

## The Decamethylferrocene(+/0) Electrode Reaction in Organic Solvents at Variable Pressure and Temperature

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Half-wave potentials  $E_{1/2}$  relative to a Ag/Ag<sup>+</sup> electrode, mean diffusion coefficients  $D$ , and standard electrode reaction rate constants  $k_{el}$  are reported for the decamethylferrocene(+/0) couple (DmFc<sup>+/0</sup>) in nine organic solvents at variable pressure and (for five solvents) temperature. Limited data on the ferrocene(+/0) (Fc<sup>+/0</sup>) and Fe(phen)<sub>3</sub><sup>3+/2+</sup> electrode reactions are included for comparison. Although  $E_{1/2}$  for DmFc<sup>+/0</sup> correlates only loosely with the reciprocal of the solvent dielectric constant  $\epsilon$  at ambient pressure, its pressure dependence expressed as the volume of reaction  $\Delta V_{cell}$  is a linear function of  $\Phi = (1/\epsilon)(\partial \ln \epsilon / \partial P)_T$  (the Drude–Nernst relation). Interpretation of the temperature dependence data is made difficult by enthalpy–entropy compensation. Measurements of  $D$  for solutions containing 0.5 mol L<sup>-1</sup> tetrabutylammonium perchlorate (TBAP) at 25 °C and ambient pressure are inversely proportional to the viscosities  $\eta$  of the pure solvents as expected from the Stokes–Einstein relation, despite the fact that increasing [TBAP] results in increased  $\eta$ . The activation volume  $\Delta V_{diff}^\ddagger$  for diffusion of DmFc<sup>+/0</sup> ranges from 7 to 17 cm<sup>3</sup> mol<sup>-1</sup> and generally increases with increasing  $\eta$  and thus with increasing [TBAP]. The activation volumes  $\Delta V_{el}^\ddagger$  for the electrode reactions of DmFc<sup>+/0</sup> and Fc<sup>+/0</sup> are all positive, equaling the corresponding  $\Delta V_{diff}^\ddagger$  values within the experimental uncertainty and contrast sharply with the negative  $\Delta V_{ex}^\ddagger$  values characteristic of the corresponding self-exchange reactions in homogeneous solution. These facts, together with the thermal activation parameters, point to solvent dynamical control of the electrode (but not the homogeneous self-exchange) reactions. The apparent radii of the electroactive species according to the Drude–Nernst and Stokes–Einstein relations cannot be satisfactorily related to their crystallographic radii and are better regarded as adjustable parameters with limited physical significance.

### Introduction

In furtherance of our continuing studies of pressure effects on the kinetics and equilibria of electrode reactions of metal complexes in solution<sup>1–8</sup>



we have carried out experiments designed to determine how the *volume of reaction*  $\Delta V_{cell}$  for an exemplary couple

(DmFc<sup>+/0</sup>, where DmFc = decamethylferrocene) relative to a particular reference electrode (Ag/(0.01 mol L<sup>-1</sup> AgNO<sub>3</sub> + 0.5 mol L<sup>-1</sup> TBAP in AN)<sup>9</sup>) varies with the nature of the solvent:

$$\Delta V_{cell} = -F(\partial E_{1/2} / \partial P)_T \quad (2)$$

Here  $E_{1/2}$  is the half-wave potential from a cyclic voltammogram (CV) and  $F$  is the Faraday constant (96 485 A s mol<sup>-1</sup>). Since CVs yield values of the mean reactant diffusion coefficient  $D$ , we also report the variation of  $D$  with pressure (expressed as a volume of activation for reactant diffusion,  $\Delta V_{diff}^\ddagger$ ) and with the nature of the solvent.

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- (9) Abbreviations: Fc, ferrocene; DmFc, decamethylferrocene; AC, acetone; AN, acetonitrile; BN, benzonitrile; DCM, dichloromethane; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; PC, propylene carbonate; PY, pyridine; MeOH, methanol; EtOH, ethanol; PrOH, 1-propanol; TBAP, tetra-*n*-butylammonium perchlorate; TEAP, tetraethylammonium perchlorate; phen, 1,10-phenanthroline; bpy, 2,2'-bipyridine; chxNC, cyclohexylisocyanide; hfac<sup>-</sup>, 1,1,1,5,5,5-hexafluoroacetylacetonate.

$$\Delta V_{\text{diff}}^{\ddagger} = -RT(\partial \ln D/\partial P)_T \quad (3)$$

Complementary measurements of the standard electrode reaction rate constants  $k_{\text{el}}$  and the corresponding volumes of activation  $\Delta V_{\text{el}}^{\ddagger}$  were obtained from alternating current voltammograms (ACVs).<sup>1–8</sup>

$$\Delta V_{\text{el}}^{\ddagger} = -RT(\partial \ln k_{\text{el}}/\partial P)_T \quad (4)$$

A limited study of temperature effects on  $E_{1/2}$ ,  $k_{\text{el}}$ , and  $D$  is included in this report.

The DmFc<sup>+0</sup> couple was selected because the large size and low charge of the DmFc<sup>+</sup> ion, together with the electrical neutrality of DmFc, offer the opportunity to minimize Coulombic complications such as ion pair formation. Although the analogous ferrocene couple Fc<sup>+0</sup> has long been used as a reference couple for electrochemistry in organic solvents and might seem to be an obvious choice for study, its measured electrochemical properties (notably  $D$  and  $k_{\text{el}}$  in the widely used solvent AN<sup>9</sup>)<sup>2,10,11</sup> often drift with time, making it unsuitable for variable-pressure or -temperature experiments which require several hours to complete. Lay et al.,<sup>12</sup> however, have shown that the DmFc<sup>+0</sup> couple is a much better electrochemical standard, especially when (as here) solvent effects are a primary object of investigation. The DmFc<sup>+0</sup> was therefore chosen for our recent study of pressure effects on its self-exchange reaction in homogeneous nonaqueous solution.<sup>13</sup> Nevertheless, we include here for comparison such limited results as we have been able to obtain for Fc<sup>+0</sup> and the highly charged couple Fe(phen)<sub>3</sub><sup>3+/2+</sup> in organic solvents.

According to the Born theory of solvation of an ion of charge number  $z_i$  and effective radius  $r_i$  in a solvent (regarded as a continuous dielectric), the molar free energy of solvation  $\Delta G_{\text{solv}}$  relative to the gas phase is given by

$$\Delta G_{\text{solv}} = -(N_A z_i^2 e^2 / 8\pi\epsilon_0 r_i)(1 - \epsilon^{-1}) \quad (5)$$

where  $\epsilon$  is the dielectric constant (relative permittivity) of the solvent and the other symbols have their usual meanings in SI. The molar volume of solvation (volume of solvent electrostriction)  $\Delta V_{\text{solv}}$  is then given by the Drude–Nernst relation

$$\Delta V_{\text{solv}} = (\partial \Delta G_{\text{solv}} / \partial P)_T = -(N_A z_i^2 e^2 / 8\pi\epsilon_0 r_i) \Phi \quad (6)$$

where  $\Phi = (1/\epsilon)(\partial \ln \epsilon / \partial P)_T$ .<sup>14</sup> Thus, for a change in charge of an ion from  $z_1$  to  $z_2$  at an electrode, the contribution of solvation change to  $\Delta V_{\text{cell}}$  is  $-[N_A \Delta(z^2/r)e^2 / 8\pi\epsilon_0] \Phi$ , where  $\Delta(z^2/r) = (z_2^2/r_2) - (z_1^2/r_1)$ . If  $r_1 = r_2 = r$  so that the intrinsic volume change  $\Delta V_{\text{int}}$  of the molecule undergoing redox is

zero, we have<sup>7,15,16</sup>

$$\Delta V_{\text{cell}} = A - [N_A \Delta(z^2)e^2 / 8\pi\epsilon_0 r] \Phi \quad (7)$$

where  $A$  is a constant representing the contribution of the reference electrode together with those of any pressure-dependent interactions between the reactants and the supporting electrolyte that affect  $E_{1/2}$ . For series of complexes Fe(CN)<sub>*n*</sub>L<sub>(3–*n*/2)</sub><sup>(3–*n*)/(2–*n*)</sup> (bidentate L = phen or bpy,  $n = 0–6$ ) for which  $r_1 \approx r_2$ , Tregloan et al.<sup>15</sup> found a linear dependence of  $\Delta V_{\text{cell}}$  on  $\Delta(z^2)$  in a particular medium, aqueous KNO<sub>3</sub> (i.e., at constant  $\Phi$  and  $r_i$ ). In the present study, we used the DmFc<sup>+0</sup> couple to test eq 7 with respect to the dependence of  $\Delta V_{\text{cell}}$  on  $\Phi$  for a series of organic solvents at constant  $\Delta(z^2)$ .

A further objective of this study was to compare the nonaqueous electrode kinetics of a “well-behaved” couple (DmFc<sup>+0</sup>) with the kinetics of the corresponding outer-sphere bimolecular electron transfer (self-exchange) reaction in homogeneous solution (rate constants  $k_{\text{ex}}$ ), particularly with respect to pressure effects (recently reported for the DmFc<sup>+0</sup> self-exchange reaction<sup>13</sup>):



In the absence of strong adsorption of a reactant on the electrode, reaction 1 is effectively the same as reaction 8 but with a “virtual” exchange partner. In simple terms, for electron transfer to occur in reaction 1, both  $\text{ML}_n^{(z+1)+}$  and  $\text{ML}_n^{z+}$  must first adjust their internal and solvational configurations to a common intermediate configuration, whereas in reaction 1 only one reactant molecule needs to reorganize to that intermediate state. Consequently, the free energy of activation  $\Delta G_{\text{el}}^{\ddagger}$  for reaction 1 can be expected to be just half the corresponding quantity  $\Delta G_{\text{ex}}^{\ddagger}$  for reaction 8, as predicted by Marcus.<sup>17</sup>

$$k_{\text{ex}} = Z_{\text{ex}} \exp(-\Delta G_{\text{ex}}^{\ddagger} / RT) \quad (9)$$

$$k_{\text{el}} = Z_{\text{el}} \exp(-\Delta G_{\text{el}}^{\ddagger} / RT) \quad (10)$$

This expectation, however, is difficult to test precisely by comparing  $k_{\text{el}}$  with  $k_{\text{ex}}$  because  $Z_{\text{el}}$  and consequently  $k_{\text{el}}$  are typically affected by the nature, history, and size of the electrode surface. On the other hand, since these electrode properties are not significantly affected by hydrostatic pressures  $P$  of a few hundred MPa, the corresponding volumes of activation  $\Delta V_{\text{ex}}^{\ddagger}$  and  $\Delta V_{\text{el}}^{\ddagger}$

$$\Delta V_{\text{ex}}^{\ddagger} = -RT(\partial \ln k_{\text{ex}} / \partial P)_T \quad (11)$$

$$\Delta V_{\text{el}}^{\ddagger} = -RT(\partial \ln k_{\text{el}} / \partial P)_T \quad (12)$$

should stand in a 2:1 ratio in the absence of complicating factors, and this is borne out for most reactions of types (1)

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and (8) in *aqueous* media.<sup>1,4,5,8</sup> Furthermore, because  $\Delta V_{\text{ex}}^\ddagger$  can be predicted<sup>1,18</sup> to be moderately negative for outer-sphere electron transfer (in the absence of mechanistic aberrations such as counterion catalysis<sup>5,18,19</sup>), it follows that  $\Delta V_{\text{el}}^\ddagger$  should also be negative and of predictable magnitude ( $-1$  to  $-10$  cm<sup>3</sup> mol<sup>-1</sup>), and this is indeed the case for aqueous systems.<sup>1,4,5,8</sup>

For *nonaqueous solvents*, however, the picture is very different. To date, in all variable-pressure studies of electrode reaction kinetics in organic solvents,  $\Delta V_{\text{el}}^\ddagger$  has been found to be positive even though  $\Delta V_{\text{ex}}^\ddagger$ , where known for the corresponding self-exchange reactions in the same solvents, is invariably negative.<sup>1-3,6</sup> Furthermore, for electrode reactions in nonaqueous media,  $k_{\text{el}}$  correlates with solvent fluidity (reciprocal of the viscosity  $\eta$ ).<sup>1-3,6,20,21</sup> There are three plausible alternative explanations for the  $k_{\text{el}}-\eta^{-1}$  correlations: (i) The experimental  $k_{\text{el}}$  and  $\Delta V_{\text{el}}^\ddagger$  values are artifacts of the uncompensated resistance  $R_{\text{u}}$ , which is proportional to  $\eta$ .<sup>22</sup> (ii) The electrode reaction rate is diffusion controlled. (iii) The activation barrier crossing frequency is controlled by solvent dynamics or solvent “friction”<sup>1-3,6,20,21</sup> (strictly speaking, in rate control by solvent dynamics, the rate constant should correlate inversely with the longitudinal relaxation time  $\tau_{\text{L}}$  of the solvent, but this is usually at least roughly proportional to  $\eta$ <sup>11,20-28</sup>). In this study, we attempt to eliminate two of these alternatives.

The effect of pressure on  $k_{\text{el}}$  is of particular interest in this context because the viscosity of nonaqueous solvents increases sharply (approximately exponentially) with rising pressure and can therefore be readily “tuned” by applied pressure *without changing the chemical identity of the solvent*. Thus, in organic solvents, the existing data<sup>1-3,6</sup> indicate that  $\Delta V_{\text{el}}^\ddagger$  correlates roughly with the volume of activation for diffusion  $\Delta V_{\text{diff}}^\ddagger$  (eq 3) which, through the Stokes–Einstein relation

$$D = k_{\text{B}}T/6\pi\eta a \quad (13)$$

can be equated with  $\Delta V_{\text{visc}}^\ddagger$  for viscous flow of the solvent, a markedly positive quantity given by  $RT(\partial \ln \eta / \partial P)_T$ . Since  $D$  is measured in the presence of a supporting electrolyte which can affect  $\eta$  substantially, we show below that  $D$  is nonetheless proportional to  $\eta$  for the pure solvent, so that the identification of  $\Delta V_{\text{diff}}^\ddagger$  with  $\Delta V_{\text{visc}}^\ddagger$  holds regardless of the presence of the supporting electrolyte. For water as the solvent,  $\eta$  is fortuitously almost independent of pressure ( $\Delta V_{\text{visc}}^\ddagger \approx 0$ , 0–200 MPa).<sup>1,6</sup> Consequently, although  $\Delta V_{\text{el}}^\ddagger$

is positive and correlates roughly with  $\Delta V_{\text{diff}}^\ddagger$  for the Co(bpy)<sub>3</sub><sup>3+/2+</sup> and Fe(phen)<sub>3</sub><sup>3+/2+</sup> couples<sup>9</sup> in organic solvents, in water it assumes the theoretically predicted negative values whereas  $\Delta V_{\text{diff}}^\ddagger$  is essentially zero,<sup>2,6</sup> leaving little doubt that viscosity is the dominant influence on measurements of nonaqueous electrode kinetics.

These inferences, however, are based on a limited set of data. Poor solubility of the electrochemically active species and irreversibility of the electrode reaction often limit the choice of reactions and solvents. Furthermore, because a cycle of pressure measurements typically extends over several hours, the system must be chemically stable enough that measurements of  $k_{\text{el}}$  are reproducible over such periods. If one wishes to compare  $\Delta V_{\text{el}}^\ddagger$  with an available  $\Delta V_{\text{ex}}^\ddagger$  value for a given couple in the same solvent, the choice is restricted further.<sup>2,3</sup> Finally, results for highly charged couples such as Co(bpy)<sub>3</sub><sup>3+/2+</sup>,<sup>6,20,21</sup> Fe(phen)<sub>3</sub><sup>3+/2+</sup>,<sup>2</sup> or even Mn(CNchx)<sub>6</sub><sup>2+/+</sup><sup>2,9</sup> in nonaqueous media are likely to be complicated to an unknown extent by ion pairing with counterions from the supporting electrolyte. To minimize such pairing as well as medium (Debye–Hückel-type) effects and Coulombic work terms, one can study oxidation or reduction of a neutral substrate. Satisfactory  $\Delta V_{\text{el}}^\ddagger$  measurements were obtained with Ru(hfac)<sub>3</sub><sup>0/-</sup><sup>3,9</sup> but were limited to four solvents and are open to interpretational difficulties if one accepts the contention of Weaver et al.<sup>29</sup> that this electrode reaction is nonadiabatic.

We report here our attempts to define more clearly the relationship among  $\Delta V_{\text{el}}^\ddagger$ ,  $\Delta V_{\text{ex}}^\ddagger$ , and  $\Delta V_{\text{diff}}^\ddagger$  for a neutral/singly charged couple over a wider range of solvents using the DmFc<sup>+0</sup> couple, which is sufficiently soluble for electrochemical measurements in at least 10 organic solvents and for which  $\Delta V_{\text{ex}}^\ddagger$  values in AC, DCM, and (with low precision) AN<sup>9</sup> are now available.<sup>13</sup> Attempts to extend our high-pressure studies of the Fc<sup>+0</sup> electrode reaction<sup>2</sup> to organic solvents other than AN yielded reproducible  $k_{\text{el}}$  data only with DMF and DMSO.<sup>9</sup> For comparison with a highly charged couple, we also obtained further data on the Fe(phen)<sub>3</sub><sup>3+/2+</sup> electrode reaction studied previously.<sup>2</sup>

## Experimental Section

**Materials.** Decamethylferrocene (Aldrich, 97%) was sublimed twice at 140 °C under reduced pressure. Ferrocene was made as described by Jolly<sup>30</sup> and purified by sublimation at 130 °C at atmospheric pressure. [Fe(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> was made as described elsewhere.<sup>2</sup> TBAP, TEAP<sup>9</sup> (Fluka, >99%, puriss electrochemical grade), and silver nitrate (Engelhardt, ACS reagent grade) were used as received. The solvents AN, AC, MeOH, EtOH, PrOH, and DCM (abbreviations as in ref 9) were purified by standard procedures.<sup>31,32</sup> PC (Aldrich, 99.7% anhydrous), DMF (Aldrich, 99.8% spectrophotometric grade or 99.9% HPLC grade), DMSO

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**Table 1.** Parameters Representing Pressure Dependences of Cell Potentials and Electrode Reaction Kinetics for  $\text{Fc}^{+/0}$ ,  $\text{DmFc}^{+/0}$ , and  $\text{Fe}(\text{phen})_3^{3+/2+}$  in Various Solvents<sup>a</sup>

couple	medium <sup>b</sup>	solvent	$E_{1/2}^{0c}/\text{mV}$	$\Delta V_{\text{cell}}^c/\text{cm}^3 \text{ mol}^{-1}$	$D^0/10^{-6} \text{ cm}^2 \text{ s}^{-1}$	$\Delta V_{\text{diff}}^{\#}/\text{cm}^3 \text{ mol}^{-1}$	$k_{\text{el}}^0/10^{-2} \text{ cm s}^{-1}$	$\Delta V_{\text{el}}^{\#}/\text{cm}^3 \text{ mol}^{-1}$
$\text{DmFc}^{+/0}$	TBAP (0.5)	AC	$-350 \pm 3$	$0.8 \pm 0.8$	$14.1 \pm 0.6$	$9.3 \pm 0.2$		
		AN	$-400 \pm 3$	$-3.3 \pm 1.1$	$12.6 \pm 0.4$	$7.7 \pm 0.1$		
		PC	$-422 \pm 2$	$-7.1 \pm 0.7$	$1.77 \pm 0.22$	$17.3 \pm 2.1$	$3.7 \pm 0.5$	$18.8 \pm 0.9$
		DMSO <sup>d</sup>	$-433 \pm 2$	$-7.2 \pm 0.2$	$3.5 \pm 0.3$	$14.8 \pm 0.2$	$9.3 \pm 1.2$	$14.5 \pm 0.8$
		PY	$-379 \pm 5$		$5.0 \pm 0.2$	$13.9 \pm 0.1$	$4.8 \pm 0.5$	$12.6 \pm 0.2$
		DCM	$-351 \pm 1$	$5.4 \pm 0.9^e$	$10.7 \pm 0.1^f$	$8.3 \pm 0.1^f$	$8.0 \pm 1.5^f$	$5.0 \pm 0.5^f$
		EtOH	$-329 \pm 2$	$-3.7 \pm 0.4$	$4.6 \pm 0.2$	$10.2 \pm 0.1$	$3.8 \pm 0.1$	$8.5 \pm 0.2$
		BN	$-367 \pm 2$	$-2.9 \pm 0.6$	$3.6 \pm 0.2$	$17.2 \pm 0.2$	$3.7 \pm 0.6$	$16.5 \pm 0.4$
		DMF <sup>d,e</sup>	$-407 \pm 2$	$-4.4 \pm 0.9$	$6.9 \pm 0.1$	$9.8 \pm 0.2$	$12.2 \pm 0.3$	$11.6 \pm 0.6$
		DMF	$-402 \pm 2^g$	$-4.9 \pm 1.0^g$	$6.0 \pm 0.4^g$	$11.3 \pm 1.0^g$	$7.7 \pm 1.5^h$	$11.4 \pm 0.7^h$
	TBAP (0.2) TBAP (0.1) TEAP (0.2)	DMF <sup>e,i</sup>	$-398 \pm 2$	$-2.2 \pm 0.7$	$5.3 \pm 0.1$	$11.3 \pm 0.2$	$4.9 \pm 0.1$	$12.8 \pm 0.3$
		DMF <sup>e</sup>	$-404 \pm 3$	$-2.7 \pm 1.6$	$7.4 \pm 0.1$	$9.6 \pm 0.1$	$5.3 \pm 0.1$	$10.2 \pm 0.3$
		DMF <sup>e</sup>	$-408 \pm 2$	$-3.3 \pm 0.7$	$9.4 \pm 0.1$	$9.0 \pm 0.1$	$8.4 \pm 0.1$	$10.0 \pm 0.4$
		AN <sup>e</sup>	$-422 \pm 1$	$-4.7 \pm 1.0$	$17.8 \pm 0.3$	$6.6 \pm 0.4$	$13.0 \pm 0.2$	$7.0 \pm 0.4$
		DMF <sup>e</sup>	$-411 \pm 2$	$-5.9 \pm 1.0$	$6.4 \pm 0.1$	$9.5 \pm 0.2$	$5.7 \pm 0.1$	$9.5 \pm 0.2$
		PC <sup>e</sup>	$-442 \pm 1$	$-8.6 \pm 0.6$	$1.59 \pm 0.01$	$14.9 \pm 0.2$	$2.6 \pm 0.1$	$16.6 \pm 0.2$
		DMSO <sup>d,e</sup>	$-446 \pm 4$	$-5.8 \pm 1.8$	$1.98 \pm 0.01$	$11.5 \pm 0.2$	$4.0 \pm 0.1$	$13.6 \pm 0.3$
		DMF <sup>f</sup>	$72 \pm 6$	$-10.2 \pm 1.0$	$7.0 \pm 0.1$	$10.9 \pm 0.6$	$9.1 \pm 0.9$	$12.2 \pm 0.3$
		DMSO <sup>d,f</sup>	$39 \pm 1$	$-12.9 \pm 1.6$	$3.7 \pm 0.2$	$13.4 \pm 0.1$	$4.8 \pm 0.2$	$12.9 \pm 0.1$
		$\text{Fe}(\text{phen})_3^{3+/2+}$	TBAP (0.5)	AN <sup>e,j</sup>	$768 \pm 1$	$2.5 \pm 0.6$	$5.4 \pm 0.1$	$8.0 \pm 0.1$
DMF <sup>e</sup>	$675 \pm 1$			$-1.7 \pm 0.6$	$2.7 \pm 0.1$	$9.9 \pm 0.3$	$5.1 \pm 0.1$	$13.5 \pm 0.6$
PC <sup>e</sup>	$725 \pm 1$			$-0.8 \pm 0.6$	$0.85 \pm 0.01$	$16.2 \pm 0.2$	$0.95 \pm 0.02$	$20.4 \pm 0.5$
DMSO <sup>d,e</sup>	$651 \pm 1$			$-3.3 \pm 0.8$	$0.91 \pm 0.08$	$11.3 \pm 1.9$	$4.7 \pm 0.6$	$16.6 \pm 2.9$
Na <sub>2</sub> SO <sub>4</sub> (0.1) <sup>k</sup>	H <sub>2</sub> O		$1040 \pm 5$	$15.3 \pm 0.7^l$	$4.0 \pm 0.1$	$\sim 0$	$30.0 \pm 0.3$	$-1.6 \pm 0.1$

<sup>a</sup> 25.0 °C, except as noted; all parameters calculated from fits to eqs 14, 15, and 18, averaged over 3 independent runs except as noted; superscript 0 indicates extrapolated value at atmospheric pressure. <sup>b</sup> Concentration in parentheses, mol L<sup>-1</sup>. <sup>c</sup> Relative to Ag/(0.01 mol L<sup>-1</sup> AgNO<sub>3</sub> + 0.5 mol L<sup>-1</sup> TBAP in AN) except as noted. <sup>d</sup> 45.0 °C. <sup>e</sup> Single run. <sup>f</sup> Average of 2 runs. <sup>g</sup> Average of 5 runs. <sup>h</sup> Average of 4 runs. <sup>i</sup> 4.7 °C. <sup>j</sup> Reference 2. <sup>k</sup> Reference 8. <sup>l</sup> Reference electrode Ag/AgCl/(saturated aqueous KCl).

(Aldrich, 99.9% ACS reagent grade), PY (Aldrich, 99.9+%), and BN (Aldrich, 99.9% HPLC grade) were used as received.

**Electrochemical Measurements.** The high-pressure apparatus and measurement techniques were essentially as described previously.<sup>1–8</sup> The working and auxiliary electrodes were of Pt wire (0.5 mm diameter); the working electrode was typically 2 mm long (calibrated effective area 0.033–0.034 cm<sup>2</sup>; cf. 0.0334 cm<sup>2</sup> calculated from geometrical dimensions). The reference electrode consisted of a silver rod in contact with a solution containing AgNO<sub>3</sub> (0.01 mol L<sup>-1</sup>) and TBAP (0.50 mol L<sup>-1</sup>) in AN. The working electrode was cleaned before each run using 0.05 μm Al<sub>2</sub>O<sub>3</sub> on a PSA nylon polishing cloth (Buehler) followed by sonication, first in K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/H<sub>2</sub>SO<sub>4</sub> and then in deionized water.

CV and ACV measurements were made using an EG&G model 273 potentiostat and model 124A or 5208 lock-in amplifier with output to an X–Y recorder (The Recorder Co., model 200). Half-wave potentials  $E_{1/2}$  (the average of the potentials of the current extrema of the forward and backward CV sweeps) and mean diffusion coefficients  $D$  were obtained from CVs run at a scan rate of 100 mV s<sup>-1</sup>. The ACV peak potentials  $E_{\text{dc}}$  and in-phase and 90°-out-of-phase (quadrature) currents were obtained with impressed ac potentials of 8–9 mV at frequencies  $f = 15–85$  Hz, and the uncompensated resistance  $R_{\text{u}}$  was measured directly at 10 kHz. From these data, the electrochemical transfer coefficients  $\alpha$  and standard electrode reaction rate constants  $k_{\text{el}}$  (corrected using the measured values of  $R_{\text{u}}$ ) were calculated as described below. For measurements at variable pressure,  $P$  was increased in ~50 MPa steps to ~205 MPa, starting at ~5 MPa to firm up seals and connections and to eliminate any small bubbles, and then dropped carefully to ~5 MPa and the initial measurement repeated; only those experiments for which the final and initial readings agreed within the experimental uncertainty ( $\pm 2$  mV in  $E_{1/2}$ ,  $\pm 2\%$  in  $R_{\text{u}}$ ,  $\sim \pm 5\%$  in  $k_{\text{el}}$ ) were accepted. Measurements at variable pressure were made at 25.0 °C with the exception of DMSO solutions (45.0

°C, to obviate pressure-induced freezing<sup>33</sup>). For consistency with the variable-pressure studies, the temperature dependences of  $E_{1/2}$ ,  $D$ , and  $k_{\text{el}}$  were measured at 5 MPa in the pressure apparatus, the temperature of which was controlled to  $\pm 0.1$  °C with an aluminum jacket through which water was circulated from an external thermostat.

## Results

The key parameters describing the pressure dependences of  $E_{1/2}$ ,  $D$ , and  $k_{\text{el}}$  are given in Table 1, and the temperature dependences in Table 2. The data from which they were derived are listed in the Supporting Information. Since the same reference electrode was used throughout these experiments, its contribution to the constant  $A$  in eq 7 was the same for all.

**Variable-Pressure Studies:  $\text{DmFc}^{+/0}$ .** Quasi-reversible CVs were observed for all three couples in all solvents. The peak separations  $\Delta E_{\text{p}}$  of the CVs (typically 70–80 mV) were not significantly dependent on pressure except in BN (80–90 mV) and PrOH (130–165 mV), for which  $R_{\text{u}}$  was unusually high (520 and 3300 Ω, respectively, increasing with pressure; cf. 120–390 Ω for the other solvents). The peak currents  $i$  were 10–15 μA for the solvents that gave the lowest  $R_{\text{u}}$  (~120 Ω) and smaller for those with higher  $R_{\text{u}}$ , such that  $iR_{\text{u}}$  corrections to  $E_{1/2}$  were never more than 1.5 mV (i.e., within the experimental uncertainty) and were therefore neglected, as were the corresponding very small contributions of the pressure dependence of  $iR_{\text{u}}$  to  $\Delta V_{\text{cell}}$ . The reproducibility of  $E_{1/2}$  and  $D$  over a pressure cycle in MeOH was poor because of the large background currents

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**Table 2.** Parameters Representing Temperature Dependences of Cell Potentials and Electrode Reaction Kinetics of  $\text{DmFc}^{+/0}$  in Various Organic Solvents<sup>a</sup>

medium <sup>b</sup>	solvent	$E_{1/2}^{298}/\text{mV}^{c,d}$	$\Delta H_{\text{cell}}/\text{kJ mol}^{-1 c,e}$	$\Delta S_{\text{cell}}/\text{J K}^{-1} \text{mol}^{-1 c,e}$	$A_{\text{diff}}/10^{-4} \text{cm}^2 \text{s}^{-1 f}$	$E_{a(\text{diff})}/\text{kJ mol}^{-1 f}$	$A_{\text{el}}/\text{cm}^2 \text{s}^{-1 g}$	$E_{a(\text{el})}/\text{kJ mol}^{-1 g}$
TBAP (0.5)	AC	-359	29.9 ± 0.8	-16 ± 3	2.53	7.1 ± 0.3		
	AN	-417	31.9 ± 0.5	-28 ± 2	1.87	6.7 ± 0.2		
	PC	-430	30.5 ± 0.9	-37 ± 3	9.6	16.5 ± 0.9	3200	29.0 ± 1.3
	DMF	-398	33.9 ± 1.8	-15 ± 6	2.76	9.6 ± 0.3	248	20.5 ± 2.4
TBAP (0.2)	AN	-416	31.2 ± 1.6	-30 ± 6	1.66	5.8 ± 0.5		
	DMF	-404	35.8 ± 2.3	-11 ± 8	1.91	8.3 ± 0.6	91	17.8 ± 1.6
TBAP (0.1)	AN	-410	27.9 ± 0.6	-39 ± 2	1.85	5.9 ± 0.1		
	DMF	-406	31.9 ± 1.4	-24 ± 5	2.43	8.6 ± 0.4	22	14.5 ± 0.7
TEAP (0.2)	AN	-422	33.0 ± 1.7	-26 ± 7	1.49	5.7 ± 0.4	682	21.0 ± 1.3
	PC	-443	30.2 ± 1.5	-42 ± 5	5.3	14.5 ± 0.8	240	22.9 ± 0.6
	DMF	-408	32.2 ± 1.8	-24 ± 6	1.38	8.3 ± 0.2	61	17.2 ± 0.3
	DMSO	-445	36.4 ± 2.8	-22 ± 9			94	20.1 ± 1.1

<sup>a</sup> At 5 MPa; measurements at 6–7 temperatures from 1 to 45 °C approximately (except DMSO: 20 to 45 °C). <sup>b</sup> Concentration in parentheses, mol L<sup>-1</sup>. <sup>c</sup> Relative to  $\text{Ag}/(0.01 \text{ mol L}^{-1} \text{ AgNO}_3 + 0.5 \text{ mol L}^{-1} \text{ TBAP in AN})$ . <sup>d</sup> Calculated from  $\Delta H_{\text{cell}}$  and  $\Delta S_{\text{cell}}$  for 25.0 °C. <sup>e</sup> Equation 19. <sup>f</sup> Equation 20. <sup>g</sup> Equation 21.

typical of this solvent due to its decomposition around the  $\text{DmFc}^{+/0}$  potential.<sup>34</sup> In  $\text{PrOH}$ , in which TBAP was soluble only to the extent of about 0.2 mol L<sup>-1</sup>,  $R_u$  was too high for reliable electrochemical measurements. Data for  $\text{MeOH}$  and  $\text{PrOH}$  are therefore not included in Table 1. For  $\text{PY}$ , slow drifting of  $E_{1/2}$  to less negative values precluded accurate measurement of  $\Delta V_{\text{cell}}$ , but  $D$  was satisfactorily reproducible over a pressure cycle. For the remaining systems,  $E_{1/2}$  was linearly dependent on  $P$  within the experimental uncertainty, so that  $\Delta V_{\text{cell}}$  was effectively constant (0–200 MPa) and was given (cf. eq 2) by

$$E_{1/2} = E_{1/2}^\circ - P\Delta V_{\text{cell}}/F \quad (14)$$

Mean diffusion coefficients  $D$  for the electroactive species were obtained from both the anodic and cathodic peak currents of the CVs, with good agreement. Values of  $D$  at 0.1 MPa for  $\text{DmFc}^{+/0}$  at constant [TBAP] were directly proportional to literature values<sup>32</sup> of  $\eta^{-1}$  for the various solvents (Figure S1 in the Supporting Information), implying that the hydrodynamic radius  $a$  of  $\text{DmFc}^+$  was effectively constant from solvent to solvent and that any ion pairing between  $\text{DmFc}^+$  and perchlorate ion from the supporting electrolyte was unimportant in this context. In all cases,  $\ln D$  was linearly dependent on  $P$ , implying that  $\Delta V_{\text{diff}}^\ddagger$  was effectively constant, 0–200 MPa, whence we have from eq 3 the following:

$$\ln D = \ln D^\circ - P\Delta V_{\text{diff}}^\ddagger/RT \quad (15)$$

Experiments with variable [TBAP] in AN and DMF showed a significant decrease in  $D$  with increasing [TBAP], and this can be ascribed to the expected increase of  $\eta$  caused by the supporting electrolyte. When the supporting electrolyte in DMF was 0.2 mol L<sup>-1</sup> TEAP, values of  $D$  and  $\Delta V_{\text{diff}}^\ddagger$  (Table 1) were not substantially different from those with 0.2 mol L<sup>-1</sup> TBAP, while for AN, PC, and DMSO these parameters are roughly comparable in TEAP and TBAP solutions (allowing for the difference in concentrations). The effects of TEAP and TBAP on  $\eta$  may therefore be taken to be closely similar.

The electrochemical transfer coefficient  $\alpha$ , calculated from the peak potentials  $E_{\text{dc}}$  of ACVs

$$E_{\text{dc}} = E_{1/2} + (RT/F) \ln [\alpha/(1 - \alpha)] \quad (16)$$

was typically in the range  $0.45 \pm 0.05$  (for reduction) and not significantly dependent on pressure or the nature of the solvent. From the ratio of the in-phase to the quadrature currents, the phase angle  $\varphi$  and thence  $k_{\text{el}}$  were calculated with correction for  $R_u$  and double-layer capacitance as previously described<sup>6,8</sup> using eq 17, in which the angular ac frequency  $\omega = 2\pi f$ .

$$k_{\text{el}} = (2D\omega)^{1/2}/[\alpha^{-\alpha}(1 - \alpha)^{-(1-\alpha)}(\cot \varphi - 1)] \quad (17)$$

Values of  $k_{\text{el}}$  were accepted only if they were consistent over at least three different selections of  $f$ . As  $\ln k_{\text{el}}$  was linearly dependent on  $P$  within the experimental uncertainty,  $\Delta V_{\text{el}}^\ddagger$  was effectively constant over the range 0–200 MPa:

$$\ln k_{\text{el}} = \ln k_{\text{el}}^\circ - P\Delta V_{\text{el}}^\ddagger/RT \quad (18)$$

Reliable  $k_{\text{el}}$  values were obtained from ACVs when the ratio of the in-phase to quadrature faradaic currents lay between 1.2 and about 5. Passage of this ratio beyond 5 was typically heralded by distortion of the quadrature peak from the ideal bell shape and tended to occur when the reaction was too slow (notably at higher pressures, since  $\Delta V_{\text{el}}^\ddagger$  was invariably positive),  $R_u$  was too high, or the chosen  $f$  was too large. The lower limit applied when the reaction was too fast, as in the case of  $\text{DmFc}^{+/0}$  in AN with 0.5 mol L<sup>-1</sup> TBAP ( $k_{\text{el}}$  values were, however, measurable in AN with 0.2 mol L<sup>-1</sup> TEAP). Murray et al.<sup>35</sup> circumvented this problem by measuring  $k_{\text{el}}$  for  $\text{DmFc}^{+/0}$  at low temperatures (130–181 K) in butyronitrile and butyronitrile–ethyl chloride solvents, but most of the solvents of interest in the present study would freeze under pressure at low temperatures.

As noted above,  $k_{\text{el}}$  is very dependent upon the nature, history, and size of the working electrode,<sup>11,36</sup> particularly for the faster reactions, so it is not surprising that the values

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of  $k_{\text{el}}^0$  for  $\text{DmFc}^{+/0}$  at a conventional 0.5 mm diameter Pt wire electrode, listed in Table 1, have rather large uncertainty limits (standard deviations of the mean of several experiments) and are consistently about 10-fold smaller than corresponding data reported by Weaver et al.<sup>37</sup> for a dropping Hg electrode. Weaver et al.<sup>37</sup> themselves found substantial variation in  $k_{\text{el}}$  depending on the mode of measurement. For the  $\text{Fc}^{+/0}$  couple,  $k_{\text{el}}$  values ranging from 0.02 to 220  $\text{cm s}^{-1}$  at 25 °C have been reported, the favored values being 1–4  $\text{cm s}^{-1}$  and the larger discrepancies being attributed to problems in defining the surface area of microelectrodes or to uncompensated resistance.<sup>11</sup> In general, conventional wire electrodes such as were used in this study give lower apparent  $k_{\text{el}}$  values than microelectrodes.<sup>11,36</sup> In this study, however, the emphasis is on the *relative* rather than absolute values of  $k_{\text{el}}$  as pressure and temperature are varied, so it is enough that  $k_{\text{el}}$  in the various solvents is proportional to the values of Weaver et al.<sup>37</sup> because, within a particular experiment, neither the size of the electrode nor the nature of its surface changes. As for the problem of uncompensated resistance, we stress that the correction for the  $iR_{\text{u}}$  potential drop in the calculation of the  $k_{\text{el}}$  values of Tables 1 and 2 was made with carefully measured  $R_{\text{u}}$  values.

**Variable-Pressure Studies:  $\text{Fc}^{+/0}$ .** Although reproducible values of  $E_{1/2}^{\circ}$  and  $\Delta V_{\text{cell}}$  were previously<sup>2</sup> obtained for  $\text{Fc}^{+/0}$  in AN (78 mV and  $-8.7 \text{ cm}^3 \text{ mol}^{-1}$  in 0.5 mol  $\text{L}^{-1}$  TBAP; cf. 103 mV and  $-9.9 \text{ cm}^3 \text{ mol}^{-1}$  found by Tregloan et al.<sup>16</sup> for 0.1 mol  $\text{L}^{-1}$  TEAP), apparent values of  $D$  and  $k_{\text{el}}$  for  $\text{Fc}^{+/0}$  in AC and PC drifted too much for measurements at variable pressure. In this work, however, satisfactory results were obtained for DMF (at 25 °C) and DMSO (at 45 °C) with 0.5 mol  $\text{L}^{-1}$  TBAP. Experimental difficulties with  $\text{Fc}^{+/0}$  in organic solvents (especially AN) arise partly because  $k_{\text{el}}$  is high but mainly because of film formation on the electrode.<sup>10</sup> The latter problem was not evident with  $\text{DmFc}^{+/0}$ .

**Variable-Pressure Studies:  $\text{Fe}(\text{phen})_3^{3+/2+}$ .** Data for DMF, PC, and DMSO solutions were added to those previously obtained for AN<sup>2</sup> and water.<sup>8</sup> The pressure dependences of  $D$  and  $k_{\text{el}}$  for DMSO, obtained at 45 °C, showed larger scatter than usual but gave  $\Delta V_{\text{diff}}^{\ddagger}$  and  $\Delta V_{\text{el}}^{\ddagger}$  values consistent with those for other solvents.

**Variable-Temperature Studies ( $\text{DmFc}^{+/0}$  Only).** The temperature dependence of  $E_{1/2}$  was small but measurable and was fitted to the expression

$$FE_{1/2} = T\Delta S_{\text{cell}} - \Delta H_{\text{cell}} \quad (19)$$

The dependences of  $\ln D$  and  $\ln k_{\text{el}}$  on  $1/T$  were linear, giving Arrhenius activation energies  $E_{\text{a}(\text{diff})}$  and  $E_{\text{a}(\text{el})}$  with quite narrow uncertainties (Table 2) except with DMSO as solvent, for which the high freezing point limited the accessible temperature range.

$$D = A_{\text{diff}} \exp(-E_{\text{a}(\text{diff})}/RT) \quad (20)$$

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$$k_{\text{el}} = A_{\text{el}} \exp(-E_{\text{a}(\text{el})}/RT) \quad (21)$$

For  $k_{\text{el}}$ , the Arrhenius eq 21 was used rather than the customary Eyring equation

$$k_{\text{el}} = (k_{\text{B}}T/h) \exp[(\Delta S_{\text{el}}^{\ddagger}/R) - (\Delta H_{\text{el}}^{\ddagger}/RT)] \quad (22)$$

because  $A_{\text{el}} (\equiv (k_{\text{B}}T/h) \exp(\Delta S_{\text{el}}^{\ddagger}/R))$  is dependent on electrode properties and suspected solvent-dynamical contributions, so clouding the meaning of the entropy of activation  $\Delta S_{\text{el}}^{\ddagger}$ ; if, however, the data are fitted to eq 22,  $\Delta S_{\text{el}}^{\ddagger}$  for the  $\text{DmFc}^{+/0}$  electrode reaction in the various solvents would be on the order of  $-200 \text{ J K}^{-1} \text{ mol}^{-1}$ . In any event,  $E_{\text{a}(\text{el})}$  may be identified with  $\Delta H_{\text{el}}^{\ddagger}$ .

## Discussion

To assist in the interpretation of the results summarized in Tables 1 and 2, selected solvent properties are collected in Table 3. Measured values of the function  $\Phi$ <sup>14</sup> are not available for all solvents of interest at the experimental temperatures. As noted elsewhere,<sup>38,39</sup> however, the effect of pressure on the dielectric constant  $\epsilon$  of a liquid follows closely the effect on its density  $\rho$ , so that  $(\partial \ln \epsilon/\partial P)_T$  can, to a generally good approximation, be equated to isothermal compressibility  $\beta$  ( $=(\partial \ln \rho/\partial P)_T$ ). Table 3 shows that  $\Phi$  is satisfactorily represented by  $\beta/\epsilon$ . For DMF, the compression data of Brummer<sup>40</sup> were fitted to the Tait-type equation<sup>38</sup>

$$1 - \rho^0/\rho = C \ln(1 + P/B) \quad (23)$$

to give the constants  $B = 137.9 \text{ MPa}$  and  $C = 0.0921$ , whence  $\beta = C/B$  when the applied pressure  $P = 0$ . It must be borne in mind, however, that the data of Table 3 are valid at atmospheric pressure, whereas the experimental values of  $\Delta V_{\text{cell}}$  and  $\Delta V_{\text{diff}}^{\ddagger}$  given in Table 1 are effectively averages over the range 0–200 MPa. Furthermore, the data for Tables 1 and 2 refer to solutions containing 0.1–0.5 mol  $\text{L}^{-1}$  TBAP or TEAP.

Other data required for the interpretation of the results summarized in Tables 1 and 2 are the effective radii  $r$  of  $\text{DmFc}$ ,  $\text{DmFc}^+$ ,  $\text{Fc}$ , and  $\text{Fc}^+$ . Crystallographic data on various solids<sup>43–48</sup> suggest a small *contraction* (4–5 pm in the mean  $\text{Fe}-\text{C}_{\text{ring}}$  distances) when  $\text{DmFc}^+$  or  $\text{Fc}^+$  gains an electron (because this will be a bonding electron), but the situation is confused by small differences in  $\text{Fe}-\text{C}_{\text{ring}}$  distances

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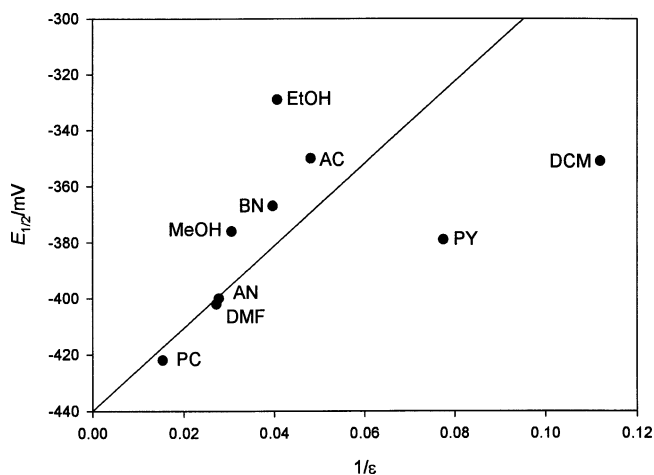
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**Table 3.** Viscosities, Isothermal Compressibilities, and Pressure Dependences of Dielectric Constants of Solvents<sup>a</sup>

solvent	$\eta/\text{mPa s}$	$\beta/10^{-10} \text{ Pa}^{-1}$	$\epsilon$	$\beta\epsilon^{-1}/10^{-10} \text{ Pa}^{-1}$	$\Phi/10^{-10} \text{ Pa}^{-1}$	refs
AN	0.341	11.1	36.0	0.308	0.298	32, 38, 39
AC	0.303	12.6	20.8	0.607	0.772	14, 32, 38
MeOH	0.551	11.5	32.7	0.352	0.366	14, 32, 38
PC	2.53	5.22	64.9	0.0804	0.0768	32, 38
DMF	0.820	6.68	36.7	0.182		32, 40
DMSO	1.383 <sup>b,c</sup>	5.67 <sup>b</sup>	43.9 <sup>b</sup>	0.129 <sup>b</sup>		32, 41
PY	0.884	8.50	12.9	0.659		32, 41
DCM	0.411 <sup>d</sup>	9.97	8.93	1.12	(1.72) <sup>e</sup>	14, 32, 38
EtOH	1.083	11.2	24.6	0.456	0.297	14, 32
BN	1.237	6.24	25.2	0.248	0.227	14, 32, 42
PrOH	1.943	9.17	20.5	0.448		32, 41

<sup>a</sup> 25.0 °C except as noted, 0.1 MPa. <sup>b</sup> 45.0 °C. <sup>c</sup> Extrapolated. <sup>d</sup> Interpolated. <sup>e</sup> 30.0 °C.



**Figure 1.** Cell potentials for  $\text{DmFc}^{+/0}$  (relative to  $\text{Ag}/(0.01 \text{ mol L}^{-1} \text{ AgNO}_3 + 0.50 \text{ mol L}^{-1} \text{ TBAP in AN})$ ) in various solvents containing  $0.50 \text{ mol L}^{-1} \text{ TBAP}$  versus the inverse of the dielectric constants  $\epsilon$  of the pure solvents at  $25.0 \text{ }^\circ\text{C}$ . The straight line has the theoretical slope of  $N_A \Delta(z^2/r)e^2/8\pi\epsilon_0 F = 1490 \text{ mV}$  and an assumed infinite- $\epsilon$  intercept of  $-440 \text{ mV}$ .

between staggered ( $D_{5d}$ ) and eclipsed ( $D_{5h}$ ) conformations (see tabulation by Miller et al.<sup>47</sup>), and it is not clear what conformations the cationic and uncharged ferrocenes adopt in solution. On average, the  $\text{Fe}-\text{C}_{\text{ring}}$  distances in  $\text{DmFc}^+$  and  $\text{DmFc}$  are respectively 209 and 205 pm. On the other hand, the average  $\text{Fe}-\text{C}$  bond lengths in solid  $\text{Fc}$  and  $\text{Fc}^+\text{PF}_6^-$ , in which both  $\text{Fc}$  and  $\text{Fc}^+$  have  $D_{5d}$  symmetry, are virtually identical ( $204.5 \pm 1.0$ <sup>45</sup> and  $204.85 \pm 1.6$  pm,<sup>46</sup> respectively). As before,<sup>13</sup> we adopt  $r = 400$  and  $480$  pm for  $\text{Fc}$  and  $\text{DmFc}$  (from crystal packing data), whence  $r = 400$  and  $484$  for  $\text{Fc}^+$  and  $\text{DmFc}^+$ , respectively. The contraction in  $\text{Fe}-\text{C}_{\text{ring}}$  bond lengths on reduction of  $\text{DmFc}^+$  is small, but it results in an estimated change in the intrinsic volume of  $\text{DmFc}^+$  (regarded as a sphere) of  $\Delta V_{\text{int}} \approx -7 \text{ cm}^3 \text{ mol}^{-1}$ .

**Cell Potentials.** From eq 5, it may be expected that, if  $\Delta G_{\text{solv}}$  is the main factor determining changes in  $E_{1/2}$  from solvent to solvent, then  $E_{1/2}$  should be a linear function of  $\epsilon^{-1}$ . For  $\text{DmFc}^{+/0}$ ,  $z_2 = 0$ , so the appropriate value of  $r$  is that for the cation (484 pm) and the slope is predicted to be  $-\Delta G_{\text{solv}}/F = -N_A \Delta(z^2/r)e^2/8\pi\epsilon_0 F \approx 1.49 \text{ V}$ . In Figure 1, which displays the  $\text{DmFc}^{+/0}$  cell potentials for media with  $0.50 \text{ mol L}^{-1}$  supporting electrolyte at  $25.0 \text{ }^\circ\text{C}$  as a function of  $1/\epsilon$ , the straight line has been drawn with slope  $1490 \text{ mV}$  and an assumed intercept of  $-440 \text{ mV}$ . Clearly, this theoretical line does not represent the experimental data well,

especially at low  $\epsilon$ . As noted above, the hydrodynamic radius of  $\text{DmFc}^{+/0}$  does not vary from solvent to solvent, so the large scatter of the data is unlikely to be due to variations in  $r$  but probably reflects the neglect of junction potentials at the reference electrode. There is also the possibility that ion pairing between  $\text{DmFc}^+$  and the perchlorate of the supporting electrolyte affects  $E_{1/2}$ , particularly at low  $\epsilon$ , although the diffusion coefficients show no evidence of this. Qualitatively, however, the general rising trend in  $E_{1/2}$  with  $1/\epsilon$  is consistent with expectations.

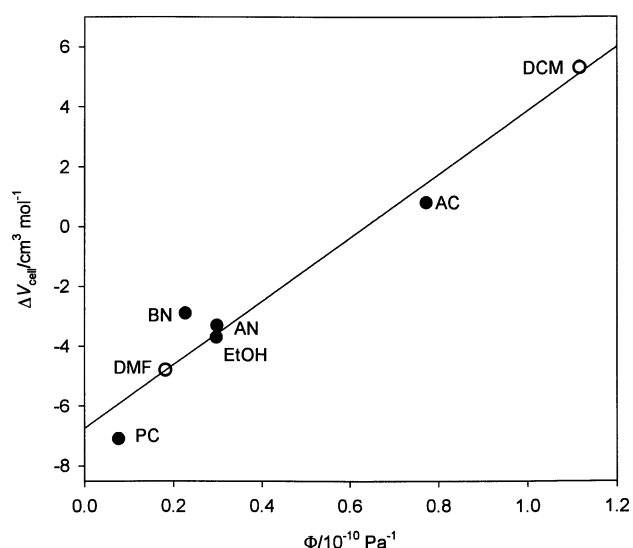
**Temperature Dependence of Cell Potentials.** The  $E_{1/2}$ ,  $\Delta H_{\text{cell}}$ , and  $\Delta S_{\text{cell}}$  data for  $\text{DmFc}^{+/0}$  in Tables 1 and 2 show that  $E_{1/2}$  is determined very largely by  $\Delta H_{\text{cell}}$ , as found by Hupp and Weaver<sup>49</sup> for low-charged couples in various nonaqueous solvents, but no strong, unequivocal trends in  $E_{1/2}$  with the nature or concentration of the supporting electrolyte are evident. Among the different solvents, PC consistently gave the smallest  $\Delta H_{\text{cell}}$  and the most negative values of  $E_{1/2}$  (at  $25.0 \text{ }^\circ\text{C}$ ) and  $\Delta S_{\text{cell}}$ , as expected from eq 5 and its temperature derivative (eq 24) if differences in solvational change largely determine the trends in  $\Delta G_{\text{cell}}$  ( $= -FE_{1/2} = \Delta H_{\text{cell}} - T\Delta S_{\text{cell}}$ ) because the dielectric constant of PC is the highest of the chosen organic solvents<sup>32,39</sup> (note that  $(\partial \ln \epsilon/\partial T)_P$  is negative and varies less from solvent to solvent than does  $\epsilon$ ).

$$\Delta S_{\text{solv}} = A' + [N_A \Delta(z^2/r)e^2/8\pi\epsilon_0 Tr](\epsilon^{-1})(\partial \ln \epsilon/\partial T)_P \quad (24)$$

$\Delta S_{\text{cell}}$  includes a contribution (represented by the constant  $A'$  in eq 24) from the temperature dependence of the reference half-cell potential; this contribution can be eliminated by use of a nonisothermal cell in which the reference half-cell is kept at a constant temperature,<sup>49,50</sup> but for consistency with the variable-pressure experiments this approach was not used here. Detailed comparisons based on  $\Delta S_{\text{solv}}$  alone, however, may be inappropriate, since Hupp and Weaver<sup>49</sup> present evidence for an additional contribution to  $\Delta S_{\text{cell}}$  that depends on the Gutmann acceptor number of the solvent, and in any event substantial compensation between  $\Delta H_{\text{cell}}$  and  $T\Delta S_{\text{cell}}$  is evident in Table 2 (i.e.,  $\Delta H_{\text{cell}}$  and  $\Delta S_{\text{cell}}$  often vary substantially in the same direction between cases with similar  $E_{1/2}$  values at  $25 \text{ }^\circ\text{C}$ ).

(49) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1984**, *23*, 3639.

(50) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131.



**Figure 2.** Reaction volumes for  $\text{DmFc}^{+/0}$  (relative to  $\text{Ag}/(0.01 \text{ mol L}^{-1} \text{ AgNO}_3 + 0.50 \text{ mol L}^{-1} \text{ TBAP in AN})$ ) in various solvents containing  $0.50 \text{ mol L}^{-1} \text{ TBAP}$  as a function of  $\Phi$  for the pure solvents, at  $25.0 \text{ }^\circ\text{C}$ : filled symbols, literature values of  $\Phi$ ; open symbols,  $\Phi$  calculated as  $\beta/\epsilon$  (Table 3).

**Volumes of Reaction.** In contrast to the very loose correlation between  $E_{1/2}$  and  $1/\epsilon$  (Figure 1),  $\Delta V_{\text{cell}}$  is seen in Figure 2 to be a linear function of  $\Phi$ , within experimental uncertainty, for  $\text{DmFc}^{+/0}$  in  $0.5 \text{ mol L}^{-1} \text{ TBAP}$  media at  $25.0 \text{ }^\circ\text{C}$ . The fit to eq 7 gives  $A = -6.7 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$  and slope  $-N_A \Delta(z^2)e^2/8\pi\epsilon_0 r = (1.06 \pm 0.10) \times 10^{11} \text{ Pa cm}^3 \text{ mol}^{-1}$  which, since  $\Delta(z^2) = -1$ , implies an effective radius of about  $650 \text{ pm}$  for  $\text{DmFc}^+$ , or  $\sim 33\%$  larger than that estimated from crystallographic data. (We note in passing that imposition of a straight line of slope  $1.1 \text{ V}$ , corresponding to  $r = 650 \text{ pm}$ , and arbitrary intercept in Figure 1 would still represent the widely scattered data poorly.) The implication is that, in the context of electrostriction of solvent, the effective radius  $r$  of a solute molecule or ion is better regarded as an adjustable parameter than a physically meaningful dimension. Indeed, Hartnig and Koper<sup>51</sup> have stressed, with particular reference to electrode reactions of neutral/singly charged couples, that the effective radius of an ion with respect to electrostriction is strongly charge dependent. Consistent with this, Hupp and Weaver<sup>49</sup> found that the  $\Delta(z^2)/r$  dependences of reaction entropies for various half-cells in organic solvents did not follow the Born predictions (eq 24) quantitatively. Tregloan and co-workers<sup>16</sup> analyzed  $\Delta V_{\text{cell}}$  values for a variety of metal complex  $3+/2+$  couples in aqueous media and remarked that the effective radii implied by their estimates of  $\Delta V_{\text{int}}$  were much smaller than the corresponding van der Waals values. Most relevantly, Wherland et al.<sup>52</sup> measured the molar volumes  $V_{\text{solute}}$  of numerous solutes including  $\text{Fc}$ ,  $\text{FcBF}_4$ ,  $\text{DmFc}$ , and  $\text{DmFcBF}_4$  in  $\text{AN}$ ,  $\text{MeOH}$ , and  $\text{DCM}$  and compared them with the computed van der Waals volumes as well as crystal unit-cell volumes. They found that the electrostrictional component of  $V_{\text{solute}}$  was large for 1:1 electrolytes in polar

solvents (e.g.,  $-38 \text{ cm}^3 \text{ mol}^{-1}$  in  $\text{AN}$  for anion + cation) but showed *no dependence on the size* of the ions. They also found that, for  $\text{DCM}$ , the electrostrictional contribution to  $V_{\text{solute}}$  was negligible, suggesting a high degree of ion pairing in that solvent.

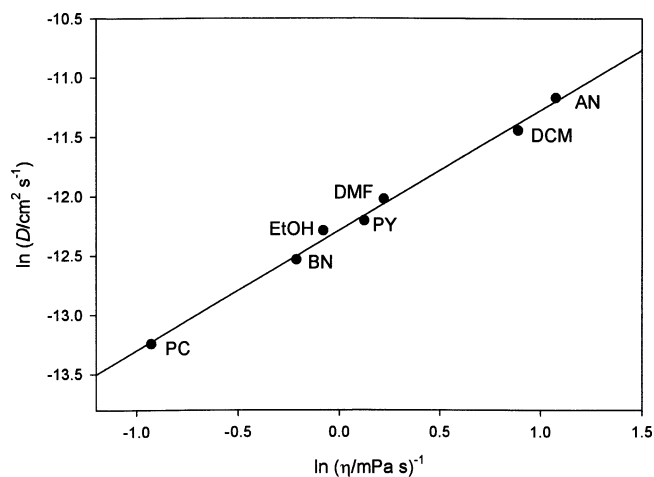
The value of  $A$  from eq 7 reflects the algebraic sum of the presumably constant intrinsic volume change  $\Delta V_{\text{int}}$  when  $\text{DmFc}^+$  is reduced to  $\text{DmFc}$  and the volumetric contribution of the  $\text{Ag}/(0.01 \text{ mol L}^{-1} \text{ AgNO}_3 + 0.5 \text{ mol L}^{-1} \text{ TBAP in AN})$  reference half-cell. If, as estimated above on the basis of the apparent crystallographic radii,  $\Delta V_{\text{int}}$  is roughly  $-7 \text{ cm}^3 \text{ mol}^{-1}$ ,  $A$  and  $\Delta V_{\text{int}}$  are fortuitously about equal within the experimental uncertainty and the contribution of this particular reference half-cell to  $\Delta V_{\text{cell}}$  can be taken to be small for solutions containing  $0.5 \text{ mol L}^{-1} \text{ TBAP}$  at  $25 \text{ }^\circ\text{C}$ . Inferences based on the ill-defined parameter  $r$  should, however, be viewed with caution. The evident constancy of  $A$  from solvent to solvent supports an earlier inference<sup>7</sup> that liquid junction potentials are effectively independent of pressure. Because  $z_2$  is zero and  $z_1$  is minimal, Coulombic work and medium (Debye–Hückel type) effects, which in any case tend to cancel each other, can be disregarded. The fit in Figure 2 of  $\text{DmFc}^{+/0}$  in  $\text{DCM}$ , the case in which ion pairing is most likely,<sup>13,52</sup> implies that pairing of  $\text{DmFc}^+$  with the perchlorate ion of  $\text{TBAP}$  either is saturated in all cases (which seems improbable) or else does not influence  $\Delta V_{\text{cell}}$  appreciably. The  $\Delta V_{\text{cell}}$  value for  $\text{DMSO}$  at  $45.0 \text{ }^\circ\text{C}$  would fall quite close to the line in Figure 2 but has been excluded because the contribution of the reference electrode to  $A$  at  $45 \text{ }^\circ\text{C}$  is unknown; nevertheless, the closeness implies that the contribution of the  $\text{Ag}/(0.01 \text{ mol L}^{-1} \text{ AgNO}_3 + 0.5 \text{ mol L}^{-1} \text{ TBAP in AN})$  reference half-cell to  $A$  is indeed fortuitously small.

The limited  $\Delta V_{\text{cell}}$  data for  $\text{Fc}^{+/0}$  in Table 1 are  $5\text{--}6 \text{ cm}^3 \text{ mol}^{-1}$  more negative than for  $\text{DmFc}^{+/0}$  in  $\text{DMF}$  and  $\text{DMSO}$  ( $25$  and  $45 \text{ }^\circ\text{C}$  respectively,  $0.5 \text{ mol L}^{-1} \text{ TBAP}$ ). On the basis of the crystallographic values of  $r$ , more *positive* values of  $\Delta V_{\text{cell}}$  would be expected for  $\text{Fc}^{+/0}$  relative to  $\text{DmFc}^{+/0}$  because  $\Delta V_{\text{int}}$  should be less negative and the Drude–Nernst electrostriction term in eq 7 should be numerically larger. This result lends weight to the foregoing assertion that, in the context of solvent electrostriction,  $r$  may be better regarded as an adjustable parameter with little physical significance. Several possible reasons for the fictitious nature of  $r$  have been suggested. For solvent close to a reactant ion, dielectric saturation may occur,<sup>49</sup> although this is not expected to be a strong effect for large ions of low charge. The reactant molecules are not spheres and the distances of closest approach of solvent molecules to them is not necessarily the van der Waals radius.<sup>52</sup> To these caveats we add the observation that van der Waals volumes take no account of the dead volume in a solid or a solution; Wherland et al.<sup>52</sup> found that the calculated van der Waals volumes accounted for 68% of the corresponding crystal unit cell volumes (cf. Kepler's conjecture that close-packing of spheres can never fill more than a fraction  $\pi/\sqrt{18}$  or 74% of the available volume) and, for uncharged solutes, 62–65% of the solute molar volumes. Finally, any attempt to

(51) Hartnig, C.; Koper, M. T. M. *J. Am. Chem. Soc.* **2003**, *125*, 9840.

(52) Tran, D.; Hunt, J. P.; Wherland, S. *Inorg. Chem.* **1992**, *31*, 2460.





**Figure 3.** log–log correlation of mean diffusion coefficients of  $\text{DmFc}^{+0}$  in solutions containing  $0.50 \text{ mol L}^{-1}$  TBAP with the fluidity of the pure solvents at  $25.0 \text{ }^\circ\text{C}$ .

extract intermolecular contact radii from crystallographic measurements involves some questionable assumptions, and the validity of these inferred radii in solution is even more doubtful.

**Diffusion Coefficients.** In AN and DMF,  $D$  decreased somewhat with increasing [TBAP] (Tables 1 and S20), presumably because TBAP increased the viscosity  $\eta$  of the solvent. Nevertheless, in accordance with the Stokes–Einstein relation (eq 13), a direct proportionality was found between the experimental values of  $D$  for  $0.5 \text{ mol L}^{-1}$  TBAP media at  $25 \text{ }^\circ\text{C}$  and values of the fluidities  $\eta^{-1}$  for the pure solvents from the literature (Table 3 and Figure S1); a plot of  $\ln D$  vs  $-\ln \eta$  (Figure 3) has slope  $1.01 \pm 0.03$  with intercept  $-12.29 \pm 0.02$  (for  $D$  in  $\text{cm}^2 \text{ s}^{-1}$  and  $\eta$  in  $\text{mPa s}$ ). These observations validate our assumption that  $\eta$  for the TBAP solutions bears the same relationship to  $\eta$  for the pure solvents for all the solvents studied. The observed relationship between  $D$  and  $\eta^{-1}$  implies that  $a$  for  $\text{DmFc}^{+0}$  does not change significantly from solvent to solvent and that ion pair formation between  $\text{DmFc}^+$  and perchlorate ion (from the TBAP) is not an important variable in this context. Because  $\eta$  is not known for solutions containing TBAP, it is not feasible to calculate  $a$  from the CV data—the intercept of Figure 3 fortuitously gives  $a \approx 475 \text{ pm}$ , essentially the crystallographic value, but this is untenable because a simple Jones–Dole<sup>53</sup>/Stokes–Einstein extrapolation of  $D$  values for DMF at  $25 \text{ }^\circ\text{C}$  (Table 1) to zero [TBAP] suggests that  $\eta$  for DMF containing  $0.5 \text{ mol L}^{-1}$  TBAP could be nearly 3 times that of pure DMF. In any event, the reservations expressed in the preceding section concerning the physical significance of  $r$  also apply to any attempt to identify  $a$  with crystallographic distances. Nevertheless, as expected qualitatively from eq 13 and the crystallographic radii,  $D$  for  $\text{Fc}^{+0}$  was a little higher than for the bulkier  $\text{DmFc}^{+0}$  couple for a given solvent and conditions (Table 1).

Stevenson and White<sup>54</sup> studied pressure effects on the electrochemistry of the  $\text{DmFc}^{+0}$  couple in acetophenone and

nitrobenzene over the range  $0 < P < 100 \text{ MPa}$  and deduced, as we have assumed,<sup>1–3,6,7</sup> that decreases in  $D$  with rising pressure are due to the increase in solution viscosity in accordance with the Stokes–Einstein relation. Thus,  $\Delta V_{\text{diff}}^\ddagger$  may be confidently identified with the volume of activation for viscous flow  $\Delta V_{\text{visc}}^\ddagger = RT(\partial \ln \eta / \partial P)_T$ . Tables 1 and 3 show that large volumes of activation  $\Delta V_{\text{diff}}^\ddagger$  for diffusion are roughly correlated with high solvent viscosities. Moreover, for  $\text{DmFc}^{+0}$  in DMF,  $\Delta V_{\text{diff}}^\ddagger$  increases with increasing [TBAP]—in other words, with increasing  $\eta$  for the solution. This effect arises because, in the absence of special effects such as hydrogen-bonding, high viscosity can originate in large part from the necessity for large displacements of surrounding solvent molecules and bulky solutes such as  $\text{TBA}^+$  to allow a diffusing molecule to hop between vacancies in the liquid.

The obvious common feature of  $\Delta V_{\text{diff}}^\ddagger$  values for  $\text{DmFc}^{+0}$ ,  $\text{Fc}^{+0}$ , and  $\text{Fe}(\text{phen})_3^{3+/2+}$  in the organic solvents of Table 1 is that they are all positive and quite large ( $7\text{--}17 \text{ cm}^3 \text{ mol}^{-1}$ ). This stands in sharp contrast to the case of  $\text{Fe}(\text{phen})_3^{3+/2+}$  in water, for which  $\Delta V_{\text{diff}}^\ddagger \approx 0$  despite a  $D$  value that is similar to that for (e.g.) DMF. This reflects the fact that the viscosity of water at near-ambient temperatures is almost independent of pressure, evidently because the fluidizing breakup of vestigial ice-I-like local structures by increasing pressure counteracts the normal increase in viscosity due to closer packing of the molecules.<sup>1</sup>

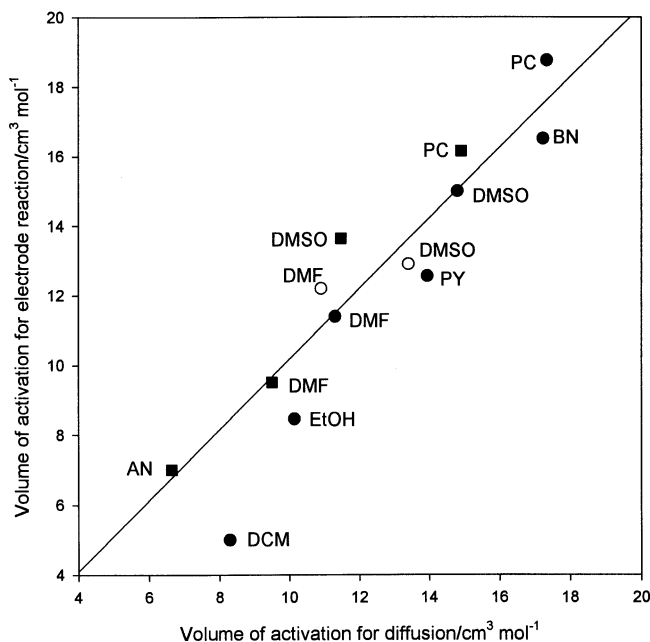
**Rate Constants and Volumes of Activation.** In Table 1,  $k_{\text{el}}$  is seen qualitatively to rise with increasing  $D$  and hence with increasing solvent fluidity ( $\eta^{-1}$ ). A plot of  $\ln k_{\text{el}}$  vs  $\ln D$  (Figure S2) shows much scatter, and the slope of the least-squares regression (0.6) is not very meaningful; this is because  $k_{\text{el}}$  is to some degree dependent on electrode surface properties and history. The nature and history of electrodes, however, are not affected by pressures up to  $\sim 200 \text{ MPa}$ , so that  $k_{\text{el}}$  showed good reproducibility within a run and the resulting values of  $\Delta V_{\text{el}}^\ddagger$  agreed well from run to run for a given couple and conditions.

The salient features of the  $\Delta V_{\text{el}}^\ddagger$  data for the metallocene couples in Table 1 are that they are all quite strongly positive and roughly equal to  $\Delta V_{\text{diff}}^\ddagger$ . In particular,  $\Delta V_{\text{el}}^\ddagger$  values for  $\text{DmFc}^{+0}$  in DCM and AN (with TEAP) ( $+5.0$  and  $+7.0 \text{ cm}^3 \text{ mol}^{-1}$ , respectively) stand in sharp contrast to the negative  $\Delta V_{\text{ex}}^\ddagger$  found<sup>13</sup> for the corresponding homogeneous self-exchange reaction in DCM, AC, and AN ( $-6.4$ ,  $-8.6$ , and  $\sim -5 \text{ cm}^3 \text{ mol}^{-1}$ , respectively). Likewise, for the  $\text{Fc}^{+0}$  self-exchange in AN, Hunt et al.<sup>55</sup> found  $\Delta V_{\text{ex}}^\ddagger = -7 \text{ cm}^3 \text{ mol}^{-1}$ ;  $\Delta V_{\text{el}}^\ddagger$  for the corresponding electrode reaction in AN is inaccessible for technical reasons,<sup>2,10</sup> but strongly positive  $\Delta V_{\text{el}}^\ddagger$  values are found for  $\text{Fc}^{+0}$  in DMF and DMSO (Table 1). As  $\Delta V_{\text{ex}}^\ddagger$  for  $\text{DmFc}^{+0}$  is “well-behaved” (i.e., can be accounted for quantitatively) on the basis of an extension of Marcus theory,<sup>13</sup> one would expect  $\Delta V_{\text{el}}^\ddagger$  to be  $\sim 1/2 \Delta V_{\text{ex}}^\ddagger$  ( $-3$  to  $-4 \text{ cm}^3 \text{ mol}^{-1}$ ) if the activation barrier height alone controlled the rate of the electrode reactions in these

(53) Jones, G.; Dole, M. *J. Am. Chem. Soc.* **1929**, *51*, 2950. Note, however, that the Jones–Dole equation was developed specifically for aqueous solutions.

(54) Stevenson, K. J.; White, H. S. *J. Phys. Chem.* **1996**, *100*, 18818.

(55) Kirchner, K.; Dang, S.-Q.; Stebler, M.; Dodgen, H.; Wherland, S.; Hunt, J. P. *Inorg. Chem.* **1989**, *28*, 3604.



**Figure 4.** Correlation between  $\Delta V_{\text{el}}^{\ddagger}$  and  $\Delta V_{\text{diff}}^{\ddagger}$  for  $\text{DmFc}^{+/0}$  (filled symbols) and  $\text{Fc}^{+/0}$  (open symbols). Circles: 0.5 mol L<sup>-1</sup> TBAP. Squares: 0.2 mol L<sup>-1</sup> TEAP. Temperature: 25.0 °C, except for DMSO (45.0 °C). The regression line represents all the data except  $\text{DmFc}^{+/0}$ /DCM and has slope  $1.01 \pm 0.12$  with intercept  $0.0 \pm 1.5$  cm<sup>3</sup> mol<sup>-1</sup>.

solvents.<sup>1,7,8</sup> Thus, some factor other than, or in addition to,  $\Delta G_{\text{el}}^{\ddagger}$  (eq 10) controls  $k_{\text{el}}$  and  $\Delta V_{\text{el}}^{\ddagger}$ . A plot of  $\Delta V_{\text{el}}^{\ddagger}$  against  $\Delta V_{\text{diff}}^{\ddagger}$  (Figure 4) has slope 1.0 and zero intercept (if the outlying point for DCM, for which strong ion pairing is expected,<sup>13,52</sup> is ignored)—in other words, on average,  $\Delta V_{\text{el}}^{\ddagger} = \Delta V_{\text{diff}}^{\ddagger}$  within the experimental scatter, and this applies to both  $\text{DmFc}^{+/0}$  (at 25 °C and, for DMSO, 45 °C) and  $\text{Fc}^{+/0}$ . Since  $\Delta V_{\text{el}}^{\ddagger}$  is much less vulnerable to electrode properties than is  $k_{\text{el}}$ , the implication is that the ideal standard electrode rate constant  $k_{\text{el}}'$  (i.e.,  $k_{\text{el}}$  in absence of electrode effects) is directly proportional to  $D^{-1}$  and hence to the solvent fluidity  $\eta^{-1}$ .

As noted in the Introduction, the direct proportionality of  $k_{\text{el}}'$  to  $\eta^{-1}$  can be interpreted in one of three ways: (i)  $k_{\text{el}}$  is an artifact of residual  $R_{\text{u}}$ . (ii) The reaction is diffusion controlled, since the flux of an electroactive species **I** by diffusion and/or migration to an electrode over a reaction zone of fixed thickness  $\delta\sigma$  is proportional to  $D_{\text{I}}$  and  $[\text{I}]$ ,<sup>56</sup> whence  $k_{\text{el}}$  is proportional to  $D_{\text{I}}$ . (iii) Solvent dynamics are rate controlling, as proposed for other electrode reactions by Murray et al.<sup>20,21</sup> and Bard et al.<sup>57–59</sup> Explanation i may be rejected because  $R_{\text{u}}$  was directly measured and specifically allowed for in every calculation of  $k_{\text{el}}$ . The case of  $\text{DmFc}^{+/0}$  in AC and AN with 0.5 mol L<sup>-1</sup> TBAP illustrates the importance of this correction: although seemingly tractable ACVs were obtained,  $k_{\text{el}}$  was actually too fast for accurate measurement, so that if corrections for  $R_{\text{u}}$  (though relatively small) were omitted, leading to an underestimation of  $k_{\text{el}}$ , false values of “ $k_{\text{el}}$ ” and “ $\Delta V_{\text{el}}^{\ddagger}$ ” were obtained, the latter

approximately equaling  $\Delta V_{\text{diff}}^{\ddagger}$ . When, however,  $k_{\text{el}}$  lay well within the range of the ACV technique, as for example with  $\text{DmFc}^{+/0}$  in DMF/TBAP, correction for  $R_{\text{u}}$  had very little impact on the calculation of  $\Delta V_{\text{el}}^{\ddagger}$ . A distinction between  $R_{\text{u}}$  artifacts and genuine electrode kinetic parameters was nevertheless possible: for  $\text{DmFc}^{+/0}$  in DMF, when [TBAP] was reduced from 0.50 to 0.10 mol L<sup>-1</sup>,  $\Delta V_{\text{el}}^{\ddagger}$  obtained with proper correction for  $R_{\text{u}}$  decreased slightly (~10%) whereas the pressure dependence of  $R_{\text{u}}$  doubled (from 0.9 to 1.8 Ω MPa<sup>-1</sup>). The latter would have caused an increase in the calculated value of  $\Delta V_{\text{el}}^{\ddagger}$  if this were an artifact of  $R_{\text{u}}$ , all or in part, because neglect of  $R_{\text{u}}$  lowers the apparent values of  $k_{\text{el}}$ .

Interpretation ii (diffusional control of the reaction rate) seems unlikely, since most of the electrode reactions considered here are not especially fast by the standards of the genre. Nevertheless, equality of  $\Delta V_{\text{el}}^{\ddagger}$  with  $\Delta V_{\text{diff}}^{\ddagger}$  is precisely what would be expected for diffusional control, whereas for solvent dynamical control one would expect in Figure 4 an intercept of about  $-4$  cm<sup>3</sup> mol<sup>-1</sup> (corresponding to a contribution of  $1/2\Delta V_{\text{ex}}^{\ddagger}$  from the activation barrier for  $\text{DmFc}^{+/0,13}$  or  $\text{Fc}^{+/0,55}$  which is mainly solvational in origin) and slope  $1.01^{-3}$  if the electrode reaction is fully adiabatic or a slope between 0 and 1 if it is not. We enlarge upon this point as follows. The incursion of solvent dynamics can be expressed as

$$k_{\text{el}}^{-1} = k_{\text{SD}}^{-1} + k_{\text{TST}}^{-1} \quad (25)$$

where  $k_{\text{SD}}$  is the electrode reaction rate constant when solvent dynamics is rate-limiting and  $k_{\text{TST}}$  is that expected from transition-state theory (TST)<sup>25,60</sup> (for diffusion control,  $k_{\text{diff}}$  would replace  $k_{\text{SD}}$  in eq 25). We will assume that  $k_{\text{SD}}$  is rate-limiting ( $k_{\text{el}} \approx k_{\text{SD}}$ ). We may rewrite eq 10 as

$$k_{\text{el}} = \kappa_{\text{e}} \nu_{\text{n}} \exp(-(\Delta G_{\text{el(IR)}}^{\ddagger} + \Delta G_{\text{el(SR)}}^{\ddagger})/RT) \quad (26)$$

where  $\kappa_{\text{e}}$  is the electronic transmission coefficient,  $\nu_{\text{n}}$  is the nuclear frequency factor, and  $\Delta G_{\text{el(IR)}}^{\ddagger}$  and  $\Delta G_{\text{el(SR)}}^{\ddagger}$  are respectively the contributions of internal reorganization of the reactants and solvent reorganization preceding electron transfer; for  $\text{DmFc}^{+/0}$ ,  $\Delta G_{\text{el(IR)}}^{\ddagger}$  is negligibly small (~0.3 kJ mol<sup>-1</sup>, i.e., half that for the self-exchange reaction)<sup>13,37</sup> relative to  $\Delta G_{\text{el(SR)}}^{\ddagger}$  which can be estimated to be ~9–10 kJ mol<sup>-1</sup> from the Marcus expression

$$\Delta G_{\text{el(SR)}}^{\ddagger} = (N_{\text{A}} e^2 / 32 \pi \epsilon_0) [(2r_1)^{-1} + (2r_2)^{-1} - \sigma^{-1}] (\epsilon_{\text{op}}^{-1} - \epsilon^{-1}) \quad (27)$$

in which the charge separation distance  $\sigma$  can be taken to be  $r_1 + r_2$  and the optical dielectric constant  $\epsilon_{\text{op}}$  can be taken to be  $n^2$ , where  $n$  is the solvent refractive index  $n$ . This being so, the one-dimensional Kramers-type approach discussed elsewhere<sup>1,3</sup> gives

(56) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; Wiley: New York, 2001; p 28.

(57) Zhang, X.; Leddy, J.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 3719.

(58) Zhang, X.; Yang, H.; Bard, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1916.

(59) Miao, W.; Ding, Z.; Bard, A. J. *J. Phys. Chem. B* **2002**, *106*, 1392.

(60) Sumi, H. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: New York, 2001; Vol. 1, Chapter 2.

$$\nu_n = \tau_L^{-1} (\Delta G_{\text{el(SR)}}^\ddagger / 4\pi RT)^{1/2} = (\epsilon/\epsilon_\infty) (RT\Delta G_{\text{el(SR)}}^\ddagger / 4\pi RT)^{1/2} / 3V_M\eta \quad (28)$$

where  $V_M$  is the molar volume and  $\epsilon_\infty$  the high-frequency dielectric constant of the solvent; it is assumed that the solvent is of the Debye type, which is reasonable for most of the non-hydroxylic liquids considered here. Thus, for a given value of  $\Delta G_{\text{el(SR)}}^\ddagger$ ,  $k_{\text{el}}$  should be directly proportional to the solvent fluidity  $\eta^{-1}$ , although this is not demonstrable with precision because of the variability of  $k_{\text{el}}$  with electrode properties, as noted above. The pressure dependence of  $\ln k_{\text{el}}$  from eq 28, however, gives

$$\Delta V_{\text{el}}^\ddagger = \Delta V_{\text{visc}}^\ddagger + \Delta V_{\text{el(SR)}}^\ddagger + Q \approx \Delta V_{\text{diff}}^\ddagger + \Delta V_{\text{el(SR)}}^\ddagger \quad (29)$$

where  $Q$  is the pressure dependence of all components of  $\ln \nu_n$  other than  $\eta$  and turns out to be small because of internal cancellations ( $\sim -0.4 \text{ cm}^3 \text{ mol}^{-1}$ )<sup>3</sup> and  $\Delta V_{\text{el(SR)}}^\ddagger$  represents the pressure dependence of the activation barrier according to TST. Thus, on the Kramers-type model,  $\Delta V_{\text{el}}^\ddagger$  should equal  $\Delta V_{\text{diff}}^\ddagger$  only if  $\Delta V_{\text{el(SR)}}^\ddagger$  is small enough to be obscured by the experimental uncertainty. For the Ru(hfac)<sub>3</sub><sup>0/-</sup> electrode reaction,<sup>3</sup> for which  $\Delta G_{\text{el(IR)}}^\ddagger$  is *not* negligible, a contribution to  $\Delta V_{\text{el}}^\ddagger$  from the pressure dependence of  $\Delta G_{\text{el}}^\ddagger$  appears to be present, but the data are limited to three solvents (including the non-Debye solvent MeOH). For DmFc<sup>+0</sup> and Fc<sup>+0</sup>, either  $\Delta V_{\text{el(SR)}}^\ddagger$  is largely canceled as a result of the numerous approximations and assumptions made or else the activation energy barrier ceases to be relevant when solvent dynamics are fully rate-controlling.

The alternative solvent-dynamical approach is the two-dimensional theory developed by Sumi, Marcus, and others,<sup>25,60–62</sup> in which solvent fluctuations and passage of the reactants over the activation barrier are separated and according to which eq 26 should be replaced by

$$k_{\text{el}} \approx \tau^{-\theta} \nu^{1-\theta} \exp(-\gamma \Delta G_{\text{el}}^\ddagger / RT) \quad (30)$$

where  $\theta$  and  $\gamma$  are positive fractions less than 1. The key feature in the present context is that  $k_{\text{el}}$  should then be proportional to a fractional power of the solvent fluidity ( $\eta^{-\theta}$ ), with  $\theta$  approaching zero as the nonadiabaticity of the electron process increases, and the experimental  $\Delta G_{\text{el}}^\ddagger$  (in effect,  $\Delta G_{\text{el(SR)}}^\ddagger$ ) should be substantially less than predicted from eq 27. In the same way,  $\Delta V_{\text{el}}^\ddagger$  should be a linear function of  $\Delta V_{\text{diff}}^\ddagger$  with slope  $0 < \theta < 1$  if a nonadiabatic two-dimensional model is appropriate. Figure 4, however, shows clearly that  $\theta$  is effectively 1.0 for the DmFc<sup>+0</sup> and Fc<sup>+0</sup> electrode reactions, and the temperature dependences of  $k_{\text{el}}$  (see below) are consistent with  $\gamma \approx 1.0$ , implying that either the one-dimensional solvent-dynamical interpretation is adequate or the reaction is diffusionally controlled. The latter possibility, however, can be eliminated by consideration of the temperature dependence of  $k_{\text{el}}$ , as follows.

(61) Nadler, W.; Marcus, R. A. *J. Chem. Phys.* **1987**, *86*, 3906.

(62) Basilevsky, M. V.; Ryaboy, V. M.; Weinberg, N. N. *J. Phys. Chem.* **1991**, *95*, 5533.

**Temperature Dependences of  $D$  and  $k_{\text{el}}$ .** It can be seen immediately from Table 2 that the Arrhenius activation energies  $E_{\text{a(el)}}$  for the electrode reactions of DmFc<sup>+0</sup> are invariably larger than the corresponding parameters for diffusion ( $E_{\text{a(diff)}}$ ) by 6–15 kJ mol<sup>-1</sup>. This effectively rules out the possibility ii, that the DmFc<sup>+0</sup> electrode reaction is diffusion controlled. Differentiating  $\ln k_{\text{el}}$  (eqs 26 and 28) with respect to  $1/T$  and neglecting  $\Delta G_{\text{el(IR)}}^\ddagger$ ,<sup>63</sup> we have

$$E_{\text{a(el)}} (= \Delta H_{\text{el}}^\ddagger) = -R(\partial \ln k_{\text{el}} / \partial (1/T)) = E_{\text{a(diff)}} + \Delta H_{\text{el(SR)}}^\ddagger + X$$

$$X = (3RT^2/2)[(\partial \ln \epsilon / \partial T)_p - 2(\partial \ln n / \partial T)_p] + RT/2 \quad (31)$$

and, calculating  $X$  as in Table S29 to be  $-3.4$ ,  $-2.2$ , and  $-3.2 \text{ kJ mol}^{-1}$  for the pure solvents AN, PC, and DMF, respectively, we can attribute the excess of  $E_{\text{a(el)}}$  over  $E_{\text{a(diff)}}$  at least qualitatively to a significant contribution of solvent reorganization  $\Delta H_{\text{el(SR)}}^\ddagger$  to the activation barrier for the electrode reaction. Detailed analysis is not possible, however, because the data in Table 2 for DMF solutions with variable [TBAP] show that  $E_{\text{a(el)}}$  and  $A_{\text{el}}$  both rise with increasing [TBAP] even though these parameters give an essentially constant  $k_{\text{el}}$  at 25 °C through mutual compensation (0.063, 0.069, and 0.064 cm s<sup>-1</sup> at [TBAP] = 0.1, 0.2, and 0.5 mol L<sup>-1</sup>, respectively).  $E_{\text{a(diff)}}$  and  $A_{\text{diff}}$ , on the other hand, show no significant dependence on [TBAP], which is in itself evidence against the interpretation ii. For DmFc<sup>+0</sup> in pure DMF, the extrapolated  $E_{\text{a(el)}}$  is about 12 kJ mol<sup>-1</sup>, whence from eq 31  $\Delta H_{\text{el(SR)}}^\ddagger \approx 6.4 \text{ kJ mol}^{-1}$ , which may be compared with a theoretical value of 7.4 kJ mol<sup>-1</sup> calculated from the  $T$  derivative of eq 27 assuming  $\sigma = 2r = 960 \text{ pm}$ . Thus, kinetic evidence for the presence of a (low) activation energy barrier consistent with solvent dynamical as distinct from diffusional rate control, though not detected in the  $\Delta V_{\text{el}}^\ddagger$  vs  $\Delta V_{\text{diff}}^\ddagger$  relationship (Figure 4), emerges in  $E_{\text{a(el)}}$  vs  $E_{\text{a(diff)}}$ .

**Possible Effect of Quaternary Ammonium Cation Desorption in Kinetic Measurements.** As a final precaution, we consider the observation by Abbott and co-workers<sup>64,65</sup> that slow desorption of quaternary ammonium ions from the working electrode in nonaqueous media may introduce voltammetric artifacts similar to those of uncompensated resistance. The Abbott effect becomes pronounced with fast scan rates and larger quaternary ammonium ions. It may be expected to interfere with measurement of  $k_{\text{el}}$  when the rate of desorption of the supporting cation becomes comparable with that of the (normally slower) electrode reaction. In this work, the highest rate constants for the DmFc<sup>+0</sup> couple were encountered in AN—as expected from solvent dynamics, as it was the most fluid solvent considered—but could be measured with confidence only in TEAP media (Tables 1,

(63) Identification of  $\epsilon_\infty$  with  $\epsilon_{\text{op}}$  ( $\approx n^2$ ) as in eq 31 is a crude approximation,<sup>37</sup> but the temperature and pressure dependences can be expected to be similar and the impact of the approximation on  $X$  trivial.

(64) Abbott, A. P.; Harper, J. C. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3981.

(65) Abbott, A. P.; Harper, J. C.; Stimson, G. J. *Electroanal. Chem.* **2002**, *520*, 6.

(66) Shalders, R. D.; Swaddle, T. W. *Inorg. Chem.* **1995**, *34*, 4815.

2, and S20–S25). With the larger TBA<sup>+</sup> as the supporting cation, ACV appeared to give inordinately high  $k_{\text{el}}$  values, as well as  $\Delta V_{\text{el}}^{\ddagger}$  that were much more positive than  $\Delta V_{\text{diff}}^{\ddagger}$  (cf. the effect of  $R_{\text{u}}$ ). When [TBAP] was decreased,  $\Delta V_{\text{el}}^{\ddagger}$  decreased toward  $\Delta V_{\text{diff}}^{\ddagger}$ , but it was not possible to dispense with substantial concentrations of supporting electrolyte because of the need to keep  $R_{\text{u}}$  low. Fortunately, these artifacts disappeared in AN when TEAP was used in moderate concentrations in place of TBAP and were not seen for DmFc<sup>+0</sup> in any other solvent—including those of low polarity, for which the Abbott effect is said<sup>64,65</sup> to be more significant but in which  $k_{\text{el}}$  for DmFc<sup>+0</sup> is not particularly fast. The failure of our earlier kinetic study<sup>2</sup> of Fc<sup>+0</sup> in AN may have been due in part to the Abbott effect, although other factors contributed to it.<sup>10</sup>

### Conclusions

Because factors such as electrode properties and size, liquid junction potentials, effective reactant radii, etc., are unaffected by the moderate range of pressure covered in this study and because the pressure-dependence parameters  $\Delta V_{\text{cell}}$  and  $\Delta V_{\text{el}}^{\ddagger}$  are derived from *relative* values of  $E_{1/2}$  and  $k_{\text{el}}$ ,  $\Delta V_{\text{cell}}$  and  $\Delta V_{\text{el}}^{\ddagger}$  correspond much better to theoretical expectations than do  $E_{1/2}$  and  $k_{\text{el}}$ . Thus, we find that the Drude–Nernst approach accounts poorly for trends in  $E_{1/2}$  with  $\epsilon^{-1}$  for DmFc<sup>+0</sup> and Fc<sup>+0</sup> in a variety of nonaqueous solvents but quite satisfactorily for the corresponding  $\Delta V_{\text{cell}}$  values in terms of  $\Phi$ . This result with constant  $\Delta(z^2)$  and varying solvents complements the finding of Tregloan et al.<sup>15</sup> concerning the dependence of  $\Delta V_{\text{cell}}$  on  $\Delta(z^2)$  in a single solvent (water). It should, however, be borne in mind that the apparent radius of the reactant required by eq 7 is somewhat larger than the crystallographically estimated value and that  $\Delta V_{\text{cell}}$  values for Fc<sup>+0</sup> are more negative than for DmFc<sup>+0</sup> rather than vice-versa as would be expected from the crystallographic radii. Reactant radii in the Drude–Nernst context may be better regarded as adjustable parameters with limited physical significance, much like the anion–cation contact distance in applications of extended Debye–Hückel theory.<sup>66</sup> We note that the Drude–Nernst theory met with only limited success in the interpretation of  $\Delta V_{\text{cell}}$  for the CoW<sub>12</sub>O<sub>40</sub><sup>5–/6–</sup> and PW<sub>12</sub>O<sub>40</sub><sup>3–/4–/5–</sup> electrode reactions in acidic aqueous solutions,<sup>67</sup> despite the nearly spherical shapes and closely similar crystallographic radii of these Keggin anions.

(67) Matsumoto, M.; Neuman, N. I.; Swaddle, T. W. *Inorg. Chem.* **2004**, *43*, 1153.

This study also reaffirms the validity of equating the readily measured  $\Delta V_{\text{diff}}^{\ddagger}$  with the less accessible  $\Delta V_{\text{visc}}^{\ddagger}$ . Again, however, the hydrodynamic radii  $a$  of the electroactive species calculable for solutions containing (by extrapolation) no supporting electrolyte are much smaller than crystallographic estimates and are better regarded as adjustable parameters.

For the DmFc<sup>+0</sup> and Fc<sup>+0</sup> electrode reactions in nonaqueous solvents,  $\Delta V_{\text{el}}^{\ddagger}$  is invariably *positive* and equal to  $\Delta V_{\text{diff}}^{\ddagger}$  within the experimental uncertainty. This stands in sharp contrast to the *negative*  $\Delta V_{\text{ex}}^{\ddagger}$  values for the bimolecular self-exchange reactions of these same couples in organic solvents.<sup>13,55</sup> These facts are consistent with solvent dynamical control of the adiabatic electrode reaction but not of the homogeneous self-exchange. Temperature and supporting electrolyte effects favor the solvent dynamical interpretation iii over diffusional control of the reaction rate. For the highly charged Fe(phen)<sub>3</sub><sup>3+/2+</sup> couple in organic solvents, for which ion pairing is likely to be important,  $\Delta V_{\text{el}}^{\ddagger}$  is always 4–6 cm<sup>3</sup> mol<sup>–1</sup> more positive than  $\Delta V_{\text{diff}}^{\ddagger}$ , which suggests that ion pairing may facilitate the electrode reaction for that couple (pressure tends to break up ion pairs). Except perhaps for the deviation of the DCM point in Figure 4, there is no clear evidence for ion-pairing effects on the DmFc<sup>+0</sup> electrode reaction.

Finally, for Fe(phen)<sub>3</sub><sup>3+/2+</sup> in water, for which  $\Delta V_{\text{diff}}^{\ddagger}$  is  $\sim 0$  even though  $D$  is comparable to  $D$  for AN, DMF, etc., the small negative  $\Delta V_{\text{el}}^{\ddagger}$  corresponds to the contribution of the activation barrier ( $\sim 1/2 \Delta V_{\text{ex}}^{\ddagger}$ ), as is more evident for other aqueous electrode reactions in the absence of counterion catalysis.<sup>1,5–8</sup> The implication here is not necessarily that solvent dynamical effects do not apply in water but rather that pressure effects do not reveal them because of the fortuitous insensitivity of  $\eta$  for water to moderate pressures at near-ambient temperatures.

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**Supporting Information Available:** Tables S1–S29, listing values of  $E_{1/2}$ ,  $D$ ,  $\alpha$ ,  $R_{\text{u}}$ , and  $k_{\text{el}}$  as functions of pressure and temperature, together with derived parameters, Figure S1, showing  $D$  as a function of  $\eta$ , and Figure S2, relating  $\ln k_{\text{el}}$  and  $\ln D$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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