

# Study of the Effects of Ion Pairing and Activity Coefficients on the Separation in Standard Potentials for Two-Step Reduction of Dinitroaromatics

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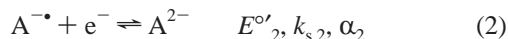
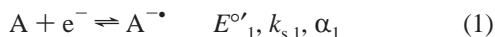
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The electrochemical reduction of 9,10-dinitroanthracene, **1**, and 3,6-dinitrodurene, **2**, occurs with potential inversion. That is, the standard potential for formation of the anion radical is shifted in the negative direction from the standard potential for the anion radical/dianion couple. This behavior has been attributed to significant structural changes accompanying the reduction steps. In this work, an assessment was made of the magnitude of the effects of activity coefficients and ion pairing, two effects which contribute to potential inversion. 1,4-Dinitrobenzene, **3**, and 2,5-dimethyl-1,4-dinitrobenzene, **4**, were studied in acetonitrile and *N,N*-dimethylformamide with  $R_4N^+$  salts as electrolytes ( $R = CH_3-$ ,  $CH_3CH_2-$ ,  $CH_3(CH_2)_3-$ , and  $CH_3(CH_2)_7-$ ) at concentrations from 0.010 to 0.100 M. Significant ion pairing between the dianion,  $A^{2-}$ , and  $R_4N^+$  was found for  $(CH_3)_4N^+$  with both **3** and **4** while the effects of the other electrolytes were smaller. The data were successfully interpreted without recourse to other ion pairs, e.g., ion pairing between the anion radical and the electrolyte cation. Ion pair formation constants are reported along with the infinite-dilution values of the difference in the two standard potentials. The effects of activity coefficients and ion pairing at 0.10 M electrolyte do not exceed 100 mV for  $(CH_3)_4N^+$  and are only 20 to 60 mV for  $(CH_3)_4N^+$ , a cation commonly used in studies of potential inversion. It is concluded that structural changes accompanying the reduction, rather than activity and ion pairing effects, are the dominant factors underlying potential inversion.

## 1. Introduction

Electrochemical reduction of neutral compounds in nonaqueous media proceeds in two or more steps, the first forming the anion radical, the second the dianion, etc. Ordinarily, the individual standard potentials occur at increasingly negative values as it becomes energetically more and more costly to insert electrons into already negatively charged species. Two steps of reduction are defined for electron acceptor A in eqs 1–3



where  $E'^{\circ}_j$ ,  $k_{s,j}$ , and  $\alpha_j$  are the formal potential, standard heterogeneous electron-transfer rate constant, and transfer coefficient of step  $j$ . Reaction 3 is the disproportionation of the anion radical, a process that can affect the electrochemical response under some conditions. The formal potential,  $E'^{\circ}_j$ , corresponds to a certain ionic strength and solvent. One objective of the present work is to evaluate the difference in the thermodynamically significant infinite-dilution standard potentials,  $E^{\circ}_1 - E^{\circ}_2$ .

The situation cited above, in which  $E'^{\circ}_1 - E'^{\circ}_2 > 0$ , i.e., the second standard potential falls at potentials more negative than the first, is called normal ordering of potentials. The separation in standard potentials is in the range of 0.3 to 0.6 V for most compounds. By contrast, there are many examples where  $E'^{\circ}_1$

–  $E'^{\circ}_2 < 0$ , i.e., insertion of the second electron occurs with greater ease than the first, a situation that has been called “potential inversion”.<sup>1</sup>

The underlying causes of potential inversion can be traced to structural changes that accompany one or both electron-transfer steps. In most cases, the structural changes have not been fully characterized, but in cases where they have, it has been found that, for reductions, the structural change has the effect of lowering the LUMO energy thus aiding the insertion of the second electron.<sup>1b</sup>

It is convenient to discuss potential inversion in terms of the free energy of disproportionation,  $\Delta G^{\circ}_{\text{disp}}$ . Estimates of  $\Delta G^{\circ}_{\text{disp}}$  in the gas phase range from about +70 to +140 kcal/mol,<sup>1b</sup>

$$\Delta G^{\circ}_{\text{disp}} = -RT \ln K_{\text{disp}} = F(E^{\circ}_1 - E^{\circ}_2) \quad (4)$$

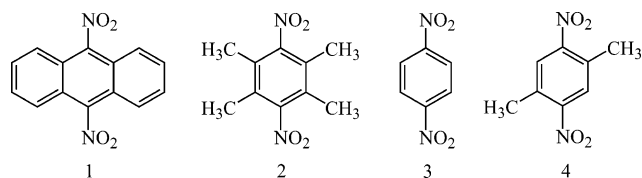
i.e., disproportionation is strongly disfavored and the hypothetical gas-phase potential separation is 3–6 V. Solvation energies reduce the magnitude of  $E^{\circ}_1 - E^{\circ}_2$  from these high gas-phase values to the range seen in solution for normal ordering, a few tenths of a volt. This effect is caused largely by the very large solvation energy of dianions, as compared to monoanions. The Born model of solvation predicts that the solvation energy will be proportional to the square of the charge so that dianions are stabilized four times as much as monoanions. This factor makes disproportionation in solution much less unfavorable and  $E'^{\circ}_1 - E'^{\circ}_2$  is reduced to normal values. In cases where potential inversion is observed, it is found that most of the effect can be traced to smaller values of the gas-phase  $\Delta G^{\circ}_{\text{disp}}$ , which, when combined with the solvation energies calibrated by the Born model, results in the correct prediction of potential inversion in most of the cases where it occurs.<sup>1b</sup>

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However, there are two other factors which affect  $E^{\circ'}_1 - E^{\circ'}_2$  in solution, both traceable to the presence of the supporting electrolyte, a necessary complication when  $E^{\circ'}_1 - E^{\circ'}_2$  is determined from voltammetric measurements. The first of these is the effect of ion pairing between the cation of the electrolyte and the anions that are formed in the reduction reactions that we are considering. Electrolytes with large tetraalkylammonium ions are usually used and it is commonly assumed that there will not be any ion pairing. However, formation of the dianion–cation pair,  $A^{2-} \cdot R_4N^+$ , cannot be ruled out and this stabilization of the dianion will lead to the same kind of contraction of  $E^{\circ'}_1 - E^{\circ'}_2$  that is caused by solvation. Significant ion pairing between the dianion of *p*-benzoquinone and  $R_4N^+$  ( $R = \text{Me}$ ,  $\text{Et}$ , and  $\text{Bu}$ ) has been reported in acetonitrile<sup>2a</sup> whereas Lehmann and Evans found no detectable ion pairing between the dianion of tetracyanoquinodimethane (TCNQ) and  $\text{Me}_4\text{N}^+$  in acetonitrile.<sup>3</sup> The effect of ion pairing on  $E^{\circ'}_1 - E^{\circ'}_2$  for nitrobenzene in liquid ammonia with KI electrolyte has been thoroughly discussed.<sup>2b</sup>

The second effect arises from activity coefficients. The concentration of the supporting electrolyte is much larger than the concentration of ions of the species being studied so the electrolyte defines the ionic strength of the solution. To first approximation, the negative logarithm of the activity coefficients of  $A^{\cdot -}$  and  $A^{2-}$  is proportional to the square of the ionic charge, making the activity coefficient of the dianion considerably smaller than that of the anion radical. This again results in an apparent stabilization of the dianion and a compression of  $E^{\circ'}_1 - E^{\circ'}_2$ , an effect that has been thoroughly discussed for TCNQ.<sup>3</sup>

The present study was prompted by our determination of the extent of potential inversion for 9,10-dinitroanthracene, **1**, and 3,6-dinitroindurene, **2**.<sup>1d</sup> The values of  $E^{\circ'}_1 - E^{\circ'}_2$  were  $-107$  and  $-280$  mV for **1** and **2**, respectively. In contrast, 1,4-dinitrobenzene, **3**, shows normal ordering of potentials. These differences in behavior were earlier interpreted as being due to differences in gas-phase  $\Delta G^{\circ}_{\text{disp}}$  among the three compounds along with Born-model estimates of solvation energies.<sup>1b</sup> The values of  $\Delta G^{\circ}_{\text{disp}}$  for **1** and **2** were affected by significant structural differences among the neutral, anion radical, and dianion so it was argued that these structural changes underlie the phenomenon of potential inversion. However, the question remains concerning the extent to which ion pairing and activity effects affect  $E^{\circ'}_1 - E^{\circ'}_2$ . Encouraged by our earlier success with TCNQ,<sup>3</sup> we decided to investigate these effects with **1–3** as well as 2,5-dimethyl-1,4-dinitrobenzene, **4**, whose behavior is similar to that of **3**.



## 2. Experimental Section

**2.1. Chemicals and Reagents.** Anhydrous acetonitrile (AN, Aldrich 99.8%,  $<0.001\%$   $\text{H}_2\text{O}$ ) and *N,N*-dimethylformamide (DMF, J. T. Baker, 99.8+%,  $<0.04\%$   $\text{H}_2\text{O}$ ) were used as received and transferred via syringe under nitrogen. Tetra-butylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ , Fluka) was recrystallized three times from absolute ethanol, tetramethylammonium hexafluorophosphate ( $\text{Me}_4\text{NPF}_6$ , Aldrich) was recrystallized twice from acetonitrile/water (9:1), and both electrolytes were dried in a vacuum oven at  $100^\circ\text{C}$  for 24 h before use. Tetraethylammonium perchlorate ( $\text{Et}_4\text{NClO}_4$ , Acros)

was purified by recrystallizing three times from deionized water and was dried under vacuum for 24 h at  $70^\circ\text{C}$ . Tetraoctylammonium bromide ( $\text{Oc}_4\text{NBr}$ , Fluka) was dried in a vacuum oven at  $40^\circ\text{C}$ . 9,10-Dinitroanthracene (**1**, Aldrich), 3,6-dinitroindurene (**2**, Aldrich), 1,4-dinitrobenzene (**3**, Aldrich, 98%), ferrocene (Aldrich), 2,5-dimethyl-1,4-phenylenediamine (Aldrich, 97%), hydrogen peroxide (50% aqueous solution, Aldrich), trifluoroacetic acid (Riedel-deHaën), and dichloromethane ( $\text{CH}_2\text{Cl}_2$ , EMD) were used as received. Nitrogen, presaturated with solvent, was used as the purge gas.

2,5-Dimethyl-1,4-dinitrobenzene (**4**) was synthesized by Emmons oxidation of the corresponding 2,5-dimethyl-1,4-phenylenediamine with peroxytrifluoroacetic acid prepared from trifluoroacetic acid and 50% hydrogen peroxide.<sup>4</sup>

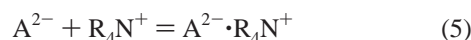
**2.2. Electrochemical Cells, Electrodes, and Instrumentation.** All electrochemical experiments were performed with an EG&G Princeton Applied Research Potentiostat/Galvanostat, model 283, using a standard, jacketed three-electrode cell (10 mL). The experiments were conducted at 298 K with use of a circulating water bath. The working electrode was a nominally 0.3-cm diameter glassy carbon electrode, a platinum wire served as auxiliary electrode, and the reference electrode was an  $\text{Ag}/\text{Ag}^+$  electrode (a silver wire immersed in 0.10 M  $\text{Bu}_4\text{NPF}_6/0.01$  M silver nitrate/acetonitrile). The reference electrode was separated from the test solution by a porous Vycor frit. (Bioanalytical Systems). The potential of the silver reference electrode was periodically measured vs the potential of the ferrocenium/ferrocene couple in the solvent being studied and all potentials are reported vs ferrocene. The highly polished glassy carbon electrode was repolished before use with 0.05- $\mu\text{m}$  alumina paste (Buhler), rinsed with water, and sonicated for 5 min in water. It was then rinsed with acetone and dried with a tissue. The area of the electrode was determined to be  $0.0814\text{ cm}^2$  based on simulations of voltammograms of known concentrations of ferrocene in acetonitrile at 298 K, using the consensus value of  $2.5 \times 10^{-5}\text{ cm}^2/\text{s}$  for the diffusion coefficient of ferrocene.<sup>5a</sup> In studies of the dinitroaromatics, the solution resistance,  $R_u$ , was totally compensated via *IR* compensation through positive feedback. Digital simulations were conducted with DigiSim from Bioanalytical Systems, version 3.03. The mechanism included reactions 1–3 and their associated parameters. Ion pairing was not explicitly included in the simulations. The effect of ion pairing was thus seen through the change in the formal potentials with changing electrolyte identity and concentration according to eq 9 below. Fits of eq 9 to the data were achieved by using the “solve” function in Microsoft Excel with *K* and *Ba* as adjustable parameters as fully described elsewhere.<sup>5b</sup>

The uncompensated resistance,  $R_u$ , depends on the electrolyte and solvent and also on the size of the working electrode, the dimensions of the cell, and the specific placement of the three electrodes. Because the effects of resistance were significant in the present work, particularly at the lower concentrations of electrolyte, accurate determination of  $R_u$  was essential. With the exception of the electrolyte  $\text{Oc}_4\text{NBr}$ , the uncompensated resistance ( $R_u$ ) for all the electrolyte solutions studied was determined by cyclic voltammetry of three different concentrations of ferrocene, with partial positive-feedback resistance compensation at scan rates where the effects of resistance are evident. Ferrocene behaved reversibly under all conditions studied. Digital simulation was used to find the particular value of residual uncompensated resistance, entered into the simulations, that would fit all three concentrations at all scan rates. The sum of the electronically applied compensation and the

residual uncompensated resistance required in the simulation is  $R_u$  for that particular electrolyte and our cell and electrodes. These quantities are specific to the working electrode used in this work and the arrangement of the electrodes in the cell, which was carefully reproduced in each experiment.

### 3. Results and Discussion

**3.1. Treating the Combined Effects of Ion Pairing and Activity.** At the outset, let us say that all of the data were satisfactorily accommodated by a treatment that included only one type of ion pair, the dianion with the electrolyte cation, reaction 5 with equilibrium constant 6:



$$K = \frac{a_{A^{2-} \cdot R_4N^+}}{a_{A^{2-}} a_{R_4N^+}} = \frac{y_{A^{2-} \cdot R_4N^+} C_{A^{2-} \cdot R_4N^+}}{y_{A^{2-}} C_{A^{2-}} y_{R_4N^+} C_{R_4N^+}} \quad (6)$$

where  $y_j$  is the activity coefficient of species  $j$  with molar standard state (as opposed to molal) and  $C_j$  is the molar concentration.

The activity coefficients are given by the extended form of the Debye–Hückel equation,

$$\ln y_j = -A \frac{z_j^2 \sqrt{\mu}}{1 + Ba \sqrt{\mu}} \quad (7)$$

where  $z_j$  is the charge on species  $j$ ,  $\mu$  is the ionic strength (molar units),  $A$  is the Debye–Hückel constant, and  $Ba$  is an adjustable ion-size parameter.  $A$  at 298 K is 3.788 for acetonitrile and 3.669 for DMF.<sup>3</sup>

The activity coefficients appear in the Nernst equations for the two electrode reactions,

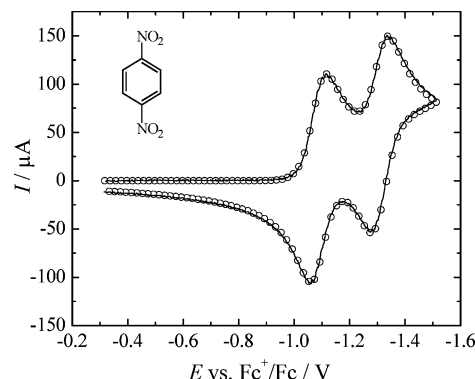
$$E = E_1^{\circ'} + \frac{RT}{F} \ln \frac{y_A C_A}{y_{A^{2-}} C_{A^{2-}}} = E_2^{\circ'} + \frac{RT}{F} \ln \frac{y_{A^{2-}} C_{A^{2-}}}{y_{A^{2-} \cdot R_4N^+} C_{A^{2-} \cdot R_4N^+}} \quad (8)$$

Equations 6–8 were combined to form an expression for  $E^{\circ'}_1 - E^{\circ'}_2$  (eq 9). This expression was fit to the data for each

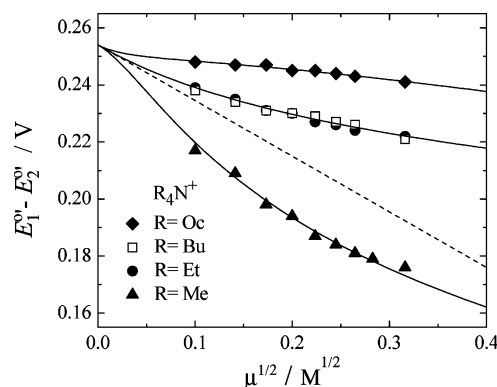
$$E^{\circ'}_1 - E^{\circ'}_2 = E^{\circ}_1 - E^{\circ}_2 + \frac{RT}{F} \ln \left( \frac{y_{A^{2-}}}{y_{A^{2-} \cdot R_4N^+}} \right) - \frac{RT}{F} \ln \left( 1 + \frac{y_{A^{2-}} y_{R_4N^+}}{y_{A^{2-} \cdot R_4N^+}} C_{R_4N^+} K \right) \quad (9)$$

electrolyte at various ionic strengths by varying  $K$  and  $Ba$ . The infinite-dilution values of  $E^{\circ'}_1 - E^{\circ'}_2$ , i.e.,  $E^{\circ}_1 - E^{\circ}_2$ , were also, in fact, adjustable but we added the reasonable constraint that they must be identical for all electrolytes because the thermodynamic  $E^{\circ}_1 - E^{\circ}_2$  should depend only on the solvent. The charges used,  $z_j$ , were the nominal charges on the species except for the ion pair,  $A^{2-} \cdot R_4N^+$ , where a charge of  $-3^{1/2} = -1.73$  was found best to account for all of the experimental data. There is no theoretical significance to this apparent charge on the ion pair.

**3.2. Results for 3 and 4.** We first confirmed that potential inversion is seen for **1** and **2** in acetonitrile with various electrolytes. Estimates of  $E^{\circ'}_1 - E^{\circ'}_2$  were consistent with those determined earlier<sup>1d</sup> but, as noted there, the precision of the determination is not high, making it difficult to detect with certainty any differences that occur upon changing the nature



**Figure 1.** Cyclic voltammogram of 1.24 mM 1,4-dinitrobenzene, **3**, at a glassy carbon working electrode in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile. Scan rate: 1.00 V/s. Temperature: 298 K. Full curve: background-corrected experimental voltammogram. Symbols: digital simulation for  $E^{\circ'}_1 = -1.084$  V,  $E^{\circ'}_2 = -1.305$  V,  $\alpha_1 = \alpha_2 = 0.5$ ,  $k_{s,1} = 0.6$  cm/s,  $k_{s,2} = 0.2$  cm/s,  $k_{f,3} = 10^3$  M<sup>-1</sup> s<sup>-1</sup>,  $D_A = 1.68 \times 10^{-5}$  cm<sup>2</sup>/s.



**Figure 2.** Fit of eq 9 to data of  $E^{\circ'}_1 - E^{\circ'}_2$  as a function of ionic strength for 1,4-dinitrobenzene, **3**, for four different electrolytes in acetonitrile at 298 K. For fitting parameters, see Table 1. Dashed line: eq 10 with  $Ba = 0$ .

or concentration of the electrolyte. Thus, we turned to **3** and **4**, whose normal ordering allows precise determination of  $E^{\circ'}_1 - E^{\circ'}_2$ , with the hope that trends seen with these two *p*-dinitroaromatics would shed some light on the behavior of **1** and **2**.

Figure 1 shows a voltammogram of 1.24 mM **3** obtained at the glassy carbon working electrode in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile at 1.00 V/s. 130 Ω of solution resistance has been compensated. The points are the result of a simulation with  $E^{\circ'}_1 = -1.084$  V and  $E^{\circ'}_2 = -1.305$  V, so  $E^{\circ'}_1 - E^{\circ'}_2$  is 221 mV under these conditions.<sup>6</sup> Both waves are accounted for by close-to-reversible electron-transfer reactions. However, noticeable quasireversibility sets in for data obtained at the lowest electrolyte concentration.

Simulations such as that shown in Figure 1 were performed for scan rates of 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 5, and 10 V/s and electrolyte concentrations of 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, and 0.10 M for each of four electrolytes, R<sub>4</sub>NX (R = Me, X = PF<sub>6</sub><sup>-</sup>; R = Et, X = ClO<sub>4</sub><sup>-</sup>; R = Bu, X = PF<sub>6</sub><sup>-</sup>; R = octyl, X = Br<sup>-</sup>). The fits of eq 9 to the experimental data are shown in Figure 2.

The data for all electrolytes fit an infinite-dilution value of  $E^{\circ}_1 - E^{\circ}_2$  of 0.254 V. No significant ion pairing is seen with the octyl, butyl, and ethyl electrolytes but  $K = 195$  M<sup>-1</sup> was found for tetramethylammonium ion, the smallest of the electrolyte cations studied. The values of  $K$  and  $Ba$  used can be found in Table 1.

**TABLE 1:** Difference in Standard Potentials ( $E^\circ_1 - E^\circ_2$ ), Formation Constant for Dianion with Electrolyte Cation ( $K$ ), and Ion Size Parameter ( $Ba$ )

Compound	Solvent/ $R_4N^+$	$E^\circ_1 - E^\circ_2$	$K / M^{-1}$	$Ba$
	CH <sub>3</sub> CN	+0.254 V		
	Me <sub>4</sub> N <sup>+</sup>		195	2.5
	Et <sub>4</sub> N <sup>+</sup>		3	3.3
	Bu <sub>4</sub> N <sup>+</sup>		4	3.3
	Oct <sub>4</sub> N <sup>+</sup>		4	30.5
	DMF	+0.390 V		
	CH <sub>3</sub> CN	+0.204 V		
	Me <sub>4</sub> N <sup>+</sup>		349	2.5
	Et <sub>4</sub> N <sup>+</sup>		40	2.4
	Bu <sub>4</sub> N <sup>+</sup>		24	8.5
	CH <sub>3</sub> CN (1.3% H <sub>2</sub> O)	+0.053 V		
	Me <sub>4</sub> N <sup>+</sup>		127	6.2
	Et <sub>4</sub> N <sup>+</sup>		27	6.8
	Bu <sub>4</sub> N <sup>+</sup>		11	10.2

<sup>a</sup> Me = methyl; Et = ethyl; Bu = *n*-butyl; Oc = *n*-octyl.

In the absence of ion pairing ( $K = 0$ ), eq 9 reduces to a much simpler form, eq 10. If, in addition,  $Ba = 0$ , eq 10 predicts that a plot of  $E^{\circ'}_1 - E^{\circ'}_2$  vs  $\mu^{1/2}$  will be linear with a slope of  $-2ART/F$  (see dashed line in Figure 2). Such behavior was seen with TCNQ.<sup>3</sup> Introduction of  $Ba > 0$  diminishes the effect of ionic strength on  $E^{\circ'}_1 - E^{\circ'}_2$  and causes curvature in the plot as can be seen for Oc<sub>4</sub>NBr in Figure 2. Finally, when ion pairing

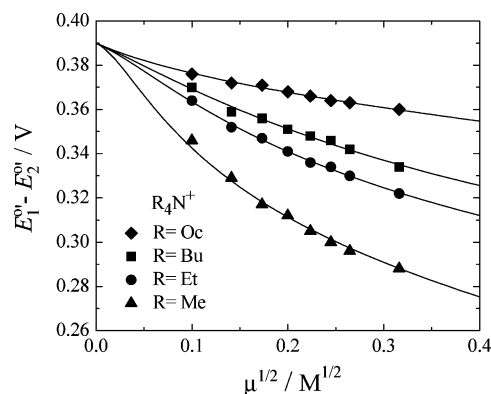
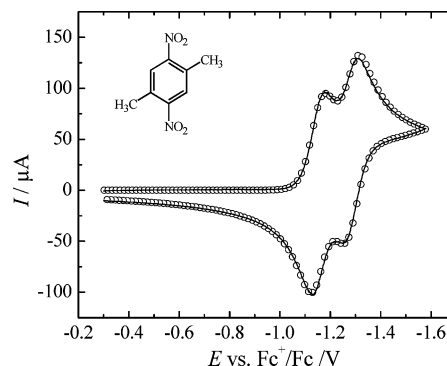
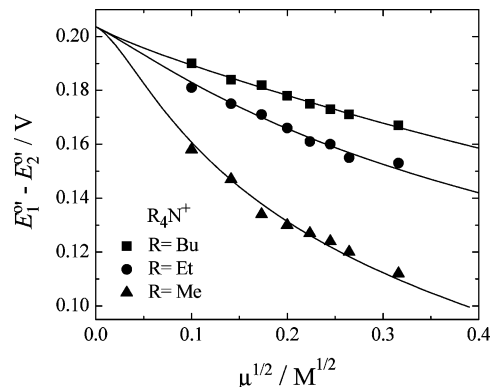
$$E^{\circ'}_1 - E^{\circ'}_2 = E^\circ_1 - E^\circ_2 - \frac{2ART\sqrt{\mu}}{F(1 + Ba\sqrt{\mu})} \quad (10)$$

occurs, larger reductions in  $|E^{\circ'}_1 - E^{\circ'}_2|$  occur due to the third term on right side of eq 9. When ion pairing was indicated, we found it impossible to fit the data solely by varying  $Ba$  with  $K = 0$ .

To put in perspective the relative effects of solvation, on one hand, and ion pairing and activity effects, on the other, we carried out DFT calculations of the gas-phase free energies of the neutral, anion radical, and dianion of **3**. The result was  $(E^\circ_1 - E^\circ_2)_{\text{vac}} = +4.496$  V. In acetonitrile solution, the infinite dilution value is  $(E^\circ_1 - E^\circ_2)_{\text{CH}_3\text{CN}} = +0.254$  (Figure 2) while in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub>, a typical electrolyte used in studies of potential inversion,  $(E^{\circ'}_1 - E^{\circ'}_2)_{\text{CH}_3\text{CN}, \text{Bu}_4\text{N}^+}$  has decreased to +0.221 V. Thus  $4.496 - 0.254 = 4.242$  V (97.8 kcal/mol) of compression is due solely to solvation while a meager  $0.254 - 0.221 = 0.033$  V (0.8 kcal/mol) can be attributed to ion pairing and activity effects.

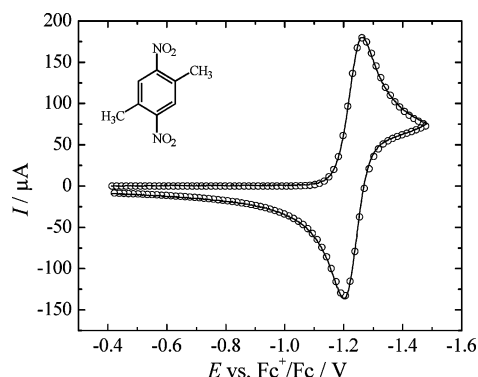
Figure 3 shows fits of eq 9 to the  $E^{\circ'}_1 - E^{\circ'}_2$  data for **3** in DMF. Detectable ion pairing is found for all electrolytes and the value for tetramethylammonium ion, 430 M<sup>-1</sup>, is more than twice that found in acetonitrile. The value of  $E^\circ_1 - E^\circ_2$  for DMF is 0.390 V, which is 136 mV greater than that seen in acetonitrile. As  $E^\circ_1 - E^\circ_2$  is not affected by electrolyte, we conclude that compression of the difference in standard potentials by solvation is greater in acetonitrile though the difference, about 3 kcal/mol, is not large. This is qualitatively consistent with the detectably larger solvation of the anion radicals of various nitrobenzenes in acetonitrile compared to DMF.<sup>7</sup>

Figure 4 shows a voltammogram of 0.92 mM **4** obtained at the glassy carbon working electrode in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile at 1.00 V/s. The points represent the simulation fit to the data (full curve). In Figure 5 are fits of eq 9 to the data for three different electrolytes with the relevant parameter values shown in Table 1. Ion pairing is weak for tetraethyl- and tetrabutylammonium ion and is quite significant for tetramethy-

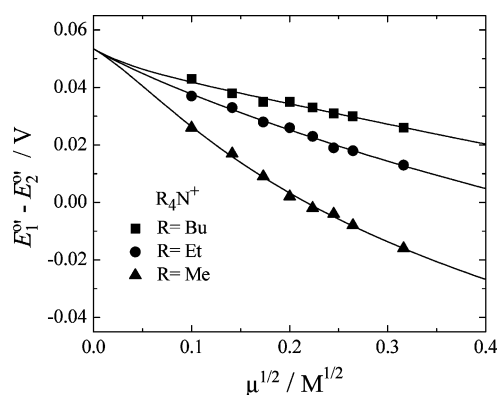
**Figure 3.** Fit of eq 9 to data of  $E^{\circ'}_1 - E^{\circ'}_2$  as a function of ionic strength for 1,4-dinitrobenzene, **3**, for four different electrolytes in DMF at 298 K. For fitting parameters, see Table 1.**Figure 4.** Cyclic voltammogram of 0.92 mM 2,5-dimethyl-1,4-dinitrobenzene, **4**, at a glassy carbon working electrode in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile. Scan rate: 1.00 V/s. Temperature: 298 K. Full curve: background-corrected experimental voltammogram. Symbols: digital simulation for  $E^{\circ'}_1 = -1.240$  V,  $E^{\circ'}_2 = -1.407$  V,  $\alpha_1 = \alpha_2 = 0.5$ ,  $k_{s,1} = 0.6$  cm/s,  $k_{s,2} = 0.17$  cm/s,  $k_{t,3} = 10^4$  M<sup>-1</sup> s<sup>-1</sup>,  $D_A = 1.60 \times 10^{-5}$  cm<sup>2</sup>/s.**Figure 5.** Fit of eq 9 to data of  $E^{\circ'}_1 - E^{\circ'}_2$  as a function of ionic strength for 2,5-dimethyl-1,4-dinitrobenzene, **4**, for three different electrolytes in acetonitrile at 298 K. For fitting parameters, see Table 1.

lammonium ion but the effects are more pronounced than with **3** in all electrolytes. A possible explanation is that the electron-donating methyl groups push greater electron density onto the nitro groups in the dianion than is the case for **3**. This slightly enhanced electron density may underlie the larger ion-pair formation constants for **4**, for example 349 M<sup>-1</sup> compared to 195 M<sup>-1</sup> for tetramethylammonium. The value of  $E^\circ_1 - E^\circ_2$  for compound **4** in acetonitrile is 50 mV smaller than that of **3**. However, this difference corresponds to only 1 kcal/mol and is too small to interpret with any degree of confidence.





**Figure 6.** Cyclic voltammogram of 0.83 mM 2,5-dimethyl-1,4-dinitrobenzene, **4**, at a glassy carbon working electrode in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile containing 1.3% water. Scan rate: 1.00 V/s. Temperature: 298 K. Full curve: background corrected experimental voltammogram. Symbols: digital simulation for  $E^{\circ'}_1 = -1.212$  V,  $E^{\circ'}_2 = -1.238$  V,  $\alpha_1 = \alpha_2 = 0.5$ ,  $k_{s,1} = 0.6$  cm/s,  $k_{s,2} = 0.2$  cm/s,  $D_A = 1.36 \times 10^{-5}$  cm<sup>2</sup>/s.



**Figure 7.** Fit of eq 9 to data of  $E^{\circ'}_1 - E^{\circ'}_2$  as a function of ionic strength for 2,5-dimethyl-1,4-dinitrobenzene, **4**, for three different electrolytes in acetonitrile containing 1.3% water at 298 K. For fitting parameters, see Table 1.

As can be seen in Figures 2, 3, and 5, the combined effects of ion pairing and activity coefficients in lowering the difference between the two formal potentials is 100 mV or less. That is, with the electrolyte cation that most strongly ion pairs (tetramethylammonium) at the highest concentration used (0.10 M),  $E^{\circ'}_1 - E^{\circ'}_2$  is within 100 mV of the infinite-dilution value,  $E^{\circ}_1 - E^{\circ}_2$ . For Bu<sub>4</sub>N<sup>+</sup>, which has been widely used in studies of potential inversion, the total effect is even smaller, 20–60 mV. This strongly suggests that these effects cannot be the dominant factors in bringing about the observed potential inversion in compounds **1** and **2**. To see if these effects might somehow be enhanced as one approached potential inversion, we artificially compressed  $E^{\circ'}_1 - E^{\circ'}_2$  for **4** by adding water. Hydrogen bonding interactions between water and the dianion are much stronger than those with the anion radical, a factor that brings about compression just as does ion pairing and the activity coefficient effect. Figure 6 shows a voltammogram of 0.83 mM **4** obtained at the glassy carbon working electrode in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile containing 1.3% water at 1.00 V/s. One can see in Figure 6 that the two reduction peaks have merged into a single peak and simulation showed that  $E^{\circ'}_1 - E^{\circ'}_2$  has decreased to 0.026 V compared to 0.167 V in the absence of water (Figure 4). However, the potentials are not quite inverted. The fits of eq 9 to the data (Figure 7) in the presence of water show detectable ion pairing for all three electrolytes but the formation constants are somewhat smaller than in the absence of water (Table 1). When water is present, the dianion will enter

**TABLE 2: Values of  $E^{\circ'}_1 - E^{\circ'}_2$  (in V) for Compounds **1**, **3**, and **4** for Two Electrolytes at High and Low Concentrations in Acetonitrile at 298 K**

	9,10-dinitro-anthracene, <b>1</b>	1,4-dinitro-benzene, <b>3</b>	2,5-dimethyl-1,4-dinitrobenzene, <b>4</b>
0.10 M Bu <sub>4</sub> NPF <sub>6</sub>	−0.053	+0.221	+0.167
0.01 M Bu <sub>4</sub> NPF <sub>6</sub>	−0.074	+0.238	+0.190
0.10 M Me <sub>4</sub> NPF <sub>6</sub>	−0.025	+0.176	+0.111
0.01 M Me <sub>4</sub> NPF <sub>6</sub>	−0.069	+0.217	+0.158

a competition between hydrogen bonding to water or ion pairing with the cation so the latter is slightly less prevalent.

The data in Figure 7 show that it is possible to generate a small inversion, −0.016 V for 0.10 M Me<sub>4</sub>NPF<sub>6</sub>, but the overall effect of activity coefficients and ion pairing is similar in magnitude to the cases where one is rather far from potential inversion. So there are no special effects associated with systems close to inversion.

**3.3. Behavior of **1** and **2**.** The determination of precise values of  $E^{\circ'}_1 - E^{\circ'}_2$  is relatively straightforward for cases of normal ordering. However, even with the compression in the difference in formal potentials seen for **4** in the presence of water, the determination of  $E^{\circ'}_1 - E^{\circ'}_2$  becomes quite difficult. Analysis of the voltammograms of **1** and **2** clearly shows that inversion has occurred but determination of  $E^{\circ'}_1 - E^{\circ'}_2$ , and particularly its dependence on electrolyte concentration, can only be estimated.

Table 2 compares  $E^{\circ'}_1 - E^{\circ'}_2$  for **1**, **3**, and **4** for high (0.10 M) and low (0.01 M) concentrations of Bu<sub>4</sub>NPF<sub>6</sub> and Me<sub>4</sub>NPF<sub>6</sub>, both in acetonitrile. The results for **3** and **4** have been discussed earlier and they show normal ordering under all conditions. By contrast, **1** shows inversion under all conditions. Note that the estimates of  $E^{\circ'}_1 - E^{\circ'}_2$  for **1** for both electrolytes and both concentrations fall in a ~50 mV range (−0.025 to −0.074 V). This is similar to but slightly smaller than the range seen for **3** (~60 mV; 0.176 to 0.238 V) and **4** (~80 mV; 0.111 to 0.190 V). Thus, the effects of ion pairing and activity coefficients on  $E^{\circ'}_1 - E^{\circ'}_2$  are not abnormally large for **1**.

## 4. Conclusion

This work has reaffirmed that solvation is by far the most important factor in reducing the difference in potentials on going from gas phase to solution, accounting in one example for over 99% of the observed compression. The combined effects of ion pairing and activity coefficients account for 100 mV or less for the compounds, solvents, and electrolytes studied here. The ion pairing and activity effects are not significantly different for cases of near potential inversion as compared to normal ordering. The original conclusion that structural effects are the primary cause of potential inversion for **1** and **2** is on a sound basis. The additional effects of ion pairing and activity coefficients are rather modest, 100 mV or less.

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