# Substituent Effects on Iron Diimine Complexes.
# II. Correlations with Thermodynamic and Spectral Properties in Acetonitrile

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*The electrochemical oxidation of nineteen iron(II) complexes, $FeL_3^{2+}$, with aliphatic diimine ligands, L = $H_3CN=C(R)-C(R')=NCH_3$, where R, R' = H, H; H, $CH_3$; $CH_3$, $CH_3$; $CH_3$, $C_2H_5$; $CH_2CH_2CH_2CH_2$; $CH_2CH(CH_3)CH_2CH_2$; H, $C_6H_5$; $CH_3$, $C_6H_5$, and mixed diimine ligands, L = $C_5H_4N-C(R_1)=N(R_2)$, where $R_1$, $R_2$ = H, $CH_3$; H, $C_2H_5$; $CH_3$, $CH_3$; $CH_3$, $C_2H_5$; $CH_3$, $C_6H_5$; $CH_3$, m- or p-$NH_2C_6H_4$; $C_6H_5$, $C_6H_5$; $C_6H_5$, m- or p-$NH_2C_6H_4$ was studied by means of cyclic voltammetry in acetonitrile, 0.2 M tetraethylammonium perchlorate at 25.0 °C. Except for compounds R, R' = H, $C_6H_5$; $CH_3$, $C_6H_5$, and for the compounds with free amino groups, reversible one-electron oxidation processes were found. For the amino containing compounds the electrochemical oxidation is more complex due to concurrent oxidation of the amino group. For the phenyl derivatives of the aliphatic series, chemical and electrochemical steps follow the primary reversible one-electrion reaction. For the compounds which exhibit reversible electrochemical oxidation, the half-wave potentials are identical to the standard electrode potentials. These potentials can be correlated with the sum of the polar Taft parameters for the substituents. Substituents presenting large steric or mesomeric effects do not fit this correlation, since these effects are excluded from the polar Taft parameters. A better correlation can be obtained by including steric effects. The frequencies of the intense absorption band in the visible region, assigned to an inverse charge transfer, are correlated with the half-wave potentials of the reversible oxidation processes. A correlation between the square-root of the molar absorptivities at the absorbance maximum of the inverse charge transfer band with the sum of the polar Taft parameters of the substituents is also obtained.*

## Introduction

In part I of this series [1, 2] a systematic study of substituent effects on iron diimine complexes relating

thermodynamic and spectral properties in aqueous sulfuric acid with substituent parameters was presented. The complexes studied had aliphatic [3] diimine ($H_3CN=C(R)-C(R')=NCH_3$) and mixed [4] diimine ($C_5H_4N-C(R_1)=N(R_2)$) ligands, analogous to the well known iron complexes of the aromatic diimine ligands 2,2'-bipyridine and 1,10-phenanthroline. The latter complexes have been extensively employed as redox indicators [5] over a wide range of acidities due to the reversibility of the chemical oxidation to the ferric form, accompanied by profound color changes. The iron complexes with aliphatic and mixed diimine ligands display reversible chemical oxidation to the respective ferric forms only if the acid concentration exceeds 10 M $H_2SO_4$ (aliphatic series) [6, 7] or 4 M $H_2SO_4$ (mixed series) [8]. At lower acid concentration ligand-oxidation occurs with the formation of new ligand-oxidized complexes [6–10]. Several aspects of the spectroscopic, thermodynamic, and kinetic properties, and reactivity of diimine complexes were reviewed by Krumholz [11], McWhinnie and Miller [12], and Dwyer, *et al.* [13].

Acetonitrile is a good solvent for spectroscopic and electrochemical studies due to the relatively high dielectric constant, low viscosity, and poor coordinating ability [14]. This solvent has been employed successfully in the study of the electrochemical reductions of aromatic diimine complexes of iron(II) [12, 15, 16]. The reversible one-electron electrochemical oxidation [17] of five iron diimine complexes (R, R' = H, H; H, $CH_3$; $CH_3$, $CH_3$ and $R_1$, $R_2$ = H, $CH_3$; $CH_3$, $CH_3$) in acetonitrile indicated that complications arising from ligand-oxidation processes can be minimized in this solvent. The electrochemical reductions on a platinum disk electrode [17] indicated that the one-electron reduced species $FeL_3^+$ is formed [18]. Therefore, the aliphatic and mixed diimine ligands stabilize, as the aromatic diimine ligands, the low valence state complexes, indicating the importance of the common structural iron diimine chromophore [19] in determining the properties of these complexes.

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TABLE I. Half-wave Potentials, $E_{1/2}$, of the Couples $FeL_3^{3+}/FeL_3^{2+}$, Wavenumbers $(\bar{\nu})$ at the Absorbance Maxima and Molar Absorptivities $(\epsilon)$ of the $FeL_3^{2+}$ Complexes in Acetonitrile, 0.2 $M$ TEAP, at 25 °C.

| No. | R or $R_1$ | $R'$ or $R_2$ | $E_{1/2}$ [a] V vs. Ag/AgCl | $\bar{\nu}_{max}$ kK | $\epsilon_{max} \times 10^{-3}$ $M^{-1}$ cm$^{-1}$ |
|---|---|---|---|---|---|
| *Aliphatic Diimine Ligands* | | | | | |
| $L = H_3CN=C(R)-C(R')=NCH_3$ | | | | | |
| 1 | H | H | 1.30 | 18.1 | 8.5 |
| 2 | H | $CH_3$ | 1.13 | 17.8 | 9.6 |
| 3 | $CH_3$ | $CH_3$ | 0.93 | 17.6 | 10.8 |
| 4 | $CH_3$ | $C_2H_5$ | 0.98 | 17.5 | 10.4 |
| 5 | $-CH_2-CH_2-CH_2-CH_2-$ | | 0.96 | 17.2 | 12.2 |
| 6 | $-CH_2CH(CH_3)CH_2CH_2-$ | | 0.95 | 17.2 | 12.3 |
| 7 | H | $C_6H_5$ | 1.11[b] | 16.6 | 11.6 |
| 8 | $CH_3$ | $C_6H_5$ | 0.98[b] | 16.9 | 10.6 |
| *Mixed Diimine Ligands* | | | | | |
| $L = C_5H_4N-C(R_1)=NR_2$ | | | | | |
| 9 | H | $CH_3$ | 1.11 | 18.2 | 10.7 |
| 10 | H | $C_2H_5$ | 1.07 | 18.0 | 10.4 |
| 11 | $CH_3$ | $CH_3$ | 0.94 | 18.0 | 11.3 |
| 12 | $CH_3$ | $C_2H_5$ | 0.99 | 17.8 | 11.0 |
| 13 | $CH_3$ | $C_6H_5$ | 1.12 | 17.6 | 8.8 |
| 14 | $CH_3$ | $m$-$NH_2C_6H_4$ | 1.11[b] | 17.6 | 8.7 |
| 15 | $CH_3$ | $p$-$NH_2C_6H_4$ | 0.97[b] | 17.2 | 8.4 |
| 16 | $C_6H_5$ | $CH_3$ | 1.14 | 17.7 | – |
| 17 | $C_6H_5$ | $C_6H_5$ | 1.31 | 17.2 | 8.1 |
| 18 | $C_6H_5$ | $m$-$NH_2C_6H_4$ | – | 17.3 | 11.1 |
| 19 | $C_6H_5$ | $p$-$NH_2C_6H_4$ | – | 16.9 | 9.7 |

[a]±0.01 V vs. Ag/AgCl.    [b]± 0.02 V vs. Ag/AgCl.

TABLE II. Analytical Data for the $FeL_3(ClO_4)_2$ of the Mixed Diimine Ligands. See Table I for the structure of the compounds.

| No. | % Fe | | % N | | % C | | % H | |
|---|---|---|---|---|---|---|---|---|
| | calcd | expl | calcd | expl | calcd | expl | calcd | expl |
| 11 | 8.50 | 8.4 | 12.79 | 12.7 | 43.83 | 43.8 | 4.57 | 4.6 |
| 12 | 7.98 | 8.05 | 12.02 | 11.9 | 46.35 | 46.1 | 5.15 | 5.1 |
| 13 | 6.62 | 6.8 | 9.96 | 9.85 | 55.52 | 54.0 | 4.27 | 4.2 |
| 14 | 6.28 | 6.3 | 14.19 | 13.5 | 52.70 | 51.0 | 4.39 | 4.3 |
| 15 | 6.28 | 6.25 | 14.19 | 14.15 | 52.70 | 50.0 | 4.29 | 4.3 |
| 16 | 6.62 | 6.6 | 9.96 | 9.85 | 55.52 | 54.4 | 4.27 | 4.25 |
| 17 | 5.42 | 5.5 | 8.16 | 8.1 | 62.97 | 59.0 | 8.16 | 8.2 |
| 18 | 5.20 | 5.2 | 11.73 | 11.7 | 60.34 | 58.5 | 4.19 | 4.15 |
| 19 | 5.2 | 5.35 | 11.73 | 11.65 | 60.34 | 56.0 | 4.19 | 4.05 |

In the present paper substituent effects on nineteen iron diimine complexes were studied by means of cyclic voltammetry and visible absorption spectra in acetonitrile. Correlations between the half-wave potentials, $E_{1/2}$, of the reversible one-electron oxidations and the frequencies of the inverse charge transfer band $t_2 \rightarrow \pi^*$ are presented, as well as correlations between $E_{1/2}$ or the molar absorptivity at the absorbance maximum and the sum of the Taft parameters of the substituents on the iron diimine chromophore.
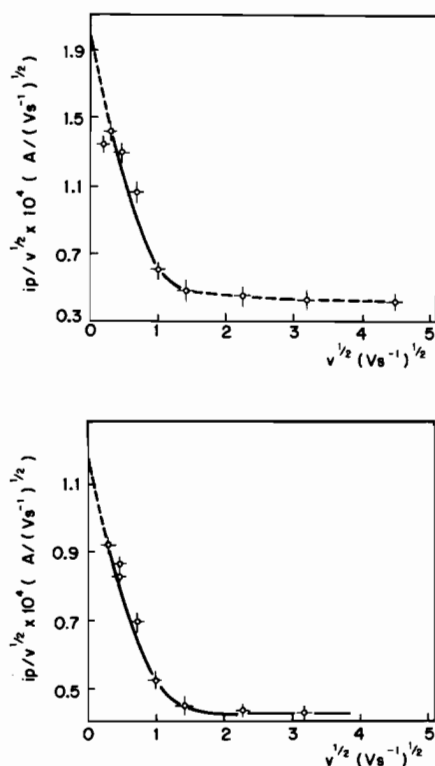
Fig. 1. The current function ($i_p v^{-1/2}$) as a function of the square-root of the potential scan rate (v) for the complexes $FeL_3^{2+}$ (L = $H_3CN=C(R)-C(R')=NCH_3$); R,R' = H, $C_6H_5$ (upper) and $CH_3$, $C_6H_5$ (lower) in acetonitrile, 0.2 *M* TEAP, at 25 °C.

## Experimental

Table I lists the compounds studied. Table II lists microanalytical results (C, H) for 9 of the complexes of mixed diimine ligands [20]. Determinations of iron and nitrogen were performed in the semimicro range by using a colorimetric technique [9, 21] and the Kjeldahl method [23], respectively. Micro-analytical data as well as preparation and purification procedures for these compounds is described elsewhere [1, 21, 22]. The electrochemical cell and instrumentation employed are described in reference 17, which also contains the purification procedure used for the solvent acetonitrile and supporting electrolyte tetraethyl ammonium perchlorate (TEAP). The visible–UV spectrophotometer Zeiss DMR-10 was used for spectral measurements, with spectrosil Coleman cells of 1 mm optical path.

## Results and Discussion

### Electrochemical Behavior in Acetonitrile

All of the complexes studied (see Table I) except 7, 8, 14, 15, 18 and 19, exhibit a reversible one-electron oxidation in the region of 0.5 to 1.8 V *vs.* Ag/AgCl for potential scan rates (v) in the 0.02–0.5 V s$^{-1}$ range. In this potential range, only one anodic and one cathodic current peak is observed, with anodic to cathodic peak ratio of 1.00 ± 0.02. Both peak currents increase linearly with the square-root of potential sweep rate, and with concentration. The current function $i_p v^{-1/2}$ is constant within the experimental error (2–3%). Experimental cyclic voltammograms and those calculated assuming a reversible one-electron transfer, according to Nicholson and Shain [24], agree within the experimental error (see reference 17 for examples). Therefore the electrochemical oxidation processes are reversible under diffusion control, and the half-wave potentials, $E_{1/2}$, obtained from the cyclic voltammograms identical to the standard electrode potentials, $E°$, provided that the diffusion coefficients of the oxidized (O) and reduced (R) species are identical: $E_{1/2} = E° + (RT/nF)\ln(D_R/D_O)^{1/2}$. Table I lists the $E_{1/2}$ for these compounds.

For compounds 7 and 8, R, R' = H, $C_6H_5$ and $CH_3$, $C_6H_5$, which have a phenyl group on the aliphatic diimine ligand, the electrochemical behavior is more complex, as illustrated by Fig. 1, where the current function $i_p v^{-1/2}$ as a function of $v^{1/2}$ is shown. The term $i_p v^{-1/2}$ decreases to a steady value at large sweep rates (v > 10 V s$^{-1}$), when a reversible one-electron oxidation takes place. The curves in Fig. 1 suggest that chemical and electrochemical reactions are coupled to the primary electrochemical step. Similar plots [25] have been obtained for the aliphatic diimine complex of iron(II), R, R' = H, H, in 0.5 *M* $H_2SO_4$, where chemical and electrochemical reactions involving solvent water were shown to be coupled with the first one-electron reversible transfer, with the formation of new complexes with oxidized ligands, *e.g.*, $H_3CN=C(OH)-CH=NCH_3$, and the total number of Faradays consumed per mole of complex $n_T = 3$. For this compound in acetonitrile the rate of the coupled chemical reactions, a function of the water activity [26], is reduced. In sulfuric acid solutions ($\sim$4.0 *M* $H_2SO_4$) the ligand-oxidation reactions for the compounds 7 and 8 are too fast to be followed by the spectrophotometric and potentiometric techniques [7] employed in the study of the R, R' = H, H compound [9, 26]. In the present investigation, the acetonitrile employed contained of the order of millimolar amounts of water, which allow ligand-oxidation reactions to take place. For the phenyl derivatives $n_T = 5$(H, $C_6H_5$) and 3($CH_3$, $C_6H_5$), as obtained from the ratio $(i_p v^{-1/2})_{v\to o}/(i_p v^{-1/2})_{v\to\infty} = n_T/n_{(v\to\infty)}$ [24], and from the Randles–Sevcik equation. Approximate values for the pseudo first-order chemical reaction step, the self-reduction of the iron(III) complex by the ligand, yielding a ligand-radical-complex can be estimated as $\sim$1.5 (H, $C_6H_5$) and $\sim$0.5 s$^{-1}$ ($CH_3$, $C_6H_5$). These

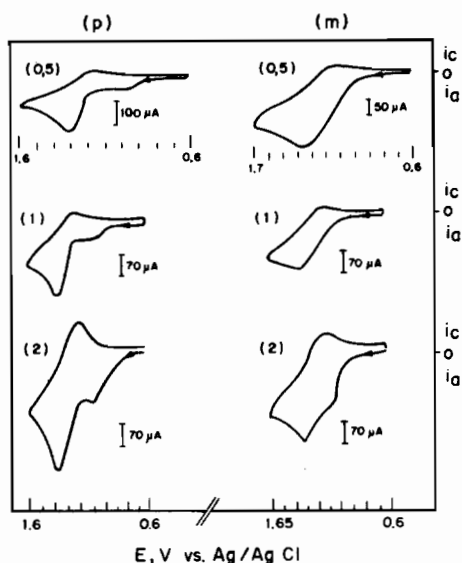Fig. 2. Cyclic voltammograms of $5.0 \times 10^{-4}$ $M$ solutions of the complexes $FeL_3^{2+}$ ($L = C_5H_4N-C(CH_3)=NR_2$) in acetonitrile, 0.2 $M$ TEAP, at 25 °C. The scan rates (V s$^{-1}$) are in parentheses. ($p$) $R_2 = p\text{-}NH_2C_6H_4$; ($m$) $R_2 = m\text{-}NH_2C_6H_4$.



Fig. 3. Cyclic voltammograms of $5.0 \times 10^{-4}$ $M$ solutions of $FeL_3^{2+}$, $L = C_5H_4N-C(CH_3)=N(p\text{-}NH_2C_6H_4)$, in acetonitrile, 0.2 $M$ TEAP, at 25 °C. The scan rates (V s$^{-1}$) are in parentheses.

preliminary results are under detailed investigation. For details on mechanisms and calculations see references 9 and 25.

The electrochemical behavior of all of the compounds with free amino groups, 14, 15, 18 and 19 is also more complex. In the case of $R_1$, $R_2 = CH_3$, $m$- or $p\text{-}NH_2C_6H_4$, Fig. 2 shows examples of cyclic voltammograms as a function of potential scan rate. At slow scan rates the $p$- or $m$-amino derivatives show two oxidation peaks but only one cathodic current peak. As the scan rate is increased, the cathodic peak current increases. Fig. 3 shows the cyclic voltammograms of the two waves separated for the $p$-amino compound. In the range of 0.6 to 1.1 V $vs.$ Ag/AgCl (Fig. 3a), one anodic and one cathodic current peak is observed in the 1–10 V s$^{-1}$ potential scan rate range. The peak potentials is independent of the scan rate and the ratio of anodic to cathodic current peak, calculated according to Nicholson's procedure [27], is unity within the experimental error (5%). The separation between peak potentials is close to 60 mV. The product $i_p v^{-1/2}$ is constant within the experimental error. These characteristics of the cyclic voltammograms indicate that this first oxidation step is a reversible one-electron step, probably associated with the oxidation of the central metal ion. The $E_{1/2}$ are also listed in Table I.

In the 1.1 to 1.6 V $vs.$ Ag/AgCl range (Fig. 3b) only one anodic current peak can be observed. The peak potential shifts approximately 80–100 mV towards more positive potentials with a ten-fold increase in potential scan rate. These data indicate that the electrode process is irreversible. It is likely
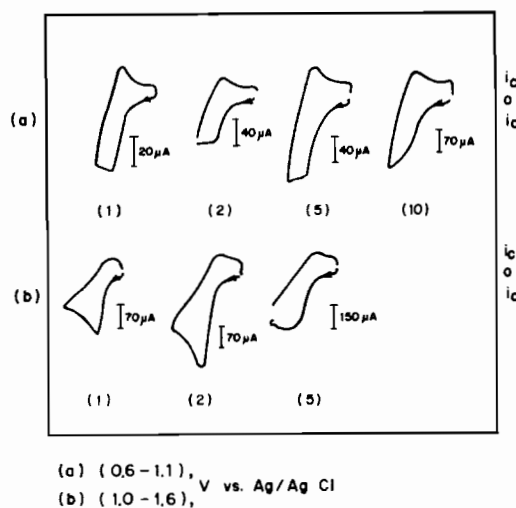
then that the second oxidation wave is associated with the irreversible oxidation of the free amino group. Literature data for the electrochemical oxidation of aromatic amines [28], *e.g.*, aniline, are also irreversible processes. It is very likely that the electrochemical step is coupled with chemical and electrochemical reactions since the oxidation of the amine radical facilitates the dissociation of the complex, as indicated by the cyclic voltammograms over the entire potential range. The irreversible oxidation occurs at 1.30–1.38 V $vs.$ Ag/AgCl (v = 0.5–5 V s$^{-1}$) for the $p$-amino compound and at 1.37–1.47 V $vs.$ Ag/AgCl (v = 0.5–5 V s$^{-1}$) for the $m$-amino derivative.

For the $R_1$, $R_2 = C_6H_5$, $p$- or $m\text{-}NH_2C_6H_4$ derivatives, one can observe only a very drawn out oxidation wave at around 1.3–1.4 V $vs.$ Ag/AgCl. Inspection of Table I for the $R_1$, $R_2 = C_6H_5$, $C_6H_5$ compound shows that $E_{1/2} = 1.31$ V $vs.$ Ag/AgCl. It is reasonable to assume that the concurrent electrochemical oxidation reactions of the central metal ion and of the free amino group are occurring.

*Correlations Between $E_{1/2}$ and Substituent Parameters*

The $E_{1/2}$'s decrease by *ca.* 0.18 V per methyl group replacing hydrogen at the methine carbon both in the aliphatic and mixed series, as can be seen by inspection of Table I. As hydrogen atoms are replaced by electron-donating methyl groups, a higher $\sigma$ bonding ability of the ligands should result, and consequently the decrease of $E_{1/2}$. A similar trend has been observed in suluric acid aqueous solutions [1]. This decrease reflects a higher stabilization of the ferric forms as compared to the stabilization of the
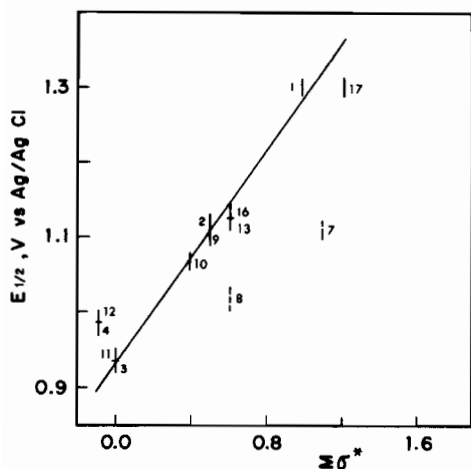
Fig. 4. Half-wave potentials, $E_{1/2}$, of the couples $FeL_3^{3+}/$ $FeL_3^{2+}$ in acetonitrile, 0.2 $M$ TEAP, at 25 °C, as a function of the sum of the polar Taft parameters of the substituents. The numbers refer to the compounds given in Table I.



Fig. 5. Half-wave potentials, $E_{1/2}$, minus steric Taft parameters $(E_s)$, $E_{1/2} - \delta \Sigma E_s$, as a function of the sum of the polar Taft parameters under the same conditions of Fig. 4.



Fig. 6. Square-root of the molar absorptivity $(\epsilon)$ at the absorbance maximum of the inverse charge transfer band as a function of the sum of the polar Taft parameters of the substituents on the iron diiming chromophore. The numbers refer to the compounds given in Table I.

ferrous forms, since the standard electrode potentials (in the case identical to $E_{1/2}$ reflect the difference of free energy of formation of the ferric and ferrous forms. Introduction of amino groups on the phenyl ring of the $R_1$, $R_2 = CH_3$, $C_6H_5$ compounds causes negligible effect in the *meta*-position but a lowering of about 50 mV in the *para*-position, indicating that mesomeric effects, important in the *para*-position, increase electron density of the coordinated nitrogen and therefore stabilize the ferric form more than the ferrous form. An interplay of inductive and steric effects can account for inversions of the direction of the $E_{1/2}$. For instance, compare $R_1$, $R_2 = H$, $CH_3$ and H, $C_2H_5$ and $R_1$, $R_2 = CH_3$, $CH_3$ and $CH_3$, $C_2H_5$.

An interesting coincidence, which has also been observed in aqueous sulfuric acid solutions, is that within the experimental error if R, $R' = R_1$, $R_2$ the resulting half-wave potentials of the compounds are identical (*cf.* compounds n. 2, 9; 3, 11; 4, 12; 13, 16). Therefore, the effect of the pyridine ring on the mixed diimine ligand must be very similar to that of the two $=NCH_3$ groups. This similarity is only broken when comparing the $CH_3$, $C_6H_5$ compounds (*cf.* 8 with 13, 16). This departure is easily explained by the fact that in the aliphatic series the phenyl groups can interact *via* mesomeric effects with the diimine structure. On the other hand, this cannot occur in the mixed diimine ligands because the pyridine moiety and the methyl groups preclude planar arrangement of the phenyl and the diimine groups, as shown by theoretical calculations by Favini and Simonetta [29] on analogous compounds.

These results can be best explained in terms of correlations of $E_{1/2}$ with substituent Taft parameters [30]. As was observed for several substituted aromatic diimine complexes [31], and in the previous
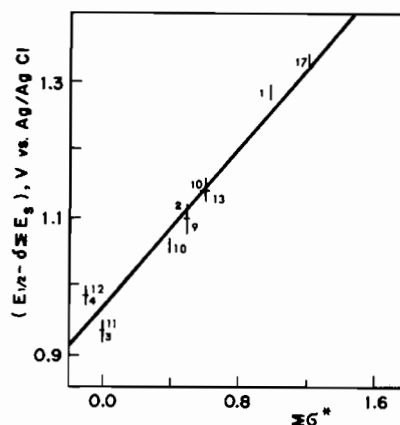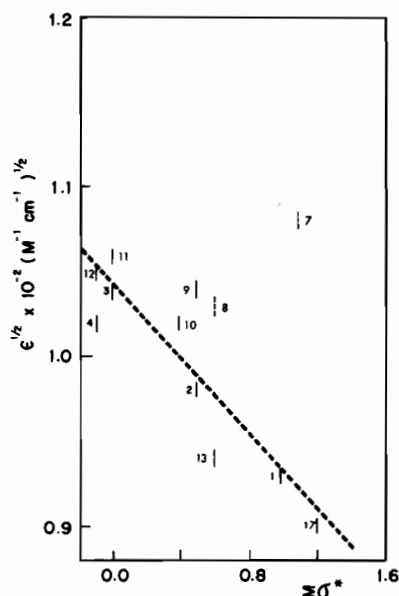
paper of this series [1], the polar effects are additive. A plot of $E_{1/2}$ *vs.* $\Sigma \sigma^*$ for all substituents on the diimine chromophore is shown in Fig. 4. This correlation considers that the effect of the pyridine ring is identical to that of two $=NCH_3$ groups, *i.e.*, zero. The figure does not include data for the cyclohexanedione derivatives or free amino-containing compounds. The correlation obtained is reasonable (C.C. = 0.93) but one notices that substituents presenting large steric effects depart from linearity. Since compounds 7 and 8 present mesomeric interaction of the phenyl group with the diimine chromophore, these compounds

should not fall in line in a correlation with polar parameters, which ostensibly exclude resonance effects.

The steric effects, $E_s$, can be considered in first approximation by considering that these effects are also additive. A general equation [30] can be

$$E_{1/2} = E_{1/2o} + \rho^*\Sigma\sigma^* + \delta\Sigma E_s$$

applied and one obtains $E_{1/2} = 0.97 + 0.29 \Sigma\sigma^* + 0.006 \Sigma E_s$. A plot of $E_{1/2} - 0.006 \Sigma E_s$ is shown in Fig. 5, where a much better linear correlation is obtained (C.C. = 0.995).

### Absorption Spectra in the 400–650 nm Region

It is well known that the visible absorption spectra of the iron diimine complexes with aliphatic [3] or mixed [22] ligands present a very strong band with a shoulder towards smaller wavelengths. This band is assigned to an inverse charge transfer from the filled metal orbitals to the empty ligand $\pi^*$ orbitals ($t_2 \rightarrow \pi^*$) [11]. Interpretation of the structure of this band as a vibrational progression of the electronic transition was first suggested by Krumholz [32] and further supported more recently by resonance Raman data by Nakamoto, et al. [33] (cf. reference 21).

Table I also contains the spectral data obtained in acetonitrile, 0.2 M TEAP, the wave numbers ($\bar{\nu}$) at the absorption maxima of the inverse charge transfer bands and the corresponding molar absorptivities ($\epsilon$) at these wave numbers.

Figure 6 shows a correlation between the square-root of the molar absorptivities ($\epsilon$) with the sum of the polar Taft parameters. Except for compounds 7, 8, which present mesomeric effects unaccounted for by Taft polar parameters, the remaining compounds seem to correlate approximately linearly $E_{1/2}$ with $\Sigma\sigma^*$ (C.C. = 0.9). A better correlation is obtained by considering only the aliphatic series. Again, steric effects may affect this correlation. Similar linear correlations between $E_{1/2}$ and polar Taft values have been found by Brown [34]. Inclusion of steric effects in this type of correlation has not been very successful [30]. From the correlation of Fig. 6 one estimates rough values for $\Sigma\sigma^*$ for the cyclohexanedione derivatives as about −0.6, in good agreement with the data estimated in 10 M $H_2SO_4$ [1]. By using this polar Taft value and the correlation of Fig. 5, one obtains for the steric effects $E_s$ ~2 × 10, of the same order of magnitude of those estimated in 10 M $H_2SO_4$.

Since the frequencies of the inverse charge transfer bands are associated with an intramolecular electron transfer, which can be considered an intramolecular redox process, one should expect correlations between these frequencies and the standard electrode potentials for a series of structurally similar compounds. Vlcek [35] has pointed out the conditions for obtaining linear correlations between $E^o$ and the
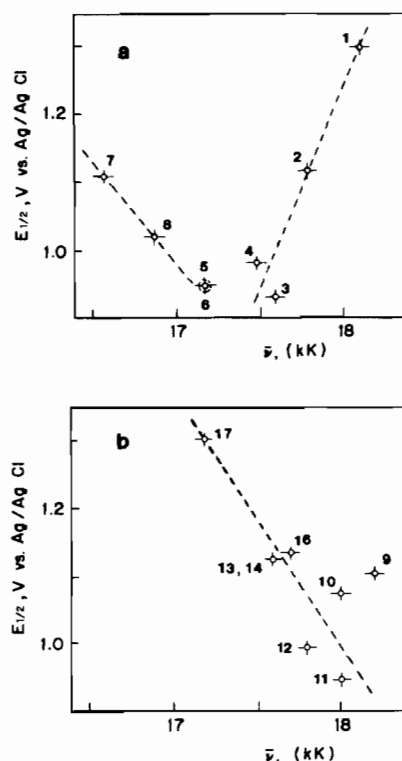


Fig. 7. Half-wave potentials, $E_{1/2}$, of the couples $FeL_3^{3+}/FeL_3^{2+}$ as a function of the wavenumbers at the absorbance maxima of the inverse charge transfer band, $t_2 \rightarrow \pi^*$, in acetonitrile, 0.2 M TEAP, at 25 °C. a) Aliphatic diimine series, and b) mixed diimine series. The numbers refer to the compounds given in Table I.

frequencies of charge transfer bands. The correlations obtained so far have been observed for series of a limited number of complexes. Fig. 7 shows a plot of $E_{1/2}$ vs. $\bar{\nu}$ for the aliphatic series (a) and mixed (b). In both series there seems to be a trend of decrease of $E_{1/2}$ with decrease of $\bar{\nu}$ for small substituents (cf. in 7a 1, 2 and 3, and in 7b 9 and 10). However, as the ligands become bulkier the reverse dependence is observed, i.e., the smaller the $\bar{\nu}$ the larger $E_{1/2}$. These opposite trends can be rationalized in terms of the difference in solvation energies of the oxidized and reduced species, which would depend strongly on the complexity of the ligands, and influence the $E_{1/2}$ values but not the energy of the charge transfer band [35]. The electronic affinity of the ligands may also be changing, principally by addition of phenyl groups. The change of this affinity would influence the frequencies of the charge transfer bands but not appreciably the values of the standard electrode potentials [35].

### Conclusion

This paper presents correlations between thermodynamic and spectral properties with the sum of

substituent Taft's [30] parameters for iron complexes of aliphatic and mixed (aliphatic–aromatic) diimine ligands. The polar effect of the aromatic pyridine moiety on the half-wave potentials is found to be identical to that of the two $=N–CH_3$ groups in acetonitrile. This fact has also been observed in aqueous sulfuric acid solutions [1]. Interesting correlations between the half-wave potentials for the reversible electrochemical oxidation processes and the frequencies of the inverse charge transfer bands have been found for fifteen complexes. Ligand-oxidation reactions were observed under certain conditions for the compounds with $H_3CN=C(H, CH_3)–C(C_6H_5) =NCH_3$ ligands.

## Acknowledgements

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