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Voltammetric Studies of Tris(1-pyrrolidinecarbodithioato)manganese(III) and -iron(III) and Bis(1-pyrrolidinecarbodithioato)copper(II) in Nonaqueous Solvents

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The voltammetric behavior of the title complexes has been studied. These complexes give a one-electron oxidation wave and a one-electron reduction wave in most solvents. A linear correlation between the ($E_{1/2}^{ox}-E_{1/2}^{red}$) values and the solubility parameters of the solvents was obtained. The ($E_{1/2}^{ox}-E_{1/2}^{red}$) values were interpreted in terms of the solvation energy of the complexes.

A number of electrochemical studies of transition metal complexes with *N,N*-disubstituted dithiocarbamates have been reported. Considerable work has been carried out at the platinum electrode in acetone or acetonitlile as the solvent, where the electrode reactions have been shown to be relatively simple; *e.g.*, the dithiocarbamato complexes of the first-row transition metals from chromium to copper give a one-electron oxidation wave as well as a one-electron reduction wave.[1–7] Solvent effects on the redox potential of complexes have been widely studied. Golding *et al.*[8] investigated the redox behavior of iron(III) dithiocarbamates and interpreted the variation in the redox potentials of the complexes in acetone–water solutions by considering the effect of the solvent as a perturbation of the energy-level scheme. Recently Austrian workers have described the solvent effects on the half-wave potentials of tetraethylammonium hexacyanoferate(III)[9] and hexacyanomanganate(III),[10] tris(ethylenediamine)cobalt(III) perchlorate,[11] and tris(acetylacetonato)manganese(III)[12] by means of the donor-acceptor approach. In the present paper the voltammetric behavior of manganese(III), iron(III), and copper(II) complexes with 1-pyrrolidinecarbodithioate [$Mn(pcd)_3$, $Fe(pcd)_3$, and $Cu(pcd)_2$] is examined in eleven nonaqueous solvents, and the solvent effects are discussed.

Experimental

$Mn(pcd)_3$, $Fe(pcd)_3$, and $Cu(pcd)_2$ were prepared according to previously described methods.[3,13,6] All the solvents used were purified in a conventional manner.[14,15] Tetrabutylammonium perchlorate (TBAP) was prepared by metathesis from an aqueous solution of sodium perchlorate and tetrabutylammonium bromide, which has been synthesized with tributylamine and butyl bromide, thoroughly washed with water, and recrystallized twice from ethanol. The voltammetric studies were carried out at the platinum disk electrode by the rotating electrode method, cyclic voltammetry, pulse voltammetry, and differential pulse voltammetry with a Yanagimoto P-1000-type polarograph. An aqueous SCE and a platinum wire were used as the reference electrode and the counter electrode respectively. All the sample solutions containing 0.1 M TBAP as supporting electrolyte were deoxygenated with pre-dried nitrogen and kept in the dark throughout the experiment because the complexes were relatively unstable to light.

Results and Discussion

Studies of the diffusion current are described for only $Fe(pcd)_3$ in this paper because $Cu(pcd)_2$ is slightly soluble in most solvents used and $Mn(pcd)_3$ decomposes slowly in solution except in the cases of *N,N*-dimethylformamide and dimethyl sulfoxide, in which $Mn(pcd)_3$ decomposes immediately. $Fe(pcd)_3$ underwent both a one-electron oxidation to $Fe(pcd)_3^+$ and a one-electron reduction to $Fe(pcd)_3^-$ in all the solvents studied. The limiting current at the rotating electrode was proportional to the square root of the rotation speed, and the peak current in cyclic voltammetry was proportional to the square root of the scan rate, indicating that both the electrode reactions in the respective solvents are controlled by diffusion. The differential pulse and the cyclyc voltammetric behavior shows that the electrode reaction of the oxi-

TABLE 1. THE PULSE VOLTAMMETRIC AND THE CONVECTIVE DIFFUSION CURRENTS OF THE OXIDATION WAVE OF $Fe(pcd)_3$

Solvent	$\frac{10^2\eta}{\text{g cm}^{-1}\text{ s}^{-1}}$	$\frac{I_dC^{*-1}}{\text{A mol}^{-1}\text{ cm}^3}$	$\frac{I_l\omega^{-1/2}C^{*-1}}{\text{A s}^{1/2}\text{ mol}^{-1}\text{ cm}^3}$	$I_dC^{*-1}\eta^{1/2}$	$10^2(I_l\omega^{-1/2}C^{*-1})(\eta^{5/6}d^{-1/6})$[a]
Acetone	0.302	68.8	4.67	3.78	3.86
Acetonitrile	0.399	69.4	4.45	4.04	4.06
Dichloromethane	0.412	61.3	4.04	3.93	3.97
Isobutyl methyl ketone	0.542	50.3	2.66	3.70	3.56
Nitromethane	0.627	50.5	2.96	4.00	4.23
N,N-Dimethylformamide	0.796	43.3	2.26	3.86	4.07
Nitrobenzene	1.811	26.1	1.13	3.51	3.88
Dimethyl sulfoxide	1.996	24.3	1.01	3.43	3.81

a) *d*: density of the solvent in g cm^{-3}.

dation and the reduction are reversible or nearly reversible, and that the oxidation process is more reversible than the reduction process in the respective solvents. Table 1 shows that there is a marked dependence of the normalized pulse voltammetric diffusion current (I_d/C^*) and the normalized convective diffusion current ($I_l/\omega^{1/2}C^*$) of the oxidation wave for Fe(pcd)$_3$ on the viscosity of the solvents (η). Fe(pcd)$_3$ is too insoluble in the alcohols for us to obtain reliable data on the normalized diffusion currents. According to the Cottrell equation, the pulse voltammetric diffusion current is proportional to the square root of the diffusion coefficient (D). Using the Stokes-Einstein relation, $I_d\eta^{1/2}/C^*$ can be expected to be constant, provided the diffusion coefficient is due solely to a change in the viscosity. The value of $I_d\eta^{1/2}/C^*$ in Table 1 are almost constant, indicating that there is no specific interaction between Fe(pcd)$_3$ and the molecule of each solvent. As is shown in Table 1, this is also confirmed by the rotating disk electrode method with the aid of the Levich equation and the Stokes-Einstein relation.

The half-wave potential of the oxidation ($E^{\text{ox}}_{1/2}$) and the reduction ($E^{\text{red}}_{1/2}$) of the pcd complexes were found to vary appreciably with different solvents. To aviod the difficulty in evaluating the liquid-junction potential between the reference electrode used (SCE) and the solvent studied, the difference between $E^{\text{ox}}_{1/2}$ and $E^{\text{red}}_{1/2}$ was used to discuss the solvent effect. The ($E^{\text{ox}}_{1/2}-E^{\text{red}}_{1/2}$) values for Fe(pcd)$_3$, Mn(pcd)$_3$, and Cu(pcd)$_2$ are listed in Table 2, together with the solubility parameter (δ),[16,17] the relative dielectric constant (ε), the donor number (DN),[18] and the acceptor number (AN),[19] of the solvents. As may be seen from Table 2, there is a correlation only between the ($E^{\text{ox}}_{1/2}-E^{\text{red}}_{1/2}$) values and the solubility parameters. When the oxidation and the reduction processes at the rotating electrode are reversible, $E^{\text{ox}}_{1/2}$ and $E^{\text{red}}_{1/2}$ can be written as follows:

$$E^{\text{ox}}_{1/2} = E^{\circ}_{\text{ox}} + (RT/F)\ln(f_{\text{M}^+}D_{\text{M}}{}^{2/3}/f_{\text{M}}D_{\text{M}^+}{}^{2/3}) \tag{1}$$

and:

$$E^{\text{red}}_{1/2} = E^{\circ}_{\text{red}} + (RT/F)\ln(f_{\text{M}}D_{\text{M}^-}{}^{2/3}/f_{\text{M}^-}D_{\text{M}}{}^{2/3}) \tag{2}$$

where E°_{ox} and E°_{red} are the standard potentials of the M/M$^+$ and M$^-$/M couples respectively, and where f is the activity coefficient, the subscripts M, M$^+$, and M$^-$ representing the neutral complex, the cation formed by oxidation, and the anion formed by reduction respectively. By applying the Born-Haber cycle, the ($E^{\circ}_{\text{ox}}-E^{\circ}_{\text{red}}$) can be written as follows:

$$F(E^{\circ}_{\text{ox}}-E^{\circ}_{\text{red}}) = I_{\text{p}} - E_{\text{A}} + \Delta G^{\text{s}}_{\text{M}^+} + \Delta G^{\text{s}}_{\text{M}^-} - 2\Delta G^{\text{s}}_{\text{M}}, \tag{3}$$

where I_{P} and E_{A} are the ionization potential and the electron affinity of the neutral complex respectively, and where ΔG^{s} is the solvation energy. From Eqs. 1—3, the ($E^{\text{ox}}_{1/2}-E^{\text{red}}_{1/2}$) can be expressed by:

$$F(E^{\text{ox}}_{1/2}-E^{\text{red}}_{1/2}) = I_{\text{p}} - E_{\text{A}} + \Delta G^{\text{s}}_{\text{M}^+} + \Delta G^{\text{s}}_{\text{M}^-} - 2\Delta G^{\text{s}}_{\text{M}} + 2RT\ln(f_{\text{M}^\pm}/f_{\text{M}}) + (2/3)RT\ln(D_{\text{M}}{}^2/D_{\text{M}^+}D_{\text{M}^-}). \tag{4}$$

Among the values of the last five terms on the right-hand side of Eq. 4, which may vary with different solvents, those of the last two terms are considered to be almost constant. The solvation energy of the ion is predominantly electrostatic in nature and is, then, expressed by the modified Born equation.[20] The variation in the ΔG_{M^+} and ΔG_{M^-} with different solvents, evaluated from the modified Born equation with the crystallographic radius of 6.42 Å for Fe(pcd)$_3$,[21] is too little to explain the difference in ($E^{\text{ox}}_{1/2}-E^{\text{red}}_{1/2}$). Consequently, the remaining term, that is, the solvation energy of the neutral complex, must be largely responsible for the difference in ($E^{\text{ox}}_{1/2}-E^{\text{red}}_{1/2}$) values. When the complex with a solubility parameter, δ_{M}, is transferred from the gas phase to the polar solvent of the molar volume, V_{S}, and solubility parameter, δ_{S}, ΔG_{M} is approximately expressed by:[22]

$$\Delta G_{\text{M}} = V_{\text{S}}\delta_{\text{S}}(\delta_{\text{S}}-\delta_{\text{M}}). \tag{5}$$

Since the first and second terms on the right-hand side of Eq. 4 are inherent in the complexes, and since the remaining terms except ΔG_{M} are considered to be almost constant in all the solvents studied, Eq. 4 can be written as:

$$F(E^{\text{ox}}_{1/2}-E^{\text{red}}_{1/2}) = -2V_{\text{S}}\delta_{\text{S}}(\delta_{\text{S}}-\delta_{\text{M}}) + k \tag{6}$$

or:

$$F(E^{\text{ox}}_{1/2}-E^{\text{red}}_{1/2}) + 2V_{\text{S}}\delta_{\text{S}}{}^2 = 2V_{\text{S}}\delta_{\text{S}}\delta_{\text{M}} + k. \tag{7}$$

Figure 1 shows the plot of the value of the left-hand side of Eq. 7 for Fe(pcd)$_3$ *vs.* $2V_{\text{S}}\delta_{\text{S}}$. It gives a straight line with a slope of 11.44 (cal cm^{-3})$^{1/2}$, corresponding to the δ_{M} of Fe(pcd)$_3$. The δ_{M} values of Mn(pcd)$_3$

TABLE 2. SOLVENT PARAMETERS AND ($E^{\text{ox}}_{1/2}-E^{\text{red}}_{1/2}$) VALUES

No.	Solvent	δ/(cal cm^{-3})$^{1/2}$	ε	DN	AN	$E^{\text{ox}}_{1/2}-E^{\text{red}}_{1/2}$/mV		
						Cu(pcd)$_2$	Fe(pcd)$_3$	Mn(pcd)$_3$
1	Isobutyl methyl ketone	8.58	13.1	—	—	1111	996	524
2	Acetone	9.62	20.7	17.0	12.5	1052	954	485
3	Dichloromethane	9.88	9.0	—	20.4	1038	930	473
4	Nitrobenzene	11.06	34.8	4.4	14.8	995	879	417
5	*N*,*N*-Dimethylformamide	11.79	36.7	26.6	16.0	960	860	—
6	Acetonitrile	12.11	36.0	14.1	18.9	924	841	387
7	Nitromethane	12.90	36.0	2.7	20.5	911	811	359
8	Dimethyl sulfoxide	12.97	46.6	29.8	19.3	865	766	—
9	1-Propanol	12.18	20.4	—	—	880	714	301
10	Ethanol	12.78	24.3	—	37.1	850	700	297
11	Methanol	14.50	32.6	19.0	41.3	808	645	231

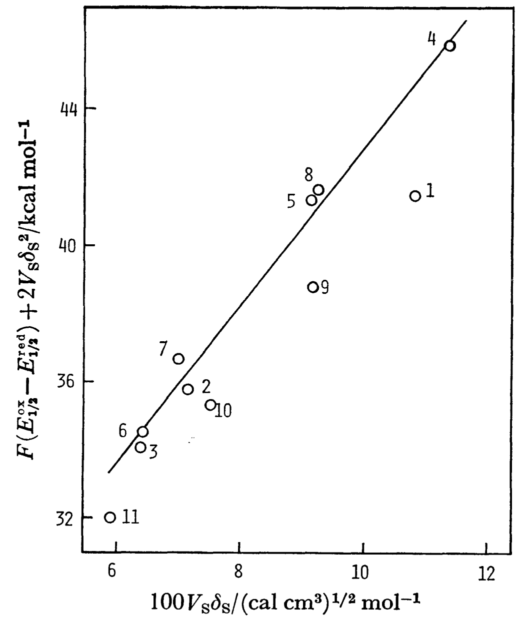

Fig. 1. Plot of Eq. 7 for $Fe(pcd)_3$.
Numbers correspond to those in Table 2.

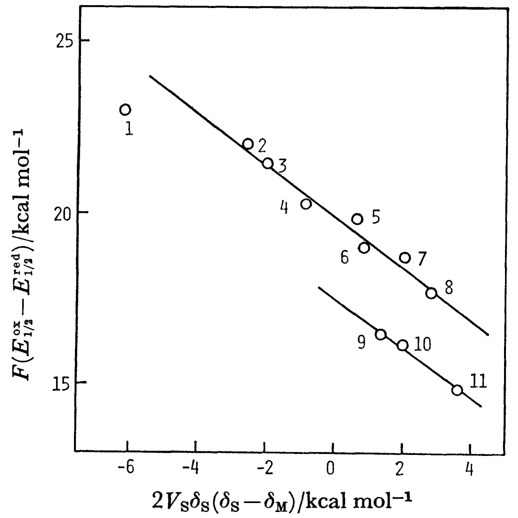

Fig. 2. Plot of Eq. 6 for $Fe(pcd)_3$.
δ_M: 11.44 (cal cm^{-3})$^{1/2}$. Numbers correspond to those in Table 2.

and $Cu(pcd)_2$, as obtained from a similar plot, are 11.40 and 11.32 (cal cm^{-3})$^{1/2}$ respectively. These δ_M values are considered reasonable compared with the value of other complexes.[23] Using the δ_M value thus evaluated, the $(E^{ox}_{1/2}-E^{red}_{1/2})$ value was plotted against $V_S\delta_S(\delta_S-\delta_M)$. The plot for $Fe(pcd)_3$ is shown in Fig. 2, which gives two straight lines, one for the aprotic solvents, and the other, for the alcohols. These linear relationship indicates that Eq. 6 is a valid expression of the solvent effect. The difference between the alcohols and the other solvents may be due to the difference in the entropy change of the solvation being neglected in Eq. 5. Similar relations were obtained for $Mn(pcd)_3$ and $Cu(pcd)_2$. It may be concluded from these results that the variation in the half-wave potential of these pcd complexes with different solvents is not dependent on the solvation energy of the ions formed by oxidation and reduction, but is dependent on the solvation energy of the neutral complexes.

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