

Low Valence States of Iron Complexes of Aliphatic and Mixed Aliphatic-Aromatic Diimine Ligands

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Received April 28, 1984

Abstract

Electrochemical reductions of iron(II) diimine complexes $[\text{FeL}_3]^{2+}$, where $\text{L} = \text{CH}_3\text{N}=\text{C}(\text{R})-\text{C}(\text{R}')=\text{NCH}_3$, aliphatic diimine series with $\text{R}, \text{R}' = \text{H}, \text{H}; \text{H}, \text{CH}_3$ and CH_3, CH_3 and $\text{L} = \text{C}_5\text{H}_4\text{N}-\text{C}(\text{R})=\text{N}(\text{R}')$, mixed diimine series with $\text{R}, \text{R}' = \text{H}, \text{CH}_3$ and CH_3] were investigated through polarography and cyclic voltammetry in acetonitrile, with tetraethylammonium perchlorate supporting electrolyte (0.2 M) as a function of temperature. In the 0 to -2.4 V vs. Ag/AgCl potential range two to four polarographic waves were observed for the aliphatic series. The first two waves can be described as one-electron reversible reduction processes. They indicate that low valence states iron(I) and iron(0) are stabilized in acetonitrile. In the mixed ligand series three one-electron reversible reduction waves were observed, indicating that in addition to the low valence states stabilized in the aliphatic diimine series the formal reduction state $\text{Fe}(-\text{I})$ is also stabilized. The stabilization of the low oxidation states is due to the electron acceptor properties of the diimine ligands, inherent to the presence of the chromophoric iron diimine group. The half-wave potential data and the stabilization of the low valence states point to the importance of analyzing both σ and π effects. The molecular electro-negativity values for the series of iron diimine complexes investigated evidences a synergistic interaction between the metal-ligand σ and π bonds. Diffusion coefficients, temperature effects on the heterogeneous electron transfer step, and electrocapillary curves were obtained for these complexes. No evidence for adsorption of the complexes on mercury electrodes was found for the one-electron reversible steps. When comparing polarographic data with those obtained on platinum disk working electrodes employed in the cyclic voltammetric experiments, we observed that for the symmetric aliphatic diimine ligands the observed cathodic currents are larger

than expected on the basis of the previously calculated diffusion coefficients. In addition, the reduction waves are shifted 0.14 V to more negative potentials. The symmetric aliphatic diimine complexes exhibit adsorption of the electroactive species on the surface of the platinum electrodes in this potential range.

Introduction

Iron(II) diimine complexes with aromatic ligands such as 1,10-phenanthroline and 2,2'-bipyridine have been known since the last century when Blau [1] discovered that these compounds were deeply red colored. This color is also characteristic of the aliphatic diimine iron(II) complexes synthesized by Krumholz in 1953 [2]. Such properties led Sone [3] to conclude that the intense color of these compounds was associated with the presence of the chromophoric group iron–diimine. Later, Busch and Bailar [4] established the structural link between the aromatic series and the aliphatic one by synthesizing the iron complexes of the mixed aromatic and aliphatic diimine type, here referred to as mixed diimine ligands [4–6]. The intense red color of these compounds was assigned [7–9] to the inverse charge transfer $t_2 \rightarrow \pi^*$, which indicates that these ligands are good electron acceptors. The existence of the low valence state iron complexes of aromatic diimine ligands with formal oxidation states (I, 0 and $-\text{I}$) is also good evidence for the electron accepting properties of these ligands [10–14]. The understanding of the similarities and differences in properties caused by the total absence (aliphatic series) or partial absence (mixed series) of the aromatic rings in the diimine complexes is of great interest [7]. The similarity of properties cannot be widely generalized throughout these series for redox behavior. The aromatic diimine complexes of iron(II) can be reversibly oxidized to the corresponding iron(III) blue compounds in aqueous sulfuric acid solutions independent of the acid concentration [15]. The chemical [16] or electrochemical [17] oxidation of the iron(II) diimine complexes with mixed or

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aliphatic ligands can only be observed as a reversible process in media of high proton acid concentration, respectively 4 M [18] and 10 M [16, 19] sulfuric acid for these series, or in high Lewis-acid concentration molten salts [20], or in aprotic media [21, 22]. At lower aqueous acid concentrations the metal oxidation is followed by fast internal redox reaction with concomitant ligand oxidation [16, 18, 19, 23, 24].

The electrochemical reduction of the aromatic diimine complexes in acetonitrile was investigated by various techniques [25–29]. These studies indicated that the stabilization of the low-valence states depends strongly on the ability of ligand to delocalize charges. Three reversible one-electron steps have been described, leading to complexes with formal oxidation states of iron of I, 0 and –I. We have investigated the electrochemical behavior of the iron(II) diimine complexes with aliphatic and mixed diimine ligands in acetonitrile on platinum electrodes using cyclic voltammetric techniques [21]. Though we did observe the stabilization of low valence states under these conditions, some of the reductions on platinum working electrodes were accompanied by adsorption of the iron compounds. In this work we investigated the polarographic behavior of various iron(II) diimine complexes with aliphatic and mixed diimine ligands (see Table I for a list of the compounds investigated) in acetonitrile and compared these data with those obtained on platinum electrodes by cyclic voltammetry. Adsorption parameters [30–32] were obtained. In addition, the present studies provide data to assess the effect of the substituents and of the structure of the diimine ligand on the reduction mechanism and on the stabilization of the low-valence states.

Experimental

The syntheses and purification of the iron(II) compounds were performed as described in the literature [9, 33]. The supporting electrolyte tetraethylammonium perchlorate was prepared and purified according to House *et al.* [34]. The electrochemical cell and the purification of the solvent are described in reference 21. The polyfunctional electrochemical instrument Princeton Applied Research Corp. Model 170 was employed in the cyclic voltammetric measurements. Polarographic measurements were performed with a Beckman Electroscan 30 using a three electrode system. The electrochemical cell was immersed in a glass compartment through which water (or appropriate circulating fluid) from a Thermostat-Circulator Lauda K-2/R was circulated. Measurements were performed at 25.0 ± 0.2 °C or at other temperatures in the 5–25 °C range.

Results and Discussion

The polarographic reduction of the investigated iron(II) diimine complexes in the potential range 0 to –2.4 V vs. Ag/AgCl in acetonitrile containing 0.2 M tetraethylammonium perchlorate (TEAP) displays two to four reduction waves, depending on the nature of the ligand. Representative polarograms for the five complexes investigated are shown in Fig. 1. The half-wave potentials of the reductions that can be described as one-electron reversible processes are assembled in Table I. The diffusion coefficients and the slopes of the plots of $\log[i/(i_d - i)]$ vs. E are assembled in Table II. Within experimental error the values of the slopes of the log plots is identical to that expected for a one-electron reversible process at 25 °C, 59 mV. The diffusion currents are proportional to the concentration of the electroactive species. The activation energies obtained from the linear plots of $\log[i_d/(m^{2/3}t^{1/6})]$ vs. $1/T$ in K^{-1} are 17 ± 2 kJ/mol and 20 ± 3 kJ/mol for the aliphatic and mixed series representatives respectively (m = mercury rate flow; t = drop time). Such values are common to diffusion-controlled processes [26]. The polarographic data indicate that the limiting current of the first two reduction waves of all these complexes is diffusion-controlled, and that the processes can be described as one-electron reversible processes:

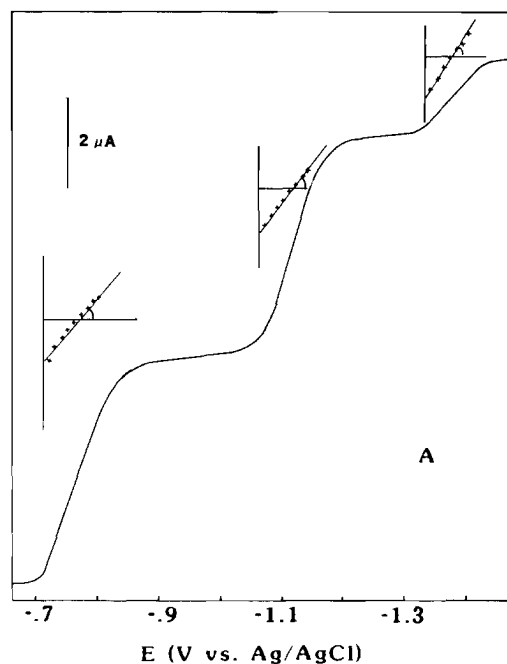
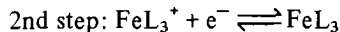
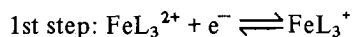


Fig. 1A. For legend, see page 153.

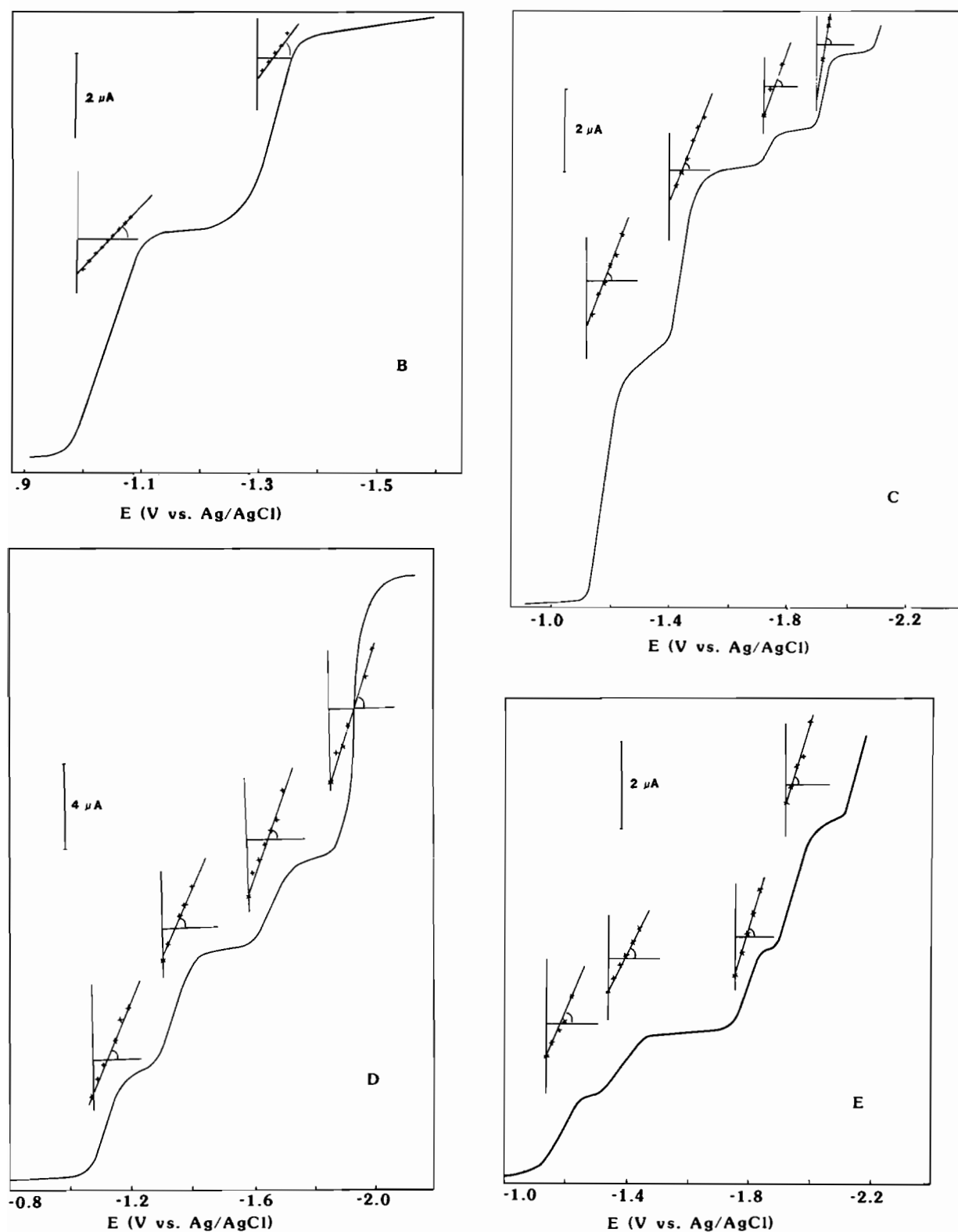
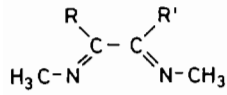
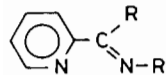


Fig. 1. Polarograms of the reduction of 1×10^{-3} M solutions of iron(II) diimine complexes in acetonitrile containing 0.2 M tetraethylammonium perchlorate at 25 °C. Also indicated the plot of $\log(i/i_d - i)$ vs. applied potential for the various corresponding waves. Ligands: A) glyoxal bis(methylimine) GMI; B) methylglyoxal bis(methylimine) (MMI); C) biacetyl bis(methylimine) (BMI); D) 2-pyridyl (methylimine) (PMI) and E) 2-pyridyl- α -methyl (methylimine) (PMM).

TABLE I. Half-wave Potentials obtained from Polarograms exemplified in Fig. 1 for the Iron(II) Tris(diimine) Complexes in Acetonitrile, containing 0.2 M Tetraethylammonium Perchlorate as Supporting Electrolyte at 25 °C. All Potentials in V vs. Ag/AgCl.

Ligand			$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)^a$
	R, R'				
	H, H	GMI	-0.77	-1.12	
	H, CH ₃	MMI	-1.04	-1.31	
	CH ₃ , CH ₃	BMI	-1.18	-1.44	
	H, CH ₃	PMI	-1.10	-1.35	-1.66
	CH ₃ , CH ₃	PMM	-1.18	-1.39	

^a $E_{1/2}(1)$; $E_{1/2}(2)$ and $E_{1/2}(3)$ correspond to the redox couples: $\text{FeL}_3^{2+}/\text{FeL}_3^+$; $\text{FeL}_3^+/\text{FeL}_3$; and $\text{FeL}_3/\text{FeL}_3^-$ respectively.

TABLE II. Diffusion Currents and Slopes (α) of the Plots of $\log(i/(i_d - i))$ vs. Applied Potential (E in V vs. Ag/AgCl) for the Iron(II) Tris(diimine) Complexes in Acetonitrile Containing 0.2 M Tetraethylammonium Perchlorate at 25 °C.

Diimine Ligand	$i_d(1)$	$i_d(2)$	$i_d(3)$	$\alpha(1)$	$\alpha(2)$	$\alpha(3)$
GMI	4.6	4.6		60	55	
MMI	5.0	4.7		65	63	
BMI	5.3	5.2		55	57	
PMI	4.8	4.8	4.0	58	61	55

In the potential range in which these two reduction reactions take place we cannot detect appreciable adsorption of the complexes on the mercury electrode. This fact is illustrated in Fig. 2, where the quantity $m^{2/3}t^{1/6}$ as a function of the increased negative potential is compared for the supporting electrolyte alone and in the presence of the various iron diimine complexes. In the case of the mixed diimine complex illustrated in Fig. 2D, the third reduction wave (half-wave potential -1.66 vs. Ag/AgCl) must involve the reduction of a partially adsorbed complex at the surface of the mercury electrode. Due to the nernstian behavior [35] of the observed wave, this third step is likely to involve adsorbed zero-valent and adsorbed iron(-I) complexes.

The stabilization of the low oxidation states Fe(I) and Fe(0) for these complexes, in addition to Fe(-I) found in the case of $\text{Fe}(\text{PMI})_3^{2+}$, is similar to that found in the literature for the iron complexes of aromatic diimine ligands [25-9]. Therefore, the electron delocalization capability of such ligands must be comparable to that of the aromatic diimine ligands.

Observation of the half-wave potentials as a function of the nature of the substituent indicates that as methyl groups replace hydrogens in the aliphatic or mixed diimine series the half-wave potentials are shifted to more negative values. This trend is to be expected since the methyl groups increase

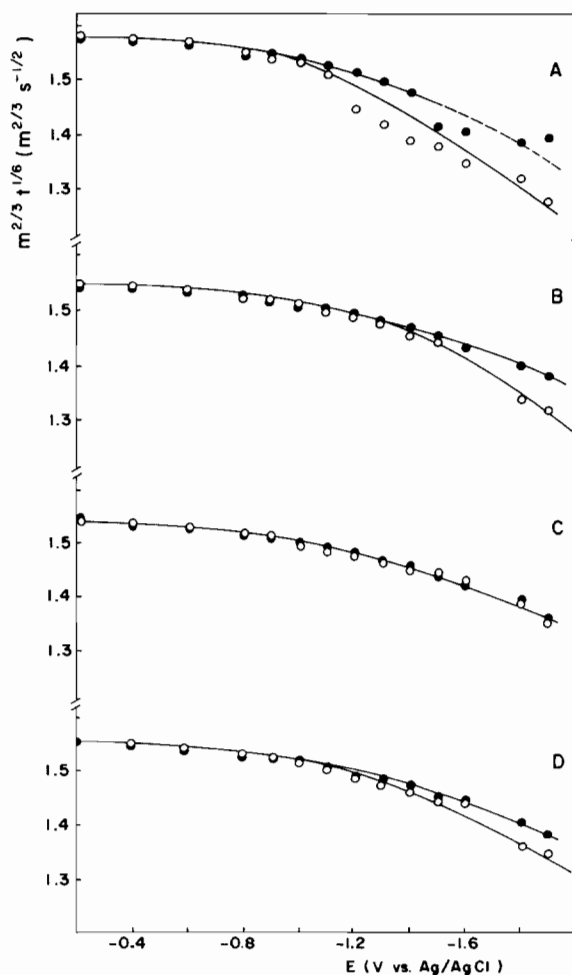


Fig. 2. Electrocapillary curves for iron diimine complexes. \circ 0.2 M tetraethylammonium perchlorate in acetonitrile; \bullet previous solution containing 5×10^{-4} M of the iron diimine complexes. Ligands: A) glyoxal bis(methylimine) (GMI); B) Methylglyoxal bis(methylimine) (MMI); C) biacetyl bis(methylimine) (BMI) and D) 2-pyridyl (methylimine) (PMI).

the σ bonding capabilities of the ligands, leading to the faster stabilization of the more positively charged metal ions as compared to the less positively charged metal ions. Thus the stabilization of the iron(II) forms is greater than that of the iron(I) forms. A similar effect is observed in the Fe(III)/Fe(II) series, with the iron(III) forms being stabilized faster than the iron(II) forms [7].

The cyclic voltammograms [21] for the first reduction step of these complexes on platinum working electrodes show some characteristics of a one-electron reversible behavior. However, the half-wave potentials for the symmetric ligands differ considerably from those obtained by the polarographic method (compare Tables I and III). In addition, whereas the diffusion coefficients calculated from the Randles and Sevcik equation for the reversible one-electron oxidation processes [36] agree with the polarographic diffusion coefficients for the complexes with asymmetric ligands, the diffusion coefficients for the complexes of symmetric ligands are different, by a factor of three to six (see Table III).

TABLE III. Half-wave Potentials (in V vs. Ag/AgCl) and Apparent Diffusion Coefficients (D_{app}) obtained from Cyclic Voltammetry of Iron(II) Tris(diimine) Complexes (1.00×10^{-3} M) in Acetonitrile containing 0.2 M Tetraethylammonium Perchlorate.

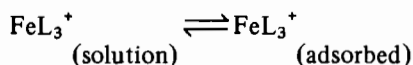
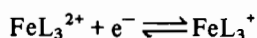
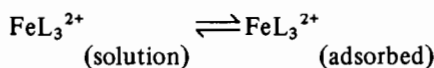
Diimine Ligand	$E_{1/2}$ (V)	$D(10^5)$ (cm^2/s)
GMI	-0.92(-0.77) ^a	3.0(1.2)
MMI	-1.09(-1.04)	1.0(0.95)
BMI	-1.31(-1.18)	5.7(1.0)
PMI	-1.10(-1.10)	1.0(1.0)

^aThe values in parentheses represent respectively the half-wave potentials (from polarography) and the diffusion coefficients calculated for the electrochemical oxidation of these complexes on platinum electrodes (a reversible one-electron process) [37].

Such cyclic voltammetric diffusion coefficients yield unrealistically small solvodynamic mean radii, smaller than those obtained from structural determinations with molecular models [37]. These data suggest that in the electrochemical reduction of the complexes with symmetric ligands adsorption must be invoked. Peak current intensity increases as a result of electron transfer to the adsorbed material which happens at potentials close to those necessary for the reduction of the material arriving at the electrode surface by diffusion [40]. The potential shift to more cathodic potentials also reflects the adsorption phenomenon – the reduction becomes more difficult [38]; Figs. 3A and B compare the voltammograms obtained experimentally (solid lines) and that calculated for a one-electron reversible pro-

cess (points) without adsorption according to Nicholson and Shain [39]. Figs. 3C and 3D display the potential displacement of the actual curves and those calculated from the polarographic data. Since pre-current peaks or post-current peaks are not observed, we can consider that both reagent and product of the electron transfer step are weakly adsorbed [38].

The reduction of the two complexes with symmetric aliphatic diimine ligands on platinum electrodes can be described as follows:



which can be treated as adsorption obeying a Langmuir isotherm (Henry's law) [38]. Adsorption parameters (P_0) of 3 and 5 are found for the two complexes of symmetric ligands GMI and BMI respectively.

It is interesting to notice that the weak adsorption phenomenon of both reactant and product of the electron transfer is only found for the symmetric ligands of aliphatic diimine complexes. Such complexes seem to have a more favorable configuration for adsorption. It is not unlikely that these reduction processes could be accompanied by reorientation by the applied electric field [41]. A more negative applied potential would be required to reorient the complex or to compensate for the free-energy of adsorption of the complexes. It would be very interesting to obtain thin-layer electrochemical results relating conformation with adsorption and reduction, as described by Hubbard and co-workers in a variety of reductions of organic and organometallic compounds [42].

In this series of complexes we can observe stabilization of low valence states – both by polarography and by cyclic voltammetry. The substituents on the diimine chromophore affect both the σ and the π bonds between the iron and nitrogen atoms. The σ bonds involve electron donations from the nitrogen to iron; the π bonds involve back-bonding from iron electrons to the resonant ligand system. In the aliphatic series as we replace hydrogens by methyl groups we observe a displacement of the half-wave potentials to more negative values. The ligand glyoxal bis(methylimine) stabilizes more easily the low oxidation states than the ligand biacetyl bis(methylimine). The methyl groups are electron-donating groups. Increased σ donating ability of the ligand increases the stabilization of the iron(II) forms versus iron(I) forms. A more marked difference in half-wave potentials is observed on going

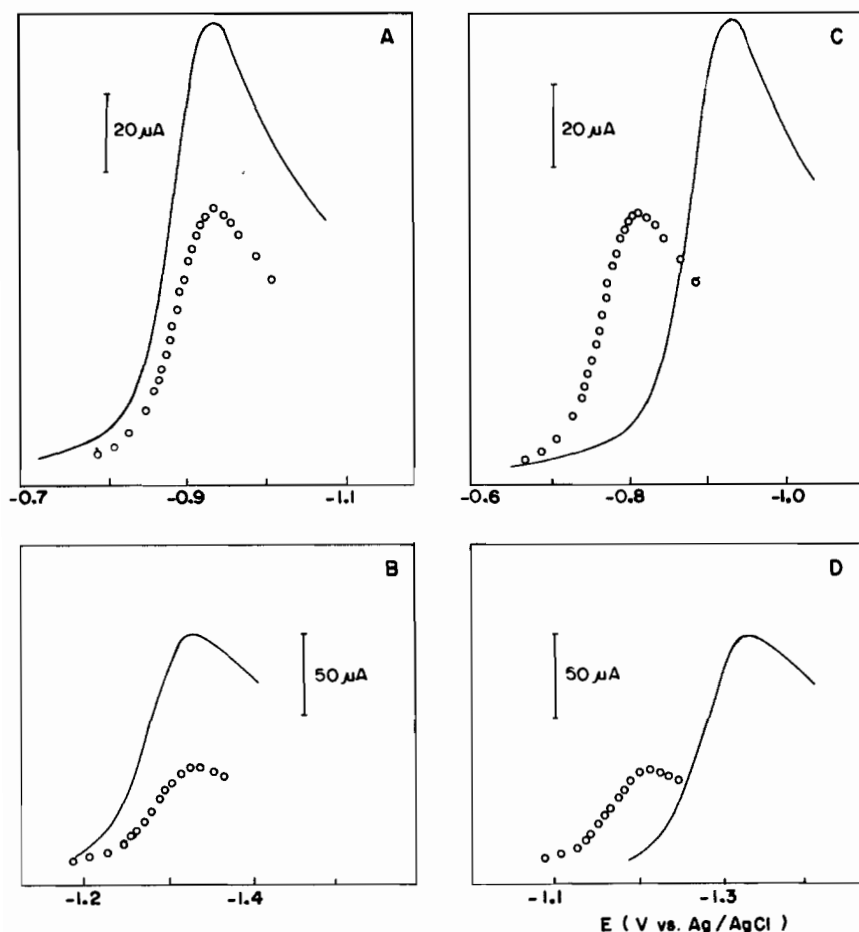


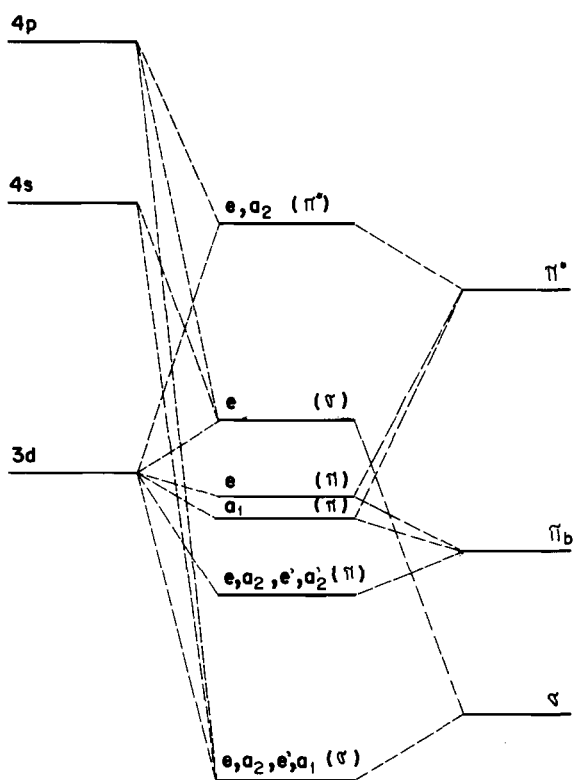
Fig. 3. Cyclic voltammograms obtained in the reduction of iron diimine complexes of symmetric ligands (—) and (○) calculated curves assuming a one-electron reversible behavior. A) ligand glyoxal bis(methylimine); B) ligand biacetyl bis(methylimine); C and D calculated curves displaced to the polarographic half-wave potential.

from glyoxal bis(methylimine) to methylglyoxal bis(methylimine) – a 0.27 V more difficult electrochemical reduction. The same trend can be observed in the mixed diimine series; however, all potential shifts are smaller than those observed for the aliphatic series. We do observe three one-electron reduction waves for the mixed ligand 2-pyridyl(methylimine). In this case, as well as in the aromatic series [25–9] there is a higher probability of charge delocalization through the ligands and the establishment of stronger bonding.

We can interpret the half-wave potential of the reductive process as corresponding to the introduction of one electron in orbital $e(\sigma)$ and the half-wave potential obtained in the oxidative process as the energy necessary to remove one electron from the orbital $e(\pi)$ [considering D_3 symmetry; see Scheme 1]. Therefore the sum of these two half-wave potentials is intimately correlated to the energetic separation between these orbitals [43]:

$$E_{\text{FeL}_3^{2+}/\text{FeL}_3^{3+}} + E_{\text{FeL}_3^{2+}/\text{FeL}_3^+} \approx M$$

The values of M of 2.07, 2.16, 2.11, 2.22, 2.13, and 2.44 have been found respectively for the complexes with ligands: GMI, MMI, BMI, PMI, PMM, and dipy. These values can be considered a measure of the ‘molecular electronegativity’ of the FeL_3^{2+} , and determine the electron acceptor-donor properties of these compounds. The small variation of M in the aliphatic series and in the mixed series indicates that the changes in π acceptor properties of the ligands is small; this effect is also partially offset by the changes in σ -donating capabilities of the ligands, mainly because of synergistic interactions between the σ and π bonding between metal and ligand [44]. However, it is interesting to notice that PMI with the largest value of M in the studied series is the complex that leads to the stabilization of the three low valence states, similarly to that observed for the aromatic derivatives. The importance of the synergistic interaction between σ and π bonding in these complexes has also been observed in electronic spectroscopic [9] and Mössbauer data [45].



Scheme 1. Simplified molecular orbital diagram for the iron(II) diimine complexes assuming D_3 symmetry.

Acknowledgements

The benefit of valuable discussions with Dr. J. H. Christie is gratefully acknowledged. The support of the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and of the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) is gratefully acknowledged.

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