{ZnPc}(\text{COOH})_4$ , the formation of dimers between the  $\text{ZnPc}(\text{QnSO}_3\text{H})_4$  molecules due to  $\pi-\pi$  interactions between parallel planes in this complex (staggered stacking) is impossible because of steric hindrance of peripheral substituents (Figs. 1 and 2).

Phthalocyanine complex association in aqueous medium is decreased (Table 1) on adding ethanol, quinoline or bulky countercharged ions like tetrabutylammonium chloride (TBAC). The influence of quaternary salts and ethanol on monomerization of charged phthalocyanine complexes has already been studied [6,7,9,23,26]. Monomerization in the presence of quinoline is enhanced due to axial coordination of the base to the central metal atom in the complexes which impedes the  $\pi-\pi$  interactions between the phthalocyanine complexes [3,17,26–28]. On increasing solvent viscosity the self-association of the phthalocyanine complexes is enhanced (Table 1, Nos. 11–18, 20–25). This indicates that the equilibrium process of dimerization is diffusion-controlled. The stronger effect of medium viscosity on phthalocyanine

cyanine complex association is due to an increased probability of molecule impacts in the solvent cage for a decreased diffusion length (geminal recombination). The geminal recombination due to a cage effect does not increase proportionally to the increase in viscosity (Table 1, Nos. 12–18, 20–25), which is specific of diffusion-controlled equilibrium processes [29,30]. The aggregation of  $\text{ZnPc}(\text{SO}_3\text{H})_4$  and  $\text{ZnPc}(\text{COOH})_4$  is strongly influenced by the viscosity of the medium whereas  $\text{ZnPc}(\text{QnSO}_3\text{H})_4$  is less affected due to steric hindrance from the substituents. A lowering of  $\text{ZnPc}(\text{SO}_3\text{H})_4$  or  $\text{ZnPc}(\text{COOH})_4$  aggregation in highly viscous solutions is observed on adding TBAC (Table 1, No. 19). The bulky tetrabutylammonium cation prevents both oligomerization and  $\pi$ - $\pi$  interactions between the phthalocyanine macrocycles of the complexes.

The catalytic and photocatalytic activity of the phthalocyanine complexes (Table 1) in the oxidation of MEA and  $\text{Na}_2\text{S}_2\text{O}_3$  is expressed by  $r$  (mol  $\text{O}_2$   $\text{min}^{-1}$ /mol Pc). The initial rates of catalytic and photocatalytic oxidation of the sulfur-containing compounds were determined from the linear part of the curve of dioxygen consumption with time (Fig. 4).

Cobalt phthalocyanine complexes, which exhibit a high catalytic activity in the dark, show no increase in the oxidation rate of MEA under irradiation [6,7,9] (Table 1). The lack of photo-

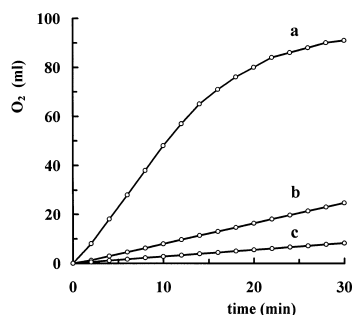
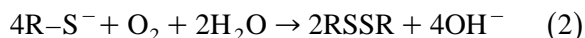


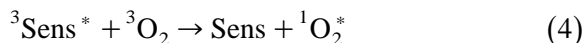
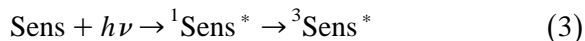
Fig. 4. Dioxygen uptake plots of the photooxidation of sulfur-containing compounds in water with no additives: (a) MEA (10 mmol) catalyzed by  $1.7 \mu\text{mol ZnPc}(\text{QnSO}_3\text{H})_4$ ; (b) MEA (10 mmol) catalyzed by  $1.7 \mu\text{mol ZnPc}(\text{COONa})_4$ ; (c)  $\text{Na}_2\text{S}_2\text{O}_3$  (30 mmol) catalyzed by  $1.7 \mu\text{mol ZnPc}(\text{QnSO}_3\text{H})_4$ . Reaction temperature  $T = 293 \text{ K}$ , atmospheric pressure of  $\text{O}_2$ .

catalytic activity of the cobalt complexes is due to a very short lifetime of the excited triplet electronic state ( $\tau_{\text{CoPc}}^T \approx 0.065 \mu\text{s}$ ) [10] and because of this they are not able to convert triplet dioxygen,  $^3\text{O}_2(^3\Sigma_g^-)$ , into singlet dioxygen,  $^1\text{O}_2(^1\Delta_g)$ . The amount of  $\text{O}_2$  consumed in the dark or under irradiation is related to formation of disulfide [3,7,9,23,27]:

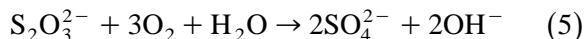


The oxidation of  $\text{Na}_2\text{S}_2\text{O}_3$  is not catalyzed by cobalt phthalocyanine complexes (Table 1) [6].

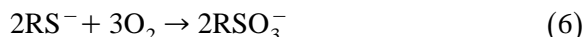
Zinc phthalocyanine complexes (Table 1) show no catalytic activity for oxidation of MEA and  $\text{Na}_2\text{S}_2\text{O}_3$  in the dark since they are not able to coordinate and activate molecular dioxygen [6–9]. They demonstrate high catalytic activity only on irradiation with visible light. These complexes (Sens) manifest long lifetimes of the excited triplet electron state ( $\tau_{\text{ZnPc}}^T \approx 245 \mu\text{s}$ ) [10]. By means of energy transfer, these complexes are able to convert triplet dioxygen,  $^3\text{O}_2(^3\Sigma_g^-)$ , into more reactive singlet dioxygen,  $^1\text{O}_2(^1\Delta_g)$ , according to the following schemes:



The rate of photocatalytic oxidation of the thiosulfate ion can be determined from the dioxygen consumption according to the stoichiometry of the following equation:



The kinetics of photocatalytic complete oxidation of MEA is somewhat more complex because the process is accomplished by a series of parallel reactions [6,7]. In alkali aqueous solution MEA is photooxidized completely to sulfonic acid according to the following general equation:



The growth of the rate of photocatalytic oxidation of MEA or  $\text{Na}_2\text{S}_2\text{O}_3$  in the presence of additives like TBAC, quinoline and ethanol (Table 1) is due to the monomerization of the

complexes and the increase of the quantum yield of  $^1\text{O}_2^*$  generation (Eqs. (3) and (4)) [6,7,9,21]. Thus, upon irradiation with visible light the quantum yield of  $^1\text{O}_2^*$ , formed from the monomeric  $\text{ZnPc}(\text{COOH})_4$  species was 0.7 whereas that from the dimeric species was 0.1 [21]. The effect of additives on the photocatalytic activity is mostly manifested with  $\text{ZnPc}(\text{SO}_3\text{H})_4$  and  $\text{ZnPc}(\text{COOH})_4$  for the high aggregation degree of these complexes in aqueous medium (Table 1, Nos. 6–9).

On increasing medium viscosity, the rates of MEA and  $\text{Na}_2\text{S}_2\text{O}_3$  photooxidation catalyzed by  $\text{ZnPc}(\text{SO}_3\text{H})_4$  or  $\text{ZnPc}(\text{COOH})_4$  are diminished (Table 1, Nos. 10–17) due to increased amounts of dimer phthalocyanine complexes. Fig. 5 presents a change of  $\text{ZnPc}(\text{COOH})_4$  activity on MEA photooxidation as a function of medium viscosity and monomer complex concentration. The amounts of ethylene glycol and glycerol in the mixed solvents (Fig. 5) did not exceed 3 wt.%. For this reason their macrodielectric constants were very close to that of water but their viscosities changed. Changes of the catalytic activity of  $\text{ZnPc}(\text{COOH})_4$  in these solvents are determined mainly by the influence of the medium viscosity on the aggregation of the complexes. By contrast with  $\text{ZnPc}(\text{SO}_3\text{H})_4$

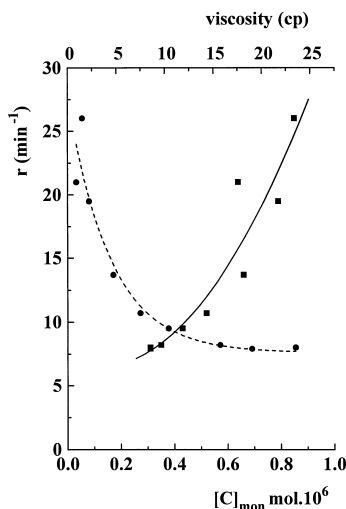


Fig. 5. Influence of the medium viscosity (---) and the monomer concentration (—) of  $\text{ZnPc}(\text{COOH})_4$  on the rates of photocatalytic oxidation of MEA (Nos. 4, 11–18, Table 1).

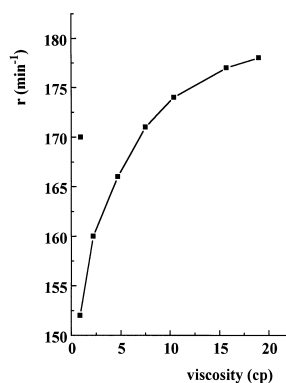


Fig. 6. Influence of the medium viscosity on the rates of photooxidation of MEA, catalyzed by  $\text{ZnPc}(\text{QnSO}_3\text{H})_4$  (Nos. 5, 10, 20–25, Table 1).

and  $\text{ZnPc}(\text{COOH})_4$ , on increasing the viscosity of the medium the rate of  $\text{ZnPc}(\text{QnSO}_3\text{H})_4$  photocatalyzed oxidation of MEA is enhanced (Fig. 6) and that of  $\text{Na}_2\text{S}_2\text{O}_3$  is lowered (Table 1, Nos. 20–25). Since the reactions of  $^1\text{O}_2(^1\Delta_g)$  are not diffusion-controlled processes [14], the different oxidation rates with the two substrates are, most likely, due to the ability of the mercaptide ion to axially coordinate itself to the central metal atom in the phthalocyanine molecules [5,31]. As the inorganic thiosulfate anion is a harder base in comparison with the mercaptide anion [32], the adduct formation of the former with the phthalocyanine complex is weakly expressed. On increasing the viscosity of the medium, the equilibrium constant of adduct formation and the local concentration of the mercaptide ion around the investigated photocatalysts are increased, thus the probability of interaction between  $^1\text{O}_2^*$  and the substrate in the solvent cage being increased. Quenching of the excited triplet state of the mercaptide ion can be neglected because it is about 10–15 times weaker than that caused by oxygen [7].

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