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Metallophthalocyanine catalysed electroreduction of nitrate and nitrite ions in alkaline media

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The electrochemical reduction of nitrite and nitrate in alkaline solution has been studied on glassy carbon electrodes modified with phthalocyanine complexes of Mn, Fe, Co, Ni, Cu and Zn (MnPc, FePc, CoPc, NiPc, CuPc and ZnPc, respectively, and Pc(-2) is phthalocyanine dianion). Voltammetry shows that the reduction of nitrite occurs at potentials slightly less negative than for nitrate reduction. The MPc complexes lower the overpotential for the reduction of nitrite and nitrate as follows: CuPc > FePc > NiPc > CoPc > MnPc > ZnPc > glassy carbon electrode. The main product for the reduction of nitrite and nitrate is ammonia, with high yields of ammonia being obtained, depending on the choices of the electrolysis potential and MPc complex.

1. Introduction

The contamination of water by nitrate ions is an increasing environmental concern due to the extensive use of nitrates in detergents and fertilizers. There is currently an interest in the development of techniques for the reduction of nitrates and nitrites and for the sensitive and selective analysis of these species [1–8]. Efficient reduction of nitrates and nitrites to harmless products would be useful in the treatment of radioactive solutions which contain high concentrations of these species, and would allow the recycling of basic electrolysis solutions used in neutralizing nitric acid containing waste. The mechanism for the chemical and electrochemical reduction of nitrates and nitrites is very complex. The reduction potential and the nature of the products of reduction of these species strongly depend on experimental conditions such as pH, coexisting ions and the choice of the electrode material. Also, the quality of the current–potential curves is highly dependent on the electrode surface.

The products of the reduction of nitrate and nitrite in alkaline media include industrially useful chemicals such as ammonia, nitrogen gas and hydroxide ions, Equations 1 to 6 (with E° values obtained from [9] and corrected to the Ag/AgCl reference).

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad -0.19V \tag{1}$$

$$NO_3^- + 3H_2O + 5e^- \rightarrow 1/2N_2 + 6OH^- \quad 0.06V \tag{2}$$

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^- \quad -0.32V \tag{3}$$

$$NO_2^- + 2H_2O + 3e^- \rightarrow 1/2N_2 + 4OH^- \quad 0.23V \tag{4}$$

$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^- \quad -0.36V \tag{5}$$

$$NO_2^- + 4H_2O + 4e^- \rightarrow NH_2OH + 5OH^- \quad -0.65V \tag{6}$$

However, research into the reduction of nitrates in alkaline media has received less attention compared to studies in acid media. With a proper choice of electrode material and applied reduction potential, good selectivity of the various products may be obtained. For example, Cattarin [1] has shown that nitrite is the main product of reduction of nitrate in basic media at a Ag cathode. Whereas reduction at a Ni cathode gave nitrogen gas [1, 10], the use of Cu and Zn cathodes gave mainly ammonia [1].

Reductions of both nitrite and nitrate in acid media occurs at more positive potentials [9], hence are more favourable, than reductions in basic media. It is thus important to lower the overvoltage required for the reduction of nitrate and nitrite in basic media. One way of achieving this is by modifying the surfaces of conventional electrodes with catalytic materials. Metallopthalocyanine (MPc, Pc(–2) = phthalocyanine dianion) complexes are well known inexpensive catalysts for many reactions [3]. Electrodes modified with MPc complexes have been used successfully in lowering the overpotential for the oxidation or reduction of a variety of electroactive species [3, 11–21]. Reduction of nitrate ions in basic media and on iron phthalocyanine (Fe(II)Pc) modified Ni or Fe electrodes has been reported [4]. Coating of Ni electrodes with FePc rendered it less active towards nitrate reduction, while the activity of the Fe electrode was unchanged by coating with FePc [4]. However, corrosion of the Fe cathode was greatly diminished when coated with FePc. No mechanism has been provided for the reduction of nitrate on MPc modified electrodes. To our knowledge, there have been no reports on the reduction of nitrite on

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MPc modified electrodes. Nitrite is known to coordinate to the central metal in some metal porphyrins [6, 8] and to be readily reduced to mainly ammonia and hydroxylamine in acidic and basic media [8]. Cobalt phthalocyanine (CoPc) complexes have been used in the selective determination of nitrite ion and there is some evidence for the coordination of the nitrite ion to the central metal in CoPc derivatives during the analysis [19]. In this work we compare the catalytic efficiencies of the phthalocyanine complexes: Fe(ɪɪ)Pc, Co(ɪɪ)Pc, Ni(ɪɪ)Pc, Cu(ɪɪ)Pc, MnPc, and ZnPc for the reduction of nitrate and nitrite ions. We study the correlation between the nature of the central metal ion in MPc and the efficiency of nitrite and nitrate reduction on MPc modified carbon electrodes.

2. Experimental details

2.1. *Materials*

Metallophthalocyanine complexes, Fe(ɪɪ)Pc, Co(ɪɪ)Pc, Ni(ɪɪ)Pc, Cu(ɪɪ)Pc, ZnPc, and MnPc were purchased from Eastman or Kodak and used without further purification. Tetrasulfonated phthalocyanine complexes of Fe(ɪɪ) and Cu(ɪɪ) ($[FeTSPc]^{4-}$ and $[CuTSPc]^{4-}$, respectively) were synthesized and purified according to published procedures [22]. Triply distilled water was used for all electrochemical experiments. Certified A.C.S grade KOH, KNO_3 and KNO_2 were used for preparing solutions. For pH studies, phosphate and phthalate buffers were employed.

2.2. *Methods*

Cyclic voltammetry was carried out in a three-electrode, two-compartment cell. Silver/silver chloride (saturated KCl) and platinum wire were used as reference and counter electrodes, respectively. The working electrode was the MPc-modified glassy carbon electrode (MPc–GCE). The adsorbed M(ɪɪ)Pc films were prepared by a drop dry method in which a drop of a saturated ($\sim 1 \times 10^{-3}$ mol dm^{-3}) solution of MPc in pyridine were placed on the glassy carbon electrode ($A = 0.07$ cm^2) and dried in air. Prior to coating with MPc complexes, the glassy carbon electrode was polished with alumina on a Buehler felt pad, followed by soaking in dilute nitric acid and rinsing in water. For some experiments an unmodified Cu electrode of 0.07 cm^2 area was employed as a working electrode.

Controlled potential coulometry experiments were also performed in a two compartment cell, a platinum plate of area 2.2 cm^2 was employed as a counter electrode and a Ag/AgCl (saturated KCl) as a reference. The working electrode consisted of a carbon rod ($A = 0.2$ cm^2) coated with the MPc complexes by the drop dry method. Electrical contact with the working electrode was established via a copper wire. The variations in the nitrite concentrations were assessed by measuring the absorbance at 354 nm, using the Cary 1E u.v. / vis. spectrophotometer. An alternative analysis of the nitrite ion was performed by treatment with sulfanilic acid to form the diazonium salt, followed by coupling to *N*-(1-naphthyl)-ethylenediamine dihydroxide and the monitoring of the absorption spectra at 550 nm. Ammonia yields were determined by the Nessler method [23] and monitoring the absorbance 400 nm. Hydroxylamine was determined qualitatively using the Nessler reagent. Voltammetry and constant potential electrolysis were performed with the Bio-Analytical Systems (BAS) CV 27 voltammograph, connected to the HP 7047A X–Y recorder.

3. Results and discussion

The catalytic effects of adsorbed MPc complexes are strongly dependent on the electrode material. For example, Co(ɪɪ)Pc and Fe(ɪɪ)Pc films adsorbed on carbon electrodes showed catalytic activity for oxygen reduction, but both complexes impeded the catalytic effect of platinum electrodes [24]. MPc adsorbed on carbon electrodes show catalytic activity for a number of reactions including the oxidation of sulfhydryl compounds [12]. We thus chose carbon electrodes for the modification with MPc complexes and the study of the reduction of nitrites and nitrates.

3.1. *Cyclic voltammetry*

Nitrite is known to disproportionate to form nitric oxide and nitrate [6]. In strongly basic media, the nitric oxide contribution is negligible [6] and its reduction at the MPc–GCE may be ignored. The cyclic voltammogram of NO_2^- on CuPc–GCE in the presence of 0.1 mol dm^{-3} KOH shows a sharp peak at −1.35 V vs Ag/AgCl and a broader peak near −1.5 V, Fig. 1(a), on the second and subsequent scans. A much weaker peak was observed at −0.6 V. The −1.35 V and −1.5 V peaks represent a shift, to more positive potentials, of the peaks observed, respectively, at −1.45 and −1.7 V during the first scan, Fig. 2. The peak observed at −0.6 V represent a shift to a more negative potential after the first scan. These shifts imply a change of the electrode surface. Similar reduction peaks have been observed for the reduction of nitrates and nitrites on copper electrodes [1]. The smaller reduction peak observed near −0.6 V was attributed to the involvement of copper oxides in the reduction process [1]. On FePc–GCE, only one peak due to the reduction of nitrite was observed at −1.6 V, Fig. 1(b). Both NiPc–GCE and CoPc–GCE, Fig. 1(c) and Fig. 1(d), respectively, showed an onset of the reduction of NO_2^- at potentials more negative than those observed for FePc and CuPc. However, no peaks for nitrite reduction were observed on CoPc–GCE and NiPc–GCE. The observation of peaks for the reduction of nitrite on FePc–GCE and CuPc–GCE is a consequence of the lowering of the potential for the reduction of NO_2^- by FePc and CuPc. The onset for the reduction of nitrite on unmodified glassy carbon electrode, Fig. 1(e), was observed at potentials

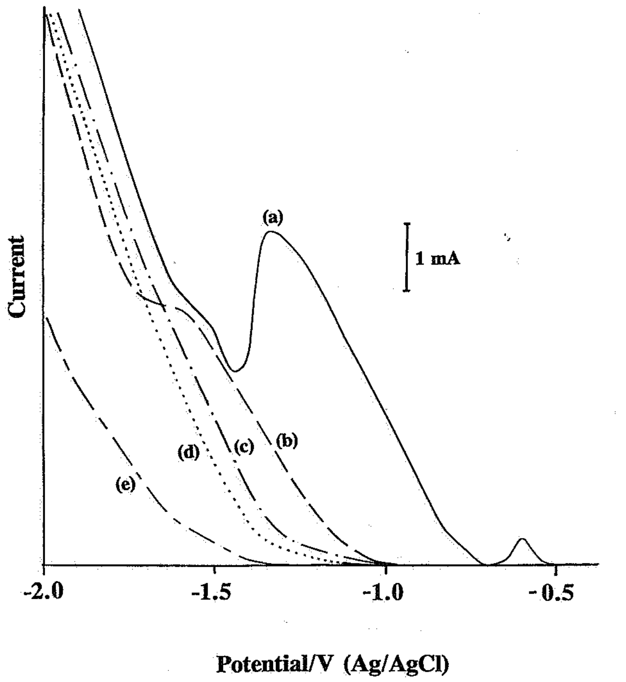

Fig. 1. Cyclic voltammograms (second scans) for the reduction of 0.1 mol dm^{-3} NO_2^- on (a) — CuPc, (b) – – – FePc, (c) –·–·– NiPc, (d) ······ CoPc modified glassy carbon electrode, and on (e) – - – unmodified glassy carbon electrode. Electrolyte: 0.1 mol dm^{-3} KOH. Scan rate: 20 mV s^{-1}.

more negative than observed on FePc, CuPc, CoPc and NiPc. The cyclic voltammograms for the reduction of nitrite on MnPc–GCE and ZnPc–GCE gave reduction potentials that were more positive than observed for the reduction of this species on the unmodified glassy carbon electrode, but more negative than for the other MPc–GCE.

The voltammograms for the reduction of NO_3^- on CuPc–GCE, Fig. 3, are similar to those observed above for the reduction of NO_2^-, in that three peaks are observed. On the first scan only one peak is observed near –1.6 V, Fig. 3(a). On second and subsequent scan, this peak shifts to –1.35 V, and two other peaks are observed at –0.5 V and –1.55 V, Fig. 3(b). This observation confirms reports on the reduction of nitrate and nitrite on unmodified Cu metal electrodes, where the voltammograms for the reduction of these species showed similar patterns [1]. No peaks were observed for the reduction of NO_3^- on FePc–GCE, contrary to the observation for NO_2^- reduction, Fig. 1(b). As observed for NO_2^-, the onset of the reduction of NO_3^- on NiPc, FePc, MnPc, ZnPc and CoPc modified glassy carbon electrodes occurred at potentials more negative than observed for CuPc–CGE, Fig. 3.

Thus, the potentials for the reduction of NO_2^- or NO_3^- in basic media and on MPc–GCE shift to positive potentials depending on MPc complexes as follows:

CuPc > FePc > NiPc > CoPc > MnPc >
ZnPc > glassy carbon electrode

CuPc lowers the overpotential for the reduction of NO_2^- and NO_3^- to a larger extent compared to the other MPc complexes. It is important to note that the catalytic currents for the reduction of NO_2^- and NO_3^- increased significantly for each following scan, Fig. 2, thus indicating the formation of a new, more catalytic, surface on the electrode. The peak current, as well as the current at the linear section of the cathodic curve, increased linearly with the increase in con-

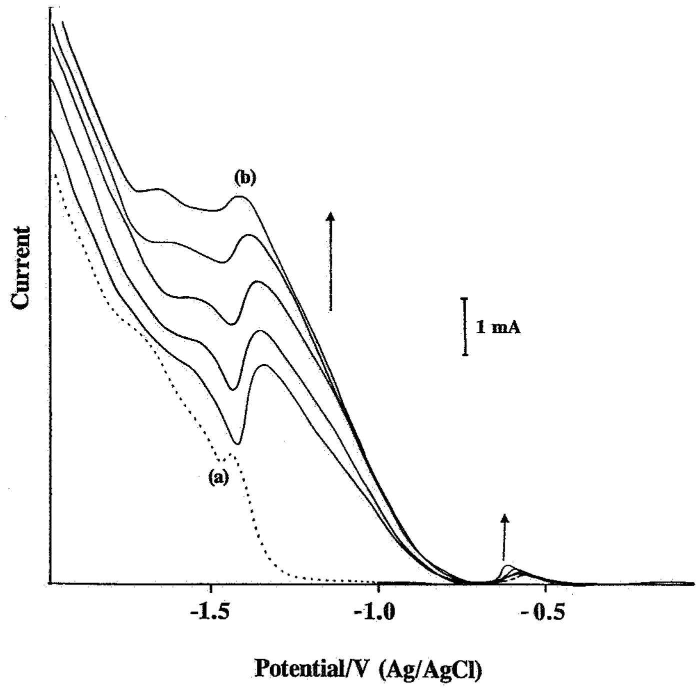

Fig. 2. Cyclic voltammograms for the reduction of 0.1 mol dm^{-3} NO_2^- on CuPc modified glassy carbon electrode. (a) First scan (dotted line) and (b) subsequent scans (undotted lines; showing an increase in current with increase in scan number). Electrolyte: 0.1 mol dm^{-3} KOH. Scan rate: 20 mV s^{-1}

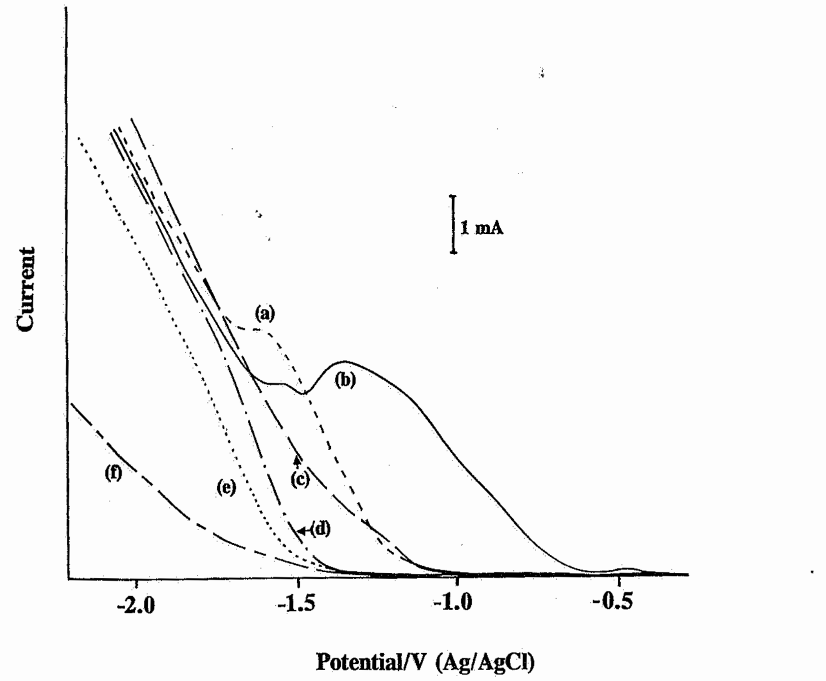

Fig. 3. Cyclic voltammograms for the reduction of 0.05 mol dm^{-3} NO_3^- on (a) - - - - CuPc, (b) —— CuPc, (c) – – – FePc, (d) –·–·– NiPc, (e) ······ CoPc and (f) – – – unmodified glassy carbon electrode. Electrolyte: 0.10 mol dm^{-3} KOH. Scan rate: 20 mV s^{-1}. (a) First scan and (b) second scan for the reduction of NO_3^- on CuPc–GCE.

centration of NO_2^- or NO_3^-, Fig. 4, confirming that these species are indeed reducible on MPc–GCEs. Fig. 4 also shows that the relative catalytic activities of CuPc and FePc complexes depend on the concentration of NO_2^- and NO_3^- with FePc showing higher catalytic currents than CuPc at low concentrations of NO_2^- or NO_3^-. The slopes of the plots in Fig. 4 are a measure of the relative catalytic efficiencies of the MPc complexes for the reduction of nitrates and nitrites. CuPc modified glassy carbon electrodes show the highest catalytic activity when compared to the other MPc–GCE, implying that the rate constant [25] for the electrochemical reaction is larger for the CuPc–GCE surface.

Figure 4 shows a very small increase in current with increase in concentration for the reduction of nitrite or nitrate on unmodified GCE when compared to currents observed on MPc modified GCE. The peak currents for the reduction of NO_2^- or NO_3^- increased with increase in scan rate, v, but were not linear with $v^{1/2}$, suggesting the presence of catalytic phenomena, as confirmed by current-time curves below.

Differences between the reduction potentials of NO_2^- or NO_3^- on unmodified glassy carbon electrode and on MPc–GCE (ΔE) varied with pH as shown in Fig. 5. The value of ΔE represents the extent to which the overpotential of the reduction of these species on unmodified glassy carbon is lowered by modification with MPc complexes. Figure, 5(a) shows that ΔE for the reduction of NO_2^- is generally higher in basic media. At low pH, a significant concentration of NO is present in solution from the disproportionation of nitrite, thus NO may contribute to the observed voltammetric behaviour of NO_2^- at low pH. For both

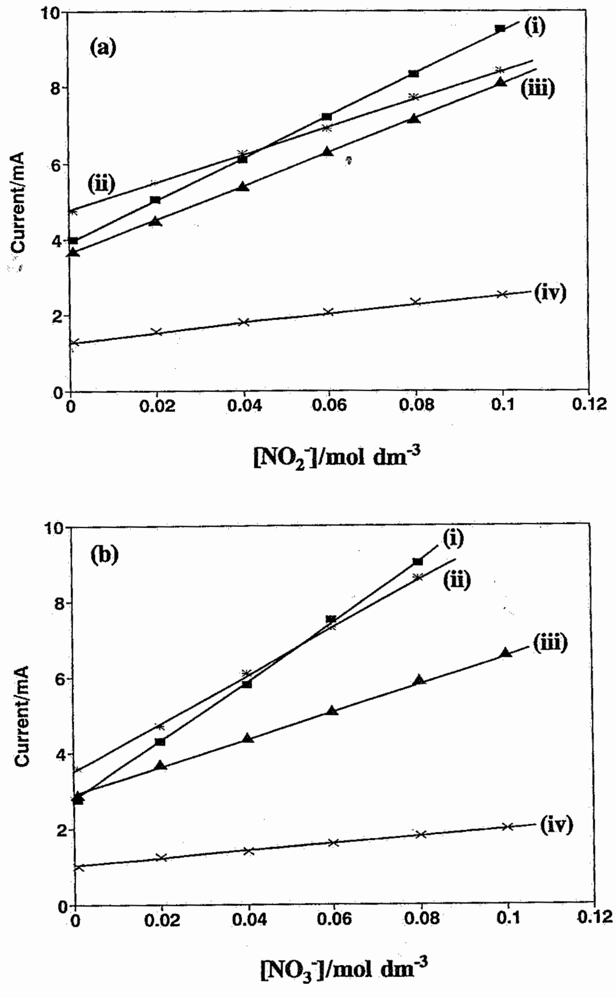

Fig. 4. Variation of the cathodic currents with (a) NO_2^- and (b) NO_3^- concentration. Reduction on (i) CuPc–GCE, (ii) FePc–GCE, (iii) CoPc–GCE and (iv) unmodified glassy carbon electrode. Scan rate: 20 mV s^{-1}. Electrolyte 0.1 mol dm^{-3} KOH. Cathode potentials: −2.0 V.

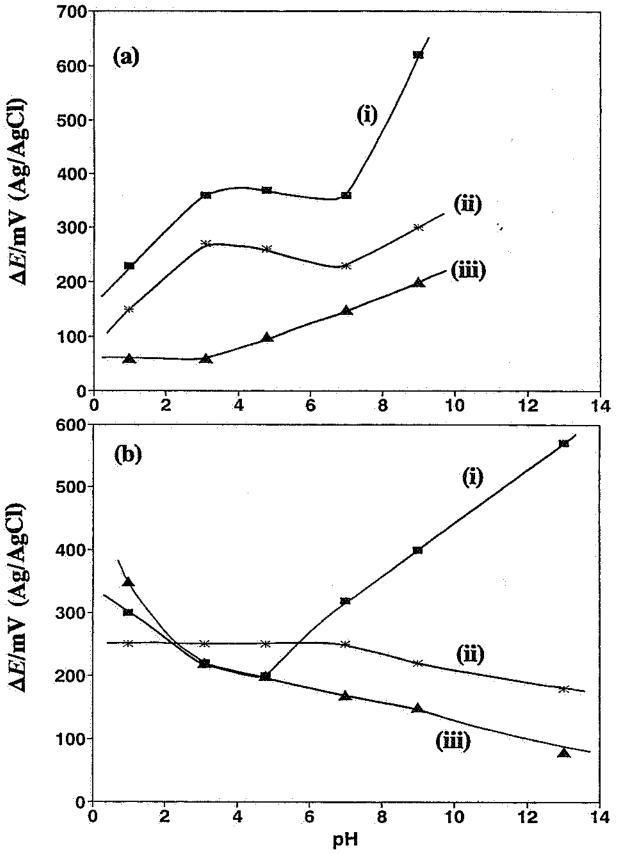

Fig. 5. The plot of pH against ΔE (V vs Ag/AgCl) for the reduction of (a) 0.1 mol dm^{-3} NO_2^- and (b) 0.1 mol dm^{-3} NO_3^- on (i) CuPc–GCE, (ii) FePc–GCE and (iii) CoPc–GCE. Current density, $j = 10$ mA cm^{-2}.

NO_2^- and NO_3^-, the largest increase in ΔE with pH was observed for the reduction of these species on CuPc–GCE. ΔE for the reduction of NO_3^- on the other MPc–GCE decreased slightly with increase in pH, Fig. 5(b). This is not surprising since the reduction of nitrates and nitrites is more favoured in acid media, as discussed in the introduction. Increasing the concentration on the MPc complex deposited onto the electrode resulted in an increase in the reduction currents for fixed concentrations of NO_2^- or NO_3^-.

The MPc catalysed reduction of oxygen is one of the few well studied catalytic reactions of MPc complexes. It has been suggested [3] that the metal ion of the MPc complex is electrochemically oxidized during the catalytic process, thereby reducing the oxygen molecule. Thus, MPc complexes such as FePc, CoPc and MnPc, which showed redox activity at the central metal exhibited higher catalytic activity than MPc complexes with ring based redox processes such as CuPc, ZnPc and NiPc [3]. Our results show CuPc to be more efficient than FePc, CoPc, NiPc, ZnPc and MnPc. CuPc does not show metal based redox activity in solution; as such the mechanism for the reduction of nitrates and nitrites on MPc modified electrodes is likely to be different from the mechanism suggested for oxygen reduction. However, it is important to note that solution electrochemistry of CuPc complexes may differ from that of adsorbed species.

MPc complexes that can bind both the reactant and the product reversibly are expected to show a high catalytic activity for the formation of the relevant products [26]. Nitrite ions have been shown to bind weakly to ring substituted CoPc complexes [19], and not to ring substituted CuPc complexes, the former shows selectivity towards nitrite ion detection [19]. The low catalytic activities of MnPc and ZnPc for the reduction of nitrite or nitrate as compared to CuPc, CoPc, FePc and NiPc implies that the products (mainly NH_3, as will be shown below) and the reactants (NO_2^- or NO_3^-) bind reversibly to CuPc and FePc and to a lesser extent, CoPc and NiPc. It is thus likely that axial binding of the reactants and/or products to either MnPc or ZnPc is not favourable. Unsubstituted MPc complexes employed for the catalysis reactions are insoluble in water; we were thus unable to confirm, using spectroscopic methods, the possible binding of NO_2^- or NO_3^- to the unsubstituted MPc complexes. Addition of nitrite or nitrate to water soluble of $[CuTSPc]^{4-}$ (TSPc(−2) = tetrasulfonated phthalocyanine dianion) complex resulted in the shift in electronic absorption spectra as shown in Fig. 6. This shift indicates that some coordination of the nitrate and nitrite to the $[CuTSPc]^{4-}$ complexes occurs. It is thus also likely that both nitrite and nitrate coordinate to unsubstituted CuPc. No significant spectral changes were observed on addition of nitrate or nitrite to solutions of $[FeTSPc]^{4-}$ in water. For many reactions, Co(II)Pc and FePc species show higher catalytic activity than Cu(II)Pc [3]. As discussed above, the central metal ion plays an important role in the catalytic activities of MPc complexes. Copper cathodes are known to be relatively efficient catalysts for the reduction of nitrates [9]. Also, we observed lower overpotentials for nitrate reduction on copper electrodes than on iron or nickel electrodes. This observation may explain the higher catalytic activity of Cu(II)Pc.

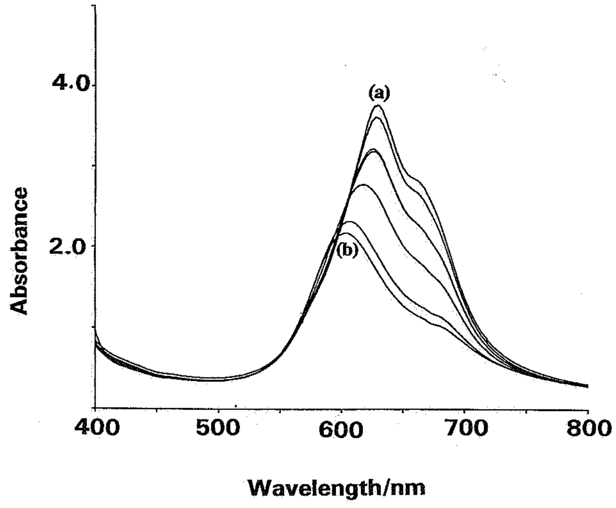

Fig. 6. Electronic absorption spectral changes observed on gradual addition of NO_2^- to solution of $[CuTSPc]^{4-}$ in water. (a) Before and (b) after the final addition of NO_2^-.

3.2. *Constant potential electrolysis*

The results of the constant potential electrolysis of nitrate and nitrite on MPc–CGE and other electrodes are shown in Table 1. The products of the reduction of nitrite and nitrate depend on factors that include (i) the type of electrode and electrode treatment, (ii) pH, (iii) applied potential and (iv) coexisting ions. The main product of the reduction of NO_3^- on FePc modified Fe electrodes was ammonia [4]. As Table 1 shows, the main product of the reduction of NO_3^- and NO_2^- on glassy carbon electrodes modified with MPc complexes is also ammonia. No NO_2^- was detected following the electrolysis of NO_3^-. This observation is contrary to the observed reduction of NO_3^- on Ag, Fe, Cu and Zn electrodes [1, 4], where significant amounts of NO_2^- were formed. It is important to note that the formation of NO_2^- from the reduction of NO_3^- was found [1, 4] to be strongly dependent on the electrolysis potential, Table 1. For example, reduction of NO_3^- on Cu at –1.1 V gave mainly NO_2^-, whereas reduction at –1.4 V gave mainly ammonia, Table 1. It is possible that the amount of NO_2^- formed under our experimental conditions is too low for detection using methods explained in the experimental section. There was some gas liberated during the electrolysis of NO_3^- and NO_2^-. One of the main products of the electrolysis of NO_3^- and NO_2^- on Ni, Pt and platinized Ni electrodes is nitrogen gas [26]. It is thus likely that the gas liberated during the electrolysis of NO_3^- and NO_2^- under the present experimental conditions is nitrogen and at high negative potentials a mixture of H_2 and N_2 may be obtained. Hydroxylamine has been reported as one of the products of the reduction of nitrite [7], especially at more positive potentials. This species was detected following the electrolysis of NO_2^- on MPc–GCE. No hydroxylamine was detected following the electrolysis of NO_3^- on MPc–GCE. The reduction of NO_3^- on MPc–GCE may thus be assumed to occur according to Equations 2 and 3, whereas the reduction of NO_2^- may occur according to Equations 4 and 6. It is interesting to note that hydroxylamine was not detected on electrolysis of NO_2^- or NO_3^- on Cu or Ag electrodes and in basic media [1].

The amount of ammonia produced during the electrolysis of NO_3^- varied with applied potential as shown in Fig. 7. Ammonia production decreased as the potential became more negative than –1.7 V, due to the contribution of the hydrogen evolution reaction. Generally, CuPc–GCE showed the highest activity for the production of NH_3, but at potentials less negative than –1.8 V, the ammonia production on FePc became higher than that of all the other MPc–GCE. The unmodified glassy carbon electrode showed lower yields for ammonia production than observed for the MPc–GCE, at potentials more negative than –1.6 V, but the ammonia yields for NO_3^- reduction on the unmodified GCE increased considerably at more positive potentials.

The current–time curves for the electrolysis (at –1.3 V) of NO_3^- and NO_2^- on CuPc–GCE, Fig. 8, showed that the process proceeds in at least two stages for these species. A gradual increase in current

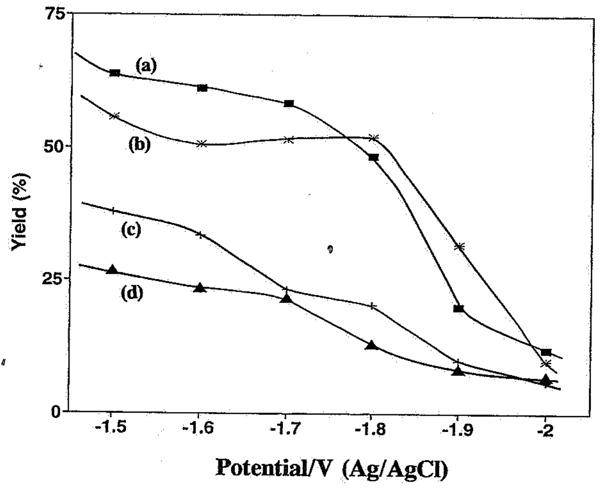

Fig. 7. Variation of the per cent yield of ammonia with electrolysis potential for the reduction of NO_3^- on (a) CuPc–GCE, (b) FePc–GCE, (c) NiPc–GCE and (d) CoPc–GCE. Electrolyte: 0.1 mol dm^{-3} KOH.

Table 1. Results of the controlled potential electrolysis of NO_3^- and NO_2^-

*Electrode**	*Starting species*	*Electrolyte* /mol dm^{-3}	η /%$^+$ NO_2^-	η /%$^+$ NH_3	E_{app}, / V (Ag/AgCl)‡	*Reference*
CuPc–GCE	NO_3^-	0.1 (KOH)	–	64	–1.5	this work
CoPc–GCE	NO_3^-	0.1 (KOH)	–	80	–1.4	this work
FePc–GCE	NO_3^-	0.1 (KOH)	–	55	–1.5	this work
NiPc–GCE	NO_3^-	0.1 (KOH)	–	85	–1.3	this work
CuPc–GCE	NO_2^-	0.1 (KOH)	–	78	–1.5	this work
GCE	NO_3^-	0.1 (KOH)	–	99	–1.5	this work
Cu	NO_3^-	1 (NaOH)	90–95	4–7	–1.1	1
Cu	NO_3	1 (NaOH)	4–8	80–88	–1.4	1
Zn	NO_3^-	3 (NaOH)		93	–1.5	4
Fe–FePc	NO_3^-	3 (NaOH)		71	–1.5	4
Ag	NO_3^-	1 (NaOH)	90–94	1–3	–1.4	1

* GCE: glassy carbon electrode.

$^+$ η, current efficiency: charge used to generate product over total charge.

‡ E_{app}, applied potential which gave the maximum per cent yield of ammonia for the particular electrode.

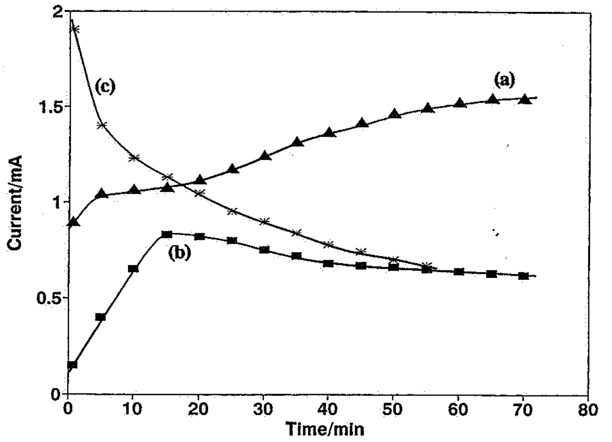

Fig. 8. The variation of the peak current versus time (min) for the reduction at −1.3 V vs Ag/AgCl of (a) NO_2^- and (b) NO_3^- on CuPc–GCE; (c) shows the reduction of NO_3^- on an unmodified Cu electrode. Electrolyte: 0.1 mol dm^{-3} KOH.

with time was observed for nitrite reduction, with a plateau being reached after 60 min of electrolysis, Fig. 8(a). The electrode activity remained high even after 8 h of electrolysis. For the reduction of NO_3^-, the electrolysis current showed an increase during the first 15 min before decreasing, Fig. 8(b), as has been observed for the reduction of this species on Pb electrodes [4]. The shape of the current-time curves reflects the autocatalytic nature of the reduction of NO_2^- and NO_3^- on MPc modified glassy carbon electrodes. Fig. 8(c) shows that the reduction NO_3^- on an uncoated Cu electrode followed the expected exponential behaviour.

4. Conclusion

Nitrite or nitrate ions are electrochemically reduced on MPc modified glassy carbon electrodes to mainly ammonia and, probably, nitrogen gas. Hydroxylamine was obtained on reduction of NO_2^-. Also the reduction of NO_3^- did not give nitrite ions. MPc–GCE are more selective towards the production of ammonia under appropriate electrolysis conditions. Even though the efficiencies for the reduction of NO_2^- or NO_3^- on MPc–GCE are not superior to the reduction of these species on unmodified metal electrodes, the MPc–GCE do not suffer the corrosion effects that affect metallic electrodes. The present work shows an improvement on the catalytic behaviour of glassy carbon electrode, for the reduction of NO_3^- to NH_3, on modification with FePc, CuPc, CoPc and NiPc complexes. We have shown that the catalytic activity of CuPc–GCE for the reduction of NO_2^- or NO_3^- is much higher in basic than in acid media, this is a very useful observation that may be of use for the treatment of nitrate and nitrite in alkaline waste.

Acknowledgements

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