Marcus [1] has shown that the activation barrier for electron transfer in a self-exchange outer-sphere redox reaction of a metal complex in solution is equal to $\lambda/4$, where $\lambda$ is a reorganization energy. $\lambda$ includes contributions from inner sphere ($\lambda_{in}$) and outer sphere ($\lambda_{out}$) reorganizations of the complex. Using a dielectric continuum model for the solvent contribution $\lambda_{out}$, Marcus [1] derived the following expression

$$\lambda_{out} = \Delta E \left( \frac{1}{2R_A} + \frac{1}{2R_B} - \frac{1}{R_{AB}} \right) \frac{1}{D_0} - \frac{1}{D_s}$$

(1)

where $\Delta E$ is the amount of charge transferred, $D_0$ and $D_s$ are the optical and static dielectric constants of the solvent medium, $R_A$ and $R_B$ are the radii of the coordination spheres about the metal centers, and $R_{AB}$ is the internuclear separation between the redox sites.

It has been suggested [2] that the intervalence transfer (IT) electronic absorption band of binuclear mixed-valence complexes [3] can be used to determine the energetics of electron transfer between the metal ions. The energy of the IT band maximum ($E_{0p}$) of a given mixed-valence complex examined in a series of solvents is predicted by eqn. (1) to vary linearly with $(1/D_0 - 1/D_s)$, and the intercept of this plot should give $\lambda_{in}$. The linear relationship was first reported by Tom, Creutz, and Taube [4] for the complex $[(NH_3)_5Ru(4,4'-bipyridine)Ru(NH_3)_5]^{5+}$ for which they found $\lambda_{out} = 15.4$ and $\lambda_{in} = 10.0$ kcal/mol. Several other weakly interacting mixed-valence complexes [5] have been shown to give linear $E_{0p}$ versus $(1/D_0 - 1/D_s)$ plots. It is important to note that Powers and Meyer [6] reported a linear correlation between $E_{0p}$ and $(1/D_0 - 1/D_s)$ for the biferrocenium cation.

We have employed pressure-induced freezing of solutions of several mixed-valence complexes to test the applicability of eqn. (1) [7,8]. Upon freezing, the dielectric constant ($D_s$) of a liquid decreases by a factor of 2 - 10 depending on its polarity, and from eqn. (1) it is predicted that pressure-induced freezing of a solution of a mixed-valence complex should result in a large (2000 - 4000 cm$^{-1}$) red shift of the IT band maximum. Figure 1 shows representative spectra for liquid and pressure-frozen solutions of biferrocenium hexafluorophosphate in nitromethane-$d_3$. As is evident in the figure, we did not observe the predicted red shift. The lack of a pronounced red shift upon freezing was also observed for this complex in a variety of other solvents (nitromethane, nitrobenzene, acetonitrile) and for other cations (biferrocenium triiodide, diferoocyenaactetylene monocation, and $[(bipy)_2ClRu^{II}(pyrazine)Ru^{III}Cl(bipy)_2]^{3+}$ where bipy = bipyridine) [7,8].
Close examination of the IT band contours from the pressure-induced freezing experiments showed that although the IT band position did not change appreciably upon freezing, the IT band position, full-width at half-maximum (fwhm), and integrated intensity were strongly correlated with the concentration of the mixed-valence complex in solution [7]. The changes in E_{op} with concentration were found to be as large as the changes observed when using a series of differing solvents. We have attributed the change in the IT band parameters with concentration to the formation of ion aggregates in solution [9]. Proof of the formation of ion aggregates in solution was established by observing the nonlinearity of plots of the solution conductivity versus the square root of the metallocene concentration for both biferrocenium triiodide and biferrocenium hexafluorophosphate in nitrobenzene and dichloromethane solutions [9].

To further probe the effect of ion aggregation on the IT band parameters (i.e., peak maximum, fwhm, integrated area), we have fit the IT band contour using the vibronic coupling model proposed by Piepho, Krausz, and Schatz [10] (the PKS model). Figure 2 shows a PKS simulation of an experimental IT band contour. The PKS model consists of three adjustable parameters: (1) $\varepsilon$ gauges the degree of electronic coupling between the metal centers, (2) $\lambda$ is the vibronic coupling parameter, and (3) $W$ gives the zero point energy difference between the two vibronic wells. In all of the systems studied we have found that $|\varepsilon|$ increases, $\lambda$ remains relatively constant, and $W$ decreases with increasing concentration. A priori we expected that an increased level of ion aggregation would result in an increase in $|\varepsilon|$, not affect $\lambda$, and increase $W$ as one of the two potential wells becomes favored. That $W$ was found to decrease with increasing concentration most likely results from the presence of a distribution of cation environments in solution. At low concentrations, an approximately equal distribution of non-aggregated and ion-paired cations exists which results in a broad IT band, but as the concentration of mixed-valence species increases, the distribution tends to favor the aggregated species and the IT band narrows and shifts to higher energies. The simple Marcus, Hush, and PKS theories assume that the IT band parameters arise from one and only one cation site and thus these models are inappropriate when a distribution of environments about the cation is present in solution. Therefore, reliable values of $\lambda_{\text{in}}$ and $\lambda_{\text{out}}$ can be obtained from fitting of the IT band contour only if it can be established that ion aggregates are not present. Accurate estimates for $\lambda_{\text{in}}$ and $\lambda_{\text{out}}$ are best obtained at very low concentration or in solvents of high dielectric constant.
References


3. For recent reviews of mixed-valence complexes see:


   (l) Meyer, T. J. In ref. 3(b), page 75.


