

Solvatochromic Behaviour of Ferrodiin & Ferroin

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The solvent-dependence of the spectral behaviour of ferrodiin and ferroin has been examined in various solvents. The results indicate a slight solvent-dependence of the charge-transfer band ($\nu_{\max}$) of $\text{Fe}(\text{LL})_3^{2+}$, but it is not as pronounced as in the case of $\text{Fe}(\text{LL})_2(\text{CN})_2$ ($\text{L}-\text{L}$ =diamine). The behaviour of hydrogen bonding solvents is different from that of the dipolar aprotic solvents.

The dependence of charge-transfer maxima ($\nu_{\max}$) on solvent has been investigated for a variety of diamine (LL) complexes of the type $\text{M}(\text{CO})_4(\text{LL})$ and $\text{Fe}(\text{LL})_2(\text{CN})_2$ ($\text{M} = \text{Cr}, \text{Mo}$ or W ; $\text{LL} = \text{Dipy}$, phen and their substituted derivatives). In all these cases, $\nu_{\max}$ of charge-transfer bands vary considerably with the nature of the solvent¹.

Though the intense red charge-transfer complexes of tris-(2,2'-dipyridyl) and 1,10-phenanthroline with ferrous ion (ferrodiin and ferroin) are well known for their analytical applications, the effects of solvents on their spectra are very little studied though the spectral aspects have been extensively studied by Lahiri and co-workers^{2,3}. The spectra of the complexes have been resolved into five distinct bands. For $\text{Fe}(\text{Dipy})_3^{2+}$, absorption maxima and extinction coefficients vary very little with the nature of solvent. However, it will be premature to conclude that the solvent has no effect on the spectra of tris-complexes like ferrodiin and ferroin without further study. The extinction coefficients of ferrodiin and ferroin have been found to vary with solvent compositions (within $\pm 3\%$) in the cases of methanol + H_2O , ethanol + water, isopropanol + H_2O , *t*-butanol + H_2O , DMF + H_2O and formamide + H_2O ⁴⁻⁸. It is, therefore, reasonable to believe slight solvent dependence of the oscillator strengths of ferrodiin and ferroin.

In order to throw more light on the solvatochromic behaviour of ferrodiin and ferroin, we have recorded the absorption spectra of these complexes in different solvents like $\text{DMSO} + \text{H}_2\text{O}$, formamide + H_2O and DMF + H_2O .

Formamide, DMSO and DMF were purified as described earlier⁹. The spectra of the ligands and

their tris-iron(II) complexes were recorded at 25°C on a Backman DU spectrophotometer.

The complexes were prepared by the addition of excess of 2,2'-dipyridyl or 1,10-phenanthroline (usually ten-fold or more) to mohr salt (dissolved in dilute HClO_4). Complete complexation was ensured by the constancy in optical density readings. The complexes are not appreciably stable in 100% (v/v) DMSO or DMF or > 60% (v/v) formamide. So we had to choose the mixed solvents for our study.

Both 2,2'-dipyridyl and 1,10-phenanthroline have two strong absorption bands in the UV region. The spectral solvent shifts of 2,2'-dipyridyl and 1,10-phenanthroline have been recently reported by us⁹. In view of the high absorption of the solvents in the UV region, the full spectra of the ligands could not be measured, only the spectra in the long wavelength region were recorded. The oscillator strength of Dipy (280nm band) in water, DMF, DMSO and formamide is 0.454, 0.252, 0.191 and 0.192 respectively. The oscillator strength of phen (264 nm band) is 1.014 and 0.658 in water and formamide respectively.

It is apparent that there is a considerable decrease in the oscillator strengths in the organic solvents compared to those in water, though the absorption maxima are very little affected. The complexes show almost the same spectra in the UV region as the pure ligands, except that the bands are slightly shifted and partly split due to the influence of H^+ and Fe^{2+} ions. Moreover, the spectra of the complexes in the UV region are complicated due to superposition of bands of ionic and molecular forms of the ligands. Therefore, it is desirable to study the spectra of the complexes in the visible region.

The solvent induced spectral shifts have been much utilized to identify $n-\pi^*$ and $\pi-\pi^*$ transitions of organic molecules or CTTS transitions. Though the solvent effects of such UV transitions are poorly correlated by the dielectric constants or functions of the dielectric constants, the transition energies have been found to be linear functions of $f(D)$ ¹⁰ [where $f(D) = \frac{2(D-1)}{D+1}$, D =dielectric constant of the medium] within limitations of the experimental error. In the case of inorganic complexes, the positions of charge-transfer maxima have been sought to be correlated with empirical solvent parameters like D , Kosower Z -values^{11,12} etc., the important parameter being Reichardt's¹³ spectroscopically based solvent E_T value. The detailed explanation of solvatochromic behaviour, however, is yet to be established.

The inorganic diimine complexes like $\text{M}(\text{CO})_4(\text{LL})$ and $\text{Fe}(\text{LL})_2(\text{CN})_2$ show appreciable solvent induced spectral shifts so that it is possible to draw plots of $\nu_{\max}$ versus solvent E_T values. But in the case of ferroin or ferrodiin i.e. $\text{Fe}(\text{LL})_3^{2+}$ complexes, slight or no such shifts have been observed. It is likely that

Table 1—Oscillator Strengths of Ferroin in Different Solvents

Complex	$\lambda_{\max}$ (cm ⁻¹)	$\epsilon \times 10^{-3}$	Half band width (cm ⁻¹)	β	Oscillator strength	Total oscillator strength
(Fe Phen ₃) ²⁺	19620	11.34	2160	6.43×10^{-7}	0.112	0.262
	21480	8.20	1680	9.68×10^{-7}	0.061	
	23100	7.40	1500	1.09×10^{-6}	0.050	
	24540	4.85	1320	1.56×10^{-6}	0.029	
	25680	2.55	960	3.36×10^{-6}	0.010	
(Fe Phen ₃) ²⁺ in 90% (v/v) aq. formamide	19600	11.23	2300	4.78×10^{-7}	0.1187	0.272
	21750	7.75	2250	5.06×10^{-7}	0.0796	
	23650	6.3	1550	1.10×10^{-6}	0.0448	
	25000	3.6	1200	1.85×10^{-6}	0.0198	
	26000	2.3	900	3.34×10^{-6}	0.0950	
(Fe Phen ₃) ²⁺ in 90% (v/v) aq. DMSO	19600	11.4	2450	4.20×10^{-7}	0.1284	0.276
	21750	7.5	2050	6.14×10^{-7}	0.0706	
	23600	6.3	1650	9.65×10^{-7}	0.0477	
	25150	3.4	1500	1.18×10^{-6}	0.0234	
	26500	1.5	1100	2.22×10^{-6}	0.0075	
(Fe Phen ₃) ²⁺ in 60% (v/v) aq. DMF	19600	11.7	2250	5.01×10^{-7}	0.1210	0.286
	21600	8.0	2000	6.45×10^{-7}	0.0735	
	23400	7.0	1700	9.10×10^{-7}	0.0547	
	24900	4.2	1400	1.36×10^{-6}	0.0270	
	26150	2.0	1150	2.03×10^{-6}	0.0105	

Table 2—Oscillator Strengths of Ferrodien in Different Solvents

Complex	$\lambda_{\max}$ (cm ⁻¹)	$\epsilon \times 10^{-3}$	Half band width (cm ⁻¹)	β	Oscillator strength	Total oscillator strength
(Fe Dipy ₃) ²⁺	19075	8.43	2000	6.07×10^{-7}	0.0775	0.203
	20725	5.50	1500	1.25×10^{-6}	0.0379	
	22000	3.35	950	3.28×10^{-6}	0.0146	
	23275	2.30	1700	8.55×10^{-7}	0.0180	
	26000	3.80	3150	2.63×10^{-7}	0.0550	
(Fe Dipy ₃) ²⁺ in 90% (v/v) aq. formamide	19150	8.90	2000	6.39×10^{-7}	0.0818	0.219
	20800	5.60	1400	1.34×10^{-6}	0.0360	
	22100	3.35	1250	1.70×10^{-6}	0.0192	
	23250	2.45	1450	1.26×10^{-6}	0.0163	
	26300	4.25	3350	2.16×10^{-6}	0.0653	
(Fe Dipy ₃) ²⁺ in 90% (v/v) aq. DMSO	19150	8.83	2200	5.24×10^{-7}	0.0892	0.222
	20750	5.00	1300	1.57×10^{-6}	0.0298	
	22000	3.00	1450	1.26×10^{-6}	0.0200	
	23250	2.30	1600	1.03×10^{-6}	0.0169	
	26300	4.00	3100	2.63×10^{-7}	0.0661	
(Fe Dipy ₃) ²⁺ in 60% (v/v) aq. DMF	19200	9.15	2100	5.77×10^{-7}	0.0883	0.228
	20800	5.70	1400	1.34×10^{-6}	0.0366	
	22150	3.35	1150	1.85×10^{-6}	0.0184	
	23250	2.40	1500	1.17×10^{-6}	0.0165	
	26300	4.25	3500	2.04×10^{-7}	0.0683	
(Fe Dipy ₃) ²⁺ in 90% (v/v) aq. isopropanol	19150	7.65	2000	6.39×10^{-7}	0.0704	0.173
	20925	4.80	1850	7.57×10^{-7}	0.0408	
	22475	2.45	1350	1.70×10^{-6}	0.0152	
	24000	1.95	1500	1.26×10^{-6}	0.0135	
	26000	3.20	2250	3.51×10^{-7}	0.0331	

the high spin complexes like Fe(LL)₂X₂ may interact strongly with the solvents to give solvent induced spectral shifts.

The solvent effects of M(CO)₄(LL) and Fe(LL)₂(CN)₂ have been ascribed to solvation changes at the small and solventophilic cyanide or carbonyl ligands affecting the energy of charge-transfer from metal to heteroatomic ligands. But the low spin complexes like Fe(LL)₃²⁺ (ferroin or ferrodien) are highly stable and no appreciable solvation at the large and solventophobic heteroatomic ligands takes place

resulting in no or slight solvent induced spectral shifts. Thus no correlation of the spectral shifts with solvent parameters is possible.

However, a slight solvent effect is apparent from the increase in extinction coefficient values of ferroin and ferrodien in mixed solvents. This indicates that the oscillator strengths are susceptible to variation in solvents. In order to investigate the nature of the variation of oscillator strengths with solvents, we resolved the visible absorption spectra of ferroin and ferrodien in the same way as described in our earlier communications^{2,3}. The results are given in Tables 1 and 2.

The number of absorption bands have been found to be the same in water and in mixed organic solvents. The curves are fitted well by the equation¹⁴,

$$\epsilon = \alpha \nu e^{-\beta(\nu_0 - \nu)^2}$$

where $\alpha = \frac{\epsilon_{\max}}{\nu_0}$ and β = a constant embodying the half-width of the band. The values of β are recorded in Tables 1 and 2.

The values of β are of the same order of magnitude in aqueous and mixed solvents though the values of β for the first two bands are greater in aqueous solutions. The values of β generally increase as we proceed towards the short wavelength regions, an effect similar to that observed by Mead¹⁵ in connection with the study of oxalate and ethylenediamine complexes of Cr and Co. The areas and oscillator strengths were calculated in the usual way.

It has been found that the oscillator strengths increase (though not appreciably) as we go from aqueous to dipolar aprotic solvents (DMSO and DMF) and polar amide solvent like formamide. The absorption maxima are only slightly affected. The

oscillator strengths of $\text{Fe}(\text{Dipy})_3^{2+}$ are almost the same in water and methanol+water solvents, decrease in the case of isopropanol+water mixtures but increase in DMSO and DMF. The results indicate that there is

a slight solvent dependence of charge-transfer band ($\nu_{\max}$) of $\text{Fe}(\text{LL})_3^{2+}$ (iron-diimine complex) but it is not so pronounced as in $\text{Fe}(\text{LL})_2(\text{CN})_2$. Further, the behaviour of polar hydrogen bonding solvents is different from the behaviour of dipolar aprotic solvents.

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