

Toward Infinite-Dilution Voltammetry

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Received: June 30, 1998; In Final Form: September 24, 1998

Steady-state microelectrode voltammetry has been used to obtain reversible half-wave potentials for the two reduction waves of 7,7,8,8-tetracyanoquinodimethane (TCNQ) and the oxidation wave of ferrocene in acetonitrile with concentrations of tetramethylammonium hexafluorophosphate electrolyte ranging from 1 to 70 mM. The dependence of the first half-wave potential of TCNQ, referred to the half-wave potential of ferrocene, on ionic strength was adequately accounted for by changes in activity coefficients of ferrocenium ions and TCNQ radical anions as predicted by the Debye–Hückel equation. Extrapolation to zero ionic strength gives -0.233 V for the infinite-dilution half-wave potential of TCNQ vs ferrocene. Application of a small correction for unequal diffusion coefficients yields -0.226 V for the standard potential of TCNQ vs ferrocene. It is concluded that there is no significant ion pairing of either ferrocenium ions with hexafluorophosphate from the electrolyte or TCNQ radical anions with tetramethylammonium ions of the electrolyte. Similarly, plots of the difference between the two half-wave potentials of TCNQ vs the square root of ionic strength can be accounted for by activity coefficients as predicted by theory. Extrapolation to infinite dilution and application of the correction for unequal diffusion coefficients gives 0.585 V for the difference between the standard potentials of TCNQ. Ion pairing between tetramethylammonium ions and TCNQ dianions is also negligible. Also, no ion pairing is detected with 10 mM CsClO₄, 5 mM RbClO₄, or 5 mM KClO₄. However, in agreement with earlier studies, results for 10 mM LiClO₄ were consistent with extensive one-to-one ion pairing between lithium ions and dianions of TCNQ.

1. Introduction

Since the inception of microelectrode voltammetry, it has been recognized that electrodes of very small dimensions allow meaningful measurements to be made in solutions with very little or no intentionally added electrolyte.^{1,2} The greatest emphasis in studies to date has been upon the measurement of limiting currents,³ particularly the influence of electromigration of charged reactants and products, though some attention has been paid to the shape and position of the steady-state voltammograms obtained with microelectrodes.^{2,4,5} An important application that to our knowledge has not yet been reported is the measurement of reversible half-wave potentials from steady-state voltammograms as a function of electrolyte concentration so that extrapolation to infinite dilution can be achieved to obtain potentials unaffected by the ions of the electrolyte (activity and ion pairing effects). This paper presents the first measurements of this kind. Specifically, the reversible potentials for reduction of tetracyanoquinodimethane (TCNQ) and for oxidation of ferrocene are reported in acetonitrile at ionic strengths as low as 1.00×10^{-3} M. Extrapolation of these values to infinite dilution produces the standard potential of the TCNQ neutral/radical anion and radical anion/dianion half reactions vs the standard potential of the ferrocene/ferrocenium half reaction. We also obtain from the data the difference in the standard potentials (at infinite dilution) for introduction of the first and second electrons into TCNQ, $E^{\circ}_{1,\text{TCNQ}} - E^{\circ}_{2,\text{TCNQ}}$. Past measurements at typical ionic strengths (0.10 M) are contaminated by contributions of unknown magnitude from activity effects and ion pairing, calling into question earlier attempts to derive solvation energies from voltammetric data.⁶

2. Background Information

2.1. Expressions for the Reversible Half-Wave Potential in Steady-State Voltammetry. The shape and position of the steady-state voltammogram for reversible reaction 1 are given



$$E = E_{1/2} + \frac{RT}{F} \ln \frac{I_{\text{lim}} - I}{I} \quad (2)$$

$$E_{1/2} = E^{\circ'} + \frac{RT}{F} \ln \frac{D_{\text{P}}}{D_{\text{R}}} \quad (3)$$

by eqs 2 and 3 for either hemispherical or disk microelectrodes.⁷ Here I is the observed current at any potential E , I_{lim} is the limiting current, D_j is the diffusion coefficient of species j , and $E^{\circ'}$ is the formal potential which is related to the infinite-dilution standard potential, E° , by eq 4 in which y_j is the activity

$$E^{\circ'} = E^{\circ} + \frac{RT}{F} \ln \frac{y_{\text{R}}}{y_{\text{P}}} \quad (4)$$

coefficient (molar scale)⁸ for species j .⁹ Thus, from observed values of $E_{1/2}$, the thermodynamically significant infinite-dilution standard potential, E° , can be extracted if it is possible to evaluate the terms involving diffusion coefficients (eq 3) and activity coefficients (eq 4). The activity coefficient term will approach zero as the ionic strength is lowered, a condition which will also minimize the single remaining factor that is known to influence $E_{1/2}$, ion pairing (ion association).

2.2. Expressions for Activity Coefficients. The Debye–Hückel equation (eq 5) will be used in the interpretation of data.

$$\ln(y_i) = -Az_i^2 \frac{\sqrt{\mu}}{1 + Ba\sqrt{\mu}} \quad (5)$$

Here, z_i is the charge on the species, μ is the ionic strength (molar), A is the Debye–Hückel constant (3.788 for acetonitrile at 298 K), B equals $4.858 \times 10^9 \text{ m}^{-1}$, and a is the ion size parameter. In this work we found that $Ba = 1$ was adequate to account for deviations from the Debye–Hückel limiting law behavior.

In the evaluation of the ionic strength of our electrolyte solutions, the known¹⁰ association constant (ion pair formation constant) of Me_4NPF_6 in acetonitrile ($K_a = 5$) was used to calculate the concentration of free ions.

2.3. Choice of Reference Electrode or Reference Couple.

When measurements of $E_{1/2}$ are made as a function of electrolyte concentration, the first practical question encountered is the reference electrode to be used. All of the common practical reference electrodes (calomel electrode, silver/silver chloride electrode, etc.) will introduce an unknown liquid junction potential into the measurement, and in fact, this liquid junction potential will change in a generally unpredictable manner as the ionic strength of the test solution is changed. In the classical determination of infinite-dilution reversible potentials in aqueous solutions, the hydrogen electrode was well suited as a reference electrode because cells with negligible liquid-junction potential could often be used in which the concentrations of acid (e.g., HCl) in the hydrogen electrode compartment and in the test electrode compartment were kept identical as the ionic strength was lowered. For example, this approach allows the determination of E° for the $\text{AgCl(s)} + e^- = \text{Ag(s)} + \text{Cl}^-(\text{aq})$ couple by measurements of cell emf for $\text{Pt(s)}|\text{H}_2, \text{HCl(aq)}||\text{HCl(aq)}, \text{AgCl(s)}|\text{Ag(s)}$ as a function of the concentration of HCl(aq). Extrapolation to infinite dilution gives $E^\circ_{\text{AgCl/Ag}}$, and the mean activity coefficient of HCl(aq) at each ionic strength can also be extracted from the data.

A similar approach was adopted in this work. All measurements of half-wave potentials were made using a nonaqueous reference electrode, $\text{Ag(s)}|\text{AgNO}_3(\text{acetonitrile})$. Then, at each ionic strength studied, the half-wave potentials of TCNQ were reported vs that of ferrocene measured with the same reference electrode. Thus, upon proper extrapolation to infinite dilution, the standard potentials for the TCNQ couples were obtained referenced to the ferrocene/ferrocenium couple, a half-reaction whose potential has been recommended as a reference for electrochemical studies in nonaqueous media.¹¹

2.4. Extrapolation to Infinite Dilution. The expressions given above were combined to obtain the form of the dependence of half-wave potential on ionic strength. For illustration, consider the half-wave potential for the first reduction step of TCNQ, $E_{1/2,1}(\text{TCNQ})$, vs the half-wave potential for the reversible ferrocene/ferrocenium ion couple, $E_{1/2}(\text{Fc})$. Combining eqs 3 and 4 gives eq 6.

$$E_{1/2,1}(\text{TCNQ}) - E_{1/2}(\text{Fc}) = E_1^\circ(\text{TCNQ}) - E^\circ(\text{Fc}) + \frac{RT}{F} \ln \frac{y_{\text{TCNQ}} y_{\text{Fc}}}{y_{\text{TCNQ}^-} y_{\text{Fc}^+}} + \frac{RT}{F} \ln \frac{D_{\text{TCNQ}} D_{\text{Fc}^+}}{D_{\text{TCNQ}^-} D_{\text{Fc}}} \quad (6)$$

Insertion of the Debye–Hückel limiting law in eq 6 gives eq 7 in which the activity coefficients of neutral species have

$$E_{1/2,1}(\text{TCNQ}) - E_{1/2}(\text{Fc}) = E_1^\circ(\text{TCNQ}) - E^\circ(\text{Fc}) + \frac{RT}{F} \ln \frac{D_{\text{TCNQ}} D_{\text{Fc}^+}}{D_{\text{TCNQ}^-} D_{\text{Fc}}} + 2A \frac{RT}{F} \sqrt{\mu} \quad (7)$$

been assumed to be unity. If the diffusion coefficient term is independent of ionic strength, a plot of the measured half-wave potential of TCNQ referred to ferrocene vs the square root of ionic strength should be linear at low ionic strengths with slope $2ART/F$. The intercept affords the infinite-dilution standard potential of TCNQ (referred to the ferrocene couple) plus a diffusion-coefficient term which must be separately evaluated.

2.5. Diffusion-Coefficient Term. In recent years, a number of reports have appeared in which the diffusion coefficients of both members of a half-reaction have been evaluated. Because the species normally are of almost identical size and differ only by the charge, the diffusion coefficients are very similar to one another, usually differing by no more than about 30%.¹² For example, for ferrocene in acetonitrile^{12d} $D_{\text{Fc}} = (2.15 \pm 0.15) \times 10^{-5}$ and $D_{\text{Fc}^+} = 1.72 \times 10^{-5} \text{ cm}^2/\text{s}$ while, for TCNQ,^{12b} $D_{\text{TCNQ}} = 1.44 \times 10^{-5}$ and $D_{\text{TCNQ}^-} = 1.35 \times 10^{-5} \text{ cm}^2/\text{s}$. When these values are inserted in the diffusion-coefficient term of eqs 6 and 7, the result is -7 mV , a rather minor correction. It is also reasonable to expect that the magnitude of this term will not change significantly with ionic strength as required by the extrapolation proposed above.

2.6. Criterion for Reversibility. The equation for the steady-state current–potential curve (voltammogram) for a reversible reaction is given by eq 2 which indicates that a plot of $\log[(I_{\text{lim}} - I)/I]$ vs potential, E , (“log plot”) should be linear with a slope of $1/0.05916 \text{ V}^{-1}$ at 298 K. This is a necessary but insufficient proof of reversibility, but it was the only practical indicator available to us. If the electron-transfer kinetics are not sufficiently facile, the slopes become smaller than the reversible limit and the plots can show curvature. Results failing to give the reversible slope within 2 mV were rejected. In such “log plots” the points were unweighted and logarithms between about -1.0 and $+1.0$ were used.

2.7. Other Factors Affecting the Measured Half-Wave Potentials. Microelectrodes were chosen so as to reduce the effects of solution resistance. The ohmic drop between working and reference electrodes will tend to reduce the slope of the “log plot” below its reversible limiting value so the observation of reversible slopes demonstrates that the ohmic drop is negligible. In addition to this experimental confirmation, we can calculate the magnitude of the error from the solution resistance and the observed steady-state currents. The solution resistance to a microdisk electrode, R_d , is given by¹³ $\rho/4r$, where ρ is the resistivity of the solution and r is the radius of the disk. Taking typical values of ρ in acetonitrile¹⁴ along with the maximum steady-state currents observed, it was found that the ohmic drop never exceeded 1 mV. In this work, the ratio of supporting electrolyte concentration to concentration of electroactive material was maintained constant at 10. Thus, the increasing resistivities encountered as the ionic strength was lowered were compensated by the decreasing currents. The currents depend linearly on the concentration of electroactive species, and the resistivities tend to vary inversely with ionic strength.^{14a}

Migration is another factor that can affect the half-wave potential. Though the electroactive species in every case was a neutral molecule, the products are ions and tend to migrate away from the electrode at low concentrations of supporting electrolyte. However, it has been shown¹⁵ that a support ratio of 10 as used in this work is sufficient to guarantee that the migration effect on the half-wave potential will be less than 1 mV. (The support ratio is the ratio of concentration of supporting electrolyte to that of the electroactive material.)

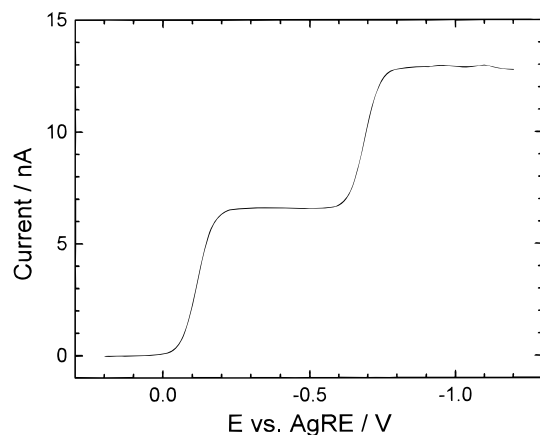


Figure 1. Steady-state voltammogram of 0.979 mM TCNQ, 10.0 mM Me_4NPF_6 in acetonitrile at a 50- μm diameter mercury-coated gold disk electrode. Scan rate: 5 mV/s. Potentials are referred to the silver reference electrode (AgRE).

3. Results

3.1. Preliminary Investigations. As indicated in section 2.3, ferrocene was chosen because it has been suggested as a standard reference couple for electrochemistry in nonaqueous media. Its electrochemical oxidation proceeds reversibly,¹⁶ the neutral form is indefinitely stable, and the cation is quite stable in nonaqueous solvents in the absence of oxygen. TCNQ is also a well-studied redox system with reversible electrode reactions and whose radical anion and dianion have been shown to be stable for at least 1 h after formation by controlled potential electrolysis in the absence of oxygen.^{12b} Thus, these systems appear to be good choices for exploratory studies of infinite-dilution voltammetry.

Preliminary investigations were conducted with platinum microdisk electrodes and 0.10 M Bu_4NPF_6 in acetonitrile. Under these conditions, the first reduction step for TCNQ showed reversible behavior but less than reversible “log plots” were obtained for the second step. Many times, the reversibility of a reaction occurring at potentials negative of the potential of zero charge is improved by using small cations in the supporting electrolyte.¹⁷ Therefore, the electrolyte was changed to Me_4NPF_6 , but the second wave was still less than reversible at platinum electrodes. Because it is often easier to maintain reversible behavior at mercury surfaces than at platinum, a mercury-coated gold disk electrode was used and the second reduction step of TCNQ remained reversible at concentrations of electrolyte as low as 2 mM.

3.2. Studies Using Tetramethylammonium Hexafluorophosphate as Electrolyte. Figure 1 shows a steady-state voltammogram obtained with 10 mM Me_4NPF_6 and 1 mM TCNQ at a mercury-coated gold microdisk electrode in acetonitrile. Two reversibly shaped waves are apparent, and quite flat limiting current plateaus are observed. The second limiting current is slightly lower than the first, an effect that is not predicted when considering individual reduction steps¹⁵ but is approximately what is predicted for the second wave of a two-step reduction as affected by migration and comproportionation with a support ratio of 10.¹⁸ The suppression of the second limiting current may also be caused in part by differences in diffusion coefficients among neutral, radical anion and dianion forms of TCNQ.^{12b}

Figure 2 shows the “log plots” of the data from Figure 1. Satisfactory linearity is observed for both waves and the slopes are equal to the reversible limit. The results for other concentrations of supporting electrolyte are summarized in Table

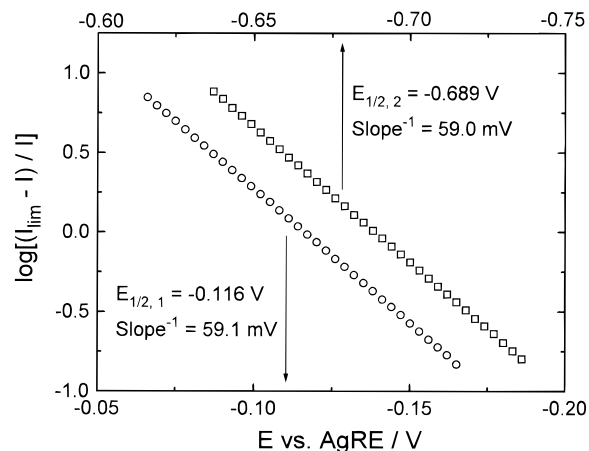


Figure 2. Plots of data taken from the voltammogram of Figure 1.

TABLE 1: Data for Reduction of TCNQ in Acetonitrile with Me_4NPF_6 Electrolyte

concn of Me_4NPF_6 (mM)	concn of TCNQ (mM)	$E_{1/2,1}$ (V)	slope ⁻¹ (mV)	$E_{1/2,2}$ (V)	slope ⁻¹ (mV)
1.01	0.102	-0.066	59.5	-0.686	61.2
2.00	0.197	-0.078	61.3	-0.667	60.4
5.00	0.500	-0.108	60.0	-0.689	59.9
10.0	0.979	-0.116	59.2	-0.689	59.1
20.0	1.98	-0.118	58.3	-0.686	60.0
30.0	2.99	-0.120	58.3	-0.680	58.2
50.0	4.96	-0.121	58.6	-0.675	58.9
69.9	6.99	-0.130	59.6	-0.682	59.4

TABLE 2: Data for Oxidation of Ferrocene in Acetonitrile with Me_4NPF_6 Electrolyte

concn of Me_4NPF_6 (mM)	concn of ferrocene (mM)	$E_{1/2}$ (V)	slope ⁻¹ (mV)
1.01	0.106	0.162	-57.5
2.00	0.196	0.149	-56.7
5.00	0.503	0.110	-59.2
10.0	0.970	0.099	-59.2
20.0	1.99	0.090	-59.9
30.0	3.02	0.084	-59.0
50.0	4.97	0.079	-59.2
69.9	6.99	0.067	-59.7

1, and Table 2 reports half-wave potentials for ferrocene. The upper limit of electrolyte concentration, 0.07 M, was determined by the solubility of Me_4NPF_6 in acetonitrile. The ferrocene data were either obtained on the same day as the TCNQ data using a separate solution of ferrocene but the same silver reference electrode or the ferrocene voltammogram was recorded after addition of ferrocene to the TCNQ solution.

The inverse slope of the “log plot” for the second wave of TCNQ with 1 mM electrolyte concentration (61.2 mV) was significantly larger than the reversible limit (59.2 mV) so this point will not be included in the analysis of the data.¹⁹

Figure 3 shows the first half-wave potential of TCNQ, referred to the ferrocene half-wave potential, plotted vs the square root of ionic strength. The straight line is the Debye–Hückel limiting law with an intercept of -0.233 V. The dashed line is based on the full Debye–Hückel equation with $Ba = 1$. The error bars (± 3 mV) represent typical day-to-day reproducibility. Reproducibility for a series of voltammograms obtained with the same solution was usually better, about ± 1 mV.

As can be seen in Figure 3, $E_{1/2,1}(\text{TCNQ}) - E_{1/2}(\text{Fc})$ differs from the infinite-dilution value by only 35 mV at an ionic strength of 0.07 M and this variation can be completely accounted for by changes in activity coefficients. A similar lowering of the difference between the half-wave potentials with

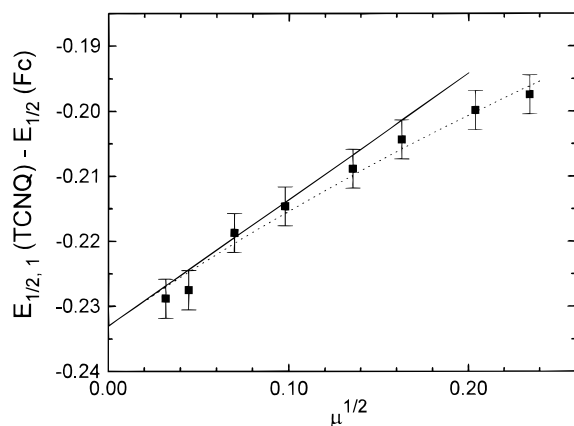


Figure 3. First half-wave potential of TCNQ with respect to the half-wave potential of ferrocene plotted vs the square root of ionic strength. Full line: Debye-Hückel limiting law. Dashed curve: Debye-Hückel equation with $Ba = 1$.

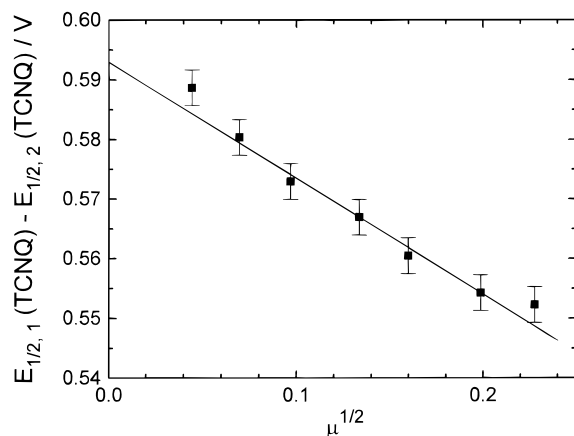


Figure 4. Difference between the two half-wave potentials for reduction of TCNQ plotted vs the square root of ionic strength. Line: Debye-Hückel limiting law.

increasing electrolyte concentration would occur if ferrocenium were to form ion pairs with hexafluorophosphate and/or if TCNQ radical anions were to form ion pairs with tetramethylammonium ion. The fact that the variation can be accounted for by changes in activity coefficients suggests strongly that no such ion pairing occurs up to an electrolyte concentration of 0.07 M. This is consistent with a recent report²⁰ that ion pairing of perchlorate anions with the ferrocenium ions from ferrocene-carboxaldehyde and 1,1'-ferrocendicarboxaldehyde in acetonitrile is significant only above about 0.05 M electrolyte.

The intercept of -0.233 V can be combined with the diffusion-coefficient term of -7 mV (see Section 2.5) in eq 7 to give $E^\circ_1(\text{TCNQ}) - E^\circ(\text{Fc}) = -0.226$ V which is our best estimate of the standard potential of the TCNQ neutral/radical anion couple referred to ferrocene. This value is about 30 mV more negative than the difference in experimental half-wave potentials measured at 0.07 M electrolyte.

Figure 4 shows a similar plot of the difference in half-wave potentials for TCNQ, $E_{1/2,1}(\text{TCNQ}) - E_{1/2,2}(\text{TCNQ})$. Here the straight line is the Debye-Hückel limiting law with intercept of 0.593 V. The deviations from limiting-law behavior are less noticeable than in Figure 3. Less weight was placed on the data point for 2 mM electrolyte ($\mu^{1/2} = 0.045$) for which we expect some irreversibility of the second wave, a factor that is clearly evident in the 1 mM voltammogram (see above). The slope of the Debye-Hückel line is equal in magnitude and opposite in sign to that of Figure 3, exactly as predicted from

TABLE 3: Data for Reduction of TCNQ in Other Electrolytes^a

electrolyte	concn (mM)	$E_{1/2,1}(\text{TCNQ}) - E_{1/2,2}(\text{TCNQ})$ (V)	$i_{\text{lim},2}/i_{\text{lim},1}$ ^b
Me ₄ NPF ₆	10.0	0.573	0.94
	5.00	0.580	0.93
CsClO ₄	10.0	0.571	0.96
RbClO ₄	5.00	0.580	0.94
KClO ₄	5.01	0.576	0.93
NaClO ₄ ^c	10.0		
LiClO ₄	10.0	0.511	0.62

^a Concentration of TCNQ was one-tenth the concentration of electrolyte. ^b Ratio of limiting currents. $i_{\text{lim},2}$ was measured from the first plateau. ^c Distorted voltammograms obtained. A red deposit formed on the electrode during the voltammetric scan.

the expression for $E_{1/2,1}(\text{TCNQ}) - E_{1/2,2}(\text{TCNQ})$ derived in an analogous fashion to eq 7. As with the first half-wave potential of TCNQ referred to ferrocene, the difference between the infinite-dilution value and the value at 0.07 M is about 35 mV and is entirely accounted for by changes in the activity coefficients. This suggests that ion pairing between tetramethylammonium and the radical anion and/or dianion of TCNQ is insignificant.

The diffusion-coefficient term for the difference between the TCNQ potentials was derived in the same way as in eq 7 and found to be $(RT/F) \ln(D_B^2/D_A D_C)$, where A–C refer to the neutral, radical anion, and dianion species, respectively. Evaluation with reported values of the diffusion coefficients^{12b} gives +8 mV which when combined with the intercept of 0.593 gives 0.585 V as our best estimate of the difference in standard potentials for TCNQ. Again, this value is about 30 mV larger than the experimental difference in half-wave potentials at an electrolyte concentration of 0.07 M.

3.3. Other Electrolytes. Another factor that can affect formal potentials is ion pairing. In the case of TCNQ, formation of ion pairs between the cation of the electrolyte and the radical anion will cause $E_{1/2,1}(\text{TCNQ})$ to shift in the positive direction. Similarly, formation of ion pairs with the dianion results in a positive shift in $E_{1/2,2}(\text{TCNQ})$. Because the latter ion pair association constant is larger than that for the radical anion, the shift of the second wave is observed at lower concentrations of electrolyte where the first wave may be unaffected. Ion pair formation has been observed²² for the case of the dianion of TCNQ and sodium or lithium ions but there is apparently no interaction with the radical anion. In terms of $E_{1/2,1}(\text{TCNQ}) - E_{1/2,2}(\text{TCNQ})$, ion pairing will cause the value to be lower for a given concentration of metal-containing salt compared to the same concentration of Me₄NPF₆, which as shown above does not ion pair with either the radical anion or dianion of TCNQ.

Results are given in Table 3. A concentration of 10 mM electrolyte was chosen for comparison with the data from Me₄NPF₆, but the solubilities of RbClO₄ and KClO₄ in acetonitrile are not large enough to reach this concentration so 5 mM was used for these salts. There are no significant differences between $E_{1/2,1}(\text{TCNQ}) - E_{1/2,2}(\text{TCNQ})$ measured in cesium-, rubidium-, or potassium-containing electrolytes and the values obtained with Me₄NPF₆, indicating that no significant ion pairing is occurring with these metal ions. In other words, all of the difference between the observed $E_{1/2,1}(\text{TCNQ}) - E_{1/2,2}(\text{TCNQ})$ and the infinite-dilution value is attributed entirely to activity effects just as we concluded for Me₄NPF₆.

By contrast, with 10.0 mM LiClO₄ there is about a 60 mV decrease in $E_{1/2,1}(\text{TCNQ}) - E_{1/2,2}(\text{TCNQ})$ compared to Me₄NPF₆, a result entirely consistent with ion pairing of lithium and the dianion of TCNQ.²² The decrease seen by Khoo et

al.^{22a} was 130 mV on going from 0.10 M Et₄NClO₄ to 0.10 M LiClO₄. The fact that we observe a 70 mV smaller change at 0.010 M electrolyte than previously seen with 0.10 M is consistent both with extensive ion pairing and with the stoichiometry of one lithium cation associating with one dianion of TCNQ.

The above analysis is qualitative both because activity effects have been neglected and because there is an anomalous feature in the voltammograms of TCNQ obtained with LiClO₄ electrolyte that suggests caution in quantitative interpretations. That feature is the ratio of limiting currents which should be exactly one at high support ratios (and identical diffusion coefficients for all TCNQ species). As discussed in section 3.2, the ratio of limiting currents is slightly less than unity for Me₄NPF₆ solutions, and almost identical values are found for CsClO₄, RbClO₄, and KClO₄ (Table 3). This value of about 0.94 appears to be consistent with predictions for a support ratio of 10.¹⁸ However, with 10.0 mM LiClO₄, the ratio of limiting currents decreases drastically to a value of 0.62. We do not have an explanation for this observation but believe that it must be related to the formation of the lithium–TCNQ dianion ion pair and the complex interplay of diffusion, migration, and the comproportionation reaction that can cause unusual effects in steady-state voltammetry with microelectrodes.¹⁸ It is interesting that no analogous decrease is seen in the second peak current in cyclic voltammetry with LiClO₄ electrolyte at an electrode of normal size with a support ratio of 100.^{22a}

4. Discussion

The results demonstrate that it is possible to obtain accurate measurements of half-wave potentials at low electrolyte concentrations using microelectrodes. Extrapolation to infinite dilution can be achieved to obtain thermodynamically significant values of the standard potentials of organic redox couples using the ferrocene/ferrocenium half-reaction as a standard. To our knowledge, this is the first time that voltammetric techniques have been used to obtain infinite-dilution standard potentials.

The measurements rely on the remarkable ability of microelectrodes to reduce the error due to solution resistance to negligible levels. Working with a support ratio (ratio of electrolyte concentration to that of the electroactive compound) of 10 guarantees that the effects of migration are also negligible. The practical lower limit of electrolyte concentration in this work was about 1 mM. At lower concentrations, the sloping background current led to difficulties in constructing “log plots”, an exercise we deemed to be essential in order to demonstrate that the reversible half-wave potential was being measured. Subtraction of background currents (obtained with electrolyte alone) from the raw data, a procedure that works well at higher concentration, was unsatisfactory below 1 mM.

An unexpected difficulty encountered at low electrolyte concentrations was the onset of electron-transfer irreversibility for the second wave of TCNQ. Though the second half-wave potential is only slightly negative of the potential of zero charge (ca. −0.5 V vs AgRE²¹), the potential at the outer Helmholtz plane may become sufficiently negative at low electrolyte concentrations to cause a transition from reversible to quasi-reversible behavior for the radical anion/dianion couple. Of course, the enhanced diffusion to microelectrodes puts stress on the electron-transfer reaction and this, combined with the aforementioned Frumkin effect, could account for the observation.

One advantage of using steady-state voltammetry to obtain infinite-dilution standard potentials is that the members of the

half-reaction being studied need not be extremely stable. Classical potentiometric measurements require the preparation of solutions containing known concentrations of the components, and these concentrations must remain constant for the duration of the solution manipulations and measurements, normally many minutes. By contrast, in steady-state voltammetry the electro-generated species can be much less stable, the only requirement being that the rates of their decomposition reactions cannot be so large as to cause shifts in the measured half-wave potentials. The present example is perhaps a poor illustration of this advantage in that the anions of TCNQ and ferrocenium ion are quite stable species and could probably be studied by the classical potentiometric procedures.

One of the motivations of this work was to assess the importance of ion pairing in affecting the observed difference in the two half-wave potentials for a substance undergoing sequential reduction or oxidation steps. In earlier work,⁶ we attempted to understand why some substances have successive half-wave potentials that are very similar or even reversed in order, with the second electron being more easily introduced or removed from the compound than the first. Calculations of the energies of gas-phase species were combined with experimental data on differences in half-wave potentials in solution to rationalize the observed solution-phase behavior in terms of the solvation energies of the ions. The experimental data that were selected were obtained using electrolytes with large counterions (for example, tetraalkylammonium ions for reduction reactions) in order to minimize the effects of ion pairing. Nevertheless, there was no experimental proof that the experimental half-wave potentials were not being affected by ion pairing. The present work demonstrates that, at least for the reduction of TCNQ in acetonitrile, ion pairing of tetraalkylammonium ions with the anions of TCNQ is not significant helping to justify our earlier neglect of ion pairing in the analysis of two-electron electrode reactions.

It is worth noting that the activity effects noted here are quite similar to the effects of ion pairing. For example, the variation of $E_{1/2,1}(\text{TCNQ}) - E_{1/2,2}(\text{TCNQ})$ with ionic strength (Figure 4) can be modeled quite precisely in terms of ion pairing rather than activity effects. The data are well accounted for using 0.587 V for the difference in potential at low electrolyte concentrations (where ion pairing is unimportant), $K_{11} = K_{22} = 12 \text{ M}^{-1}$ (K_{11} is the association constant of the radical anion with Me₄N⁺; K_{22} is the association constant for the second Me₄N⁺ ion with the dianion) and $K_{21} = 115 \text{ M}^{-1}$ (K_{21} is the association constant for the first Me₄N⁺ ion with the dianion). The fact that this alternative interpretation works well points to the danger of interpreting small changes in potentials in terms of ion pairing without considering the effect of changing activity coefficients.

5. Experimental Section

5.1. Chemicals and Reagents. Optima grade acetonitrile from Fisher was used as received. Tetramethylammonium hexafluorophosphate (Me₄NPF₆) from Aldrich was recrystallized twice from acetonitrile/water (9:1) and dried in a vacuum oven at 70 °C. 7,7,8,8-Tetracyanoquinodimethane (Aldrich) and ferrocene (Aldrich) were used as received. Lithium perchlorate (Aldrich), sodium perchlorate (Aldrich), potassium perchlorate (Alpha AESAR), rubidium perchlorate (Alpha AESAR), and cesium perchlorate (Aldrich) were all dried in a vacuum oven at 70 °C.

5.2. Electrochemical Cells, Electrodes, and Instrumentation. A standard, jacketed three-electrode cell (20 mL) was

used for voltammetry. The temperature was maintained at 25 °C using a circulating water bath. The working electrode was a mercury-coated gold disk microelectrode (50 μm diameter), a platinum wire served as auxiliary electrode, and the reference electrode was a silver/silver nitrate electrode. This electrode was composed of a silver wire in contact with 0.010 M AgNO_3 , 0.10 M Bu_4NPF_6 in acetonitrile. The reference electrode was separated from the test solution by a porous Vycor plug (Bioanalytical Systems).

The method used for preparation of the mercury-coated electrode was a modification of a previously published procedure.²³ A 50- μm gold wire (Alfa AESAR) was sealed in glass tubing, and a copper wire was attached to the gold wire using conductive epoxy (Epoxies Etc.). The copper wire was sealed at the top of the glass tubing with epoxy-patch (Hysol Aerospace & Industrial Products Division) after the conductive epoxy had cured. The tip of the capillary was polished using superfine 400 silicon carbide paper (3M) which was dampened with water. Further polishing was carried out with 5.0 μm alumina paste (Buehler) followed by 1.0, 0.3, and 0.05 μm alumina on a polishing wheel. The electrode was rinsed in deionized water, sonicated for 5 min in water, rinsed again with deionized water, and finally rinsed with acetone between each polishing step. After the final polish with 0.05 μm alumina, the electrode was sonicated for a total of 20 min in deionized water with the water being changed three times. After air-drying, the electrode was dipped in a small volume of 99.9995% mercury (Aldrich) for 30 min. After removal from the mercury, the electrode was allowed to stand for 15 min, after which it was rinsed with deionized water followed by acetone. The quality of the coating was assessed by examination under an optical microscope (50 \times). To renew the coating of mercury on the electrode, the mercury was first dissolved by soaking the electrode in concentrated nitric acid for 10 min. Then the gold electrode was treated as above starting with the 5.0 μm alumina polishing step.

The potentiostats for all steady-state voltammetry were EG&G Princeton Applied Research 263 and 283 models. The scan rate was 5 mV/s. The solutions were purged with purified nitrogen saturated with acetonitrile.

Acknowledgment. This research was supported by the National Science Foundation, Grant CHE-9704211.

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