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Electrochemical Investigation on Porphyrazines with Peripheral Crown-Ether Groups

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Summary. In this study, the electrochemical properties of novel porphyrazines with eight crown ether substituents appending on the periphery through flexible chains were investigated by using cyclic voltammetry and controlled potential coulometry. Cyclic voltammetry measurements showed that the metal free porphyrazine gave all of the six possible redox reactions of common porphyrazine derivatives. Cobalt porphyrazine exhibited a metal-based reduction and a metal-based oxidation processes followed by two ligand-based reduction and two oxidation processes. I_p *vs.* $v^{1/2}$ plots of redox processes of the two compounds indicated the diffusional mass transfer mechanism of the complexes. Copper porphyrazine gave an oxidation process having adsorption properties and three reduction reactions. The variations of peak current ratios of electrochemical reactions for all three complexes with scan rate showed that electron transfer processes of complexes were followed by reversible or irreversible chemical reactions. Aggregation and sandwich adduct formation properties of complexes were determined by CV measurements. Peak potentials of redox processes for all complexes were shifted towards positive potentials by addition of alkali metal cations. Addition of K^+ formed sandwich type adducts with 15-crown-macrocycles diminishing aggregation of planar molecules by intramolecular rather than intermolecular complexation.

Keywords. Electrochemistry; Cobalt; Copper; Porphyrazines; Crown ether.

Introduction

Intensive research interest in peripherally functionalized porpyrazines during the last decade has shown that these tetrapyrrol derivatives could be considered as alternatives to the phthalocyanines that have found extensive applications in many fields [1–5]. Despite the structural similarities, porphyrazines have been less studied compared to the phthalocyanines. Peripherally-functionalised porphyrazines have the potential to exhibit novel optical, magnetic, and electronic properties; also

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the presence of S donor atoms play an important role in affecting the solid state interactions [6–10]. The physical and chemical properties of the porphyrazines can be enhanced by the addition of macrocyclic substituents on the periphery suitable to interact with alkali ions. The transition metal ion in the inner core, on the other hand, offers new ways to induce, modify, and control molecular properties [11].

In our previous paper [11] we reported novel porphyrazines with eight crown ether substituents appending on the periphery through flexible chains. Easy interaction of the crown ether groups with alkali cations had been used to evaluate the direction of the crown ether units with respect to the porphyrazine inner core.

Although the electrochemical properties of phthalocyanines and porphyrins have been extensively studied, especially by *Lever* [12–14] and *Kadish*'s group [15–19], there has been limited interest in porphyrazines up to recent years. There are a few detailed electrochemical studies on the porphyrazine derivatives using cyclic voltammetry (CV) and controlled potential coulometry (CPC) [20, 21].

In this paper we present the first detailed electrochemical properties of the porphyrazines with peripheral crown-ether groups (Fig. 1), the synthesis of which have been reported earlier [11]. The redox properties of these compounds are essential for their implementations in many technological areas such as electrophotography, photovoltaic cells, fuel cells, and electrochromic displays [22–32].

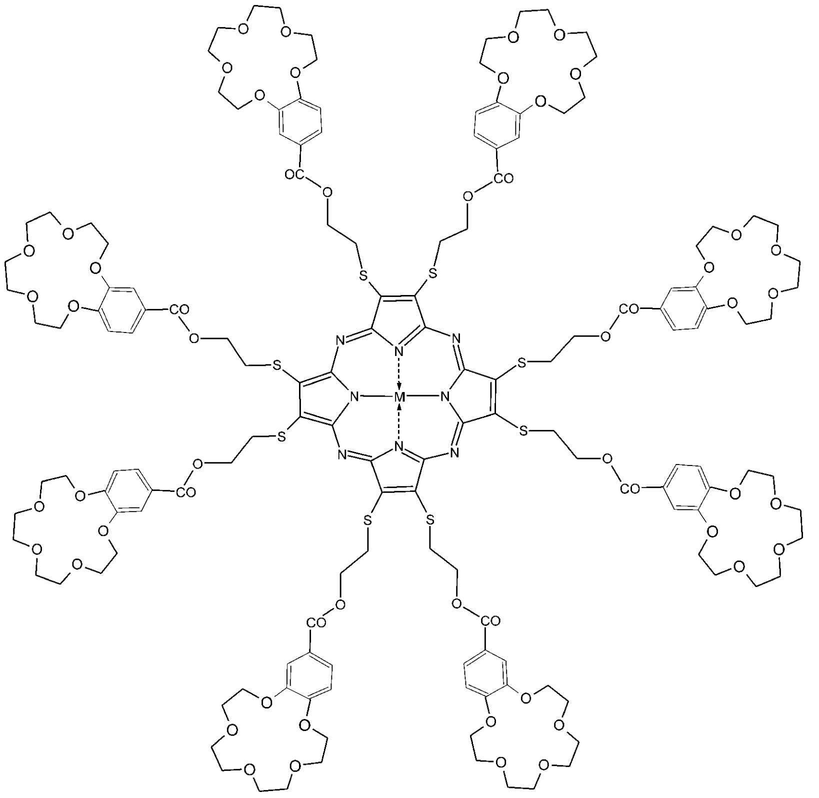

Fig. 1. Structures of compounds: octakis crown ether porphyrazine (**1**, M = 2H), octakis crown ether cobalt porphyrazine (**2**, M = Co), and octakis crown ether copper porphyrazine (**3**, M = Cu)

Result and Discussion

The reduction and oxidation behaviors of metallophthalocyanine and metalloporphyrazine derivatives are due to the interaction between the ring and the metal center. Despite the fact that porphyrins, phthalocyanines, and porphyrazines are liable to undergo two ring oxidation and up to four ring reduction steps, all these processes have not been discussed in most studies dealing with their electrochemistry [5, 8, 9, 20, 21, 32–38]. In this study all possible redox processes of a porphyrazine were recorded with **1**. As shown in Fig. 2, **1** exhibited four reduction waves at about -0.212, -0.495 -0.911, and -1.183 V and two irreversible oxidation waves at 0.898 and 1.090 V at a scan rate of $0.10\,\mathrm{V\,s^{-1}}$ within the accessible potential range of the *DCM*/*TBAP* solvent systems. $E_p/\log v$ plots of all these redox processes are given in Fig. 3 and peak separations are given in Table 1. The variations of peak separations (ΔE) and $E_p/\log v$ values with the scan rate are used to identify the reversibility of a redox process. ΔE is not proper for the determination of the reversibility of a peak following with a chemical reaction, so the $E_p/\log v$ value is more convenient for the reversibility of a redox couple [20, 39]. The $E_p/\log v$ value of the Ic/Ia redox couple is 64 mV. ΔE of this couple is 128 mV at $0.010\,\mathrm{V\,s^{-1}}$ and increases with increasing scan rates. These data indicate that this couple is out of the reversible range. The IIc process gave the corresponding peak (IIa) during the reverse scan only at the scan rate higher than $0.10\,\mathrm{V\,s^{-1}}$ and has very high ΔE (442 mV at $0.01\,\mathrm{V\,s^{-1}}$) together with moderate level of $E_p/\log v$ (59) value, therefore it can not be considered as a totally irreversible peak. The IIIc process has a reverse couple but its ΔE (259 mV at $0.10\,\mathrm{V\,s^{-1}}$) and $E_p/\log v$ (121) values are out of reversible peak properties. The $E_p/\log v$ (56) value of the IVc shows that this process is not totally irreversible even though it has not a reverse couple. As shown in Fig. 2, the cathodic peak of the IIIc/IIIa redox couple shifts towards negative potential much more than that of the IVc; the

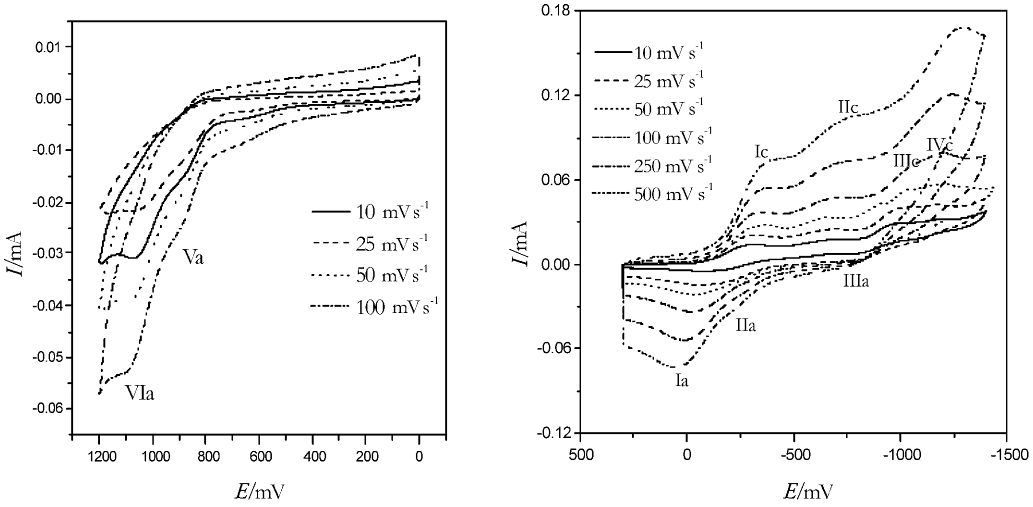

Fig. 2. Cyclic voltammogram of $5.0\cdot10^{-4}\,\mathrm{mol\,dm^{-3}}$ octakis crown ether porphyrazine (**1**) in $0.1\,\mathrm{mol\,dm^{-3}}$ *TBAP*/*DCM* *vs.* SCE

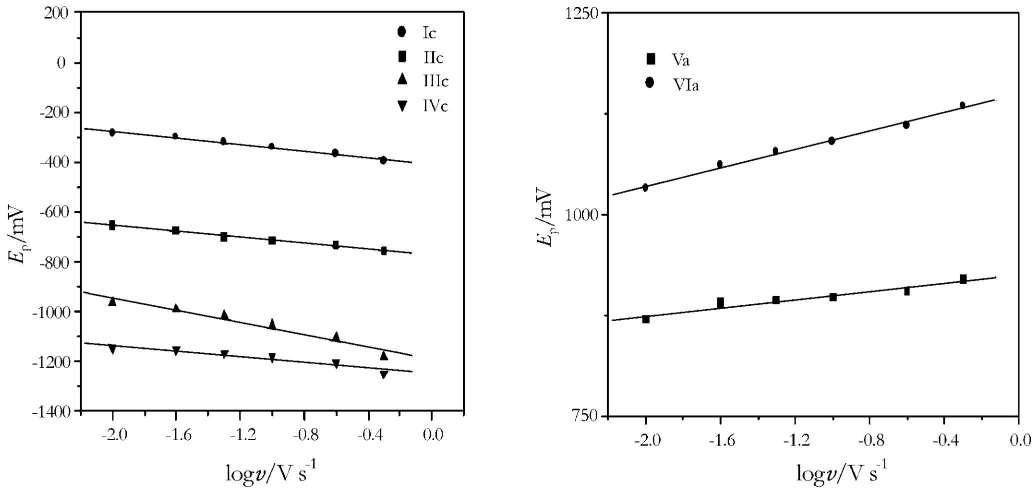

Fig. 3. Change in the cathodic peak potentials (E_{pc}) with the logarithm of scan rates ($\log v$) for octakis crown ether porphyrazine (**1**)

Table 1. Potential data of complexes **1–3**

Compounds	Redox process	E_{pc} (V)	E_{pa} (V)	$1/2(E_{pc}+E_{pa})^a$ (V)	ΔE (mV)	$\delta E_p/\delta \log v$
1	Ic/Ia	−0.328	−0.096	−0.212 (−0.712)	232	64
	IIc/IIa	−0.692	−0.297	−0.495 (−1.000)	397	59
	IIIc/IIIa	−1.024	−0.797	−0.911 (−1.416)	259	121
	IVc	−1.183	–	−1.183 (−1.688)	–	54
	Va	–	0.898	0.898 (0.393)	–	25
	VIa	–	1.090	1.090 (0.585)	–	56
2	Ic/Ia	−0.177	−0.025	−0.101 (−0.592)	152	55
	IIc/IIa	−0.451	−0.277	−0.364 (−0.855)	174	65
	IIIc/IIIa	−1.205	−0.868	−1.037 (−1.528)	337	118
	IVc/IVa	0.637	0.768	0.702 (0.211)	131	43
	Va	–	0.904	0.904 (0.413)	–	58
	VIa	–	1.148	1.148 (0.657)	–	54
3	Ic/Ia	−0.460	0.288	−0.086 (−0.581)	748	32
	IIc/IIa	−0.850	−0.065	−0.428 (−0.923)	785	146
	IIIc	−1.316	–	−1.316 (−1.811)	–	149
	IVc/IVa	0.476	0.768	0.622 (0.127)	292	113

[a] E_p for irreversible processes; potentials are given with respect to Fc/Fc^+ in parenthesis

consequence of which is the convergence of these to peaks to an intense peak at higher scan rates.

The plot of the peak current ($I_{p,c}$) as a function of the square root of the scan rate ($v^{1/2}$) for all redox processes of **1** gave straight lines (Fig. 4). However, the line for the IIIc does not intercept the *y*-axis at the origin. This may result from the existence of a chemical reaction coupling to the electron transfer process.

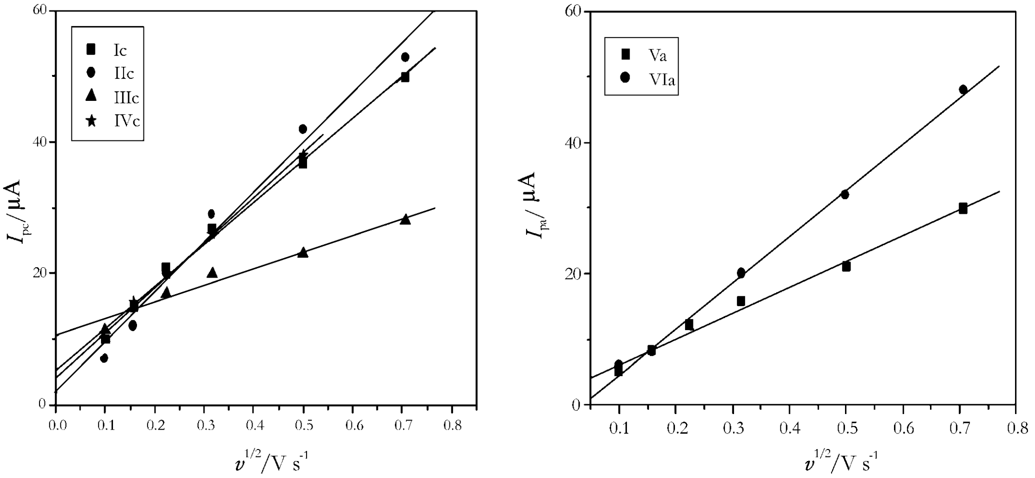

Fig. 4. Change in the cathodic peak current (I_{pc}) with the square root of scan rates ($v^{1/2}$) for octakis crown ether porphyrazine (**1**)

The linear dependences of the other processes are characteristic of a behavior associated with a diffusional process of **1** [20, 39–42].

Figure 5 shows the change in the ratio of the anodic to the cathodic peak current ($I_{p,a}/I_{p,c}$) as a function of the scan rate. The relationship between $I_{p,a}/I_{p,c}$ ratios with the scan rates serves as a quick test for the electrochemical mechanism associated with preceding or succeeding chemical reactions. In the case of the ratio, $I_{p,a}/I_{p,c}$, with increasing scan rate, v, is unity, it is a simple electron transfer reaction. In the case of the $I_{p,a}/I_{p,c}$ decreases with v, it is assigned as a reversible electron transfer reaction followed by a reversible chemical reaction. While the $I_{p,a}/I_{p,c}$ increases with v, it is assigned as a reversible electron transfer reaction followed by an irreversible chemical reaction [36]. In the case of the Ic/Ia redox process of **1**, the $I_{p,a}/I_{p,c}$ ratio starts from a small value and increases towards unity with increasing scan rate. This can be taken as an indication of an irreversible chemical reaction succeeding the electron transfer reaction. In the case of the IIc/IIa redox process, the anodic peak is recorded only at very high scan rates. This results from an irreversible chemical reaction succeeding the electron transfer reaction or the instability of the reduced species. The $I_{p,a}/I_{p,c}$ ratio of the IIIc/IIIa redox process decreased with increasing scan rate indicating the existence of a reversible chemical reaction following this electron transfer process (Fig. 5).

As shown in cyclic voltammograms given in Fig. 6, **2** exhibited a reversible metal-based reduction couple at -0.101 V. It was assigned to Co(II)/Co(I) followed by two *quasi*-reversible ring reductions at -0.364 and -1.037 V and a *quasi*-reversible metal-based oxidation associated to Co(II)/Co(III) at 0.702 V and two ligand-based oxidations processes at 0.904 and 1.148 V. First-row transition metaloporphyrazines differ from those of the main-group metal porphyrazines due to the fact that metal "d" orbitals may be positioned between HOMO and LUMO of the porphyrazine [3, 12, 15, 34, 42]. According to these studies, the first oxidation and the first reduction processes occur on the metal center in the metal porphyrazines only for Mn, Fe, and Co derivatives. For Ni, Cu, and Zn porphyrazine derivatives, redox processes take place on the ring. Thus, in the case of **2**, the

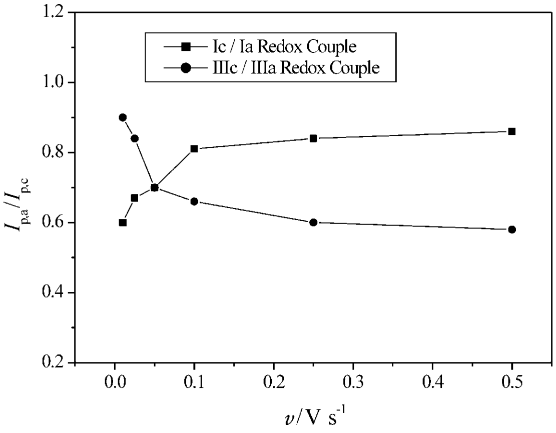

Fig. 5. Change in the anodic to cathodic peak current ratio (I_{pa}/I_{pc}) with scan rate (v) for octakis crown ether porphyrazine (**1**)

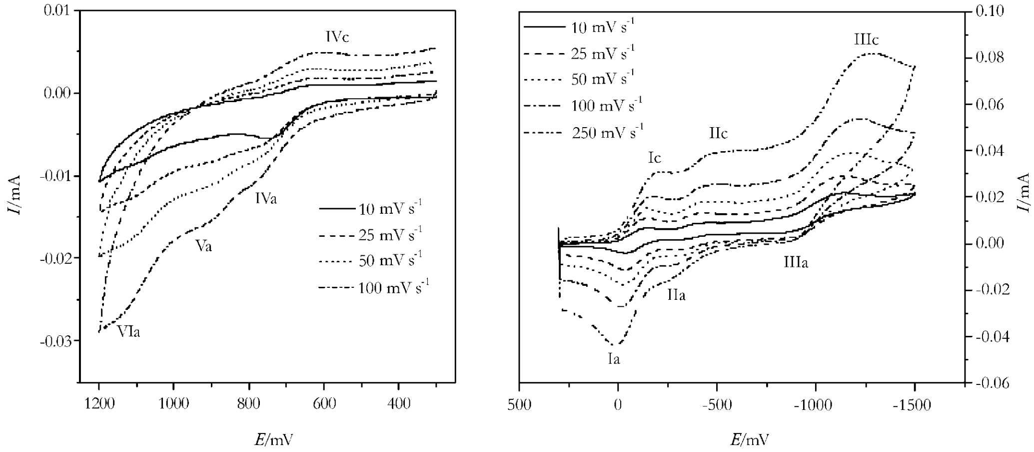

Fig. 6. Cyclic voltammogram of $5.0 \cdot 10^{-4}$ mol dm^{-3} octakis crown ether cobalt porphyrazine (**2**) in 0.1 mol dm^{-3} *TBAP/DCM vs.* SCE

first reduction at -0.101 V and the first oxidation at 0.702 V are expected to take place at the Co center of the complex and the remaining ones are attributed to the porphyrazine group.

The ΔE and $E_p/\log v$ values of **2** given in Table 1 indicate that while the IIIc process has an irreversible behavior, all other redox processes have *quasi*-reversible peak character. The linear dependences of $I_{p,c}$ to the $v^{1/2}$ for all redox processes of **2** show a diffusional mass transfer mechanism of the complex. The change in the ratio of the anodic to the cathodic peak current ($I_{p,a}/I_{p,c}$) with the scan rate for the Ic/Ia redox process of **2** (Fig. 7) indicates a simple electron transfer mechanism of the complex. For the IIc/IIa and IIIc/IIIa redox processes, it is understood from the $I_{p,a}/I_{p,c}$ ratios given in Fig. 7 that there is a fast reversible chemical reaction succeeding the electron transfer reaction. The $I_{p,a}/I_{p,c}$ ratio for the IVa/IVc redox process has a very small value (≈ 0.3) and does not change considerably with increasing scan rates. This may be due to a succeeding fast irreversible chemical

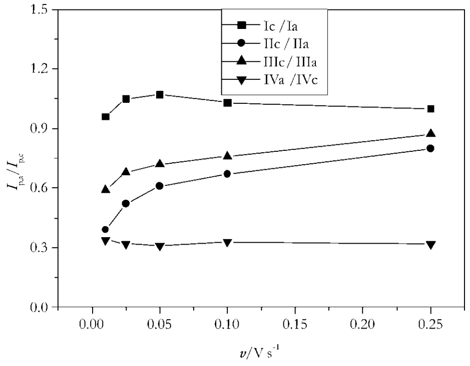

Fig. 7. Change in the anodic to cathodic peak current ratio (I_{pa}/I_{pc}) with scan rate (v) for octakis crown ether cobalt porphyrazine (**2**)

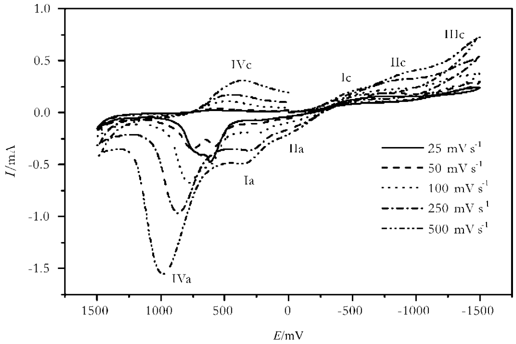

Fig. 8. Cyclic voltammogram of $5.0 \cdot 10^{-4}$ mol dm^{-3} octakis crown ether copper porphyrazine (**3**) in 0.1 mol dm^{-3} *TBAP*/*DCM vs.* SCE

reaction. The ring oxidation processes (Va and VIa) recorded only at higher scan rates proved the presence of this succeeding chemical reactions.

Complex **3** gives rather interesting and different voltammograms as presented in Fig. 8. During the cathodic scan it gives two *quasi*-reversible and an irreversible reductions at -0.086, -0.428, and -1.316 V and during the anodic scan it gives an adsorption couple at 0.624 V. The anodic peak of the couple splits into two peaks at low scan rates. The first one was attributed to the dissolved species while the second one was attributed to the adsorbed species. When the scan rate was increased, the first peak disappeared and only the adsorption peak remained. Different from **1** and **2**, the ring oxidation process of **3** was recorded at a less positive potential due to the adsorption of the complex on the electrode. As a result of the high intensity of the adsorption peak, the remaining ones could not be discovered on the voltammograms in the same scale.

Although in the phthalocyanines and porphyrazines with fused crown ether groups, it is known that addition of alkali metals of sufficiently large radii enhances aggregation as a result of intermolecular sandwich formation [43–45], interaction of K^+ with the flexible crown ether of porphyrazines examined in this study revealed just the opposite effect. This means that alkali metal complexation is increasing the concentration of monomeric units by formation of intramolecular

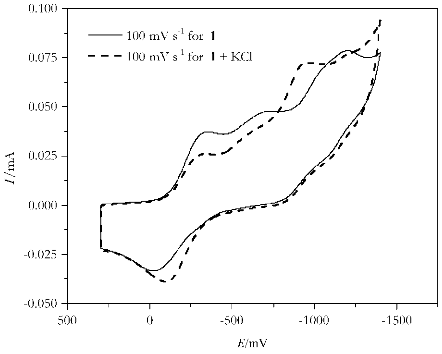

Fig. 9. Effect of addition of K^+ to the cyclic voltammogram of octakis crown ether porphyrazine (**1**)

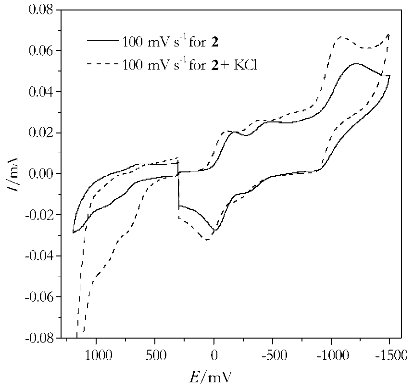

Fig. 10. Effect of addition of K^+ to the cyclic voltammogram of octakis crown ether cobalt porphyrazine (**2**)

sandwich formation between the neighboring crown ether moieties of the same molecule and the K^+ ion [11]. This tendency of the porphyrazines was clearly verified by spectral data through the diminishing aggregation which causes the monomers of the compound to form a tetramer after alkali metal interaction. Supporting data were obtained by a CV measurement. Cyclic voltammograms of the complexes with and without K^+ are given in Figs. 9–11. Thus, addition of K^+ shifts the electron transfer processes of the complexes toward positive potentials, increases peak currents, and affects the reversibility and adsorption properties of the complexes. The intramolecular sandwich formation between the neighboring crown ether moieties of the same molecule and K^+ results in a decreasing effect on the electron releasing ability of the inner core and this enables the porphyrazine reduction more easily. Increasing the concentration of monomeric units by formation of intramolecular sandwiches also causes an increase in the peak currents of the electron transfer processes. It is well known that the peak current corresponding to an electrochemical reaction is directly proportional with the concentration of the electroactive species [39]. For **3**, the splitted adsorption peaks were converted into a single peak after the addition of K^+ (Fig. 11). This may be due to the positively charged sections formed on the periphery of the porphyrazine unit, which diminishes the adsorption ability of the complex.

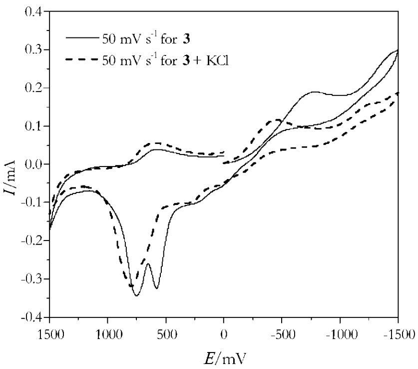

Fig. 11. Effect of addition of K^+ to the cyclic voltammogram of octakis crown ether copper porphyrazine (**3**)

Using the controlled potential coulometry (CPC), complete electrolysis of the solution at the working electrode at constant potential (E_{pc} of redox couple) was achieved. The time integration of the electrolysis current was recorded and the charge, Q, at the end of electrolysis was calculated using the current-time response of the solution. *Faraday*'s law was used to estimate the number of electrons transferred. The CPC studies indicated that the number of electrons transferred for the first reductions and the first oxidation processes is approximately one. However, the number of electrons transferred for the remaining processes is found to be a little smaller than one. This may be due to the chemical reactions succeeding the electron transfer reactions.

Conclusion

This study showed that **1** gave all possible electron transfer reactions of common porphyrazine derivatives. Complex **2** gave a one electron metal based reduction followed by two one electron ring reduction and one electron metal oxidation couple followed by two one electron ring oxidation processes. Differently, **3** exhibited an adsorption peak which split into two peaks at slow scan rates assigning to adsorbed and dissolved species. Alkali metal complexation is increasing the concentration of monomeric units by formation of intramolecular sandwiches between the neighboring crown ether moieties of same molecule and K^+. Additions of K^+ shift the electron transfer processes of the complexes toward positive potentials, increase the peak currents, and affect the reversibility and adsorption properties of the compounds.

Experimental

CV was carried out with a Princeton Applied Research Model 273 potentiostat/galvanostat controlled by an external PC using the computer program HEADSTRT [46] and utilizing a three electrode configuration at 25°C. An Origin 6.0 graph program [47] was used to evaluate the HEADSTRT data, to draw voltammograms, and to analyze them. Peak currents were also measured and the baseline for subsequent peaks was obtained by using the Origin 6.0 graph program. A Pt wire served as the counter electrode. A saturated calomel electrode (*SCE*) was employed as the reference electrode and separated from the bulk of the solution by a double bridge containing saturated *KCl* adjacent to SCE and solvent and carrier adjacent to the solution. Ferrocene was used as internal reference, and potentials are also reported in Table 1 with respect to the Fc/Fc^+ redox potential in *DCM*. The working electrode was a Pt plate with an area of $1.0\,cm^2$. The surface of the working electrode was polished with a H_2O suspension of Al_2O_3 before each run. The last polishing was done with a particle size of 50 nm. Electrochemical grade tetrabutyl ammonium perchlorate (*TBAP*) in extra pure *DCM* was employed as the supporting electrolyte at a concentration of $0.1\,mol\,dm^{-3}$. High purity N_2 was used for deaeration and to maintain a nitrogen blanket for at least 15 minute prior to each run. For the CPC studies, a Pt gauze working electrode ($10.5\,cm^2$ surface area), a Pt wire counter electrode separated with a double bridge, a SCE as reference electrode, and a model 377/12 synchronous stirrer were used. The potential of the working electrode was set to the E_p obtained in the CV experiments. Then the solution was electrolyzed with efficient stirring.

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