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Effects of Ion Aggregation on the Intervalence Transfer Band of the Mixed-Valence Biferrocenium Cation in Solution

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Abstract: The concentration dependence of the energy (E_{op}) of the intervalence transfer (IT) electronic absorption band of mixed-valence biferrocenium triiodide dissolved in either nitrobenzene or dichloromethane is examined. In nitrobenzene, E_{op} increases rapidly from ~5.57 to ~6.05 × 10^3 cm^{-1} in the 0.24–0.4 mM range, whereupon further increases in the concentration of biferrocenium triiodide lead to E_{op} increasing more gradually to a value ~6.3 × 10^3 cm^{-1} at 24 mM. On the other hand, the full width at half maximum ($\Delta\bar{\nu}_{1/2}$) and the transition moment of the IT band decrease with increasing concentration for biferrocenium triiodide in nitrobenzene. E_{op} increases, $\Delta\bar{\nu}_{1/2}$ remains constant, and the transition moment of the IT band increases with increasing concentration for biferrocenium triiodide in dichloromethane in the more limited range of 0.30–0.95 mM. These concentration dependencies of the IT band for biferrocenium triiodide are attributable to variable degrees of ion aggregation in solution. The concentration dependencies of the electrical conductivity of solutions of biferrocenium triiodide in either nitrobenzene or dichloromethane substantiate this proposal. IT band contours obtained at different concentrations are fit to the PKS vibronic model to yield parameters that characterize the electronic and vibronic coupling within the mixed-valence biferrocenium cation. It is concluded that in the 0.24–24 mM range the IT band contour of biferrocenium triiodide in nitrobenzene is likely a superposition of variable amounts of two IT bands, one for an ion-paired cation and the other for a non-ion-paired cation. The increase in E_{op} with increasing concentration reflects an increasing percentage of ion-paired mixed-valence cations that have a higher energy IT band than the non-ion-paired cation because the ion pairing probably introduces a zeropoint energy separation between the two vibronic states of the cation.

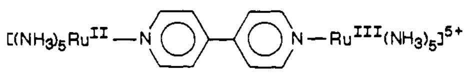
Marcus[3] has shown that the activation barrier to electron transfer for a self-exchange outer-sphere redox reaction of a metal complex in solution is equal to $\lambda/4$, where λ is a reorganization energy. λ includes contributions from inner (λ_i) and outer (λ_o) sphere reorganizations of the complex. Using a dielectric continuum model for the solvent, Marcus[3] showed that λ_o is given by eq 1, where e is the unit electron charge, n^2 and D_s are the

$$\lambda_o = e^2\left(\frac{1}{2r_1}+\frac{1}{2r_2}-\frac{1}{d}\right)\left(\frac{1}{n^2}-\frac{1}{D_s}\right) \qquad (1)$$

optical and static dielectric constants of the solvent medium, r_1 and r_2 are the molecular radii at the redox sites (i.e., the two complexes), and d is the internuclear separation between redox sites.

It has been suggested[4] that the intervalence transfer (IT) electronic absorption band of binuclear mixed-valence complexes[5] can be used to determine the energetics for electron transfer between two metal ions. For a symmetric binuclear mixed-valence complex with a relatively weak interaction between the two metal ions, $E_{op} = 4E_a$, where E_a is the activation energy for thermal electron transfer and E_{op} is the energy of the IT band. Furthermore, Hush[4] has shown that $E_{op} = \lambda = \lambda_i + \lambda_o$, where λ_o can be calculated as given in eq 1.

It was not too long after the report[6] in 1969 by Creutz and Taube of the preparation of the first stable binuclear mixed-valence complex that eq 1 was applied to an analysis of IT bands. E_{op} for the IT band of a given mixed-valence complex examined in a series of solvents is predicted by eq 1 to vary linearly with $(1/n^2 - 1/D_s)$, and the intercept of the plot should give λ_i. The expected linear relationship was first reported by Tom, Creutz, and Taube[7] for ion I, for which they found λ_o = 15.4 and λ_i = 10.0 kcal/mol.



I

In ref 13 of this same paper it was noted that only in the case of D_2O was a specific salt effect examined and found to be absent and that acetone gave a point considerably off the E_{op} vs $(1/n^2 - 1/D_s)$ line obtained for the other solvents.

Several other weakly interacting mixed-valence complexes have been shown[8] to give linear E_{op} vs $(1/n^2 - 1/D_s)$ plots. A few exceptions have been reported.[9] Of course, electronically delocalized mixed-valence complexes would not be expected to have IT bands with solvent-dependent E_{op} values.[10] Finally, it is relevant to this paper to mention that Powers and Meyer[11] reported linear E_{op} vs $(1/n^2 - 1/D_s)$ correlations for mixed-valence biferrocenium cation II.

In spite of all the apparent success in using eq 1 to explain the solvent dependence of E_{op} for mixed-valence complexes, we very recently reported[12] definitive evidence that eq 1 does *not* properly explain the solvent dependence of E_{op}. No appreciable changes

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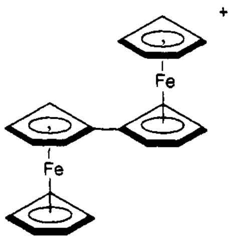

II

in the energy of the IT band were seen for solutions of mixed-valence complexes when pressure-induced freezing was employed to vary D_s such that $1/D_s$ would become comparable in magnitude to $1/n^2$. The results presented in this paper for a detailed study of the concentration dependence of E_{op} for biferrocenium cation II and the electrical conductivity of solutions of cation II clearly indicate that appreciable effects on the IT band of ion aggregation are present. Therefore, in comparing the peak location of the IT band of a particular complex in different solvents, even at the same concentration, a significant part of the differences may be due to differences in the degree of ion pairing and/or solvation.

Results and Discussion

Concentration Dependence of the IT Band of Mixed-Valence Biferrocenium Cation II. The NIR spectrum of biferrocenium triiodide dissolved in nitrobenzene-d_5 was carefully measured over a range of concentrations from 0.24 to 24 mM. Two different path length cells (0.1 and 1 cm) were used, and data were collected for each cell such that the concentration ranges overlapped. The data were normalized by using this overlap region. The IT band which was clearly visible in each of these NIR spectra was least-squares fit to a Gaussian line shape. In this manner values for E_{op} and $\Delta\bar{\nu}_{1/2}$, the energy and full width at half-maximum of the IT band, respectively, were determined. A plot of E_{op} versus concentration of biferrocenium triiodide in nitrobenzene is illustrated in Figure 1. In passing, it should be pointed out that in previous studies[8-10] IT band profiles were apparently not fit to Gaussians, but values for E_{op} and $\Delta\bar{\nu}_{1/2}$ were apparently evaluated by eye. Furthermore, in most[8-10] of the previous studies of IT bands the concentrations of the mixed-valence species were not given.

As can be seen in Figure 1, there is an appreciable concentration dependence in E_{op} for biferrocenium triiodide in nitrobenzene-d_5. In the concentration range of 0.24 to ~0.4 mM E_{op} increases rapidly from ~5.57 to ~6.05×10^3 cm^{-1}. As the concentration is further increased, E_{op} continues to increase, but more gradually than it does below ~0.4 mM. Throughout the concentration range of 1–24 mM the magnitude of E_{op} varies as $E_{op} = 5.58 + 0.43(\ln C) - 0.065(\ln C)^2$ in units of 10^3 cm^{-1}, where C is the concentration. It is also interesting that throughout the 0.24–24 mM concentration range there is a total change in E_{op} of ~700 cm^{-1}, a value that is comparable to the 680 cm^{-1} range of E_{op} values given by Powers and Meyer[11] for the biferrocenium cation in a series of solvents. They gave values of $E_{op} = 5.21 \times 10^3$ cm^{-1} and $\Delta\bar{\nu}_{1/2} = 3750$ cm^{-1} for the IT band of the biferrocenium cation in nitrobenzene-d_5 at an unspecified concentration.

In Figure 2 it can be seen that not only does E_{op} for biferrocenium triiodide in nitrobenzene-d_5 change with concentration but also $\Delta\bar{\nu}_{1/2}$ changes with concentration. $\Delta\bar{\nu}_{1/2}$ decreases rapidly from ~2450 cm^{-1} at 0.24 mM to ~2050 cm^{-1} at ~4 mM, whereupon it decreases more gradually with further increases in concentration, eventually to a value of $\Delta\bar{\nu}_{1/2} = 1870$ cm^{-1} at 24.0 mM. Throughout the concentration range of 1–24 mM we find $\Delta\bar{\nu}_{1/2} = 2160 - 89(\ln C)$ in units of cm^{-1}. The data presented in this paper were taken at a constant slit width of 1.0 mm, which corresponds to a spectral line width of 13.2 nm. The true widths would, if anything, be smaller than those determined in our experiments. Apparently the commercial spectrometers used in previous work[7,8,11] employ very wide slits in this region since they are operating near the limit of their detectors. Of course, it is imperative that the IT band profile be accurately represented by experimental data in order that either the simple Hush theory[4]

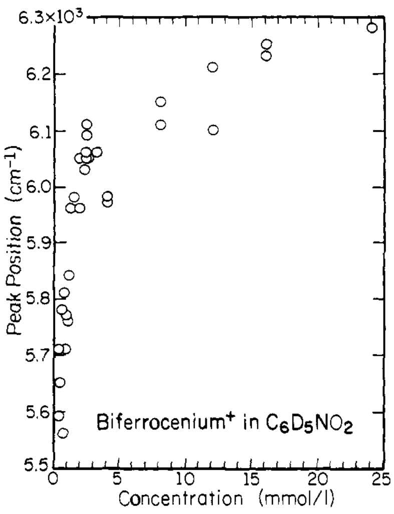

Figure 1. Plot of the peak position of the IT band, E_{op}, versus the concentration of biferrocenium triiodide in nitrobenzene. Values of E_{op} were determined by least-squares fitting each of the IT band contours to a Gaussian function.

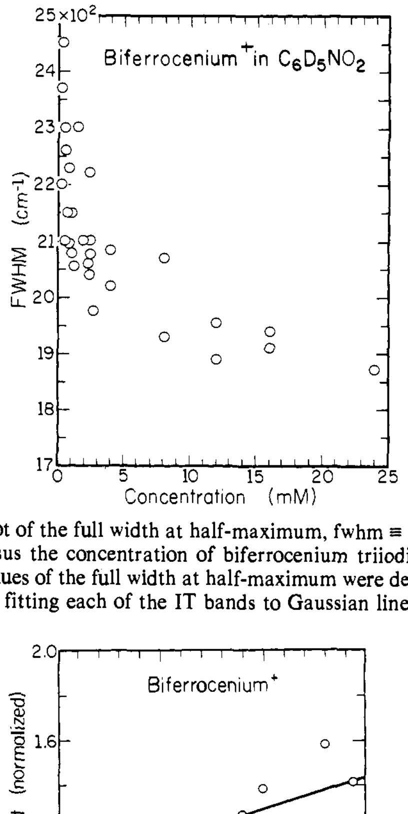

Figure 2. Plot of the full width at half-maximum, fwhm ≡ $\Delta\bar{\nu}_{1/2}$, of the IT band versus the concentration of biferrocenium triiodide in nitrobenzene. Values of the full width at half-maximum were determined by least-squares fitting each of the IT bands to Gaussian line shapes.

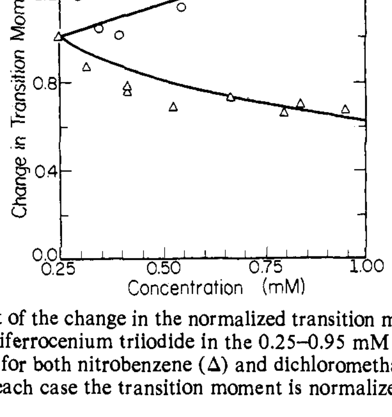

Figure 3. Plot of the change in the normalized transition moment of the IT band for biferrocenium triiodide in the 0.25–0.95 mM range. Data are presented for both nitrobenzene (Δ) and dichloromethane (○) solutions, and in each case the transition moment is normalized to unity at 0.25 mM.

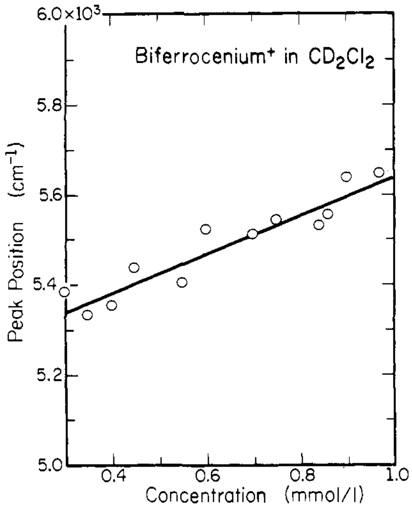

Figure 4. Plot of the peak position of the IT band, E_{op}, versus the concentration of biferrocenium triiodide in dichloromethane. Values of E_{op} were determined by least-squares fitting of each of the IT band contours to a Gaussian function.

or the more detailed PKS vibronic model[13] be used to analyze the IT band contour.

Not only do the magnitudes of E_{op} and $\Delta\bar{\nu}_{1/2}$ for the biferrocenium cation in nitrobenzene-d_5 change with increasing concentration but also the integrated transition moment (i.e., oscillator strength) of the IT band changes. The transition moment is the integrated area of the band divided by the concentration of the complex. In Figure 3 it can be seen that the transition moment of the IT band decreases approximately 60% in the range of 0.30–0.95 mM for the biferrocenium cation in nitrobenzene-d_5. When the concentration is further increased, the integrated transition moment continues to decrease but at a more gradual rate. Throughout the concentration range of 1–24 mM the *normalized* value for the transition moment, NTM, varies as NTM = $-0.63 - 0.22(\ln C) + 0.02(\ln C)^2$. In fact, the concentration dependence characteristics (i.e., rates of changes in certain concentration ranges) are similar for E_{op}, $\Delta\bar{\nu}_{1/2}$, and the integrated transition moment of the IT band.

In Figure 4 is depicted the concentration dependence of E_{op} for biferrocenium triiodide dissolved in CD_2Cl_2. The solubility of biferrocenium triiodide in dichloromethane is less than that in nitrobenzene. As a consequence, the concentration range for biferrocenium triiodide was limited to 0.30 to almost 1.0 mM. Higher concentrations may be possible; however, we wanted to be sure that all of the compound was dissolved. In spite of this more limited concentration range it can be seen in Figure 4 that E_{op} increases essentially linearly from $\sim 5.34 \times 10^3$ cm^{-1} at 0.30 mM to $\sim 5.63 \times 10^3$ cm^{-1} at 0.98 mM and can be fit to $E_{op} = 5.22 + 0.42C$ in units of 10^3 cm^{-1}. In this relatively limited concentration range $\Delta\bar{\nu}_{1/2}$ remains essentially constant at 1850 $\mp$ 50 cm^{-1}. Powers and Meyer[11] reported $E_{op} = 5.00 \times 10^3$ cm^{-1} and $\Delta\bar{\nu}_{1/2} = 3700$ cm^{-1} for the biferrocenium cation at an unspecified concentration in CD_2Cl_2.

In contrast to the behavior of the IT band in nitrobenzene-d_5, the integrated transition moment of the IT band for the CD_2Cl_2 solution increases with increasing concentration in the 0.30–0.95 mM range (see Figure 3). In this case NTM = $1 + 0.055(C - 0.25)$.

Electrical Conductivity of Solutions. One possible explanation for the above concentration dependencies of the biferrocenium IT band is the presence of ion aggregates. In order to examine this possibility, conductivity measurements were carried out for solutions of biferrocenium triiodide in nitrobenzene, biferrocenium hexafluorophosphate in nitrobenzene, and biferrocenium triiodide in dichloromethane.

Table I. Conductivity Data for Biferrocenium Triiodide in Nitrobenzene

concn (C), mM	$\sqrt{C}$, M$^{1/2}$	cond, Λ_M	concn (C), mM	$\sqrt{C}$, M$^{1/2}$	cond, Λ_M
21.55	0.1468	21.91	2.06	0.0454	28.70
20.12	0.1418	22.10	1.83	0.0428	29.03
18.86	0.1373	22.27	1.65	0.0406	29.24
17.75	0.1332	22.44	1.50	0.0387	29.45
16.76	0.1295	22.69	1.31	0.0362	29.75
15.88	0.1260	22.94	1.17	0.0342	29.84
15.09	0.1228	23.13	1.05	0.0324	30.18
14.37	0.1199	23.30	0.954	0.0309	30.39
13.72	0.1171	23.37	0.835	0.0289	30.70
13.12	0.1145	23.54	0.742	0.0272	30.98
12.43	0.1115	23.67	0.670	0.0259	31.06
11.81	0.1087	23.91	0.607	0.0246	31.48
11.24	0.1060	24.15	0.531	0.0230	31.53
10.73	0.1036	24.25	0.472	0.0217	31.87
9.54	0.0977	24.59	0.425	0.0206	32.05
8.59	0.0927	24.89	0.386	0.0196	32.35
7.81	0.0884	25.32	0.338	0.0184	32.47
6.89	0.0830	25.61	0.301	0.0173	32.69
6.16	0.0785	25.95	0.270	0.0164	33.15
5.58	0.0747	26.11	0.246	0.0157	33.19
5.09	0.0713	26.58	0.215	0.0147	33.57
4.53	0.0673	26.73	0.191	0.0138	33.88
4.07	0.0638	27.19	0.172	0.0131	34.16
3.m0	0.0608	27.49	0.156	0.0125	34.44
3.24	0.0569	27.64	0.137	0.0117	34.63
2.88	0.0537	28.02	0.122	0.0110	34.89
2.59	0.0509	28.23	0.109	0.0104	35.45
2.36	0.0486	28.42	0.0996	0.0100	35.62

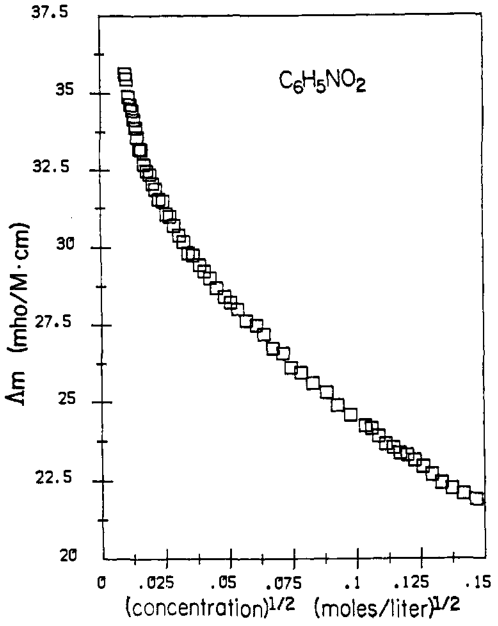

Figure 5. Plot of molar conductivity, Λ_m, versus the square root of the concentration of biferrocenium triiodide in nitrobenzene.

The electrical resistance of a 21.55 mM biferrocenium triiodide solution in nitrobenzene was determined at 25 °C. Through standard dilution techniques the resistance of the solution was determined as a function of the solute concentration in the range 21.55–0.0996 mM. The conductance, L, and molar conductivity, Λ_m, calculated from these resistance values employing a measured cell constant are given in Table I. In Figure 5 is shown a plot of Λ_m versus the square root of the concentration ($\sqrt{C}$) of biferrocenium triiodide. For a dilute solution of a well-behaved uni-univalent electrolyte, the decrease in Λ_m with decreasing concentration is closely linear in $\sqrt{C}$. It is clear from Figure 5 that ion aggregation occurs for a nitrobenzene solution of biferrocenium triiodide, since Λ_m does not vary linearly with $\sqrt{C}$ throughout the concentration range examined. There appears to

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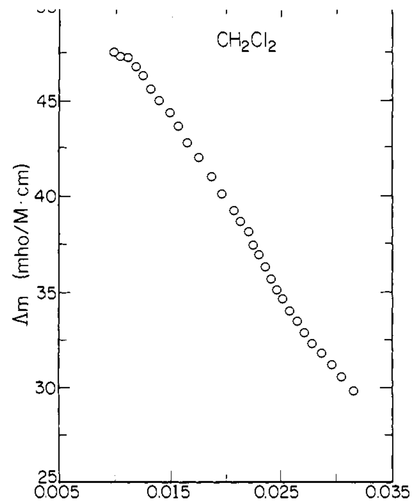

Figure 6. Plot of molar conductivity, Λ_m, versus the square root of the concentration of biferrocenium triiodide in dichloromethane.

Table II. Conductivity Data for Biferrocenium Triiodide in Dichloromethane

concn, mM	$\sqrt{C}$, M$^{1/2}$	cond, Λ_M	concn, mM	$\sqrt{C}$, M$^{1/2}$	cond, Λ_M
1.000	0.0316	29.85	0.458	0.0214	38.73
0.933	0.0305	30.62	0.432	0.0208	39.25
0.875	0.0296	31.25	0.389	0.0197	40.16
0.778	0.0287	31.80	0.354	0.0188	41.02
0.737	0.0279	32.34	0.309	0.0176	42.05
0.700	0.0271	32.92	0.275	0.0166	42.83
0.667	0.0265	33.51	0.247	0.0157	43.70
0.636	0.0258	34.04	0.225	0.0150	44.46
0.609	0.0252	35.11	0.197	0.0140	45.04
0.583	0.0246	35.70	0.175	0.0132	45.68
0.556	0.0241	36.32	0.157	0.0125	46.40
0.530	0.0236	36.95	0.143	0.0120	46.84
0.507	0.0225	37.50	0.125	0.0112	47.30
0.486	0.0220	38.15	0.111	0.0105	47.39
			0.100	0.0100	47.58

be a straight line Λ_m versus $\sqrt{C}$ behavior only in the high concentration range, and this must be due to achieving a totally aggregated species. Furthermore, Λ_m changes most rapidly in the ~0.1–4 mM range. This is the same concentration range in which E_{op} for the IT band is seen to change most rapidly for the biferrocenium triiodide solution in nitrobenzene. Thus, the concentration dependence of E_{op} can be qualitatively attributed to an increasing concentration of ion pairs, presumably of biferrocenium triiodide pairs, as the concentration is increased. From Figure 5 it appears there is some appreciable fraction of ion pairs even at the lowest concentration, 0.24 mM, of the E_{op} determinations.

A plot of Λ_m versus $\sqrt{C}$ for biferrocenium hexafluorophosphate in nitrobenzene runs nearly parallel to the plot for the triiodide salt shown in Figure 5. The values of Λ_m for the PF_6^- salt solution are somewhat larger than those for the I_3^- salt solution at the same concentration. Ion aggregation occurs substantially also for biferrocenium hexafluorophosphate dissolved in nitrobenzene.

A plot of Λ_m versus $\sqrt{C}$ for a solution of biferrocenium triiodide in CH_2Cl_2 is shown in Figure 6, and data are given in Table II. As mentioned above, solubility considerations limit the concentration range to 0.1–1.0 mM. From the almost linear dependence of Λ_m on $\sqrt{C}$ it appears that the level of ion aggregation is not changing very much throughout this range. Obviously we did not carry out measurements to low enough concentrations to determine the limiting value of $\Lambda_m°$. In a recent paper[14] $\Lambda_m°$ for $[(\eta^5\text{-}C_5H_5)_2Co]PF_6$ in CH_2Cl_2 was measured as 103.6 ∓ 1.0 Ω/(M·cm). The ion-association constant for formation of a $[(\eta^5\text{-}C_5H_5)_2Co]^+\cdots PF_6^-$ pair in CH_2Cl_2 was evaluated as $K_A = 25\,000 \mp 10\,000$ by employing the Fuoss equation[13] in an iterative least-squares fitting procedure. Thus, it is very probable that biferrocenium triiodide is largely ion paired in CH_2Cl_2.

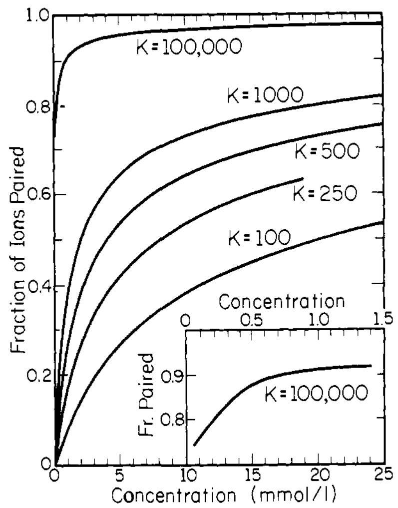

Figure 7. Plot of the fraction of ion pairs as a function of solute concentration evaluated for various values of the equilibrium constant K for the ion association of the form $BF_c^+ + I_3^- \rightleftharpoons BF_c^+\cdots I_3^-$. The inset shows an expanded view of the fraction of ion pairs for the K = 100 000 case in the low concentration range.

An iterative computer program was written in an attempt to try to fit our Λ_m data to the equation proposed by Fuoss[15] for an associated 1:1 electrolyte. In eq 2, Λ_η is the molar conductance

$$\Lambda_\eta = \Lambda_o - S(c\gamma)^{1/2} + E(c\gamma)\log(c\gamma) + J'(c\gamma) - K_a(c\gamma)f^2\Lambda_\eta \tag{2}$$

corrected for solute volume effects; Λ_o is the limiting conductance at infinite dilution; c is the stoichiometric electrolyte concentration; γ gives the fraction of ions that are not paired (i.e., the product $(c\gamma)$ gives the number of free ions in solution); K_a is the ion-pairing equilibrium constant; f is the activity coefficient; S, E, and J' are as defined by Fuoss.[15] Values for the activity coefficients were estimated by using the Debye–Hückel relationship

$$-\log f^2 = \beta''(c\gamma)^{1/2}/(1 + \kappa a\gamma^{1/2}) \tag{3}$$

with β'' and κ as defined by Fuoss.[15]

Equation 2 was solved for Λ_o, K_a, and J' with use of standard multiple linear regression techniques and is subject to the constraint that $\kappa a \leq 0.2$. The method of Fuoss requires an initial estimate of Λ_o and a (the distance between the centers of the two ions). The initial Λ_o value was obtained by extrapolating the Λ_m versus concentration plot to zero concentration, and estimates of the cation/anion radii were obtained from crystallographic data of biferrocenium triiodide (approximately 7 Å). The value of Λ_o obtained after the least-squares fit was recycled until a constant value was obtained. In neither case did we get good fits of our data to the Fuoss equation. However, for biferrocenium triiodide in the 0.2–1 mM range the best estimates from fitting our data to the Fuoss equation of the equilibrium constant for ion association are K = 100 000 (∓25 000) for dichloromethane and K = 400 (∓100) for nitrobenzene. Thus, it is evident in Figure 7 that in the case of biferrocenium triiodide in CH_2Cl_2 the fraction of ion pairs varies from ~80% to ~90% in the ~0.2 to ~1.0 mM range, whereas in the same concentration range for $C_6H_5NO_2$ the fraction of ion pairs varies from ~20% to ~40%. It must be emphasized that further experiments are needed to establish whether in fact only ion pairs are present, not larger ion aggregates.

Origin of Concentration Dependence of E_{op}, $\Delta\nu_{1/2}$, and NTM. In order to rationalize the concentration dependencies of the

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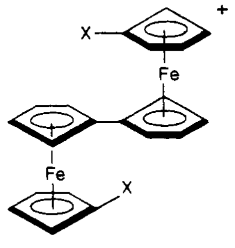
[15] Fuoss, R. M.; Accascina, F. In *Electrolytic Conductance*; Interscience: New York, 1959; Chapters XV–XVIII.

energy, half-width, and transition moment of the IT band for biferrocenium triiodide in either nitrobenzene or dichloromethane, the contours of the IT bands were computer fit to the PKS vibronic model by using numerical methods as suggested in ref 13. In this model ϵ is the parameter that gauges the electronic coupling between the d-manifolds on the two ferrocenyl moieties and λ is the parameter that gauges the degree of vibronic coupling in the mixed-valence complex. In the absence of environmental effects, a symmetric mixed-valence complex such as cation II would have $W = 0$, where W gauges the zero-point energy difference between the two vibronic states of the complex, i.e., $Fe_a^{II}Fe_b^{III}$ and $Fe_a^{III}Fe_b^{II}$. We decided to fit the IT bands with the parameters ϵ and λ only. It should be noted that when $W \neq 0$ the sum $(\lambda^2 + W)$ replaces λ^2 in the equations of the PKS theory.[13] In applying the theoretical analysis of ref 13 it is customary to express the electronic coupling energy ϵ in quanta of some vibrational mode of the complex, usually in the range 300–500 cm^{-1}. In this paper we use 400 cm^{-1} as the energy associated with a quantum. The fitting is not sensitive to the precise number used. λ^2 is a coupling energy and the units are established as above for ϵ.

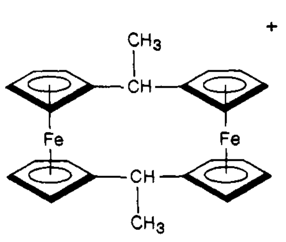
Values of ϵ and λ obtained by fitting the IT band of biferrocenium triiodide at different concentrations in either nitrobenzene or dichloromethane are given in Table III. For CH_2Cl_2 the value of ϵ increases from 8.2 to 8.7 (in units of $h\nu = 400$ cm^{-1}) over the concentration range 0.24–1.0 mM. λ was found to be constant at 3.2 (in units of $h\nu = 400$ cm^{-1}), where a change of ∓ 0.1 in λ was found to be sufficient to make the fit at any concentration measurably poorer.

In comparison, for the nitrobenzene medium ϵ increases from 8.7 to 9.7 $h\nu$ over a range of concentration of 0.24–24 mM. (Over the range 0.24–1.0 mM ϵ increases from 8.7 to an estimated value of ~9.0.) However, in order to fit the data obtained in nitrobenzene it was necessary to let λ increase from 3.12 to 3.40 over the range of $C = 0.24$ to 1.87 mM. At concentrations above ~1.87 mM no further change in λ was needed.

The above experimental data and the theoretical parameters for biferrocenium triiodide in nitrobenzene are more revealing than the data for the dichloromethane medium, for a larger concentration range could be covered with nitrobenzene. It is clear from the conductivity data that the degree of ion aggregation changes appreciably over the concentration range 0.24–24 mM. Furthermore, it is likely that there are differences in ϵ, λ, and W between the non-ion-paired biferrocenium cation and the ion pair $[Fe_2(\eta^5\text{-}C_5H_5)_2(\eta\text{-}^{10}C_{10}H_8)]^+\cdots I_3^-$. In particular, in the case of the solvated non-ion-paired complex W probably equals zero, whereas, for the ion pair W is likely to be non-zero as the result of the I_3^- ion sitting closer to one iron center than the other in cation II. Valence trapping as the result of asymmetric positioning of the anion relative to a mixed-valence biferrocene-like cation is well documented for complexes in the solid state.[16–18] For example, the $I_3^-\cdot{}^1/_2I_2$ salt of cation III with X = Cl has been shown to have a valence-trapped cation as the result of the positioning of the I_3^- anion relative to the cation.[16] On the other hand, the I_3^- salts of cation III with X = I or Br substituents exhibit a fast rate ($k \gtrsim 10^9$ s^{-1}) of intramolecular electron transfer even at 4.2 K.[16] The I_3^- anions in these X = I or Br compounds are symmetrically disposed relative to the two iron ions in the mixed-valence cation. Finally, the X-ray structure[17] of the I_3^- salt of cation IV shows that there are ion pairs in the solid state. Cation IV is valence trapped in this salt, which is the result of the asymmetric disposition of the I_3^- ion relative to the two iron ions in the nearest cation IV.



III



IV

Table III. Parameters Resultant from Fitting Biferrocenium Triiodide IT Band Contours to the PKS Vibronic Model[13]

concn, mM	ϵ[a]	λ[b]
	In CD_2Cl_2	
0.30	−8.2	3.2
0.97	−8.7	3.2
	In $C_6D_5NO_2$	
0.32	−8.7	3.15
0.67	−8.9	3.25
1.87	−9.3	3.35
2.40	−9.4	3.40
12	−9.5	3.40
24	−9.7	3.40

[a] Electronic coupling parameter in units of $h\nu = 400$ cm^{-1}. [b] Vibronic coupling parameter.

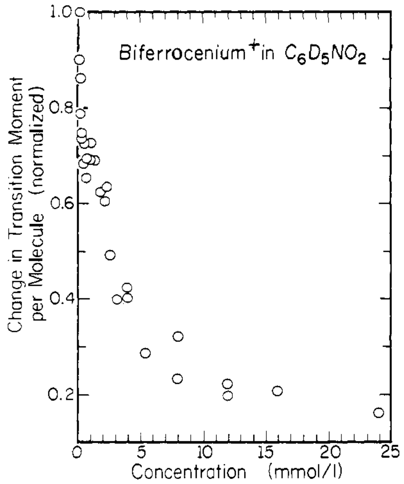


Figure 8. Plot of the change in the normalized transition moment of the IT band for biferrocenium triiodide in nitrobenzene in the full concentration range of 0.25–24 mM. The transition moment is normalized to unity for the IT band observed at a concentration of 0.25 mM.

In the concentration range 0.24–24 mM in nitrobenzene the IT band contour is likely a superposition of two IT bands, one for non-ion-paired cation II and the other for ion-paired cation II. Because ion-paired cation II probably has $W \neq 0$ and non-ion-paired cation has $W = 0$, an increase in the concentration of the ion pairs will lead to an increase in E_{op} as it is evaluated. This is what is seen for biferrocenium triiodide in nitrobenzene as the concentration is increased. The decrease in transition moment of the IT band with increasing concentration is also explicable, for ion-paired cation II with $W \neq 0$ would be expected[13] to exhibit a less intense IT band than non-ion-paired cation II. The fact that the transition moment decreases as the concentration of biferrocenium triiodide is increased in nitrobenzene could also be explained by an ion-association equilibrium with $K \simeq 400$. Figure 8 shows a plot of the transition moment over the full concentration range examined for biferrocenium triiodide in nitrobenzene. It is clear that the greatest change in transition moment occurs in the low concentration range. Above a concentration of ~5 mM, the rate of decrease is appreciably less than below ~5 mM. This is in keeping with the conductivity data which show less change in degree of ion-aggregation above ~5 mM compared to that seen below ~5 mM. The decrease in half-width with increasing

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concentration is also consistent with the idea that there are more different types of species present at low than at high concentration where all ions are probably paired.

From the above simplified fitting of the IT band for cation II in nitrobenzene it was found that λ increases with increasing concentration in the 0.32–2.4 mM range. Because λ^2 and W are found together as a sum in the theoretical equations[13] for the $W \neq 0$ case, a change of 3.15 to 3.4 for λ (λ^2 is in units of $h\nu = 400$ cm^{-1}) is equivalent to a change from $W = 0$ to $\simeq 500$ cm^{-1}. Since λ and W are strongly correlated, it is not possible to determine uniquely either parameter when $W \neq 0$. Furthermore, if the idea that the IT band is in reality a superposition of variable amounts of two or more IT bands is correct, then a fitting of the band contour to the theoretical equations is made to be very difficult.

The data observed for biferrocenium triiodide in dichloromethane present more of a challenge to explain in detail. This is in large part due to the fact that, because the static dielectric constant of CH_2Cl_2 is so small ($D_s = 9.08$) compared to that for $C_6H_5NO_2$ ($D_s = 34.82$), it is likely that there are more than just ion pairs present in CH_2Cl_2. As the concentration of biferrocenium triiodide in dichloromethane is increased, E_{op} increases, $\Delta\bar{\nu}_{1/2}$ remains unchanged, and the transition moment increases. Seemingly these observations could be explained by having ϵ increase, λ remain constant, and $W = 0$ or be any constant value as the concentration is increased. W could remain relatively constant even if there is a shift from ion pairs to triads of ions. It does seem quite reasonable that λ would remain constant, for λ reflects a difference in the totally symmetric ring–iron–ring stretching vibrational normal coordinate of the Fe^{II} metallocene moiety compared to the Fe^{III} metallocene moiety. There would seem to be no reason that λ would change very much from ion pairs to triads, for example. On the other hand, it is conceivable that ϵ would change from an ion pair to a triad as a result, for example, of a change in the conformation of cation II. Considerably more physical and spectroscopic data, such as ^1H and ^{13}C NMR data, are needed to characterize thoroughly the structure of the ion aggregates in CH_2Cl_2 and, for that matter, $C_6H_5NO_2$.

Conclusions and Comments

It has been shown that the energy of the IT band of biferrocenium triiodide in various solutions exhibits concentration dependencies that are comparable to the shift range seen for the IT band as this mixed-valence complex is moved from one solvent to another. From solution electrical conductivity measurements we have conclusively shown that these concentration dependencies are attributable to variations in the level of ion aggregation in the solvents. Thus, proper care has to be exercised before analyzing the countour of a given IT band with the PKS vibronic model.[13] The possibility that the observed IT band is a superposition of IT bands for different ion aggregates is real. It must be emphasized here that obviously cation II carries a 1+ charge, whereas, the well-known ruthenium mixed-valence complexes of composition $[(bpy)_2ClRu\text{-}B\text{-}Ru(bpy)_2Cl]^{3+}$ and $[(NH_3)_5Ru\text{-}B\text{-}Ru(NH_3)_5]^{5+}$ (B = bridge and bpy is 2,2′-bipyridine) have charges of 3+ and 5+, respectively. These ruthenium complexes very likely form ion aggregates with degrees of aggregation that vary considerably from one solvent to another. In this regard care should be exercised in accepting the very recent suggestion[19] that high-frequency vibrational modes are to be associated with the water structure about mixed-valence $[(bpy)_2ClRu\text{-}B\text{-}Ru(bpy)_2Cl]^{3+}$ complexes. This suggestion was made as a result of the observation that the E_{op} value found for water does not fit in a correlation of E_{op} versus $(1/n^2 - 1/D_s)$ established for three different ruthenium complexes in a series of solvents.

There are two other general points that should be made about the study of mixed-valence complexes. First, there has been no direct check of using a fit of an IT band to the PKS theory to assess the rate of intramolecular electron transfer. Thus, even after one knows ϵ, λ, and W very accurately, the contribution of quantum mechanical electron and nuclear tunneling to the electron-transfer rate has to be evaluated. Is one vibrational mode active, or is the quantum mechanical tunneling a multiphonon process? Direct evidence for an appreciable rate of tunneling has been reported[16] for several biferrocenium-type cations *in the solid state*. Certain mixed-valence complexes exhibit an intramolecular electron-transfer rate in excess of $\sim 10^9$ s^{-1} at 4.2 K, even though IR data clearly show that these same complexes do have a potential energy barrier present. This very fast rate of $\sim 10^9$ s^{-1} can only be explained by a tunneling mechanism.

The second general point is that, although most researchers[6-8,10] prefer to use a solution medium to study mixed-valence complexes, much more detailed data bearing on the rate of intramolecular electron transfer are obtainable by studying mixed-valence complexes in the solid state.[16-18] Only in the solid state can one know the position of the atoms that serve as the environment about the mixed-valence complex. Much more detailed results are available from spectroscopic studies of mixed-valence complexes in the solid state than in solution. For example, studies of mixed-valence $[Fe_3O(O_2CCH_3)_6(L)_3]S$, where L is a (substituted) pyridine and S is a solvate molecule, in the solid state have made it possible to show how the onset of motion of S relative to the Fe_3O complex in the crystal affects the intramolecular rate of electron transfer in the Fe_3O complex.[20] Information about the impact of solvent molecule motion is obtainable from studies of species in the solid state, whereas it would be hard to deduce for mixed-valence species in solution. Recent experimental and theoretical results[21,22] on the rate of electron transfer either between two small molecules or between a metalloprotein and an attached ruthenium complex suggest that the relative motion of nearby solvent molecules strongly affects intermolecular rates of electron transfer.

Experiment Section

Physical Measurements. NIR electronic absorption spectra were recorded with use of quartz optical cells of 10 and 1 mm path lengths. A 100 W Oriel quartz tungsten–halogen lamp with a Kratos quartermeter monochromator with 2100 blaze gratings at a slit width of 1 mm was used. Transmitted light was detected by an Opto Electronics OE-25-52 lead sulfide photoconductor that was operated on a 100 V DC bias. A light chopper was placed between the light source and the monochromator. The AC component of the PbS cell was measured with a PAR Model 8 lock-in amplifier.

The conductivity measurements were performed on a YSI Model 35 conductance meter employing a YSI Model 3402 conductivity cell (0.1 cm^{-1}). The solutions were maintained at 25.0 ∓ 0.1 °C with use of a Forma Scientific constant temperature bath. The cell constant was determined by measuring the conductivity of an aqueous 0.1 M KCl solution. The conductivity measurements were done with spectral grade (99%+) dichloromethane and nitrobenzene which were used without further purification.

Compound Preparation. Biferrocene,[23] biefrrocenium triiodide,[24] and biferrocenium hexafluorophosphate[16] were prepared according to literature procedures. Good microanalytical data were obtained. The deuteriated dichloromethane and nitrobenzene used in the optical study were purchased from Aldrich Chemical Co. and used without further purification.

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