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Solvent Effects on Intervalence Electron-Transfer Energies for Biferrocene Cations: Comparisons with Molecular Models of Solvent Reorganization

by

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with the predictions of the two-sphere model (but not ellipsoid models), although the E_{op} values for BF^+ are larger than expected, most probably due to electron delocalization effects. Taking into account anticipated "electronic-state modulation" effects (ref. 38) on the potential-energy well improves somewhat the overall match with the observed E_{op} values, but cannot account for the scatter in the E_{op} - ($\varepsilon_{op}^{-1} - \varepsilon_s^{-1}$) plots. Comparisons are made with the recent mean spherical approximation (MSA) treatment of solvent reorganization ~~(ref. 10)~~. The MSA model can account semiquantitatively for the smaller E_{op} values relative to E_{op}(con) observed in a number of solvents, but does not predict the especially large such deviations observed for methanol and D_2O. The latter are shown to be qualitatively consistent with local "solvent structuring" effects deduced on the basis of a "nonlocal dielectric" approach ~~(refs. 4, 5)~~ as well as on empirical grounds.

Solvent Effects on Intervalence Electron-Transfer Energies for Biferrocene Cations: Comparisons with Molecular Models of Solvent Reorganization

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ABSTRACT

Outer-shell electron-transfer reorganization energies, λ_o, as evaluated from intervalence band maxima, E_{op}, for biferrocenylacetylene (BFA^+), 1,4-biferrocenylbutadiyne (BFB^+), and biferrocene (BF^+) cations in thirteen solvents are compared with the predictions of some contemporary models of solvent reorganization in order to ascertain the importance of "noncontinuum", or solvent molecularity, factors to λ_o. Measurements of E_{op} were made in relatively polar media in solutions containing low concentrations (< few m$\underline{M}$) of PF_6^- so to minimize complications from ion pairing. While E_{op} correlates roughly with (ϵ_{op}^{-1} - ϵ_s^{-1}) (ϵ_{op}, ϵ_s are optical, static dielectric constants), the plots display considerable scatter; smaller slopes and larger intercepts are obtained than anticipated from such dielectric continuum treatments, so that E_{op} tends to be smaller than the "two-sphere" continuum estimates, E_{op}(con). However, the relative E_{op} values for all three biferrocenes are essentially independent of the solvent; E_{op} for BFB^+ relative to BFA^+ is in good agreement with the predictions of the two-sphere model (but not ellipsoid models), although the E_{op} values for BF^+ are larger than expected, most probably due to electron delocalization effects. Taking into account anticipated "electronic-state modulation" effects (ref. 38) on the potential-energy well improves somewhat the overall match with the observed E_{op} values, but cannot account for the scatter in the E_{op} - (ϵ_{op}^{-1} - ϵ_s^{-1}) plots. Comparisons are made with the recent mean spherical approximation (MSA) treatment of solvent reorganization (ref. 10). The MSA model can account semiquantitatively for the smaller E_{op} values relative to E_{op}(con) observed in a number of solvents, but does not predict the especially large such deviations observed for methanol and D_2O. The latter are shown to be qualitatively consistent with local "solvent structuring" effects deduced on the basis of a "nonlocal dielectric" approach (refs. 4,5) as well as on empirical grounds.

A topic of abiding interest in electron transfer concerns the ability of simple dielectric continuum models to describe and predict solvent reorganization energies. The most direct experimental information on this question can be extracted in suitable cases from optical electron-transfer spectra for symmetrical mixed-valence complexes.[1,2] Generally speaking, continuum models are tolerably successful in at least correlating the solvent dependence of the optical electron-transfer energies, E_{op}.[2,3] Nevertheless, several significant deviations of the experimental data from these predictions have been noted.[4-6] While dielectric continuum treatments have long provided the mainstay in descriptions of the solvent reorganization energetics in thermal as well as optical electron transfer,[8] several analytic treatments[4,7,10,11] and molecular dynamical simulations[12-14] have appeared recently that consider various noncontinuum ("molecular") solvent effects upon the free-energy barrier.[4,7,10] So far, however, specific evaluation of these treatments in comparison with experimental information has been surprisingly limited.

As part of a detailed exploration of solvent dynamical effects in electron transfer, we have been examining the solvent-dependent self-exchange kinetics of various metallocene redox couples.[15] In order to extract the required barrier-crossing dynamics from the measured rate constants, it is necessary to have reliable information on the solvent-dependent intrinsic barriers, ΔG^*. While approximate estimates can be obtained[15a] using the Marcus continuum model,[8] we have recently preferred to utilize ΔG^* values extracted from E_{op} values for analogous biferrocene cations, especially biferrocenylacetylene (BFA^+).[15d-f] A virtue of biferrocene cations for this purpose is that they should mimic closely the precursor complex geometries for the $Cp_2M^{+/o}$ self-exchange processes, enabling ΔG^* to be obtained simply from[1]

$$\Delta G_c^* = E_{op}/4 \tag{1}$$

where ΔG_c^* is the ("cusp" limit) value of ΔG^* in the absence of donor-acceptor resonance splitting.[15e]

While such kinetic applications provide the major motivation for our interest in such optical measurements, biferrocene cations also provide interesting systems in their own right with which to examine noncontinuum solvent effects upon the reorganization energy. Unlike mixed-valence ruthenium complexes that have been the focus of most experimental work,[2,3] the ferrocenium-ferrocene moiety should engage in relatively weak nonspecific interactions with the surrounding solvent given its +/o charge type. Indeed, the ferrocenium-ferrocene redox couple has long been utilized as a supposedly noninteracting "reference" system for electrochemical thermodynamic measurements.[16] These features suggest that measurements of electron-transfer barriers for suitable biferrocene cations could provide worthwhile tests of contemporary models of solvent reorganization energetics in the absence of complications from specific solute-solvent interactions and/or high solute charges.

Measurements of E_{op} for BFA^+ and the parent biferrocene cation, BF^+, in several solvents were reported some years ago by Powers and Meyer.[17] More recently, Lowery et al[18] and Blackbourn and Hupp[19] have uncovered substantial "ion aggregation" and ion-pairing effects upon E_{op} for BF^+ and BFA^+, respectively, under some conditions. However, the latter authors have shown that these effects for BFA^+ are typically small in relatively polar media for low concentrations ($\leq$ 1 m$\underline{M}$) of noncoordinating anions such as PF_6^- or BF_4^-.[19b]

In the present report we summarize measurements of E_{op} for BF^+, BFA^+, and also 1,4-biferrocenylbutadiyne, BFB^+, in thirteen solvents chosen so to provide a range of molecular size and structure as well as continuum reorganization energies. While BF^+ has a C-C bond linking directly the two ferrocene units, BFA^+ and BFB^+ contain one and two acetylenic groups, respectively, separating these moieties. This has the effect of diminishing the electronic interaction between the two redox centers; while BF^+ exhibits some characteristics of electronic delocalization (vide infra), BFA^+ and BFB^+ appear to approximate valence-trapped ("class II") behavior.[17,20] [The latter circumstance is required for Eq. (1) to be valid.[1]] Examination of solvent-dependent E_{op} values for BFB^+ as well as BFA^+, featuring differing distances between the redox sites, enable the electronic and electrostatic interaction effects between the redox centers to be disentangled from the desired solvent reorganization energetics of the "isolated" redox centers.

Of central interest here is the comparison of these experimental reorganization energies with the predictions of some contemporary theoretical treatments in order to elucidate the manner in which noncontinuum, or "molecular", solvent factors may influence E_{op} and hence ΔG_c^* for such weakly interacting solutes. In particular, we consider a recent "mean spherical approximation" (MSA) treatment of nonequilibrium solvent polarization[10] and a model based on so-called "non-local" dielectric theory which attempts to describe the spatial correlations of solvent structure.[4,5]

EXPERIMENTAL SECTION

Acetonitrile, acetone, and propylene carbonate were obtained from Burdick and Jackson. The first two were distilled over P_2O_5 and $CaSO_4$, respectively, in a nitrogen atmosphere; the last solvent was used as received. Nitrobenzene, benzonitrile, and nitromethane (Fluka), as well as nitroethane, and ortho- and meta-nitrotoluene (Aldrich) were purified by column chromatography using activated alumina, Propionitrile and butyronitrile (Aldrich) were distilled over P_2O_5 in a nitrogen atmosphere. Deuterated water, methanol, acetonitrile, and nitrobenzene were obtained from Aldrich.

Biferrocenylacetylene (BFA), 1,4-biferrocenylbutadiyne (BFB), and biferrocene (BF) were synthesized as described in refs. 21 to 23. Purity was verified by means of proton NMR and cyclic voltammetry as well as from the cation near-infrared spectra. The corresponding biferrocene monocations were generated using either an in situ oxidation of the neutral molecules with one equivalent of $Fe(bpy)_3(PF_6)_3$ (bpy = bipyridyl) or by isolating the cation salt following oxidation with stoichiometric amounts of $AgBF_4$ (Aldrich) in nitromethane. $Fe(bpy)_3(PF_6)_3$ was prepared by adding three equivalents of 2,2'-bipyridine (Aldrich) to one equivalent of $Fe(SO_4)\cdot 7H_2O$ (J. T. Baker) in dilute H_2SO_4. The blood-red $Fe(bipy)_3^{2+}$ solution was filtered and was made 2 M in H_2SO_4. Subsequent oxidation of the acidic solution with an excess of PbO_2 was conducted at 0°C. The baby-blue hexafluorophosphate salt was crystallized following addition of a solution of NH_4PF_6 (Apache Chemicals).

Near-infrared spectra were acquired between 800 and 2000 nm by means of a double-beam Cary Model 17D spectrometer, using pairs of 1 cm path length quartz cuvettes. Typically ca 0.5 mM BF^+, 1 mM BFA^+, and 1-2 mM BFB^+ were used so to yield maximum near-infrared absorbances around 0.2-0.5.

RESULTS AND DISCUSSION

A summary of the energies of the intervalence charge transfer (IT) band maximum, E_{op} (cm^{-1}), measured here for BF$^+$, BFA$^+$, and BFB$^+$ in thirteen solvents is given in Table I, together with a few additional values taken from refs. 17 and 19a. Whenever the present data overlap with those in ref. 17, the E_{op} values agree within our experimental uncertainty of typically ± 50 cm^{-1}. The bandshapes and intensities extracted from the present measurements are also in good agreement with those given in ref. 17. The range of solvents examined was limited by several factors, including solubility and chemical decomposition. The former factor, for example, limited measurements in D_2O to BF$^+$ (see ref. 15f for details); measurements for all three biferrocenes in amide media were precluded due to ferrocene decomposition and/or solvent oxidation (cf. ref. 17).

As noted above, a possible complication is that the E_{op} values can be affected significantly by ion pairing, even at the low anion concentrations (~ 1 m*M*) utilized here. This effect will shift E_{op} to higher energies since the optical transition then refers to a nonsymmetrical system where the initial ground state is stabilized by ion pairing but the final state is not.[19b] The effect of ion pairing is substantial for BFA$^+$ in methylene chloride.[19a] However, recent measurements, also by Blackbourn and Hupp, have shown that the ion-pairing correction required to E_{op} for BFA$^+$ in more polar media, such as acetonitrile, acetone, nitromethane and nitrobenzene, for the conditions employed here is relatively small, amounting typically to a few percent or less.[19b] Especially given the comparable uncertainties in the measurement of E_{op} itself and the more modest requirements of the present analyses (vide infra), almost no ion-pairing corrections to E_{op} obtained here were deemed necessary.

The simplest as well as the conventional means of comparing the solvent-dependent E_o values with theoretical predictions involves plotting E_{op} versus the "Pekar factor", $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$, where ϵ_{op} and ϵ_s are the solvent optical and static dielectric constants, respectively.[1,2] Such a plot for all three biferrocene cations constitutes Fig. 1; the $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ as well as E_{op} values used are summarized in Table I. The points for BF^+, BFA^+, and BFB^+ are shown as circles, squares, and triangles, respectively. The solvent numbering scheme is taken from Table I; the entries referring to hydrogen-bonded solvents D_2O and CH_3OD are displayed as open points in Fig. 1, and those in the other media as filled symbols. The crossed-square point (14) is for BFA^+ in methylene chloride after correction for ion-pairing effects, taken from ref. 19a.

The solid and dashed straight lines in Fig. 1 are the E_{op} - $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ plots for BFA^+ and BFB^+, respectively, predicted from the well-known dielectric continuum formula[1,2]

$$E_{op}(con) = e^2 (\epsilon_{op}^{-1} - \epsilon_s^{-1})(a^{-1} - R^{-1}) \tag{2}$$

where e is the electronic charge, a is the effective radius of each redox center and R is the center-to-center internuclear separation between them. The radius, a, is taken as the average value, 3.8 Å, extracted from crystallographic data for ferrocene.[26] The values of R chosen for BFA^+ and BFB^+ are 7.6 and 10.3 Å. The former value is appropriate to the trans configuration;[17] the latter value is obtained by adding the distance corresponding to the additional C=C-C linkage, 2.7 Å[27] (cf. ref. 17). No calculated line is included for BF^+ in Fig. 1; the estimated internuclear separation is sufficiently small such that $2a < R$ (i.e. the reactant spheres are interpenetrating) whereupon Eq. (2) should be invalid (vide infra).

Comparison between the experimental points and these calculated lines for

BFA^+ and BFB^+ shows reasonable agreement, especially given the uncertainties in the spatial parameters a and R, in that the experimental reorganization energies are generally within ca 20% of the corresponding predictions. Nevertheless, even ignoring the points for methanol (2) which are especially discrepant (vide infra), least-squares fits to the experimental points yield slopes, 22.5 and 37 kcal mol^{-1} for BFA^+ and BFB^+, respectively, that are substantially below the corresponding calculated values, 43.5 and 55 kcal mol^{-1}. The same qualitative behavior was noted previously in ref. 17. Moreover, although a necessarily long extrapolation is involved, these experimental "best-fit" lines yield sizable y-intercepts, about 10 and 9 kcal mol^{-1} for BFA^+ and BFB^+, respectively. Although a positive y-intercept is expected, comprising the (solvent-independent) inner-shell contribution to the reorganization energy, E_{op}^{in},[28] this component is estimated to be about 3 kcal mol^{-1} or less.[29]

Before accepting these findings as signaling significant deficiencies in the dielectric continuum treatment, however, it is necessary to consider the possible influence of electron delocalization upon E_{op}. While the validity of Eqs. (1) and (2) is not contingent upon the absence of electronic coupling, the analysis will eventually fail in the presence of large electronic matrix coupling elements, H_{12}: for "complete" electron delocalization, $E_{op} = 2H_{12}$, so that E_{op} becomes independent of the solvent.[2a] On the basis of the conventional Hush analysis of the IT band intensities, and from comproportionation equilibria as well as from geometric considerations,[17,20a] we expect the order of electronic overlap to be $BF^+ > BFA^+ > BFB^+$. Indeed, at least a vestige of delocalized behavior may be apparent for BF^+ from the observation of a relatively small slope (9 kcal mol^{-1}) and substantial y-intercept (11 kcal mol^{-1}) obtained from the experimental points in Fig. 1 (again excluding the hydrogen-bound solvents CH_3OD and D_2O). Evidence suggesting substantial electron delocalization for BF^+ - markedly greater than predicted from the Hush treatment - has been obtained by applying the Peipho-Krausz-Schatz (PKS) vibronic coupling model,[30] although such analyses for such "class II/III borderline" systems can be fraught with uncertainties.[2a,31] (We have shown recently that the analogous bicobaltocene cation exhibits substantially more electron delocalization than BF^+.[32])

As a consequence, it is conceivable that the larger E_{op} - $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ intercepts as well as smaller slopes for BFA^+ and BFB^+ than expected from the dielectric continuum treatment may be due in part to electronic delocalization effects. This influence, however, seems unlikely to be dominant. Thus the y-intercepts for BFB^+ as well as BFA^+ are similar to that for BF^+; markedly smaller values for the former system would be expected if the intercept was attributable primarily to $2H_{12}$. (The Hush analysis applied to BFA^+ and BF^+ in acetonitrile yields $2H_{12}$ estimates of about 1.5 and 3 kcal mol^{-1}, respectively.[32]) Moreover, the observed marked increases of the E_{op} - $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ slopes in the sequence $BF^+ > BFA^+ > BFB^+$ suggest that even if BF^+ is extensively delocalized, the behavior of the latter systems is primarily valence-trapped in character. We therefore feel justified in interpreting the observed solvent-dependent E_{op} values in terms of nuclear solvent reorganization as in Eq. (1).

Donor-Acceptor Geometry Effects

In order to utilize the experimental E_{op} values as a monitor of the solvent reorganization energy around each redox center, even when Eq. (1) is valid (i.e. electronic delocalization effects upon E_{op} are unimportant), it is necessary to understand how E_{op} depends upon the binuclear geometry. This is especially the case for comparisons between the experimental data and the predictions of the MSA model (vide infra), since the latter (as currently formulated[10]) describes the solvent reorganization energy for an *isolated* spherical redox center, λ_o, and therefore does not account for the modifications to this energy caused by its redox partner nearby. Specifically, then, it is desirable to deconvolute the influence upon E_{op} arising from the spatial proximity of the redox partners in the binuclear complex so to uncover the underlying solvent-dependent variations in λ_o.

The simplest means of accounting for such "geometric site" interactions utilizes the "two-sphere" model [Eq. (2)]. A more detailed comparison of the solvent-dependent E_{op} values for BFA^+ (squares) and BFB^+ (triangles) in Fig. 1 with the corresponding predictions of Eq. (2) (solid and dashed lines, respectively) shows that this simple model accounts surprisingly well for the differences in E_{op} between BFA^+ and BFB^+ in each solvent. Although the extent of the scatter in the experimental E_{op} values with respect to the corresponding calculated line in Fig. 1 varies substantially with the solvent, the *relative* deviations in a given solvent are very similar for BFA^+ and BFB^+. In other words, the changes in E_{op} in each solvent brought by altering the internuclear site separation scale generally as predicted by the solvent-independent factor $(a^{-1} - R^{-1})$ in Eq. (2). Such an E_{op} - R dependence is well established for several other systems.[34]

This point is demonstrated more quantitatively in Table II, which consists of ratios of E_{op} values in each solvent for BFB^+ versus BFA^+, $E_{op}(BFB)/E_{op}(BFA)$, and also corresponding values for BF^+ versus BFA^+,

E_{op}(BF)/E_{op}(BFA). Also listed (in parentheses) are the corresponding ratios calculated from Eq. (2), taking a = 3.8 Å and R = 5.0, 7.6, and 10.3 Å for BF^+, BFA^+, and BFB^+, respectively (cf ref. 17). Interestingly, the E_{op}(BFB)/E_{op}(BFA) ratios are not only virtually independent of the solvent (1.27 ± 0.04), but are essentially consistent with the calculated value, 1.26. Although this agreement is somewhat fortuitous given the uncertainties in R and a, it demonstrates clearly that the response of E_{op} to an alteration in the site internuclear distance is virtually independent of the solvent.

Table I shows that this finding extends to BF^+ versus BFA^+ in that E_{op}(BF)/E_{op}(BFA) is also essentially solvent independent. However, this experimental ratio, ca 0.75, is substantially larger than the calculated value, 0.48. This disparity is unsurprising not only in view of the likely effect of electron delocalization upon the BF^+ values (vide supra), but also given the limitations of the "two-sphere" model. (This continuum treatment is predicted to be valid only when $R \geq 2a$[9c,35].)

As an alternative to the "two-sphere" model, a dielectric continuum approach treating the redox partners as an ellipsoid[36] has been touted.[3,9b,c] A recent detailed discussion is provided in ref. 3. We undertook a series of model calculations using this approach for geometric parameters appropriate for the present biferrocenes, primarily in order to provide a numerical comparison with the predictions of the two-sphere model. Specifically, these calculations utilized the expressions given in Eqs. (3)-(5) of ref. 3. In addition to ϵ_{op} and ϵ_s, the calculations require estimates of the "cavity dielectric constant", ϵ_{in}, the lengths of the major and minor ellipsoid axes, 2A and 2B, respectively, and the reactant internuclear ("charge separation") distance R as before. We assumed that ϵ_{in} = 1.8; the numerical results were found to be relatively insensitive to ϵ_{in}, at least in the range 1.8 to 2.2 (cf ref. 3). Values of 2A and 2B were selected using the "eve" model,[3] involving an ellipsoid cavity just large enough to enclose totally the binuclear complex. For BFA^+ and BFB^+, for example, we used the values 2A = 9.0 and 9.5 Å, and 2B = 4.4 and 4.8 Å, respectively, although other combinations of A and B also yielded reasonable geometric fits.

The resulting E_{op} values for BF^+, and especially BFA^+ and BFB^+, are substantially (2-3 fold) smaller than both the corresponding quantities calculated from Eq. (2) and the experimental values. Although the approximately linear E_{op} - $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ plots calculated from the eve model extrapolated to small positive y-intercepts (ca 1 kcal mol^{-1}),[37] the slopes are markedly smaller than those observed experimentally. Enhancements of the ellipsoid E_{op} values so to yield rough consistency with the experimental results demanded substantially smaller values of A and/or larger values of B than appear to be geometrically reasonable. This lack of success of this ellipsoid model in comparison with the two-sphere treatment for describing the reorganization energies of BFA^+ and BFB^+ can be attributed to their "dumbbell-like" structure. Unlike bipyridyl-bridged diruthenium systems, for example, which can in some cases be described successfully as an ellipsoid,[3] the acetylenic bridges in BFA^+ and BFB^+ appear sufficiently "slim" to enable solvent to penetrate between the ferrocene partners. This should increase E_{op} substantially above the ellipsoid predictions,[2e,3] in accordance with experiment. Nevertheless, the ellipsoid treatment can account for the relatively mild E_{op} - $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ dependence observed for BF^+ (Fig. 1), as might be anticipated given that the "spherical" reaction partners are effectively interpenetrating in this case.

Reactant "Electronic-State Modulation" Effects

Before proceeding to a discussion of solvent molecularity effects on the observed E_{op} values, it is appropriate to consider briefly an interesting prediction of Kuznetsov that the reorganization energy will contain an additional solvent-dependent component associated with reactant "electronic-state modulation".[38] Specifically, the effect arises from the interaction between the transferring electron and the fluctuating solvent polarization. As the polarization of the surrounding medium changes, corresponding to progress along the solvent reaction coordinate, the spatial characteristics of the donor-acceptor wave functions can vary.[38] This effect concerns the diagonal part of the interaction matrix, that influences the *diabatic* potential-energy surfaces forming the initial and final states, as distinct from the off-diagonal components which affect the electronic matrix coupling element, H_{12}. The predicted effect is to diminish the effective reorganization energy because the alteration in the solvent polarization configuration corresponding to motion from the reactant well towards the transition state should act to make the reactant electronic wave function more "diffuse".[38] Since the effective "force constants" (i.e. the shape) of the potential-energy wells will thereby be altered, the effect is expected to influence E_{op} as well as ΔG_c^* [Eq. (1)].

A simple, albeit somewhat crude, expression for ΔG_c^* (and hence E_{op}) can be obtained by neglecting the mutual influence of the donor and acceptor sites on the zeroth-order initial and final state wavefunctions.[38b] For the present purpose, this can be expressed conveniently as the following dimensionless factor, f_e, that can be included as a multiplicative correction term in conventional dielectric continuum expressions [such as Eq. (2)]:

$$f_e = \frac{3 + (64/5P\epsilon_s) + (64R/5\beta e^2 P)^2}{4[1 + 16/5P\epsilon_s]} \qquad (3)$$

where P is the Pekar factor $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ and $\beta = (k_B T)^{-1}$, k_B being the Boltzmann constant. Specific calculations were performed using Eqs. (2) and (3) for the solvents of interest here (Table I) and for R = 7.6 and 10.3 Å, appropriate to BFA^+ and BFB^+, respectively. In both cases, essentially linear E_{op} - $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ plots were obtained with little scatter in the individual points ($\leq$ 0.4 kcal mol^{-1}). [Slightly smaller E_{op} values are predicted for solvents with high ϵ_s values.] However, the E_{op} - $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ slopes calculated for both BFA^+ and BFB^+ are only about 0.7 times as large as the conventional continuum prediction [Eq. (2)], and significant y-intercepts (3 and 4.5 kcal mol^{-1}, respectively) are obtained. Use of a more sophisticated treatment[38a] apparently yields similar results, although the extent of the predicted correction is slightly smaller (i.e. f_e is slightly larger).

Interestingly, this predicted behavior mimics roughly the deviations observed in the approximate functional form of the experimental E_{op} - $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ plots in Fig. 1 from the conventional continuum predictions [Eq. (2)]. It is important to note, however, that the substantial "scatter" in the observed E_{op} values from the E_{op} - $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ correlation seen in Fig. 1 cannot be accounted for by *any* of the continuum-based models considered here.

Comparisons with the MSA Solvent Reorganization Model

Having established that the functional dependence of E_{op} upon the solvent is virtually independent of the internuclear geometry, and additionally that the "scaling factor" $(a^{-1} - R^{-1})$ can uniformly describe such geometrical variations, this E_{op}-solvent functionality can confidently be ascribed to solvent reorganization around the individual redox centers rather than to the pecularities of their interaction. We therefore feel justified in examining the significant observed deviations in the E_{op}-solvent functionality from the dielectric continuum prediction ($\epsilon_{op}^{-1} - \epsilon_s^{-1}$) in terms of "solvent molecularity" (noncontinuum) factors.

A recent theory of nonequilibrium solvation in terms of the MSA model, formulated initially by Wolynes[10a] and extended by Rips, Klafter and Jortner,[10b,c] is of particular interest in this regard. In the MSA treatment, the solvent is modeled as a collection of hard spheres with embedded point dipoles, rather than merely a dielectric continuum. We have recently utilized this approach to estimate solvent molecularity effects upon the barrier-crossing dynamics as well as the reorganization energy of thermal electron-exchange processes.[39] The solvent reorganization energy for electron transfer involving an isolated pair of redox sites (i.e. $R \to \infty$[40]), $E(MSA) = 2\lambda_o$, according to this treatment is given by[10b,39,40]

$$E(MSA) = (2e^2/a)\{[1 + \delta_{re}(\omega = 0)]^{-1}(1 - \epsilon_s^{-1}) - [1 + \delta_{re}(\omega = \infty)]^{-1}(1 - \epsilon_{op}^{-1})\} \qquad (4)$$

where δ_{re} is a frequency(ω) - dependent correction factor to the solute radius, which is well approximated by[10b]

$$\delta_{re}(\omega) = (3r_{sol}/a)\ \{108^{1/3}\ [\epsilon(\omega)]^{1/6}) - 2\}^{-1} \qquad (5)$$

where r_{sol} is the "hard-sphere" solvent radius. The frequency-dependent dielectric constant, $\epsilon(\omega)$, is set equal to ϵ_{op} and ϵ_s for $\omega \to \infty$ and $\omega \to 0$, respectively. Physically, δ_{re} is a frequency-dependent analog[10] of the well-known "Gurney cosphere".[41]

In the limit where $\delta_{re} \rightarrow 0$ at all frequencies, ω, Eq. (4) reduces to Eq. (2) with $R \rightarrow \infty$. At least when $r_{sol} > 0$, however, E_{MSA} will differ from E_{op}(con) since then the radius correction factor $\delta_{re} > 0$. This "solvent molecularity" correction will usually act to diminish E_{MSA} below the corresponding continuum-limit value, and increasingly so as r_{sol} increases since $\delta_{re} \propto r_{sol}$ [Eq. (5)].[39]

Figure 2 is a plot of E_{op} values estimated from this MSA treatment, E_{op}(MSA), for each of the solvents considered here, versus $(\epsilon_{op}^{-1} - \epsilon_{s}^{-1})$. The E_{op}(MSA) values were obtained from Eq. (3), assuming that $E_{op}(\text{MSA}) = 0.5$ E(MSA). This procedure, although somewhat arbitrary, yields E_{op}(MSA) values that should be appropriate for BFA^{+} given that E_{op} for this system (for which $2a \approx R$) should be one half as large as for an entirely isolated redox pair, where $R \rightarrow \infty$. As in Fig. 1, the solid line in Fig. 2 is that predicted for BFA^{+} from the dielectric continuum formula [Eq. (2)]; the E_{op}(MSA) values shown would fall on this line in the limit where $\delta_{re} \rightarrow 0$. The "hard-sphere" solvent radii, r_{sol}, utilized in Fig. 2 are taken (or estimated) from values listed in ref. 42, extracted from molar volume data. The reactant radius is again set at 3.8 Å. The ϵ_{op} and ϵ_{s} values used for these calculations, along with the r_{sol} values, are listed in the caption to Fig. 2.

Inspection of Fig. 2 reveals more than one feature of interest. Most importantly, while it is seen that uniformly $E_{op}(\text{MSA}) < E_{op}(\text{con})$, the degree to which the MSA reorganization energies deviate below the corresponding continuum predictions varies significantly, by up to 3 kcal mol^{-1}. Generally speaking, the largest deviations [i.e. the smallest $E_{op}(\text{MSA})/E_{op}(\text{con})$ ratios] are seen for the solvents methylene chloride, acetone, and butyronitrile, having the smallest ϵ_{s} values. Differences in r_{sol} also play a significant role in some cases. However, varying this parameter for each solvent over the range, 2-3 Å, by which the r_{sol} values differ (with the exception of D_2O) yielded only minor (≤ 1 kcal mol^{-1}) alterations in E_{op}(MSA).

At least qualitatively, the low value of E_{op}(MSA) obtained for methylene chloride (point 14) relative to E_{op}(con) is in harmony with the abnormally small experimental E_{op} value in this solvent (Fig. 1). More quantitative agreement with experiment can be obtained by decreasing somewhat the effective ϵ_s value utilized in the MSA calculations, thereby mimicing the effect of partial "dielectric saturation". Physically, such smaller values of E_{op}(MSA) relative to E_{op}(con) can be thought to arise because the *effective* reactant radius is enhanced above the unsolvated value, a, by the "Gurney cosphere" term δ_{rs}, describing the "thickness" of the solvent region that is perturbed by the charged solute.[40,43] When ϵ_s is diminished, $\delta_{rs}(\omega = 0)$ increases so that E_{op}(MSA)/E_{op}(con) is decreased further [Eqs. (4),(5)]. Note that altering ϵ_{op} has the opposite effect in that when $\delta_{rs}(\omega = 0)$ increases, E_{op}(MSA)/E_{op}(con) tends to increase. (Note that δ_{rs} is inherently frequency dependent since $\epsilon_{op} \neq \epsilon_s$.)

Broadly speaking, the MSA predictions are also in harmony with the substantial positive y-intercepts obtained for the experimental E_{op} - $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ plots (Fig. 1) in that qualitatively similar behavior is discerned in Fig. 2. A careful comparison of Figs. 1 and 2, however, shows that the MSA model mimics only incompletely the details of the solvent-dependent deviations of the observed E_{op} values from E_{op}(con). While plots of the observed E_{op} values versus E_{op}(MSA) show a marginally better correlation than with $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$, substantial scatter is still obtained. In particular, the relatively low E_{op} values observed for all three biferrocenes in methanol, and the similarly small value for BF^+ in D_2O (Fig. 1) are not predicted by the MSA model. Indeed, the E_{op}(MSA) value for D_2O is close to E_{op}(con), resulting from the combined influence of a large ϵ_s and small r_{sol} for this solvent. It may be surmised, then, that the solvent molecularity effects observed in these hydrogen-bonded media arise from specific solvent-solvent interactions rather than from the nonspecific "solvent size" effects considered in the MSA.[43] In a qualitative vein, the smaller experimental E_{op} values in methanol and D_2O might be rendered consistent with the MSA model by surmising that such "solvent structuring" leads to larger "effective" r_{sol}, and hence smaller E_{op}(MSA), values. In actuality, however, these effects are beyond the scope of the MSA treatment.

"Nonlocal" Dielectric Solvent Effects

One formal means of accounting for such solvent-solvent interactions is provided by the so-called "nonlocal" dielectric treatment[44] applied to nonequilibrium solvent polarization by Kornyshev and Ulstrup.[4,5] The approach considers the effect of solvent structure on its polarization properties in terms of a "correlation length", Λ. This parameter provides a measure of the distance over which polarization motion is "correlated", that is, the range over which local solvent structure extends.[44] Generally speaking, Λ is expected to lie in the range ca 1-3 solvent diameters. In the commonly anticipated circumstance where $\Lambda > a$, we can express the effect in terms of a correction, ΔE_{op}, to the reorganization formula energy, E_{op}(con), obtained from the usual dielectric continuum, Eq. (2); which following Kornyshev and Ulstrup[4,5] can be expressed as

$$\Delta E_{op} = -e^2(\epsilon_*^{-1} - \epsilon_s^{-1})[a^{-1} - \Lambda^{-1} - R^{-1} \exp(-R\,\Lambda^{-1})] \qquad (6)$$

The solvent dielectric constant ϵ_* is taken at a frequency which separates the rotational and vibrational regions of the spectrum, thereby neglecting the spatial correlation for the higher-frequency branch.[5] To a first approximation, identification of ϵ_* with the so-called "infinite-frequency" value ϵ_∞ seems appropriate.[45]

Given the requirement that $\Lambda > a$, the form of Eq. (6) predicts that E_{op} will fall increasingly below E_{op}(con) as the solvent correlation length increases. Although Λ values are difficult to predict a priori, estimates were extracted by inserting experimental values of ΔE_{op} for BFA^+ and BFB^+ into Eq. (6) along with literature values of ϵ_∞ and ϵ_s.[45] This procedure yielded estimates of Λ between 4 and 12 Å. (Somewhat smaller and less variant values, in the range 3.6-4.5 Å, were obtained by assuming that $\epsilon_\infty = \epsilon_{op}$.) Interestingly, the observed solvent dependence of Λ correlates qualitatively with intuitive expectations. Thus the strongly hydrogen-bound liquids D_2O[49] and methanol yield Λ values, 7-12 Å, that are substantially larger than for relatively non-associated solvents[50] such as acetone, for which $\Lambda \approx 4$ Å. The former values are suggestive of the presence of substantial solvent "structure-making" in the vicinity of the ferrocenium-ferrocene redox center. Given the likely additional presence of other factors as noted above along with the approximations inherent in Eq. (6), however, a more detailed analysis seems unwarranted.

Other, more empirical, correlations involving the deviations of the observed E_{op} values from E_{op}(con) are also of interest in this context. An example of such a relationship is shown in Fig. 3, which consists of a plot of ΔE_{op} [$= E_{op} - E_{op}$(con)] for BFA^+ (filled circles) and BFB^+ (open circles) against the solvent "acceptor number", AN. (As before, the solvent numbering scheme is given in Table I.) The acceptor number is one of several empirical parameters which reflects partly the solvent polarity.[51] Since larger values of AN correspond broadly to a greater degree of solvent "internal order",[52] the rough correlation between $-\Delta E_{op}$ and AN observed in Fig. 3 suggests further that specific solvent-solvent interactions contribute significantly to the solvent molecularity effects upon the reorganization energy.

The unexpectedly small E_{op} values observed here for biferrocene cations in D_2O as well as methanol contrast with the relatively *large* E_{op} values obtained in D_2O for some biruthenium complexes.[6] Similar findings in this regard are obtained for biruthenium complexes containing relatively hydrophobic (bipyridine)[6a] as well as hydrophilic (ammonia) ligands.[6b] These latter results have been discussed in the context of nonlocal dielectric effects by Ulstrup.[5] Perhaps the most likely reason for this contrasting behavior for the diruthenium and biferrocene mixed-valence systems lies in the high cationic charges (3+/2+ and 2+/+) for the former redox couples, possibly yielding solvent "structure-breaking" in the vicinity of the ruthenium redox couple and hence small Λ values.[5]

Concluding Remarks

While at least the semiquantitative validity of the dielectric continuum treatment of solvent reorganization energetics is not called in question by the present results, they provide further evidence that additional molecular factors can yield significant and even important deviations from this simple picture. Given that dielectric continuum formulas are conventionally used in descriptions of thermal electron-transfer kinetics,[9] and bearing in mind the sensitivity of the rate constants to ΔG^*, it is clearly a matter of some importance to characterize and rationalize such noncontinuum factors in detail. The marked differences in the nature of some noncontinuum solvent effects upon E_{op} for the biruthenium and biferrocene systems suggests the additional importance of solute structure and/or charge. Further experiments, for example involving biferrocene cations suitably modified so to alter the solute-solvent interactions, would be instructive in this regard.

It is interesting to note that the inclusion of the additional molecular factors considered here in the solvent reorganization models yields predicted electron-transfer barriers that are almost uniformly smaller than are obtained in the dielectric continuum limit. That the experimental electron-transfer energies are, broadly speaking, roughly in accord with these predicted trends is encouraging, even though the utility of the MSA and nonlocal dielectric treatments appears to be primarily explanative rather than predictive at present. The anticipated emergence of molecular dynamics and other computer simulation descriptions of electron-transfer processes[12-14] may well contribute substantially to this problem. Given the sensitive, as well as uniquely direct, monitor of the solvent reorganization energetics provided by intervalence optical measurements, they could provide an important proving ground for such approaches.

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TABLE I **Energies of Intervalence Band Maxima, E_{op}, for Biferrocene (BF^+), Biferrocenylacetylene (BFA^+), and Biferrocenylbutadiyne (BFB^+) Cations in Various Solvents.**

		E_{op} (cm^{-1})		
Solvent[a]	$(\epsilon_{op}^{-1} - \epsilon_s^{-1})^b$	BF^+ [c]	BFA^+ [d]	BFB^+ [e]
1. D_2O	0.549	5400	--	--
2. CH_3OD	0.538	5330	7250	8690
3. Acetonitrile	0.528	5680[i]	7500	9900
4. Propionitrile	0.503	--	7170	--
5. Acetone	0.495	5640[f]	7520	--
6. Nitromethane	0.497	5460	7200	9170
7. Butyronitrile	0.483	--	7140	9430
8. Nitroethane	0.482	--	6990	--
9. Propylene Carbonate	0.480	5550	7380[f]	9090
10. Benzonitrile	0.390	--	6340[f]	8330
11. Nitrobenzene	0.390	5230[i]	6410	8065
12. *o*-nitrotoluene	0.382	--	6450	8000
13. *m*-nitrotoluene	0.376	--	6490	--
14. Methylene Chloride	0.382	--	(4440)[g]	--

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[a] Protiated solvents used, except for D_2O and CH_3OD, and where noted otherwise.

[b] Values of optical and static dielectric constants, ϵ_{op} and ϵ_{st}, respectively (at 25°C), are taken from ref. 24, except for ortho- and meta-nitrotoluene which are extracted from ref. 25.

[c] Measured using ca 0.5 mM BF^+; total anion concentration (PF_6^-) ca 0.5 mM.

[d] Measured using ca 1 mM BFA^+; total anion concentration (PF_6^-) ca 1-3 mM.

[e] Measured using 1-2 mM BFB^+; total anion concentration (PF_6^-) ca 2-5 mM.

[f] Values from ref. 17.

[g] Value taken from ref. 19a, which refers to infinite dilution.

[h] Value diminished by 3% to correct for ion pairing (from ref. 19b).

[i] Deuterated solvents used for these measurements.

TABLE II **Ratios of Intervalence Band Energies for Biferrocene (BF^+) and Biferrocenylbutadiyne (BFB^+) Cations Relative to Biferrocenylacetylene Cation (BFA^+) in Each Solvent.**

Solvent	$E_{op}(BF)/E_{op}(BFA)$[a]	$E_{op}(BFB)/E_{op}(BFA)$[b]
2. Methanol	0.74	1.20
3. Acetonitrile	0.75	1.31
5. Acetone	0.75	
6. Nitromethane	0.76	1.27
7. Butyronitrile		1.32
9. Propylene Carbonate	0.75	1.23
10. Benzonitrile		1.31
11. Nitrobenzene	0.81	1.26
12. o-Nitrotoluene		1.24
Calculated [Eq. (2)]	(0.48)[c]	(1.26)[d]

[a] Ratio of measured E_{op} value in listed solvent for BF^+ relative to that for BFA^+ (from Table I). Solvent numbering system is as in Table I.

[b] Ratio of measured E_{op} value in listed solvent for BFB^+ relative to that for BFA^+ (from Table I).

[c] Calculated E_{op} ratio, obtained from Eq. (2) assuming that a = 3.8 Å and R = 5.0 and 7.6 Å, respectively, for BF^+ and BFA^+ [see text and ref. 17; the ratio involving $E_{op}(BF)$ is given within parentheses since the circumstance $R < 2a$ strictly invalidates the use of Eq. (2)].

[d] Calculated E_{op} ratio, obtained from Eq. (2) assuming that a = 3.8 Å and R = 10.3 and 7.6 Å, respectively, for BFB^+ and BFA^+ (see text).

Figure Captions

Fig. 1

Plot of optical electron-transfer energies, E_{op} (kcal mol^{-1}) for biferrocene (BF^+, circles), biferrocenylacetylene (BFA^+, squares), and 1,4-biferrocenylbutadiyne cations (BFB^+, triangles) in various solvents against the Pekar factor $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$, where ϵ_{op} and ϵ_s are the solvent optical and static dielectric constants, respectively. E_{op} and $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ values from Table I. Solvent numbering scheme as given in Table I. Open symbols refer to hydrogen-bound solvents methanol and D_2O; crossed square refers to BFA^+/methylene chloride datum, taken from ref. 19a. Solid and dashed straight lines are dielectric continuum predictions from Eq. (2) for BFA^+ and BFB^+, respectively, with a = 3.8 Å, and R = 7.6 and 10.3 Å, respectively (see text for details).

Fig. 2

Plot of optical electron-transfer energies, E_{op}(MSA) (kcal mol^{-1}), calculated using the mean spherical approximation model versus the Pekar factor $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$ (Table I), for solvents considered in Fig. 1. E_{op}(MSA) values calculated from Eqs. (4) and (5) by assuming that E_{op}(MSA) = 0.5 E(MSA) and a = 3.8 Å (see text); dielectric parameters taken from refs. 24 and 25, and effective solvent radii, r_{sol}, taken from ref. 42 (or estimated); r_{sol} values and solvent numbering scheme (Table I) as follows (estimated values in parentheses): 1, D_2O, 1.4 Å; 2, methanol, 2.05 Å; 3, acetonitrile, 2.15 Å; 4, propionitrile, (2.45 Å); 5, acetone, 2.45 Å; 6, nitromethane, 2.15 Å; 7, butyronitrile, 2.95 Å; 8, nitroethane, (2.4 Å); 9, propylene carbonate, 2.65 Å; 10, benzonitrile, 2.65 Å; 11, nitrobenzene, 2.65 Å; 12, o-nitrotoluene, (2.7 Å); 13, *m*-nitrotoluene, (2.7 Å); 14, methylene chloride, (2.15 Å).

Fig. 3

Plot of deviations of the observed optical energy-transfer energies from the corresponding dielectric continuum predictions, E_{op} - E_{op}(con), for biferrocenylacetylene (filled circles) and 1,4-biferrocenylbutadiyne (open circles) versus the solvent acceptor number, AN. Values of AN taken from ref. 54. See Table I for solvent numbering scheme.

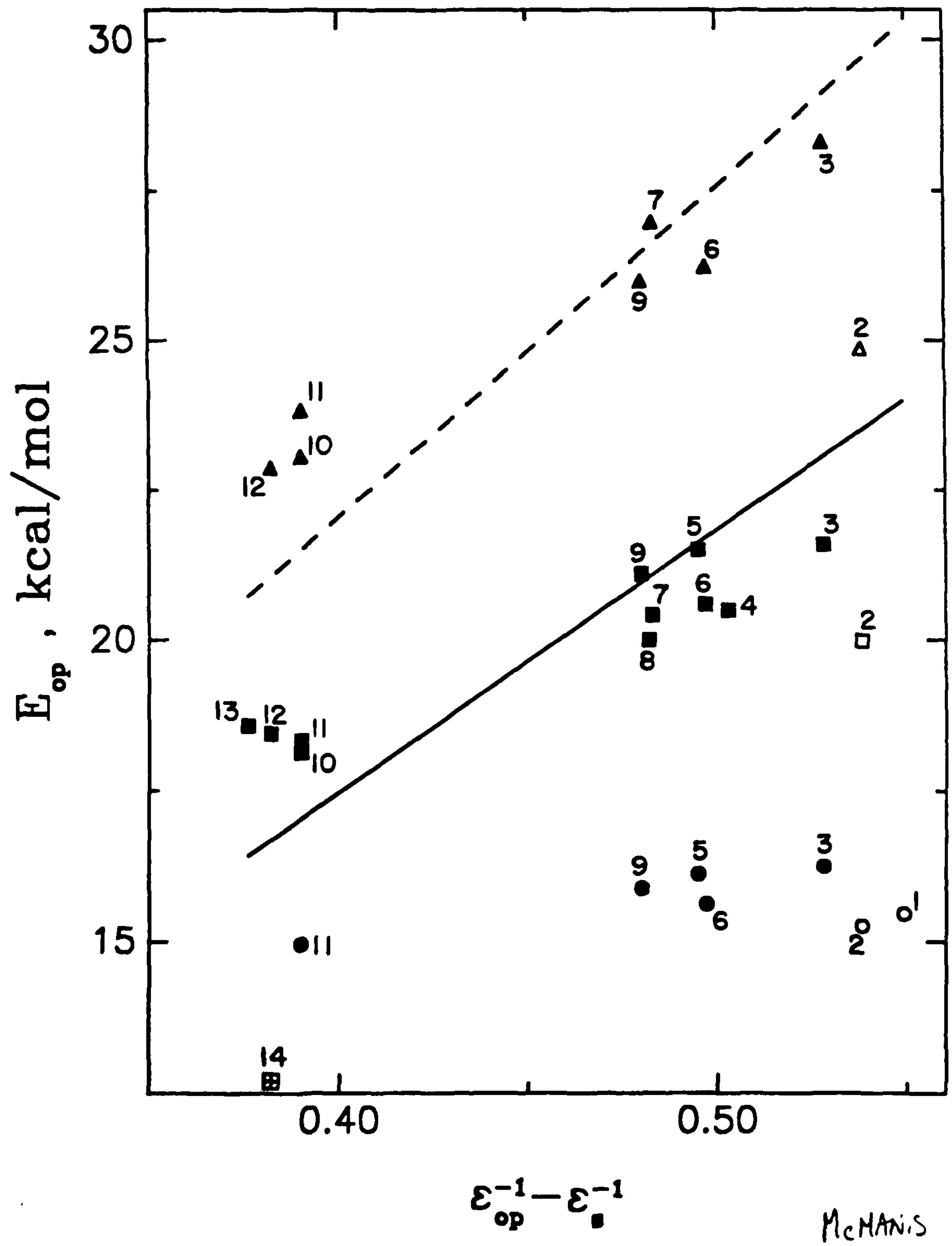

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FIG 1

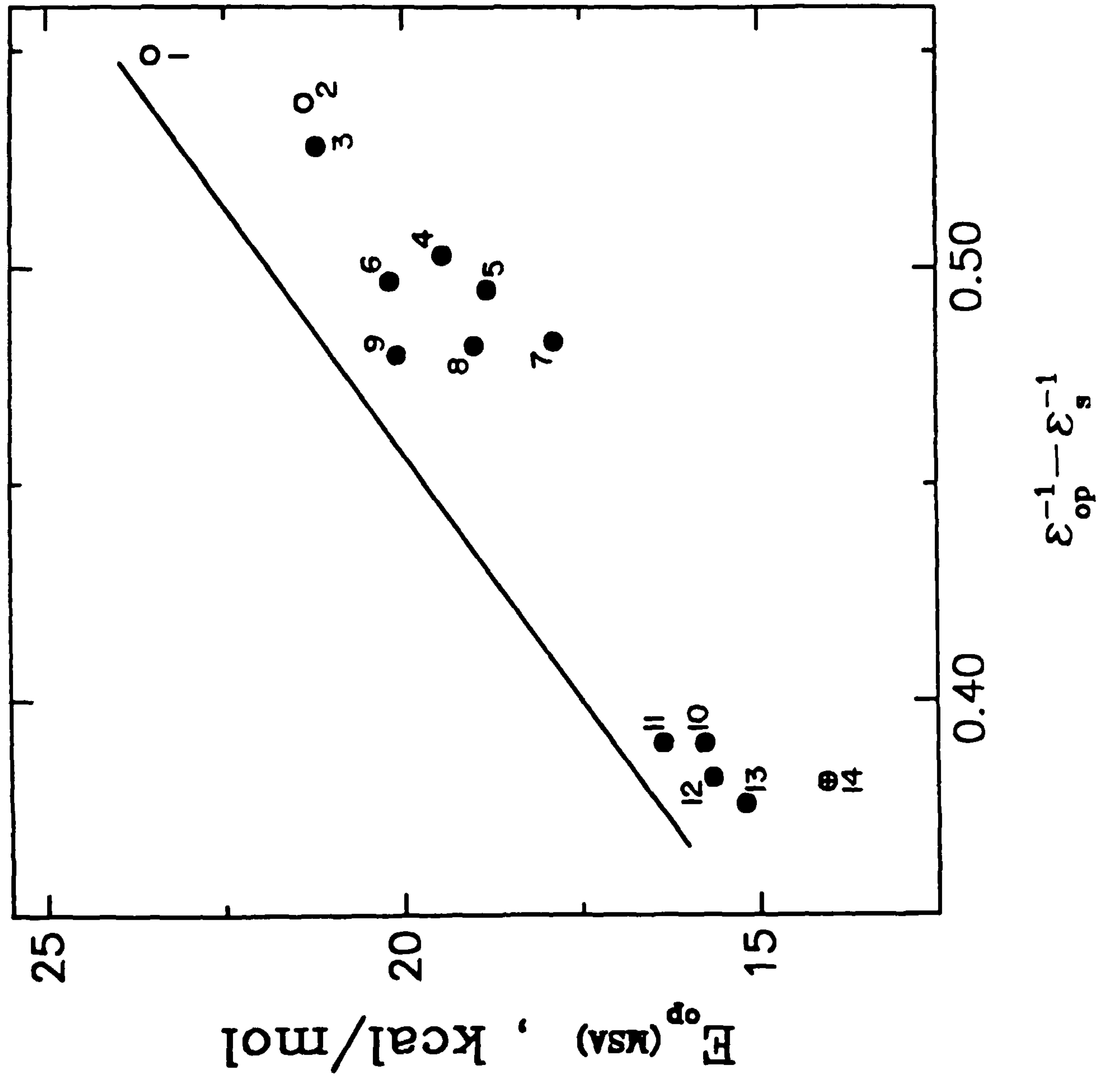

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FIG 2

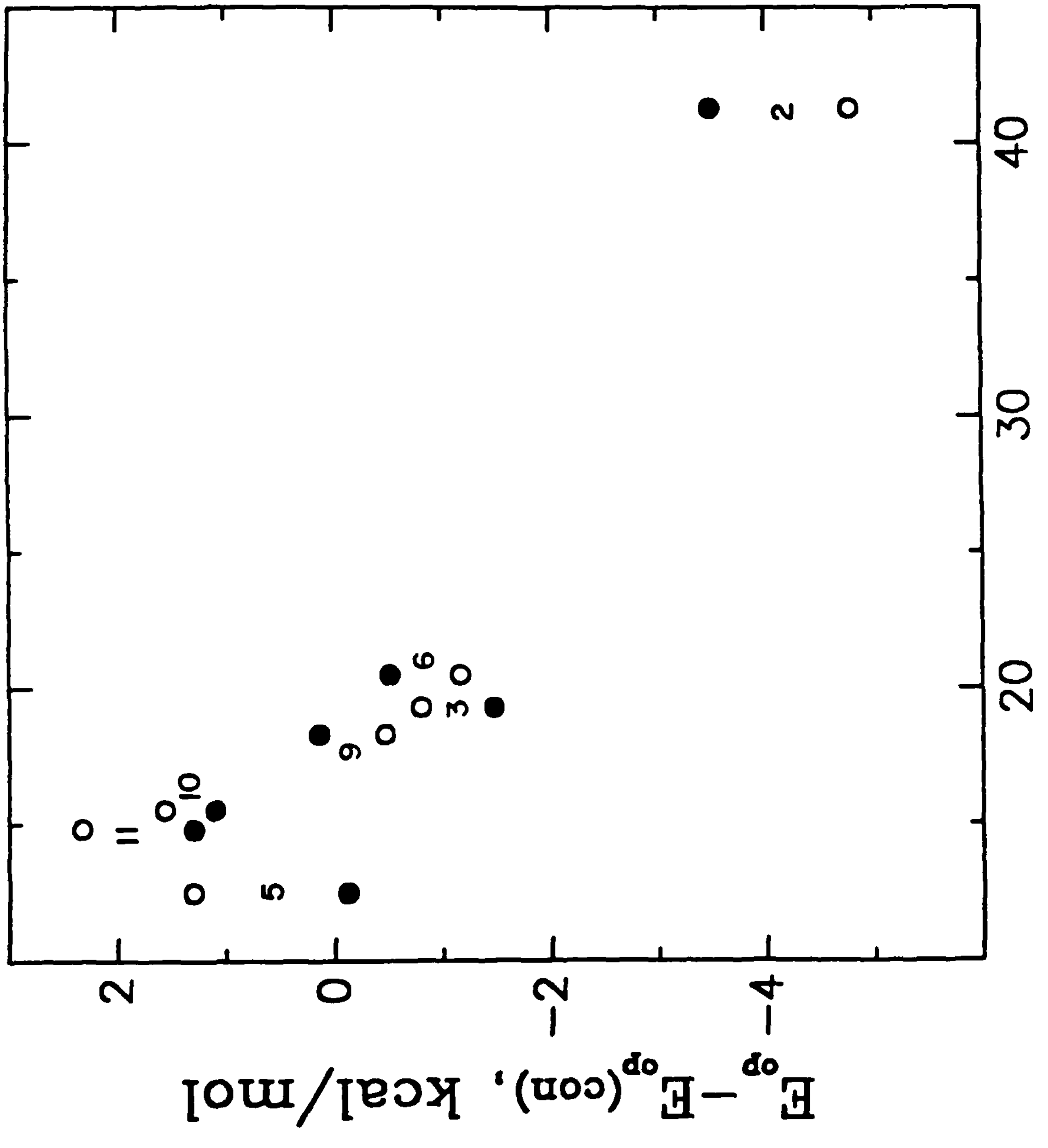

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FIG 3