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Ionic Atmosphere Effects on the Energetics of Thermal and Optical Electron-Exchange Reactions: Application to Ferrocenium-Ferrocene Self Exchange

by

A. M. Kuznetsov, D. K. Phelps, and M. J. Weaver

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Purdue University
Department of Chemistry
West Lafayette, Indiana 47907

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ABSTRACT

A treatment of ionic-atmosphere effects upon symmetrical electron-transfer reactions resulting from added electrolyte is outlined. Relationships are derived on the basis of the extended Debye-Huckel model for the increase in the activation free energy, ΔG^*_{ia}, associated with reorganization of the ionic atmosphere for homogeneous-phase reactions involving a pair of spherical reactants with varying internuclear distance R. Similar relationships apply to the energetics of symmetrical optical electron transfer, since the increase in the optical transition energy, ΔE^{ia}_{op}, should equal the corresponding ionic atmosphere reorganization energy, E^{ia}_r; under the anticipated linear response conditions, $E^{ia}_r = 4\Delta G^*_{ia}$. The predicted ΔG^*_{ia} (and hence ΔE^{ia}_{op}) values increase sharply with increasing R, as a consequence of the diminished "sharing" of the ionic cloud surrounding the donor and acceptor sites under these conditions. Outer-sphere electrochemical reactions, featuring a single "near-isolated" reactant, are predicted to feature substantially larger ΔG^*_{ia} values than for homogeneous processes proceeding with the reaction partners in contact. The influence of more specific "ionic atmosphere" effects upon ΔG^*_{ia}, especially involving reactant-electrolyte ion pairing, is also discussed. Unlike that of the nonspecific ionic atmosphere, the nuclear reorganization process associated with counterion transport between donor and acceptor sites coupled with electron transfer is nonlinear in nature, so that $E^{ia}_r \neq 4\Delta G^*_{ia}$. Some recent experimental data for electrolyte effects upon the rate constants for ferrocenium-ferrocene self exchange and related systems are examined in the light of these considerations.

Exploring the role of the ionic as well as the solvent environment on the kinetics of electron-transfer reactions is a longstanding topic of fundamental importance. For reactions between pairs of ions, the observed electrolyte effects are often expected to be dominated by variations in the electrostatic work of forming the precursor complex from the separated reactants.[1] Nevertheless, when one of the reactants is uncharged such work terms should be essentially zero, enabling other electrostatic phenomena to be exposed. Two related effects of particular interest involve the influence of the non-specific ionic atmosphere and of reactant-electrolyte ion pairing upon electron-transfer rates. Both involve the reorganization of the electrolyte countercharge surrounding the reactant pair that is required to form the transition state so that electron transfer can take place. This "ionic atmosphere" component of the reorganization barrier, ΔG^*_{ia}, is predicted on the basis of the Debye-Huckel model to increase monotonically with the ionic strength, so that the rate constant should diminish correspondingly under these conditions.[2] The occurrence of specific ion pairing between the charged reactant and supporting electrolyte ions, can also be anticipated to yield qualitatively similar kinetic effects, arising from the need to move the counterion(s) between the donor and acceptor sites commensurate with electron transfer.

Experimental examination of these effects is most straightforward for self-exchange reactions, since the inherent symmetry of such processes avoids complications associated with ion pairing-induced alterations in the thermodynamic driving force. We have recently scrutinized electrolyte effects upon the self-exchange kinetics of ferrocenium-ferrocene ($Cp_2Fe^{+/o}$), decamethyl-(ferrocenium-ferrocene) ($Cp'_2Fe^{+/o}$), and cobaltocenium-cobaltocene ($Cp_2Co^{+/o}$) in several solvents,[3] in connection with detailed examinations of solvent dynamical effects in electron transfer.[4] Independently, extensive measurements of optical electron-transfer energies for a related mixed-valence biferrocene, biferrocenylacetylene cation (BFA^+), have been undertaken by Blackbourn and Hupp[5] in some of the same media examined in ref. 3. The latter measurements indicate the presence of substantial ion-pairing effects upon the electron-transfer energetics under some electrolyte conditions relevant to the self-exchange kinetic measurements. Some evidence for ion pairing under these conditions was also provided earlier from conductance data.[6]

The present paper examines in a unified fashion electrolyte ionic atmosphere effects upon self-exchange kinetics as predicted from simple theoretical models. These considerations provide a semiquantitative rationale for the observed modest effects of the ionic environment upon the kinetics of metallocenium-metallocene self exchange.

Treatment of Nonspecific Ionic-Atmosphere Effects

The contribution to the intrinsic free-energy barrier associated with reorganization of the ionic atmosphere, ΔG^*_{ia}, can readily be described on the basis of the extended Debye-Huckel theory as follows. Consider the generalized one-electron reaction

$$Ox_1 + Red_2 \rightleftarrows Red_1 + Ox_2 \tag{1}$$

The activation free energy for reaction (1) can be expressed generally as[7]

$$\begin{aligned} \Delta G^* &= \alpha(1-\alpha)E_r + \Delta G^\circ + \alpha(G_{z_1-1,z_2+1} - G_{z_1,z_2}) \\ &+ [G_{z_1-\alpha,z_2+\alpha} - G_{z_1,z_2} - \alpha(G_{z_1-1,z_2+1} - G_{z_1,z_2})] \end{aligned} \tag{2}$$

Here α is the symmetry factor (0.5 for symmetrical reactions), ΔG° is the overall free-energy driving force and E_r is the reorganization energy of the reactants and surrounding solvent. [The last quantity corresponds to the energy which is required to alter the nuclear configuration of the reactant (precursor) state to that corresponding to the product state *without* electron transfer taking place.] The G_{Z_1,Z_2} and G_{Z_1-1,Z_2+1} terms describe the interaction energies of the reactant and product states [having charges Z_1, Z_2 and (Z_1-1) and (Z_2+1) respectively] with the ionic atmosphere; $G_{Z_1-\alpha,Z_2+\alpha}$ describes the corresponding interactions in the transition state for electron transfer. The terms within the square brackets in Eq. (2) refer to the reorganization of the ionic atmosphere. For a self-exchange (i.e. a symmetrical) reaction, the free energy of interaction of the reactant charges with the surrounding ionic atmosphere will be identical in the initial and final (strictly precursor and successor) states. Nevertheless, the ionic atmosphere (along with the solvent polarization) is required to reorganize to a more symmetrical configuration prior to electron transfer, necessarily yielding nonzero ΔG^*_{ia}. In that case ΔG^*_{ia} can be expressed simply as

$$\Delta G^*_{ia} = (G_{Z_1-\alpha,Z_2+\alpha} - G_{Z_1,Z_2}) \qquad (3)$$

If the response of the ionic atmosphere to the external charge is linear (as would be expected for a nonspecific "ionic cloud", vide infra), the free energy due to the ionic atmosphere formed around a pair of such charges can be expressed in the functional form

$$G_{Z_1,Z_2} = E_1 Z_1^2 + E_2 Z_2^2 + E_{12} Z_1 Z_2 \qquad (4)$$

Since $E_1 = E_2$ and $\alpha = 0.5$, and $Z_2 = Z_1 + 1$ for a symmetrical one-electron reaction, the reorganization energy of the ionic atmosphere, E_r^{ia}, can be expressed in this case as

$$E_r^{ia} = 4\Delta G_{ia}^{*} = |E_1 + E_2 - E_{12}| \tag{5}$$

From the form of Eq. (5), E_r^{ia} for a one-electron transfer reaction is equivalent to the absolute value of the interaction energy of two reactant charges, $Z_1 = 1$ and $Z_2 = -1$, with the surrounding ionic atmosphere.[2] On this basis, then, we can express E_r^{ia} as a superposition of potentials[2]

$$E_r^{ia} = |0.5\ (q_1\psi_1 + q_2\psi_2)| \tag{6}$$

where $q_1 = +e$ and $q_2 = -e$, and ψ_1 and ψ_2 are the electrostatic potentials at the reactants due to the ionic atmosphere.

For spherical reactants having the same radius, a, according to the extended Debye-Huckel model the expression for ψ is[2]

$$\psi_1 = -\left(\frac{e}{\epsilon_s} \cdot \frac{\kappa_D}{1 + \kappa_D a}\right) - \frac{e}{\epsilon_s R}\left\{\frac{\exp\ [\kappa_D (a-R)]}{1 + \kappa_D a} - 1\right\} \tag{7}$$

where κ_D is the inverse Debye screening length and R is the distance between the reacting centers. The corresponding formula for ψ_2 differs from Eq. (7) only in the sign. Inserting these expressions for ψ_1 and ψ_2 into Eq. (6) yields the following equation for ΔG_{ia}^{*}:

$$\Delta G_{ia}^{*} = 0.25\ E_r^{ia} = \frac{e^2}{4\epsilon_s}\left\{\frac{\kappa_D}{(1 + \kappa_D a)} + \frac{1}{R}\left[\frac{\exp[\kappa_D (a-R)]}{1 + \kappa_D a} - 1\right]\right\} \tag{8}$$

A closely related expression has been given previously by Marcus[8]; however the preceding deviation is decreased sufficiently instructive to warrant inclusion here. For the commonly anticipated circumstance where the reacting spheres are in contact, so that $R = 2a$, this expression becomes

$$\Delta G^*_{ia} = \frac{e^2}{8a\epsilon_s}\left[\frac{\exp(-\kappa_D a) + \kappa_D a - 1}{1 + \kappa_D a}\right] \tag{9}$$

which was given previously in ref. 2. For large distances between the reacting centers ($R \rightarrow \infty$), Eq. (8) reduces simply to

$$\Delta G^*_{ia}\ (R\rightarrow\infty) = \frac{e^2}{4\epsilon_s}\left(\frac{\kappa_D}{1 + \kappa_D a}\right) \tag{10}$$

Inspection of Eq. (8) shows that ΔG^*_{ia} increases markedly with increasing R, in a qualitatively (but not quantitatively) similar fashion to that predicted for the solvent reorganization energy on the basis of the dielectric continuum model[8a] (vide infra). This can be understood physically from the smaller extent of medium reorganization required when the reacting centers are on sufficiently close proximity so that their ionic atmospheres are partly shared.

Neglecting electrode-ion imaging interactions, ΔG^*_{ia} for the corresponding electrochemical exchange process, ΔG^*_{ia}(elect), will simply be one half that [Eq. (10)] for an isolated pair of reactants, i.e.

$$\Delta G^*_{ia}(\text{elect}) = \frac{e^2}{8\epsilon_s}\left[\frac{\kappa_D}{1 + \kappa_D a}\right] \tag{11}$$

It is interesting to note that Eq. (11) has the same form as the *equilibrium* free energy of interaction of an ion with its ionic atmosphere, as prescribed by the extended Debye-Huckel model.[9] Indeed the reorganization energy, $E_r^{ia} = [4\Delta G^*_{ia}(\text{elect})] = (e^2/2\epsilon_s)[\kappa_D/(1 + \kappa_D a)]$, is equal to the corresponding equilibrium interaction energy for a univalent ion, ΔG^{o}_{ia}, except for the difference in sign. This sign difference reflects the instability of the *nonequilibrium* ionic atmosphere as compared with the stabilization necessarily afforded in the equilibrium case.

The underlying physical reason for the equality between E_r^{ia} and $|\Delta G^{o}_{ia}|$ under these conditions can be readily seen as follows. Imagine an uncharged sphere present in a (1-1) electrolyte solution being charged to yield, say, a univalent cation either (i) instantaneously, or (ii) infinitely slowly. While the cation formed in the latter case will experience the full ionic atmosphere stabilization, equal to $|\Delta G^{o}_{ia}| = (e^2/2\epsilon_s)[\kappa_D/(1 + \kappa_D a)]$ as prescribed by the Debye-Huckel model, no such ionic cloud is generated in the former case, so that $\Delta G^{r}_{ia} = 0$. Since the reorganization energy is defined as the difference in free energy of the state formed by route (i) minus that produced by route (ii),[10] then clearly $E_r^{ia} = - \Delta G^{o}_{ia}$.

It is instructive to consider the difference in the form of this result with that for the solvation component of E_r, E_s^r. In contrast to the ionic atmosphere component, the instantaneous charging step [route (i)] yields a substantial change in solvation energy, which according to the dielectric continuum model is equal to $e^2/2a\epsilon_{op}$ for the above conditions, where ϵ_{op} is the solvent optical dielectric constant.[10] Although the "slow" charging step [route (ii)] also produces an energy change, $e^2/2a\epsilon_s$, yielding the well-known expression $E_s^r = (e^2/2a)(\epsilon_{op}^{-1}-\epsilon_s^{-1})$, the former optical term usually provides the dominant contribution to E_s^r. This latter "fast" component, however, is entirely absent in the ionic atmosphere case, yielding the present unusually close relationship between the equilibrium and nonequilibrium free-energy quantities.

The attainment of expressions having the same functional form for E_r^{ia} and ΔG^{o}_{ia} also suggests that the extensive experimental information on activity coefficients which characterizes the latter may also be utilized to yield estimates of E_r^{ia} and hence ΔG^*_{ia} under some circumstances. In view of the foregoing analysis, this would only appear to require that linear response conditions be attained, certainly a milder requirement than the applicability of the Debye-Huckel or other particular ionic atmosphere models.

The foregoing treatment of ionic atmosphere reorganization can also be applied directly to optical electron transfer between spherical reacting centers. At least for valence-trapped cases, the energy of maximum light absorption, E_{op}, will essentially equal the overall reorganization energy, E_r.[11] Consequently, the contribution to the energy for optical electron transfer due to reorganization of the nonspecific ionic atmosphere, ΔE^{ia}_{op}, is

$$\Delta E^{ia}_{op} \approx E^{ia}_r = \frac{e^2}{\epsilon_s}\left\{\frac{\kappa_D a}{a(1+\kappa_D a)} + \frac{1}{R}\left[\frac{\exp[\kappa_D(a-R)]}{1+\kappa_D a} - 1\right]\right\} \tag{12}$$

Note that the relationship

$$\Delta G^*_{ia} = 0.25\ E^{ia}_r \approx 0.25\ \Delta E^{ia}_{op} \tag{13}$$

will apply for any linear response condition, merely requiring that the system free energy varies quadratically along the reaction coordinate. This is commonly considered to be the case for the solvent as well as inner-shell components of the activation energy.[8] Perhaps surprisingly, nonspecific ionic atmosphere effects upon optical electron-transfer energies do not appear to have been considered previously.

Given the involved structure of Eqs. (2) and (5), the nature of the predicted dependence of ΔG^*_{ia} and ΔE^{ia}_{op} upon the electrolyte ionic strength, I, is not immediately evident. To this end, Fig. 1 shows illustrative plots of ΔE^{ia}_{op} calculated from Eq. (5) versus I for a reactant radius of 3.5 Å in a solvent having $\epsilon_s = 30$ with three different R values, corresponding to reactant contact (7 Å), a relatively small separation (R = 10 Å), and for entirely isolated reactants ($R \rightarrow \infty$). Given that κ_D is given by the well-known expression

$$\kappa_D = (8\pi\ e^2/10^3 \epsilon_s k_B T)^{1/2}\ I^{1/2} \tag{14}$$

where k_B is the Boltzmann constant, with I in mol ℓ^{-1}, the results can readily be transposed to solvents having other ϵ_s values.

While the predicted ΔE^{ia}_{op} values for R = 2a are relatively small (≤ 0.2 kcal mol^{-1}) for I < 0.25 M and roughly linear with I at the higher electrolyte concentrations, for larger R the ΔE^{ia}_{op} values are increased substantially and display a noticeable curvilinear dependence upon I (Fig. 1). While the energetic effects are not especially large, such dependencies have possible implications for the interpretation of optical electron-transfer data (vide infra). It is interesting to note that the dependence of ΔE^{ia}_{op} upon R is much greater than is expected for the solvent reorganization component, E^s_r. According to the dielectric continuum treatment,^{8} E^s_r should only increase by twofold from a geometry where R = 2a to that where $R \rightarrow \infty$. For optical systems where the observed intervalence band arises from a distribution of conformations having significantly varying R, hence reflecting an envelope of differing E_{op} values, this suggests that the bandwidth should increase with increasing ionic strength.

From Eq. (8), identical ΔG^*_{ia} - I plots for thermal self-exchange reactions are predicted as in Fig. 1 but with fourfold smaller energy values. On this basis, the predicted ΔG^*_{ia} values should commonly be small or even negligible (<0.1 kcal mol^{-1}), at least for precursor configurations approaching reactant contact ($R \approx 2a$). Given that substantially larger ΔG^*_{ia} values are predicted for $R \to \infty$, and that $\Delta G^*_{ia}(\text{elect}) = 0.5\ \Delta G^*_{ia}(R\to\infty)$ [Eqs. (10), (11)], ionic atmosphere effects are anticipated to be rather larger for outer-sphere electrochemical processes. This reflects the absence of substantial "sharing" of the ionic cloud between the donor and acceptor sites that characterizes homogeneous-phase reactants in close proximity.

Comparison with Experimental Kinetic Data

Even though the foregoing treatment is oversimplified, especially in that it does not consider ion-pairing effects (vide infra), it is nonetheless of interest to compare the observed influence of added electrolyte upon the rate constants for metallocene self exchange, k_{ex} ($\underline{M}^{-1}\ s^{-1}$), with the corresponding predictions. It is conventional to express k_{ex} in the form[12-14]

$$k_{ex} = K_p \kappa_{el} \nu_n \exp(-\Delta G^*_{int}/RT) \tag{15}$$

where K_p describes the statistical probability of forming a precursor configuration (encounter reactant pair) suitable for electron transfer, κ_{el} is the electronic transmission coefficient, ν_n is the nuclear frequency factor (s^{-1}), and ΔG^*_{int} is the overall intrinsic barrier. For simplicity, we will assume that the added electrolyte only alters ΔG^*_{int}, no influence being felt on the preexponential factor. The "kinetically observed" ΔG^*_{ia} value, $\Delta G^*_{ia}(\text{ob})$, at a given ionic strength is then given by the measured k_{ex} value ratioed to the corresponding rate constant at zero ionic strength, k^o_{ex}, according to

$$\Delta G^*_{ia}(\text{ob}) = -RT\ell n(k_{ex}/k^o_{ex}) \tag{16}$$

Values of ΔG^*_{ia}(ob), extracted from rate data for $Cp_2Fe^{+/o}$ self exchange in acetone,[3] are plotted against ionic strength, I, in Fig. 2. The added electrolyte was tetraethylammonium hexafluorophosphate (Et_4NPF_6; filled circles) or perchlorate (Et_4NClO_4; filled triangles). Although there are only a limited number of data points which exhibit some scatter (a consequence of the small rate variations involved), evidence of ionic specificity is seen in that the addition of ClO_4^- yields larger ΔG^*_{ia}(ob) values than are observed with PF_6^- (cf. ref. 3). For comparison, a pair of corresponding ΔG^*_{ia} versus I plots calculated from Eq. (8) are included in Fig. 2 (solid traces). The reactant radius was taken as 3.8 Å;[4] the lower and upper curves refer to R values of 7.6 Å (=2a) and 10 Å, respectively.

Comparison between the experimental results and calculated curves shows them to be not greatly different, at least for PF_6^-, although the ΔG^*_{ia}(ob) values are clearly larger than the calculated values obtained for reactant contact (i.e. for R = 2a). Also shown in Fig. 1 (open squares) are corresponding ΔG^*_{ia} values extracted from reaction rates for the $Co(dmg)_3(BF)_2^+$ - Cp_2Fe reaction (dmg = deprotonated dimethylglyoxime) studied by Borchardt and Wherland.[14] In this case, the added electrolyte was tetrabutylammonium tetrafluoroborate. (For $Cp_2Fe^{+/o}$ self exchange, the addition of BF_4^- yields rate changes intermediate between those for PF_6^- and ClO_4^-.[3]) The I-dependent ΔG^*_{ia} values for the $Co(dmg)_3(BF)_2^+$-Cp_2Fe reaction are markedly larger than those for $Cp_2Fe^{+/o}$ self exchange. Even though the reaction is of the same charge type as $Cp_2Fe^{+/o}$ self exchange, its nonsymmetrical nature complicates the interpretation of electrolyte effects; in particular, the thermodynamic driving force may be significantly dependent on ionic strength.

Figure 3 contains corresponding results obtained in acetonitrile. In addition to the pair of calculated curves, obtained as before, experimental points are shown for $Cp_2Fe^{+/o}$ and $Cp_2Co^{+/o}$ self exchange (filled circles and diamonds, respectively),[3] and for $Co(dmg)_3(BF)_2{}^+$-Cp_2Fe (open squares).[15] (See caption to Fig. 3 for other details.) Again the metallocene self-exchange processes exhibit substantially smaller ΔG^*_{ia} values than for the cross reaction. While the results for $Cp_2Fe^{+/o}$ and $Cp_2Co^{+/o}$ are comparable, the ΔG^*_{ia} values are now noticeably larger than predicted by Eq. (8). Comparable findings are also obtained upon analysis of the corresponding metallocene self-exchange data in nitrobenzene and methanol provided in ref. 3. Slightly larger electrolyte effects for $Cp_2Fe^{+/o}$ self exchange in acetonitrile have been reported previously;[6] however, as discussed in ref. 3 these earlier NMR line-broadening measurements are somewhat unreliable for quantitative purposes.

Deviations from Debye-Huckel Predictions: Ionic Association

The discrepancies between the experimental electrolyte effects for metallocene self exchange and the ionic atmosphere predictions may be attributed in part to the well-known limitations of the underlying Debye-Huckel treatment. For example, larger ΔG^*_{ia} values, more closely in accord with experiment, can be obtained by employing smaller effective ϵ_s values as should be appropriate in the vicinity of the reacting ion. Indeed, the predicted ΔG^*_{ia} values increase sharply as ϵ_s decreases. This is due to the Debye screening length, κ_D^{-1}, decreasing under these conditions, so that the ionic atmospheres surrounding the two reactant spheres become more "isolated" (i.e. shared to a smaller extent), thereby increasing ΔG^*_{ia} for a similar reason to that brought about by increasing R (vide supra). On the other hand, electrolyte self-association, expected increasingly at higher salt concentrations, will tend to decrease the effective ionic strength below the values plotted in Figs. 2 and 3, thereby increasing the disparity between experiment and theory.

As noted above, there is reason to believe that more specific "ionic atmosphere" effects, arising in part from ion pairing between the cationic reaction partner and electrolyte anions, contribute significantly to the observed electrolyte effects for metallocene self exchange.[5] Indeed, ion pairing may dominate the electrolyte effects seen for some systems involving cation-neutral and anion-neutral reaction partners, especially in relatively nonpolar media.[5] While the formation of such an ion pair may not eliminate the surrounding ionic atmosphere, at least in more polar media where $\kappa_D^{-1} >> a$, it will modify it substantially so that the above simplified theoretical description of ΔG^*_{ia} will no longer be entirely appropriate.

For cases where a distinct geometry of the ion pair within the precursor complex can be presumed, progress along the reaction coordinate describing the elementary electron-transfer step may be conceived as requiring motion of the associated counterion towards the redox site which will become charged upon electron transfer. (In actuality, of course, the reorganization of more than a single electrolyte counterion will probably be involved, as for nonspecific ionic atmospheres.) On energetic grounds, the transition state for self-exchange reactions will feature the countercharge still associated within the encounter complex, but now situated roughly midway between the reaction centers. At least at sufficiently high electrolyte concentrations so that ion pairing within the precursor complex is virtually complete, the value of ΔG^*_{ia} should be determined by the energy cost of transporting the counteranion from the equilibrium position in the precursor complex to this transition-state configuration prior to electron transfer. (By the usual Frank-Condon arguments, electron transfer itself takes place within an essentially fixed reactant nuclear configuration.)

While such specific ionic atmosphere ion-pairing effects can be regarded as increasing the electron-transfer reorganization energy, E_r, in qualitatively the same fashion as for the nonspecific ionic atmosphere, two significant differences are immediately evident. Firstly, unlike ion-ion interactions as prescribed by the Debye-Huckel and other linear response theories, the short-range interactions responsible for ion pairing are inherently *nonlinear* in nature. This has the consequence of yielding deviations from Eq. (13), in that the G_{ia} - reaction coordinate profile is no longer quadratic. Secondly, the resulting ΔG^{*}_{ia} values should be very sensitive to the details of the precursor-state geometry inasmuch as this effects the degree to which counterion(s) motion is required so to form the transition state. Such a "geometric specificity" in ΔG^{*}_{ia} is related to the marked dependence upon the reactant separation predicted in the nonspecific ionic atmosphere case (Fig. 1, vide supra); however, ΔG^{*}_{ia} in the presence of ionic association will be sensitive to the ion-pair geometry even for a given juxtaposition of reactants.

As described by the authors,[5] some information on the energetics of this ion transport process for the $Cp_2Fe^{+/o}$ system can be obtained from recent optical electron-transfer measurements for BFA^+ by Blackbourn and Hupp. In some respects, the structure of BFA^+ should resemble the precursor complex for the thermal self exchange of $Cp_2Fe^{+/o}$. (Indeed, we have recently utilized measurements of electron-transfer energies of BFA^+ and related biferrocene cations[16] to extract solvent-dependent activation energies for metallocene self-exchange reactions, required for discerning solvent dynamical effects in such processes.[4c,d]) Blackbourn and Hupp observed increases in the energy of the intervalence band maximum, E_{op}, for BFA^+ with increasing concentration of added electrolyte in several solvents, including acetonitrile, acetone, and nitrobenzene of relevance to the $Cp_2Fe^{+/o}$ self exchange data in ref. 3. These E_{op} increases, ΔE^{ia}_{op}, have a qualitatively similar dependence upon electrolyte concentration as the ΔG^{*}_{ia} values derived from the present kinetic data. The former were considered[5] to arise from the additional energy for the optically induced process

$$X^- Fc^+ \text{-} Fc \xrightarrow{h\nu} X^- Fc \text{-} Fc^+ \quad (17a)$$

compared to that

$$Fc^+ \text{-} Fc \xrightarrow{h\nu} Fc \text{-} Fc^+ \quad (17b)$$

in the absence of X^--Fc^+ ion pairing. The ΔE_{op}^{ia} - I dependence was interpreted in ref. 5 in terms of the increasing proportion of the ion pair $X^- Fc^+$-Fc relation to free BFA^+ present in solution as $[X^-]$ is increased. In view of the foregoing, part of these electrolyte-induced optical energy shifts are probably due to nonspecific ionic atmosphere effects as well as to ionic association, at least at lower ionic strengths, although it is hard to refute the evidence for ion pairing marshalled in ref. 5.

For sufficiently large $[X^-]$ so that such ion pairing is essentially complete, ΔE_{op}^{ia} provides a measure of the free energy required to transport the anion from geometrically equivalent positions on the charged (ferrocenium) to uncharged (ferrocene) redox sites.[5] (This is because the optical transition involves electron transfer while the nuclear coordinates remain in their initial ground-state configuration.) In view of the above reasoning, the influence upon the activation energy of the corresponding thermal process, ΔG_{ia}^*, should roughly equal the energy required to move the anion one half this distance. As noted above, the coefficient, β, relating ΔG_{ia}^* and ΔE_{op}^{ia}, i.e. for

$$\Delta G_{ia}^* = \beta \Delta E_{op}^{ia} \quad (18)$$

will generally differ from that (0.25) predicted for the nonspecific ionic atmosphere case [Eq. (13)]. Model electrostatic calculations were undertaken for the present $Cp_2Fe^{+/o}$ system assuming a coulombic force field and utilizing crystallographic data for the Cp_2Fe^+/Cp_2Fe reaction partners.[17] These yield β values in the range ca. 0.4-0.45, depending somewhat upon the precursor geometry and the anion radius.

In spite of these uncertainties, it is of interest to undertake a rough comparison of the ΔE_{op}^{ia} and ΔG_{ia}^* values extracted from optical data for BFA^+ and from the $Cp_2Fe^{+/o}$ self-exchange kinetics, respectively. The plots of ΔE_{op}^{ia} versus ionic strength in acetonitrile and acetone extracted from the data in ref. 5b show a distinctly more curvilinear shape than the corresponding ΔG_{ia}^* - I plots for $Cp_2Fe^{+/o}$ and $Cp_2Co^{+/o}$ self exchange in Figs. 2 and 3; the former display a near-plateau at higher I.[5b] This shape is at least qualitatively consistent with ionic association, the onset of the plateau being attributed to the completion of ion-pair formation.[5] A worrisome point is that the Cp_2Fe^+-X^- association constants, K_a, extracted from the optical data in several solvents, including acetonitrile and acetone,[5b] are substantially larger than corresponding values for Cp_2Co^+-PF_6^- as determined from conductance data.[6] The latter K_a values are sufficiently small ($\lesssim 20$) in acetonitrile, acetone, and nitrobenzene for example, to deduce that little ion pairing occurs within the concentration range, ca. 0-20 m<u>M</u>, where extensive association is inferred from the optical measurements.[5b] The use of such optical data for these purposes should therefore be used with some caution.

Nevertheless, Table I contains illustrative numerical comparisons of ΔE_{op} and ΔG_{ia}^* extracted from the optical and thermal electron-transfer data given in refs. 5b and 3, respectively. In each solvent, values of $\Delta G_{ia}^*(op)$ (taken as 0.4 ΔE_{op}^{ia}), obtained from the shift in the BFA^+ optical band upon the addition of either 0.025 or 0.25 <u>M</u> electrolyte, are given alongside the corresponding values of $\Delta G^{*}_{ia}(\mathrm{ob})$ extracted as before from the $Cp_2Fe^{+/0}$ rate data by using Eq. (16). (The lower and higher electrolyte concentrations were chosen so to correspond to partial and essentially complete ion pairing as deduced in ref. 5b.)

Comparison between the corresponding $0.4\Delta E^{ia}_{op}$ and ΔG^{*}_{ia} values shows that the former are markedly (ca. 3-5 fold) larger than the latter at both ionic strengths. These results therefore indicate that the ionic-atmosphere effects observed for optical electron transfer in BFA^{+} are muted considerably in the ostensibly similar $Cp_2Fe^{+/0}$ thermal self-exchange process. Somewhat smaller disparities can be obtained by relating ΔE^{ia}_{op} and ΔG^{*}_{ia} instead by means of Eq. (13), although it is doubtful if this quadratic-based expression is applicable when ion-pair formation is extensive.

While the extent of the discrepancies between ΔE^{ia}_{op} and ΔG^{*}_{ia} is not entirely unexpected given the assumptions involved in both Eq. (16) and (18), they do nonetheless suggest that different electron-transfer pathways are being followed in these optical and thermal systems. One likely possibility is prompted by recent theoretical calculations for $Cp_2Fe^{+/0}$ self exchange by Newton which indicates that markedly larger electronic coupling matrix elements (i.e. donor-acceptor "orbital overlap") are obtained for approach of the reacting pair along a common fivefold axis ("axial" geometry) than for a "side-by-side" configuration.[18] Especially given that the reaction appears to follow nonadiabatic pathways under most conditions (i.e. $\kappa_{el} << 1$),[4d] the thermal reaction is therefore expected to proceed preferentially via the former transition-state geometry. The latter type of configuration, however, is more characteristic of the BFA^{+} structure given that the two ferrocene ring structures are tethered via an in-plane acetylenic bridge. It is possible that ion pairing within the "axial" geometry, preferred for the thermal bimolecular process, is less prevalent than for the "side-by-side" configuration. Given the anticipated sensitivity of ΔG^*_{ia} to the precise juxtaposition of the redox centers, both in the absence and presence of ion pairing, even subtle changes in the precursor complex structure may yield substantially different electrolyte effects. Such factors could easily be responsible in part for the marked differences seen in the electrolyte effects for $Cp_2Fe^{+/0}$ self exchange and the $Co(dmg)_3(FB)_2^+$-Cp_2Fe cross reaction (Figs. 2,3). Bearing in mind that the measured thermal electron-transfer rates will reflect predominantly *pathways yielding* the lowest energy barriers, the observed muting of the ion-pairing effect anticipated for $Cp_2Fe^{+/0}$ self exchange is not entirely surprising.

Nevertheless, it would seem desirable to formulate a more general treatment of ionic atmosphere effects upon electron-transfer energetics which incorporates ionic association, as well as nonspecific factors in a more satisfactory fashion than provided by the Debye-Hückel model. We hope to elaborate further on this topic in the near future.

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TABLE I. Illustrative Comparisons between Energetics of Electrolyte Effects upon $Cp_2Fe^{+/o}$ Self Exchange and BFA^+ Optical Electron Exchange

Solvent	Ionic Strength [a] M	Anion	$0.4\Delta E^{ia}_{op}$ [b] kcal mol^{-1}	$\Delta G^*_{ia}(ob)$ [c] kcal mol^{-1}
Acetonitrile	0.025	PF_6^-		0.04
	0.025	BF_4^-	0.35	
	0.25	PF_6^-		0.15
	0.25	BF_4^-	0.7	
Acetone	0.025	PF_6^-	0.35	0.07
	0.025	BF_4^-	0.45	
	0.25	PF_6^-	0.45	0.20
	0.25	BF_4^-	0.65	
Nitrobenzene	0.025	PF_6^-		0.04
	0.025	BF_4^-	0.25	
	0.25	PF_6^-		0.12
	0.25	BF_4^-	0.55	

[a] Essentially equal to concentration of added electrolyte, either tetrabutylammonium tetrafluoroborate or tetraethylammonium hexafluorophosphate, as indicated by anion noted in adjacent column.

[b] ΔE^{ia}_{op} is observed increase in intervalence band maximum for BFA^+ upon addition of electrolyte indicated; data taken from ref. 5b.

[c] Increase of activation free energy for $Cp_2Fe^{+/o}$ self exchange upon addition of electrolyte indicated, as obtained from kinetic data in ref. 3 by using Eq. (8).

Figure Captions

Fig. 1

Increase in energy of optical electron transfer (or reorganization energy) between a pair of spherical reactants of radius 3.5 Å as calculated from Eq. (12) versus the electrolyte ionic strength, for three internuclear separations, R, as indicated. Solvent dielectric constant, ϵ_s, taken as 30.

Fig. 2

Comparison between increases in activation free energy due to ionic atmosphere effects, ΔG^*_{ia}, versus ionic strength, as predicted from Eq. (8) (solid traces) and from experimental kinetic data (points) in acetone. Latter ΔG^*_{ia} values obtained by using Eq. (16) from experimental kinetic data for $Cp_2Fe^{+/0}$ self exchange (filled symbols)[3] and for $Co(dmg)_3(BF)_2{}^+$ reduction by Cp_2Fe[15] (open squares). Added electrolytes are tetraethylammonium hexafluorophosphate (filled circles), tetraethylammonium perchlorate (filled triangles), and tetrabutylammonium tetrafluoroborate (open squares). Calculated ΔG^*_{ia} - I traces were obtained using the following parameters: $\epsilon_s = 21$, $a = 3.8$ Å, $R = 7.6$ Å (lower trace), $R = 10$ Å (upper trace).

Fig. 3

Similar to Fig. 2, but in acetonitrile. Key to experimentally derived ΔG^*_{ia} values as follows. Filled squares: $Cp_2Fe^{+/0}$ self exchange with added tetraethylammonium hexafluorophosphate.[3] Filled diamonds: $Cp_2Co^{+/0}$ self exchange with added tetraethylammonium tetrafluoroborate.[3] Open squares: $Co(dmg)_3(BF)_2^+$ reduction by Cp_2Fe, with added tetrabutylammonium tetrafluoroborate.[15]

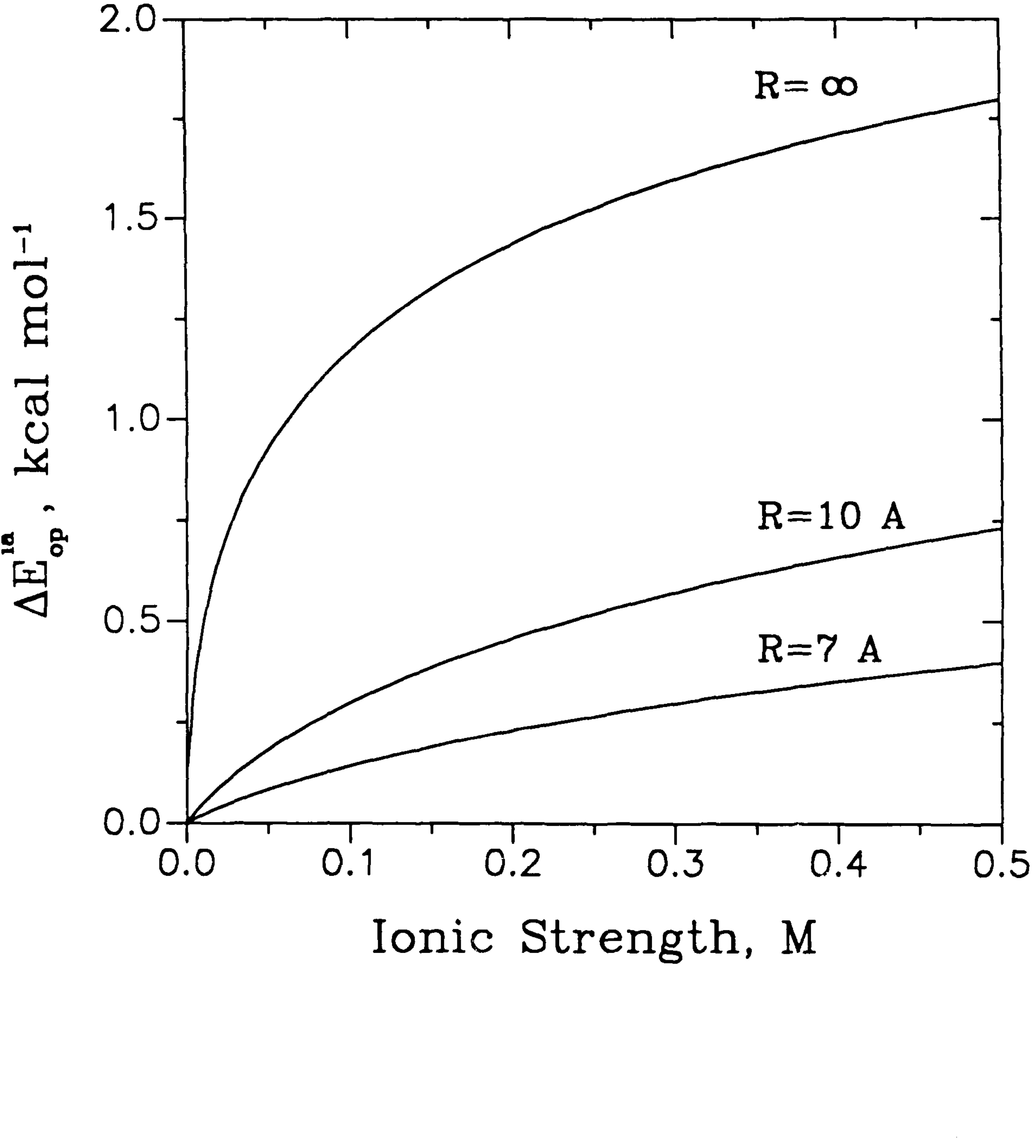

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Figure 1

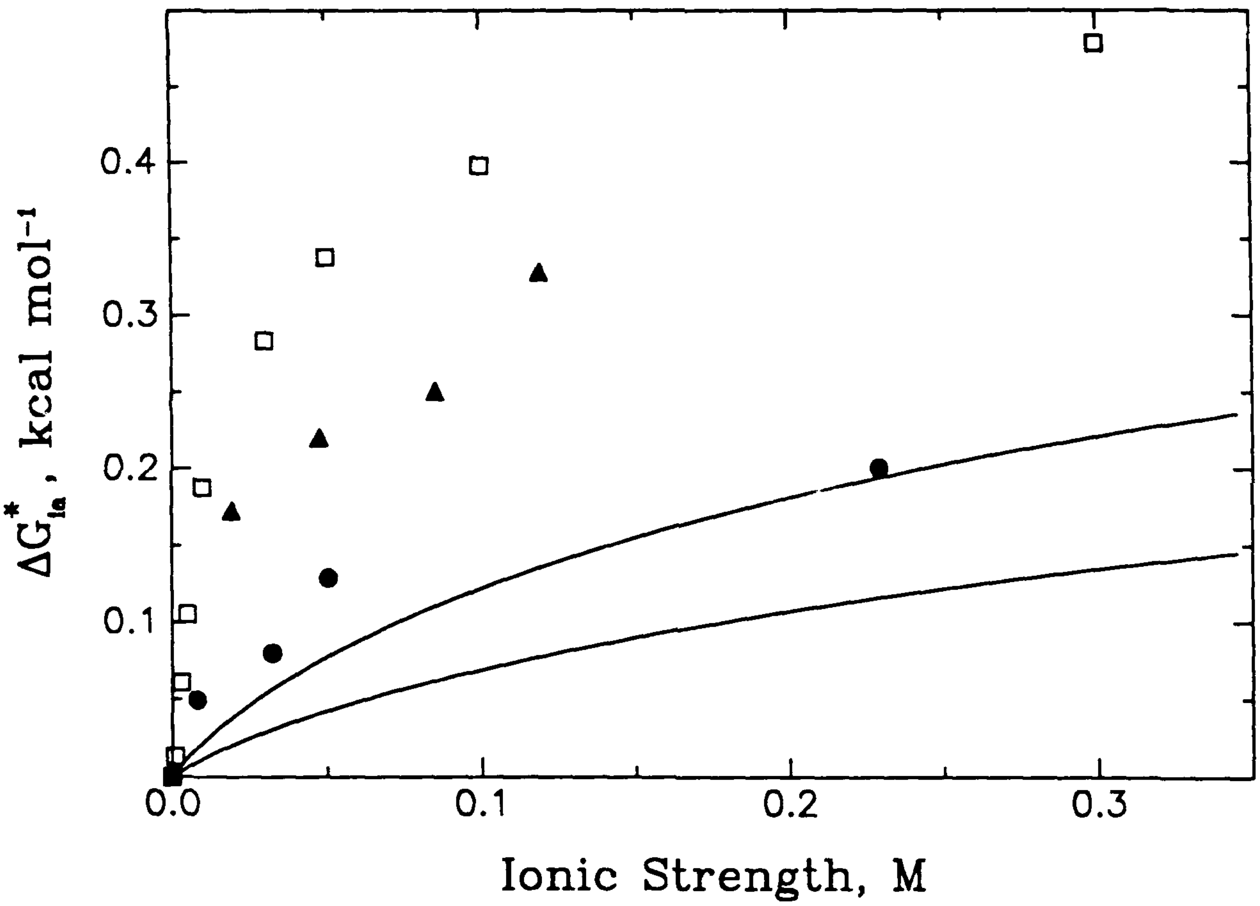

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Figure 2

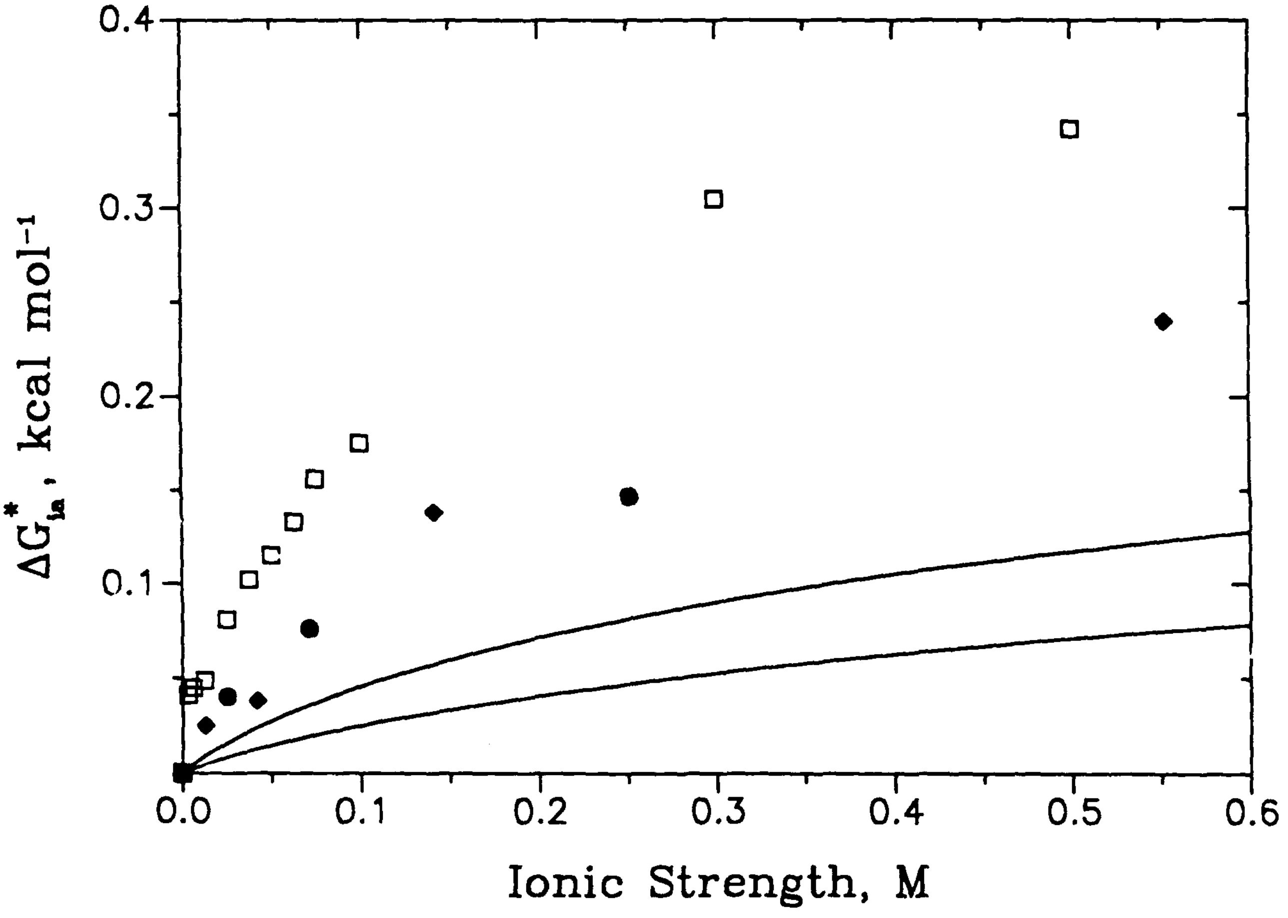

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Figure 3