Whether this proceeds completely or equilibria similar to (2) exist in the solutions cannot be decided on the basis of the present results.

The spectral behavior is qualitatively similar to that of the salicylaldimines.[12,54–56] Interestingly, whereas ((sal)$_2$en)Cu exists as a dark green dimer[57,58] in the crystalline state and gives violet monomeric solutions in, *e.g.*, chloroform, the complex ((hac)$_2$en)Cu is violet both in the solid state and in solution. Electronic spectra are very similar in both phases. Apparently solid-state dimerization does not occur in the case of ((hac)$_2$en)Cu.

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Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Electrochemistry of Transition Metal Dithienes. I. Bis(maleonitriledithiolate)nickel(II) in Acetonitrile

By PETER JAMES LINGANE

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Chronopotentiometry and linear-scan voltammetry are used to demonstrate that the oxidation of $Ni(mnt)_2^{2-}$ and the reduction of $Ni(mnt)_2^-$ are diffusion controlled in acetonitrile in the presence of $(C_2H_5)_4NClO_4$ and that neither species is electroactively adsorbed onto platinum. Electron transfer is exceedingly rapid, $k_{s,h} > 1$ cm sec^{-1}. The substantial decrease in anionic mobility with increasing negative charge is attributed to the electrostriction effect. Vapor pressure osmometry demonstrates that $Ni(mnt)_2^{2-}$ but not $Ni(mnt)_2^-$ is ion paired, $K_f \approx 500\ M^{-1}$. After correction for ion-pair formation and changes in activity coefficients, $E° = -(0.17 \pm 0.01)$ V *vs.* Ag$^+$(0.01 *M*)|Ag.

Introduction

Voltammetric and polarographic current–potential curves proved to be exceedingly useful for demonstrating the existence and interconversion of the several members of particular transition metal 1,2-dithiene oxidation–reduction series. Such experiments have also demonstrated ligand exchange between complexes and the dimeric nature of certain iron and cobalt bis complexes in dichloromethane. Half-wave potentials have guided synthetic work and served for the comparison of relative thermodynamic stabilities.[1,2] We are investigating the kinetics of the electrochemical interconversion of representative dithiene complexes and in this communication we present our results for nickel complexes with the maleonitriledithiolate ligand in acetonitrile. We have demonstrated that the electron-transfer step for the oxidation of bis(maleonitriledithiolate)nickel(II), $Ni(mnt)_2^{2-}$, is exceedingly rapid at platinum and is uncomplicated by electrochemically significant solution reactions. This complex and its one-electron oxidation product $Ni(mnt)_2^-$ are not adsorbed onto platinum. $Ni(mnt)_2^{2-}$ but not $Ni(mnt)_2^-$ is ion paired with the supporting electrolyte cation. Activity coefficient and ion-pairing corrections accurately reproduce the shift of half-wave potential with supporting electrolyte concentration. The fortuitous use of larger cation electrolytes and/or a single electrolyte concentration doubtless prevented the earlier observation of this ion-pairing phenomenon.

Experimental Section

The synthesis of transition metal dithiolates has been reviewed.[3] The salts $[(CH_3)_4N]_2Ni(mnt)_2$, $[(C_2H_5)_4N]_2Ni(mnt)_2$, $[(C_2H_5)_4N]_2$-$Pt(mnt)_2$, and $[(C_2H_5)_4N]Ni(mnt)_2$ were prepared as previously described;[4] elemental analyses were in excellent agreement with the theoretical stoichiometries.

This system appears to be insensitive to small amine and unsaturated nitrile impurities in the acetonitrile since no differences were observed using Eastman practical grade acetonitrile purified by method F of Forcier and Olver,[5] the second distillation being from sulfuric acid, as compared with Matheson Coleman and Bell Spectro Grade solvent. Water content is also relatively unimportant since the deliberate addition of 1% water does not affect the position or shape of linear-scan voltammograms.

Tetraethylammonium perchlorate was obtained from Eastman Chemical Co. (White Label) and was recrystallized from water and dried at room temperature in a vacuum desiccator. Benzil of unknown origin was recrystallized three times from ethanol–water.

The Ag–Ag$^+$(0.01 *M*),$(C_2H_5)_4NClO_4$(0.1 *M*) electrode in acetonitrile solvent was used as the reference electrode in order to avoid any possible difficulties in reproducing the liquid junction

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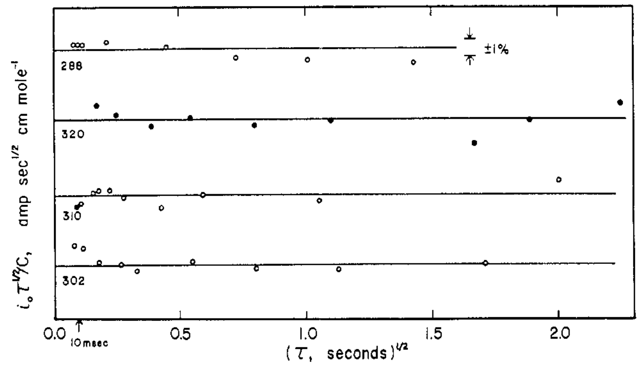

Figure 1.—Plots of the chronopotentiometric constant *vs.* square root of transition time for oxidation of $Ni(mnt)_2^{2-}$ and $Pt(mnt)_2^{2-}$ in AN. From top to bottom: $Ni(mnt)_2^{2-}$ in 0.4 M $(C_2H_5)_4NClO_4$, 0.1 M $(C_2H_5)_4NClO_4$, and 0.032 M $(C_2H_5)_4NClO_4$; and $Pt(mnt)_2^{2-}$ in 0.1 M $(C_2H_5)_4NClO_4$. Intercept values are indicated on the figure.

between acetonitrile and an aqueous calomel reference electrode. This electrode was isolated from the test solution with a cracked-glass frit. The potentials reported here may be converted to potentials *vs.* the aqueous KCl saturated calomel electrode by *adding* 291 ± 1 mV.[6] These potentials may be converted to potentials *vs.* the aqueous NaCl saturated calomel electrode used by Davison, *et al.*,[7] by adding 283 ± 2 mV.

The linear-sweep voltammetric experiments were carried out with operational amplifier circuitry of conventional design.[8] The chronopotentiometric experiments employed a 360-V battery bank in series with a large dropping resistor as the constant-current source; a break-before-make relay was employed to avoid shorting the working and auxiliary electrodes momentarily during the switch from the dummy circuit to the cell circuit.[9]

The working electrode was an unshielded planar platinum disk, Beckman No. 39273, of area 0.203 cm². The auxiliary electrode was a flat coil of platinum wire immersed in the test solution. The cell resistance was measured to be 280 ohms at 1000 Hz for a solution 0.4 M in $(C_2H_5)_4NClO_4$.

The vapor pressure measurements employed a Hewlett-Packard Model 302 vapor pressure osmometer and were carried out at 37° All other experiments were conducted at 25.0 ± 0.1°.

Solutions for the electrochemical experiments were deaerated with argon.

Chronopotentiometric Results

Measured values of the chronopotentiometric constant $i_0\tau^{1/2}/C$[10] are plotted as a function of $\tau^{1/2}$[11] in Figure 1 for the oxidation of $Ni(mnt)_2^{2-}$ and $Pt(mnt)_2^{2-}$ for several supporting electrolyte concentrations. Data for the reduction of $Ni(mnt)_2^{-}$ are similar. Because no upturn is observed at the shorter transition times, we can conclude that these species are not electroactively adsorbed to a significant extent under these conditions.[12] Because no downturn is observed at the shorter transition times, we can conclude that the electron-transfer step is not preceded by a chemical transformation of half-life comparable to the shortest transition times (about 10 msec) employed. Current-reversal experiments with these systems using forward electrolysis times of about 1 sec yielded the theoretical ratio within about 5%. Consequently, the reaction $Ni(mnt)_2^{-} + e = Ni(mnt)_2^{2-}$ appears to be diffusion controlled and free of any complications. Less extensive data at other concentrations indicate that this conclusion is independent of the complex concentration over the range 1–10 mM.[13]

TABLE I

	$[(C_2H_5)_4NClO_4]$, M					
	0.4		0.10		0.032	
	Volt.	Chrono	Volt.	Chrono	Volt.	Chrono
			1. $Ni(mnt)_2^{2-}$			
$E_{1/2}$, mV	−56	−56	−84 ± 3[a]	−83	−102	−100
10^5D, cm²/sec	1.12	1.14	1.36 ± 0.04[a]	1.40	1.42	1.32
			2. $Ni(mnt)_2^{-}$			
$E_{1/2}$, mV	−58		−87	−89[b]	−110	
10^5D, cm²/sec	1.49		1.76 ± 0.06[a]	1.77	1.78	
Mean $E_{1/2}$, mV	−57[c]		−86		−105[c]	

[a] Mean of two determinations. [b] Precipitate appeared subsequently in reference electrode compartment. [c] Neglects slight correction (±2 mV) for difference in liquid-junction potentials.

Diffusion coefficients calculated from eq 1, the Sand equation, are summarized in Table I for the nickel

$$i_0\tau^{1/2}/C = F\pi^{1/2}D^{1/2}/2 \qquad (1)$$

complexes. For $Pt(mnt)_2^{2-}$, D is 1.26×10^{-5} cm² sec^{-1} in 0.1 M supporting electrolyte. The significant decrease in D for the nickel complexes in 0.4 M $(C_2H_5)_4NClO_4$ probably results from the increased viscosity of this solution.

The chronopotentiometric potential–time curve for a one-electron oxidation process is given by eq 2 and was obtained by combining eq 2-14, 8-5, and 8-6 in ref 10.

$$\left(\frac{\pi D_R}{4k_{s,h}{}^2\tau}\right)^{1/2} = \left(\frac{tD_R}{\tau D_O}\right)^{1/2}\gamma_O \exp\left(\frac{-\alpha F}{RT}(E - E^\circ)\right) - \left[1 - \left(\frac{t}{\tau}\right)^{1/2}\right]\gamma_R \exp\left(\frac{(1-\alpha)F(E - E^\circ)}{RT}\right) \qquad (2)$$

This equation is applicable to the oxidation $Ni(mnt)_2^{2-} = Ni(mnt)_2^{-} + e$, where γ_O and γ_R are the activity coefficients of the $Ni(mnt)_2^{-}$ and $Ni(mnt)_2^{2-}$ species and E° is the standard (reduction) potential of the couple. Here, $\gamma_R/\gamma_O \approx \gamma_\pm{}^3$.

If $k_{s,h}\tau^{1/2}$ is very large, eq 2 reduces to the form familiar for a "reversible" process at 25°

$$E = E_{1/2} - 0.059 \log [(\tau/t)^{1/2} - 1] \qquad (3)$$

where $E_{1/2}$ is the (polarographic) half-wave potential and is given by

$$E_{1/2} = E^\circ - 0.059 \log [\gamma_\pm{}^3(D_O/D_R)^{1/2}] \qquad (4)$$

Plots of E *vs.* log $[(\tau/t)^{1/2} - 1]$ are linear for the oxidation of both $Ni(mnt)_2^{2-}$ and $Pt(mnt)_2^{2-}$ and for the reduction of $Ni(mnt)_2^{-}$ and have the expected slope even at very short transition times (Figure 2). Conse-

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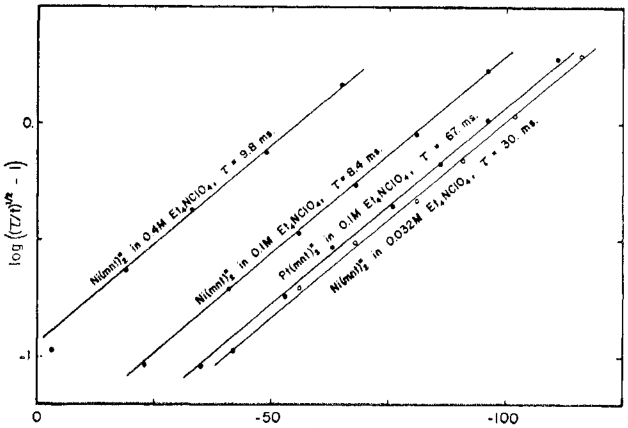

Figure 2.—Plots for electrochemical reversibility for the oxidation of $Ni(mnt)_2^{2-}$ and $Pt(mnt)_2^{2-}$ in AN. The potentials have been corrected for uncompensated resistance. The lines are drawn with slopes of 59 mV.

quently, the rate constants for these heterogeneous electron-transfer reactions must be quite large.

Although we cannot determine rate constants from our data since the systems appear reversible even at the highest current densities, we can set lower limits by determining the smallest values of $k_{s,h}$ such that the fit of the data to eq 2, assuming α equal to 0.5 and $D_O/D_R = 1$, is equally good as the fit of the data to eq 3. The χ^2 test was chosen as the goodness of fit criterion.[14]

This novel approach is preferred to the log plots of Figure 3 because the result is less qualitative and, of most importance, because the limit set on $k_{s,h}$ will automatically reflect the magnitude of the experimental error, moving to lower values for data of lower precision, and the magnitude of the transition time, moving to higher values for data at shorter transition times.

In Figure 3, χ^2 is plotted as a function of $k_{s,h}/D^{1/2}$ for the nickel data of Figure 2. As anticipated, the values of χ^2 decrease rapidly with increasing $k_{s,h}$ and then become constant. From the position of the transition we conclude that $k_{s,h}$ must be at least 1 cm sec^{-1}. Assuming the Marcus relationship, $k_{el} \gtrsim \sqrt{k_{ex}/10^3}$, this translates into a homogeneous electron-exchange rate of at least 1000 M^{-1} sec^{-1}. The shifts in the position of the transition for the three curves in Figure 3 most likely reflect differences in the precision of the data and in the values of τ and should not be interpreted as implying that $k_{s,h}$ is a function of supporting electrolyte concentration. The heterogeneous exchange rate for the $Pt(mnt)_2^{-}$–$Pt(mnt)_2^{2-}$ couple appears equally fast. $k_{s,h}$ values of this magnitude are rare; they exceed the constants appropriate to the halogen–halide couples at platinum electrodes, for example.[15]

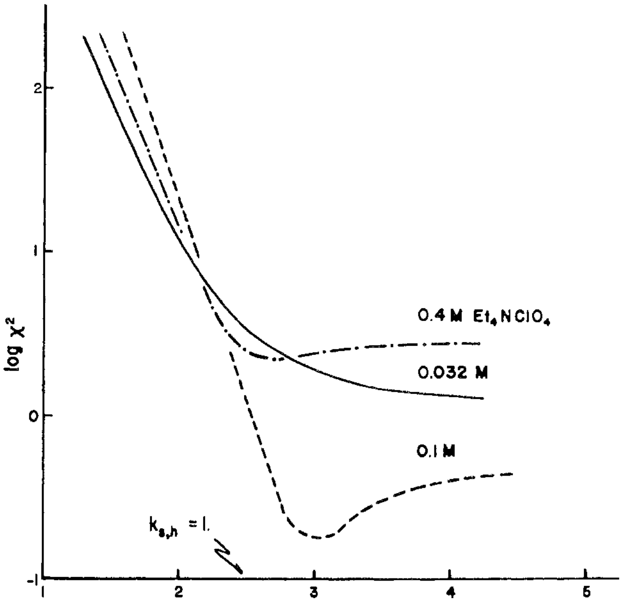

Figure 3.—χ^2 plots to set lower limit on $k_{s,h}$ for oxidation of $Ni(mnt)_2^{2-}$ in AN for three supporting electrolyte concentrations.

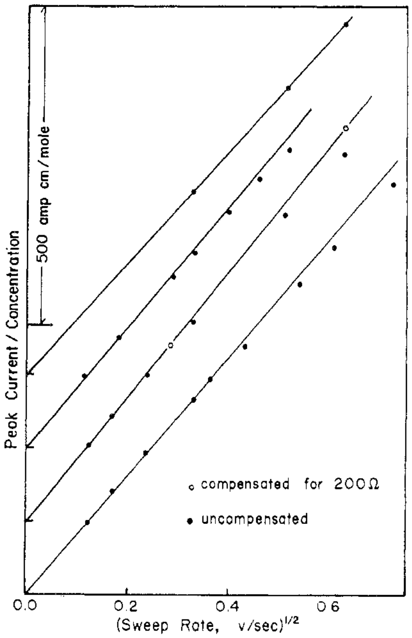

Figure 4.—Plots of normalized peak current *vs.* square root of sweep rate for oxidation of $Ni(mnt)_2^{2-}$ and $Pt(mnt)_2^{2-}$ in AN. From top to bottom: $Ni(mnt)_2^{2-}$ in 0.4 M $(C_2H_5)_4NClO_4$, 0.1 M $(C_2H_5)_4NClO_4$, and 0.032 M $(C_2H_5)_4NClO_4$; and $Pt(mnt)_2^{2-}$ in 0.1 M $(C_2H_5)_4NClO_4$.

Linear-Scan Voltammetric Results

The peak current density for the initial scan is given by eq 5 for a diffusion-controlled, reversible system.[16]

$$i_p = 2.72 \times 10^5 n^{3/2} D^{1/2} \nu^{1/2} C \qquad (5)$$

ν is the sweep rate in volts per second. As may be seen in Figure 4, the peak current densities fall slightly below the theoretical values at the higher sweep rates due to the presence of uncompensated resistance, R_u. As may also be seen in Figure 4, the curvature of the plots disappears upon feeding back to the summing point of the control amplifier a signal equal to iR_u.[8] Values of D calculated from the slopes of these plots are summarized in Table I and are in agreement with the chronopotentiometric values.

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Both the chronopotentiometric quarter-wave potential, which is given by eq 3 with $t = \tau/4$, and the linear-scan peak potential, which is given by eq 6,[16] should be independent of either the current density or sweep rate

$$E_p = E_{1/2} \pm 0.028 \text{ V} \qquad (6)$$

since the system under study is reversible. Since there is significant uncompensated resistance, however, we would expect both these quantities to be shifted by an amount iR_u and that therefore plots of quarter-wave potential *vs.* the constant current and of peak potential *vs.* the peak current should be linear with slopes R_u. Values of R_u determined in this fashion were about 10% of the total cell resistance. The values of $E_{1/2}$ appearing in Table I were calculated from the $i = 0$ intercepts.

Vapor Pressure Measurements

The shift of $E_{1/2}$ with supporting electrolyte concentration might indicate that one or both members of this couple are ion paired with $(C_2H_5)_4N^+$. To test this possibility, the vapor pressure of acetonitrile was determined as a function of $[(C_2H_5)_4N]_2Ni(mnt)_2$ and $(C_2H_5)_4NNi(mnt)_2$ concentrations by the thermoelectric differential vapor pressure method.[17–19] This method rests on the *assumption* that the observed temperature lowering upon the addition of a solute is proportional to the difference in chemical potential between the pure solvent and the solvent in the solution. Since this temperature lowering is accurately proportional to the change in the resistance of the thermistor used to monitor the temperature, it can be shown[18] that

$$\Delta R = kn\phi m \qquad (7)$$

where k is the calibration constant, nm is the number of particles (units: kg^{-1}), and ϕ is the molal osmotic coefficient of the solvent.

Figure 5 is a plot of the ΔR values observed for the two nickel salts and for benzil (which was assumed to be monomeric with osmotic coefficient unity for calibration purposes). The data for $(C_2H_5)_4NNi(mnt)_2$ fall on the calibration curve, up to the solubility limit, which suggests that it is not associated; this conclusion agrees with the conductance data for this salt.[20] The data for $[(C_2H_5)_4N]_2Ni(mnt)_2$ fall well below the calibration curve which is consistent with ion-pair formation. $[(CH_3)_4N]_2Ni(mnt)_2$ and $[(C_2H_5)_4N]_2Pt(mnt)_2$ are also significantly ion paired by this criterion.[13]

The osmotic coefficients for these salts were calculated[21] assuming the extended Debye–Hückel equation[22] with the constants evaluated for a dielectric constant of 36.0[23] and an ion-size parameter of 6 au. The latter value was chosen to be compatible with the sum of the hydrodynamic radii calculated[24,25] from the limiting conductivities[20] of these salts. As may be seen by examining the data in Table II, the osmotic coefficients are changed only a few per cent upon changing the ion-size parameter over the range 4–8 au and thus the qualitative conclusions inherent in Figure 5 are justified.

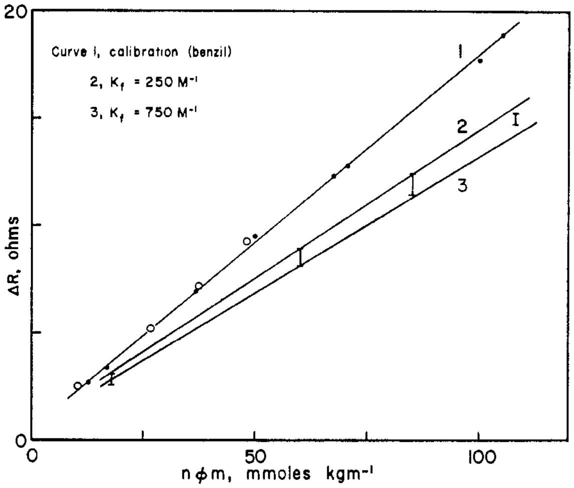

Figure 5.—Experimental ΔR values *vs.* osmotic concentration, in AN at 37°: benzil and $(C_2H_5)_4NNi(mnt)_2$, curve 1; $[(C_2H_5)_4N]_2Ni(mnt)_2$, curves 2 ($K_f = 250$ M^{-1}) and 3 ($K_f = 750$ M^{-1}).

TABLE II

MOLAL OSMOTIC COEFFICIENTS OF ACETONITRILE AT 25° AS A FUNCTION OF IONIC STRENGTH

	Ion-size parameter, au		
$I^{1/2}$	4	6	8
0.02	0.976	0.977	0.978
0.04	0.955	0.957	0.960
0.06	0.936	0.941	0.945
0.08	0.919	0.927	0.933
0.10	0.904	0.915	0.924
0.12	0.890	0.904	0.916
0.14	0.878	0.895	0.909
0.16	0.866	0.888	0.904
0.20	0.847	0.876	0.896
0.30	0.813	0.857	0.887

Quantitative interpretation is less definitive, however, because the value of the formation constant is very sensitive to experimental error and because activity corrections are extremely important. Nevertheless, it would appear that a formation constant of about 500 M^{-1} (37°) is compatible with the observations. The theoretical curves in Figure 5, calculated for $k_f = 250$ and 750 M^{-1}, were obtained by attributing the deviation from the calibration curve to a deficit of $x - 1$ particles where x, the fraction of the ion pair dissociated, is calculated from eq 8. C is the molar

$$(1 - x)/x(1 + x) = K_f C \gamma_{\pm}{}^4 \qquad (8)$$

concentration of the complex and the activity coefficients are based on the (molar) ionic strength at equilibrium, *i.e.*, assuming 40–80% ion pair.

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Discussion

Although the structural parameters of $Ni(mnt)_2^{2-}$ and $Ni(mnt)_2^-$ are very similar,[2] the diffusion coefficient of the former and, hence, its mobility are considerably smaller than those of $Ni(mnt)_2^-$; the diffusion coefficients of $Ni(mnt)_2^{2-}$ and $Pt(mnt)_2^{2-}$ and, hence, their mobilities are similar, however. This apparent dependence of the mobility of the charge of the ion appears to be a general phenomenon. For example, limiting ionic equivalent conductances for a variety of dithiolate anions, calculated from the conductance parameters of Davison, *et al.*,[20] taking the equivalent conductances of $(n\text{-}C_4H_9)_4N^+$ and $(C_2H_5)_4N^+$ as 61.93 and 85.05 cm²/ohm equiv, respectively,[25] are presented in Table III. The limiting conductances of the dinegative monomers are in excellent internal agreement, as are the conductances of the mononegative monomers, but the relative conductances of these two groups are not in the 2:1 ratio that would be expected were the mobilities of these two groups equal. Further evidence is found by examining the conductivities of HSO_4^- and SO_4^{2-} in acetonitrile, 100 *vs.* 120 cm²/ohm equiv,[26] again suggesting a lower mobility for the dinegative species.

TABLE III[a]

	Λ_0	λ_0^-
I. Dinegative Monomers		
$((C_4H_9)_4N)_2Cu(mnt)_2$	187	125
$((C_4H_9)_4N)_2Co(mnt)_2$	188	126
$((C_4H_9)_4N)_2Ni(mnt)_2$	190	128
II. Mononegative Monomers		
$((C_2H_5)_4N)Ni(mnt)_2$	169	84
$((C_4H_9)_4N)Ni(tdt)_2$	145	83
$((C_4H_9)_4N)Co(tdt)_2$	142	80
III. Dinegative Monomers		
$((C_4H_9)_4N)_2[Co(mnt)_2]_2$	166	104
$((C_4H_9)_4N)_2[CoS_4C_4(CF_3)_4]_2$	160	98
$(C_2H_5)_4N)_2[CoS_4C_4(CF_3)_4]_2$	184	99

[a] mnt = maleonitriledithiolate; tdt = toluene-3,4-dithiolate.

Tuan and Fuoss[27] have explained the abnormally large *B* (viscosity) coefficients of small ions in acetonitrile by proposing an interaction of these ions with the dipolar solvent molecules; this interaction effectively "solvates" the moving ion, thereby increasing the viscosity of the solution. This "electrostriction" must also act to decrease the mobility of the moving ion and, since it should increase with increasing charge, it is probably the explanation for the effect observed here. It would be of interest to test this possibility by measuring the conductance of these anions in less polar solvents.

If the $Ni(mnt)_2^{2-}$ entity is significantly ion paired, an additional term must be added[28] to eq 4, *viz.*

$$E_{1/2} = E^\circ - 0.059 \log \gamma_\pm^{3}(D_O/D_R)^{1/2} + 0.059 \log [1 + K_f C \gamma_\pm^{4}] \quad (9)$$

where *C* is the supporting electrolyte concentration. $(C_2H_5)_4NClO_4$ is not associated in acetonitrile.[29]

In calculating values of E° from eq 9, activity coefficients were again estimated by the extended Debye–Hückel equation, K_f was taken as 500 M^{-1}, and the term 0.059 log $(D_O/D_R)^{1/2}$ was taken equal to 3 mV. The results are summarized in Table IV. It would appear that the activity coefficient and ion-pairing corrections adequately explain the observed shift in half-wave potential with supporting electrolyte concentration and that the standard potential of the $Ni(mnt)_2^-$–$Ni(mnt)_2^{2-}$ couple is −172 ± 10 mV *vs.* $Ag^+(0.01\ M)|Ag$ or about +120 mV *vs.* aqueous sce.

TABLE IV

C, *M*	$E_{1/2}$,mV	177 log $\gamma_\pm$, mV	59 log $(1 + KC\gamma_\pm^4)$, mV	E°, mV
0.4	−57	−63.3	49.6	−172
0.1	−86	−47.1	38.2	−173
0.032	−105	−33.8	29.8	−170

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