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Dyes and Pigments 43 (1999) 241–251

DYES and PIGMENTS

The colours of charge-transfer complexes of methyl viologen: effects of donor, ionic strength and solvent

Paul M.S. Monk*, Neil M. Hodgkinson[1], Robert D. Partridge

Department of Chemistry and Materials, Manchester Metropolitan University, Manchester M1 5GD, UK

Received 11 May 1999; accepted 11 June 1999

Abstract

The methyl viologen dication (MV^{2+}) is electron deficient and readily undergoes outer-sphere charge-transfer complexation with donor species. Equilibrium constants of complexation (K) have been determined optically for a series of nine donors; some were found to form charge-transfer complexes while others merely formed association ion pairs. K is directly related to the ionization energy I of the donor moiety. For hexacyanoferrate(II), the transition dipole of complexation is anomalously large. A plot of the spectral width at half peak height against standard functions from classical electrostatics is also given, and is discussed in terms of the CT transition incorporating molecular movement. The absorbance of an optical charge-transfer (CT) band decreases as an inert electrolyte is added to the solution. A simple treatment of a competing association reaction is used to explain why the absorbance (Abs) changes with anion concentration $[X^-]$, according to the relationship $\log(Abs) = k\log([X^-]) + k'$, where k and k' are collections of constants. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Methyl viologen; Bipyridilium; Charge transfer

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1. Introduction

Viologen species have the structures shown in Scheme 1, and are formally named as salts of 1,1′-disubstituent-4,4′-bipyridilium.

The bipyridilium dication has a relatively high electron affinity [1] and therefore behaves as a good Lewis acid (electron acceptor A). Accordingly, this species readily forms outer-sphere charge-transfer (CT) complexes [2,3] with Lewis base-type species possessing low ionization potentials (electron donors D) [Eq. (1)]:

$$\underset{\text{not coloured}}{A^{x+} + D^{y-}} \rightarrow \underset{\text{coloured}}{A^{(x-\delta)+}\!:\!D^{(y-\delta)-}} \qquad (1)$$

where typical donors D are electron-rich species such as anions or organic moieties possessing lone pairs.

The formation of the new dative bond is evinced by a new optical absorption band (i.e. a new colour). The methyl viologen dication–hexacyanoferrate(II) complex, for example, absorbs strongly in the wavelength range ca. 420–670 nm, thus imparting a purple colour to the complex, whereas both methyl viologen and hexacyanoferrate(II) are colourless in aqueous solution [2].

Complex formation is an important aspect of viologen electrochemistry. It follows that donor-type species are often one of the components added to

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* Corresponding author. Tel.: +44-(0)161-247-1421; fax: +44-(0)161-247-6357.

E-mail address: p.monk@mmu.ac.uk (P.M.S. Monk)

[1] Current address: Baxenden Chemicals Ltd., Accrington, Lancashire, BB5 2SL, UK.

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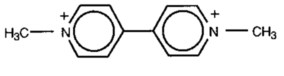
PII: S0143-7208(99)00063-7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Scheme 1.

solution within, for example, electrochromic displays as electron mediators [4].

It has been noted that the absorbance of a CT-couple decreases when an inert electrolyte is added to the solution [5–7]. Examples of solution-phase acceptors and donors yielding charge-transfer complexes include the hexacyanoferrate(II) (as donor) with dicationic heptyl viologen [5] as acceptor, or again, methyl viologen with donors such as hexacyanoferrate(II) [6], Rose Bengal [7] or Eosin Y (a xanthene dye) [7]. A relationship is described here between absorbance (*Abs*) and anion concentration $[X^-]$, viz. $\log(Abs) \propto -\log[X]$. Reference [6] attributes the decrease of optical absorbance with increasing ionic strength I to competing equilibria, while Ref [7], in finding a correlation between $\log(K_{CT})$ with $\sqrt{I}$, appears to imply an activity coefficient effect.

It is also worth noting that a recent study of CT-complexation used zwitterionic viologen species [7] (i.e. a viologen-type nucleus bearing no overall ionic charge), and found the equilibrium constant of charge-transfer complexation to be essentially independent of I. This behaviour is expected using the model above, since ionic-association effects will be almost non-existent; (the donor in that study was Rose Bengal [7]).

There are many theories of charge transfer [8]. The theory we have used here is that of Mulliken, whose treatment of charge transfer was wave mechanical in origin [9], and states that the energy of the charge-transfer transition is proportional to the ionization potential I_D of the donor D [Eq. (2)]:

$$h\upsilon_{CT} = I_D - E_A + \Delta \tag{2}$$

where the energy of the CT band is obtained via the frequency maximum υ of the CT band, and the electron affinity of the acceptor A is E_A. Δ represents the difference between Σ (van der Waals, repulsion, exchange and CT resonance energies) and the excited- and ground-states of the charge transferred [8].

Using first-order perturbation theory, Δ can be approximated to (constant/I_D−constant′) for a series of donors with a single, invariant acceptor (as here), and so it might be expected that a graph of I_D against $h\upsilon$ would be parabolic, with a gradient of unity only at very high I_D. Using a single solvent and but one acceptor species allows for further simplification, such that Eq. (2) becomes Eq. (3):

$$h\upsilon_{CT} = xI_D - y \tag{3}$$

where the constants x and y are empirical fitting parameters. The factor x is expected to be less than unity owing to solvent ionizations processes [Eq. (4)]:

$$\mathrm{A{:}D} + \text{solvent} \xrightarrow{K_{\text{solv}}} \mathrm{A}^-_{(\text{solv})} + \mathrm{D}^+_{(\text{solv})} \tag{4}$$

The driving force for reaction is the solvation energies of the ions [10,11]. (Only in less-polar solvents is it realistic to describe these CT complexes as having a straightforward 1:1 stoichiometry because of these solvent interactions.)

Finally, we have used methyl viologen (MV), since it is water soluble without forming micelles, and because extensive literature relating to its charge-transfer properties is available [1–9,12–23]. All the donors used were also soluble in water, and all concentrations were chosen to ensure that the complexes remained in solution (the increased covalency of the complex tends to decrease its water solubility; the MV^{2+}–$[Fe(CN)_6]^{4-}$ complex, for example, precipitates readily from water [24] at concentrations above ca. 20 mmol dm^{-3}).

2. Experimental

2.1. Materials

The methyl viologen (MV) dication was prepared as the *bis*(methosulphate) salt by dissolving 4,4′-bipyridine (Aldrich) with excess dimethyl sulphate (Fisons) in dry DMF at room temperature. Crystals were apparent after ca. 2 h. Recrystallisation from aqueous ethanol produced white needle-like crystals.

The purity of the methyl viologen was confirmed by the following characterisation data:

^{1}H NMR	$\delta = 9.1$ ppm, d of d, 4H (bipyridine); 8.5 ppm, d of d, 4H (bipyridine); 4.6 ppm, s, 6H, (Me) and 3.7 ppm, s, 6H, ($MeSO_4^-$).
^{13}C NMR	$\delta = 153$ ppm (Carbon-2);149 ppm (C-4); 129 ppm (C-3); 58 ($MeSO_4^-$) and 51 ppm (Me).
IR	3200 cm^{-1}, C-H; 1650 cm^{-1}, C=C, C=N; 1600, 1540, 1430 cm^{-1} (C=C); 1200, 1080 cm^{-1}; 880 cm^{-1}.
m.p.	decomposed at $T > 270$°C.

Benzyl viologen (BzV), as the dichloride salt, was made similarly by reflux of 4,4′-bipyridine and benzyl chloride in DMF with subsequent recrystallisation from aqueous ethanol.

All donor species were Aldrich reagents unless stated otherwise. Donors were the potassium salts of fluoride, chloride, bromide, iodide, sulphate (BDH) or hexacyanoferrate(II) (Fisons). Perchlorate was used as the lithium salt (Hopkin and Williams); and ethylamine and hydroquinone were obtained as the neutral species.

All solvents used when obtaining data for Fig. 6 were dried over molecular sieves before use, or were distilled.

2.2. Equilibrium constants

Solutions contained 0.1–1.0 mmol dm^{-3} of MV^{2+} and various concentrations of donor to maintain a complex stoichiometry of 1:1. The equilibrium constant K of complexation between the methyl viologen dication and donor species was determined spectroscopically using the method of Rose and Drago [25], a variant of the well-known Benesi–Hildebrand equation. This method was chosen since donor and complex had overlapping optical absorption bands. A single-beam Philips PL 8720 instrument was used for these measurements.

All solutions were of pH 4.8–5.5 with the exception of ethylamine, for which the solution pH was 6.2.

For the ionic strength experiments, solutions were prepared using doubly distilled water. The ionic strength was adjusted using sodium chloride as inert electrolyte to prevent the competitive effects of using common ions. The concentrations of NaCl used were in the range 1–500 mmol dm^{-3}. The concentration of both acceptor and donor species was 2.5 mmol dm^{-3}.

Since the complex was the only species to have an appreciable absorbance, its concentration was determined optically using Beer's law. The amounts of acceptor and donor bound up within a complex moiety therefore being known, the amounts of uncomplexed material remaining in solution were thus calculated. Alternatively, the ionic strength I could be calculated using terms for starting materials, that is, assuming the complex to be in a dynamic equilibrium with reagents; both counter ions and inert electrolyte were included in these sums.

3. Results and discussion

3.1. Absorbance–ionic-strength dependence

Addition of hexacyanoferrate(II) to a solution of methyl viologen dication MV^{2+} causes a deep purple colour to form with λ_{max} at 525 nm. This is a 1:1 charge-transfer complex. Subsequent addition of sodium chloride to this solution causes the intensity of the colour to diminish (see Fig. 1).

Absorbance was determined as a function of ionic strength for the methyl viologen dication–hexacyanoferrate(II) anion charge-transfer couple. Fig. 2 shows a plot of log(Abs) vs log(I) for the methyl viologen: hexacyanoferrate(II) system. The plot is seen to be linear over a wide range of ionic strengths, i.e. linear except at extremely low and at very high ionic strengths.

Using an straightforward speciation approach, it is readily shown that $\log(Abs) \propto \log(I)$ at intermediate ionic strengths, (see Appendix). The 1:1 complex with hexacyanoferrate(II) is characterised by an equilibrium constant K of [2] 54.2 (mol dm^{-3})$^{-1}$ and the complex with chloride has a much smaller K of [22] 1.7 (mol dm^{-3})$^{-1}$. The solid line in Fig. 2 was calculated using these values of K in Eq. (18) (a computer-based iteration is necessary for each value of I) and the agreement between calculation and experiment is seen to be satisfactory for most ionic strengths.

The deviation in Fig. 2 at low ionic strengths is thought to arise from the formation of a separate

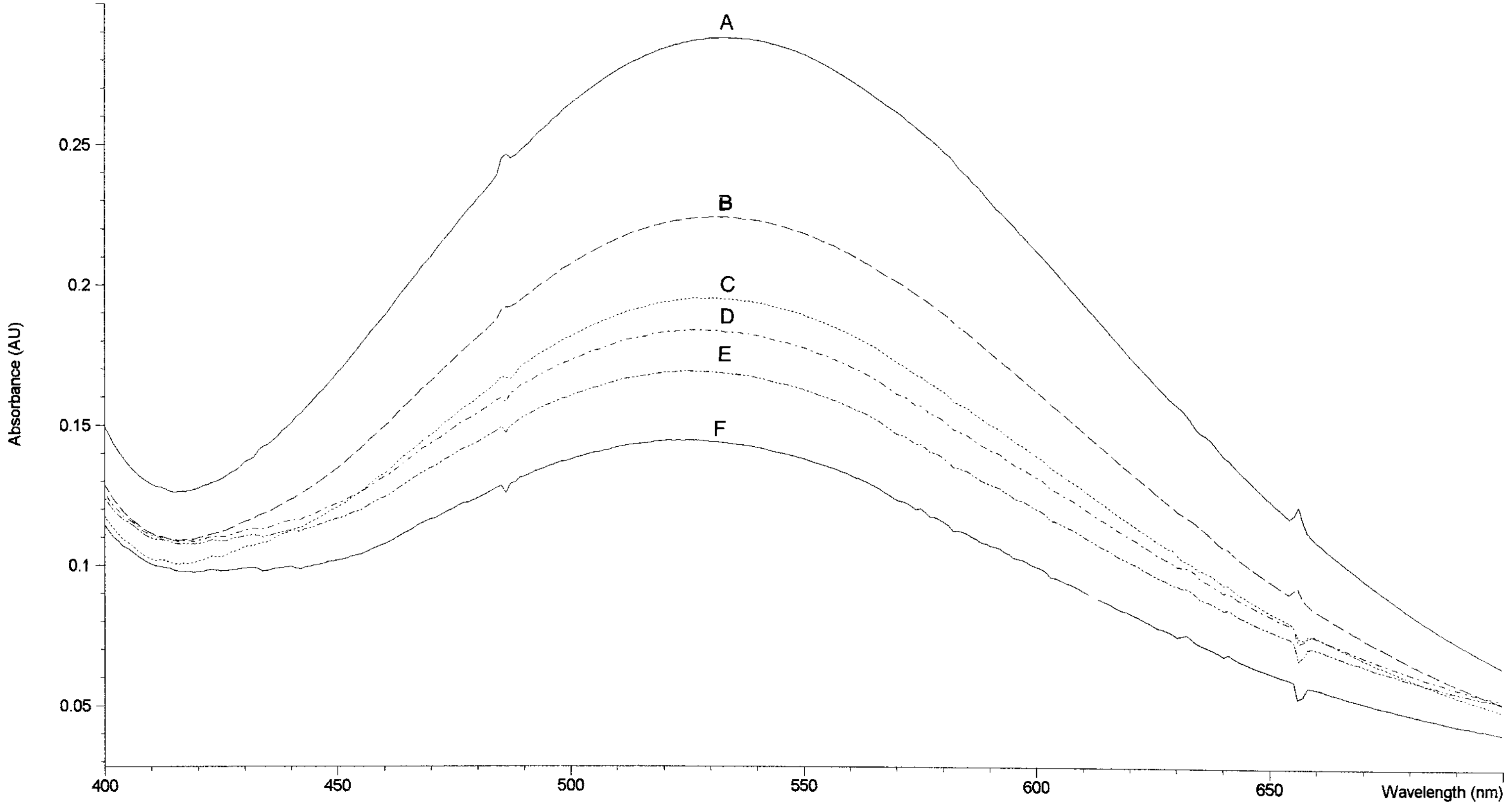

Fig 1. UV–visible spectrum of the CT 1:1 complex formed between MV^{2+} and $Fe(CN)_6^{4-}$ in water (both present at a concentration of 10 mmol dm^{-3}). The ionic strength I of solution was adjusted using solid NaCl: the concentration of NaCl in solution was (a) 4.14, (b) 8.27, (c) 12.4, (d) 16.5, (e) 20.7 and (e) 28.9 mmol dm^{-3}.

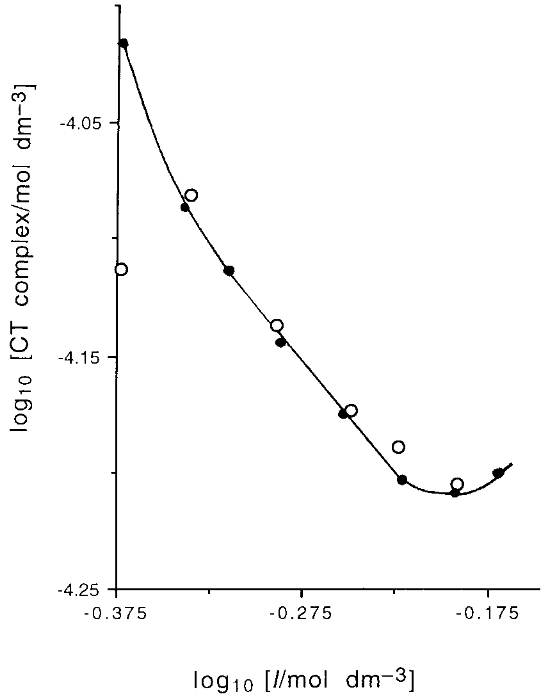

Fig 2. Plot of log(concentration of CT complex) against log(ionic strength) for the optical charge transfer complex formed between the MV^{2+} and Fe(CN)$_6^{4-}$ in water at 298 K. [MV^{2+}] = 5 mmol dm^{-3} and [Fe(CN)$_6^{4-}$] = 10 mmol dm^{-3} throughout and ionic strength was increased by adding NaCl. The concentration of CT complex was determined using the optical absorbance i.e. assuming that the complex was the only absorbing species in solution. The points 'O' are experimental data and the solid line is the absorbance calculated iteratively from Eq. (18) in the Appendix using K_{CT} = 1.7 (mol dm^{-3})$^{-1}$ for the MV^{2+}–Cl complex and 54.2 (mol dm^{-3})$^{-1}$ for the MV^{2+}–[Fe(CN)$_6$]$^{4-}$ complex, and ignoring 2:1 CT complexes.

2:1 complex of MV^{2+} ([Fe(CN)$_6$]$^{4-}$)$_2$; we find the equilibrium constant of formation for this species to be 0.21 (mol dm^{-3})$^{-2}$, which is identical with the literature value of Nakahara and Wang [2]. This complex has an optical absorption band that is partially coincident with that of the 1:1 complex, but of lower ε, hence the overall optical absorbance measured is lower than the treatment here would predict.

The deviations in Fig. 2 at high ionic strength I are almost certainly caused by strong and extensive interactions between ion and solvent, and between ions; such interactions are not accounted for using the extended Debye-Hückel equation alone.

Table 1
Values of equilibrium constant K, extinction coefficient ε, wavelength maximum λ_{max} and ionization potential I, for the complexes formed between the methyl viologen dication and a series of nine donor species in water at 25°C

Donor	K (M^{-1})	K_{Lit} (M^{-1})	ε (M^{-1} cm^{-1})	λ_{max} (nm)	I (eV)
Associating ions					
Fluoride	1.00	–	121.0	344	17.42[a]
Perchlorate	1.01	–	125.0	299	19.4[b]
Sulphate	0.98	–	132.1	305	18.7[b]
Ions forming charge-transfer complexes					
Chloride	1.70	1.7[c]	148.2	362	12.97[a]
Bromide	3.40	3.3[c]	176.8	377	11.81[a]
Iodide	3.80	3.9[c]	184.4	387	10.45[a]
Ethylamine	5.70	–	187.2	605	9.19[d]
Hydroquinone	5.90	5.23[e]	191.3	406	9.68[f]
Hexacyanoferrate	54.2	50.3[g]	690.0	525	3.5[b]

[a] Weast WJ, editor. Handbook of chemistry and physics, 66th ed. Boca Raton (FL): CRC Press, 1985. p. E-74.

[b] Determined spectroscopically from Fig. 1 of this work.

[c] Bertolotti SG, Cosa JJ, Gsponer HE, Previtali CM. Can J Chem 1987;65:2425.

[d] Collin J. Can J Chem 1959;37:293.

[e] Murthy AJN, Bhardwaj AP, Spectrochim Acta 1982;38B:207.

[f] Vilesov FI, Dokl Akad Nauk SSSR 1960;132:632 (as cited in Vedeneyev VI, Gurvich LV, Kondrat'yev, VN, Medvedev VA, Frankevich YeL, Bond energies, ionization potentials and electron affinities. London: Edward Arnold Ltd., 1962).

[g] Nakahara A, Wang JH, J Phys Chem. 1963;67:496.

3.2. Optical constants of charge transfer

The methyl viologen salt prepared comprised the methylsulphate anion, MeSO$_4^-$; this anion is a very weak donor. All other donors are acting as donors relative to methylsulphate, except perchlorate. It is thus assumed that the MeSO$_4^-$ anion is not a *donor* since the only spectroscopic peaks seen in solutions of MeSO$_4^-$ and MV^{2+} are the same as in spectra of the constituent species. These peaks are all in the UV.

For most of the species studied here, the presence of a charge-transfer complex was discerned optically, since a new colour was seen on mixing solutions of acceptor (A) and donor (D). For example, mixing methyl viologen (MV) with a solution of hexacyanoferrate(II) yielded an intense purple colour [2], and the complex between MV and iodide ion was yellow [22]. In the cases of the weaker complexes such as chloride, a faint colour was visible in concentrated solutions, and solid samples possessed a pale yellow colour. The very weakest association species, e.g. that with sulphate, were invisible to the eye but revealed a new, weak spectroscopic band on spectrophotometric analysis. Perchlorate did not form a CT complex as gauged by spectroscopy.

Values of the equilibrium constant K and the extinction coefficient ε for the nine charge-transfer complexes were determined optically, and optical constants are listed in Table 1.

The donors were simple halide anions of fluoride, chloride, bromide and iodide; polyatomic anions of sulphate, perchlorate and hexacyanoferrate(II), and neutral organic donors of hydroquinone and ethylamine. The values are cited following extrapolation to zero ionic strength I. Values are seen to compare well with those in the literature, where applicable.

Fig. 3 shows a plot of $h\nu_{CT}$ vs I_D, and linear albeit of gradient 0.91. White [1] has reported such a plot for methyl viologen using data for a series of arene donors (all species in methanol), and obtained a linear plot of gradient $x = 0.9$. Similarly, Murthy and Bhardwaj [23] used MV^{2+} with a series of donors (in ethanol) and determined a gradient of 0.6. Foster [26] has apparently found gradients of between 0.82 and 0.86 for such plots using non-viologen acceptors in non-aqueous solvents.

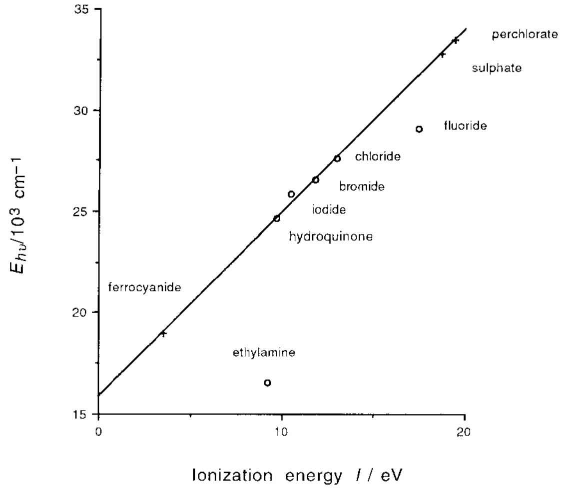

Fig 3. Plot of hn_{CT} for the maximum of charge-transfer bands and the ionization energy I_D of the electron-donor species D (see legend to Table 1 for the source of I_D values).

The point for 'ethylamine' in Fig. 3 does not lie on the line at all, implying either that the donor is not ethylamine but is probably the ethylammonium ion, since the pH for this solution was 6.2. However, as the ethylammmonium donor would be expected to have a *higher* ionization potential than ethylamine (the donor nitrogen has already donated charge to a proton), the anomaly in the position of the point for ethylamine is probably due to a low transition energy. The true nature of the ethylamine donor also explains why the intensity of the CT band is so weak when using 'ethylamine' here).

No values of ionization energy I could be found for the donors of ClO_4^-, SO_4^{2-} and $[Fe(CN)_6]^{4-}$. Assuming that Mulliken's relationship in Eq. (2) is obeyed, we have estimated values of I_D using the energy of optical band maxima in Fig. 3. These values are included in Table 1 for archiving purposes alone. The value for fluoride in this figure also shows a rather poor fit. We assume that ion–solvent effects are responsible for the deviations. The anions of F^-, ClO_4^- and SO_4^{2-} did not evince a CT complex, as gauged by the small equilibrium constant: figures quoted below refer to the association complex instead.

Next, values of equilibrium constant K for complexation were compared with ionization potentials I, and a graph of $\log(K)$ against I was drawn, (Fig. 4). This figure is seen to be linear except for F^-, SO_4^{2-} and ClO_4^- i.e. the three anions not evincing charge-transfer (i.e. the 'complexes' formed with methyl viologen are association pairs).

The linearity of Fig. 4 implies that the extent of charge-transfer is a straightforward function of the ease of ionization of the donor. It also lends legitimacy to the value of I obtained optically for the $[Fe(CN)_6]^{4-}$ anion as donor.

The molar extinction coefficient (ε) and associated oscillator strength (f) of the CT band are enhanced owing to the delocalisation of the electronic charge donated datively on charge transfer.

If the CT absorption band is gaussian (when drawn with the ordinate axis having an energy-related

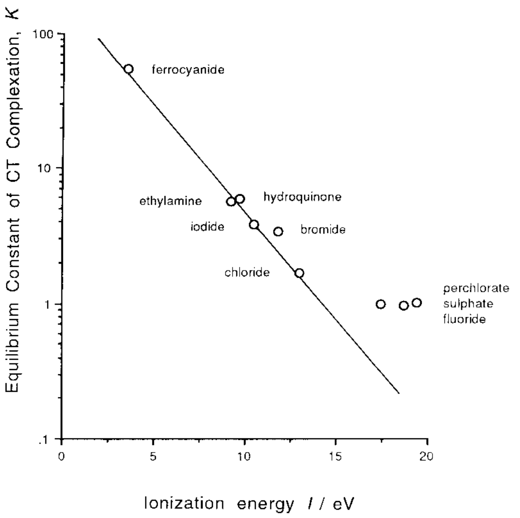

Fig 4. Plot of $\log_{10}(K)$ for the charge-transfer complex against ionization energy I_D of the electron-donor species D (see legend to Table 1 for the source of I_D values).

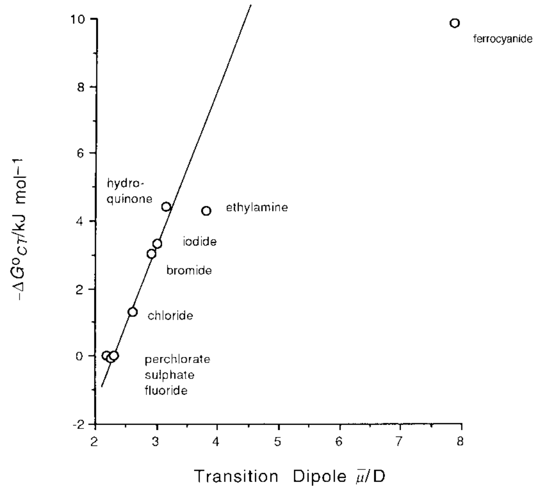

Fig 5. Plot of transition dipole (calculated from the optical charge-transfer band) against the Gibbs function change ΔG^o on charge-transfer complexation.

scale), then the transition dipole $\bar{\mu}$ may be gauged from the optical constants [27] $\upsilon_{\max}$ and $\varepsilon_{\max}$, as Eq. (5):

$$|\bar{\mu}|^2 = 4.25 \times 10^{-20}\left(\frac{\varepsilon_{\max}\bar{\upsilon}_{1/2}}{\bar{\upsilon}_{\max}}\right) \qquad (5)$$

where $\bar{\upsilon}_{1/2}$ is the bandwidth at half band height.

The only optical band in this study that was not of gaussian shape was that for ethylamine: this band was unsymmetrical, probably owing to the presence of a slight (overlapping) second band. There is an equilibrium in solution for this donor ($EtNH_2 + H^+ = EtNH_3^+$), so it is assumed that both amine and ammonium species act as donors, each forming a CT band of different energy. An approximate band width for ethylamine was obtained as $\bar{\upsilon}_{1/2} = 2\times$(frequency range: $\upsilon_{\max}$ to υ at half-height on the low-frequency side of the band). A plot of transition dipole for the CT transition $\bar{\mu}$ against the Gibbs function change on complexation ΔG is relatively linear, (Fig. 5), implying that dipole changes on complexation are actually related to the *extent* of complexation.

The only points not fitting closely on the line in Fig. 5 are those for ethylamine and hexacyanoferrate(II). [The deviation of the point for $EtNH_2$ from the line in Fig. 5 is taken to arise simply from the non-gaussian shape of the band i.e. the value of $\bar{\mu}$ calculated using Eq. (5) is wrong.]

The band for hexacyanoferrate(II) *is* gaussian, so the deviation of the point from the line implies that either the band is broader, and/or of lower energy than expected. In fact, Ulstrup et al. [6] have also analysed the MV^{2+}–$[Fe(CN)_6]^{4-}$ CT band, and similarly found it to be both red-shifted and slightly broader than expected from classical theory. These authors discuss several possible causes for the deviation and state that the most likely reason for the broadening is a range of configurational distances between the two ion-pair components, as argued from the strong dependence of the interionic transition dipoles on the mutual distances and orientation of the components. The large equilibrium constant of complexation evinced by the MV^{2+}–$[Fe(CN)_6]^{4-}$ complex (see Table 1) is again unusually large, suggesting a different energetic route might be involved. An XRD structure of MV^{2+} with the donor of $Ni(CN)_4^{2-}$ shows that the nitrogen of a cyanide ligand points toward the nitrogen of the pyridine rings [28]; solution-phase NMR studies of the MV^{2+}–$[Fe(CN)_6]^{4-}$ complex arrive at the same conclusion [29].

Finally, the deviation of the point for the MV^{2+}–$[Fe(CN)_6]^{4-}$ complex on Fig. 5 yields a further problem: the value of I_D for the $[Fe(CN)_6]^{4-}$ ion (Table 1, as obtained from Fig. 5) could to be in error since other data for this ion (e.g. Fig. 5) deviate strongly from the general trends. It can be argued that the assumptions made in compiling Figs. 3 and 4 are very similar, in which case taking a value of I_D from Fig. 3 for the $[Fe(CN)_6]^{4-}$ ion, and using it in Fig. 4, could be tautologous. Conversely, however, values of I_D for sulphate and perchlorate are more likely to be reliable since the relationship in Fig. 5 *is* obeyed by these polyatomic anions. If the value of I_D for hexacyanoferrate(II) is removed from Fig. 3, then the resultant graph is probably parabolic.

3.3. *Effect of solvent permittivity*

The solubility of methyl viologen *bis*(methosulphate) is rather poor in organic solvents, so we prepared benzyl viologen (BzV, as the dichloride salt) to utilise its superior solubility. The charge-transfer band of BzV^{2+}–$[Fe(CN)_6]^{4-}$ was determined in a range of eight solvents ranging in permittivity [30] from methanol ($\varepsilon_r = 32.7$) to formamide of relative permittivity $\varepsilon_r = 109$. Decreasing the solvent permittivity causes the width of the CT band to decrease, as expected. The CT band width at half peak height (Δ) was determined for each solvent system and plotted against $\sqrt{1/n_D^2 - 1/\varepsilon_r}$. This variable derives from classical electrostatics and represents the movement of a charge through a medium of constant dielectric constant; so, ε_r is the relative 'static' dielectric constant and n_D is the refractive index of the solvent, itself the square root of the optical dielectric constant.

Ulstrup et al. [6] studied a CT system comprising the hexacyanoferrate(II) ion as donor and a novel pyridinium betaine as acceptor. With this system, a plot of Δ vs $\sqrt{1/n^2 - 1/\varepsilon_r}$ was relatively linear but did not pass through the origin indicating that "…small molecular structural changes accompany the [optical CT] excitation…" Although Ulstrup used a betaine system, for which there can be notable redistributions of electronic charge following the charge-transfer transition, even then there was no *overall* charge on the CT complex before and after photo-excitation. The energy of solvent re-organisation should therefore be merely a function of the reciprocal of the distance between the ions of the CT couple. Since there are discrepancies between experimental and calculated values of Gibbs function for solvent re-organisation on excitation (i.e. motion has occurred within the couple) [6], and since changes in structure following electron transfer are so negligible for the $[Fe(CN)_6]^{3-/4-}$ couple that they can be ignored [31], it is perhaps not too fanciful to suppose that the major changes in molecular structure occur *on the viologen*. The non-zero intercept on Ulstrup's graph thus implies that the CT transition is a non-Condon process. We have recently shown [32],

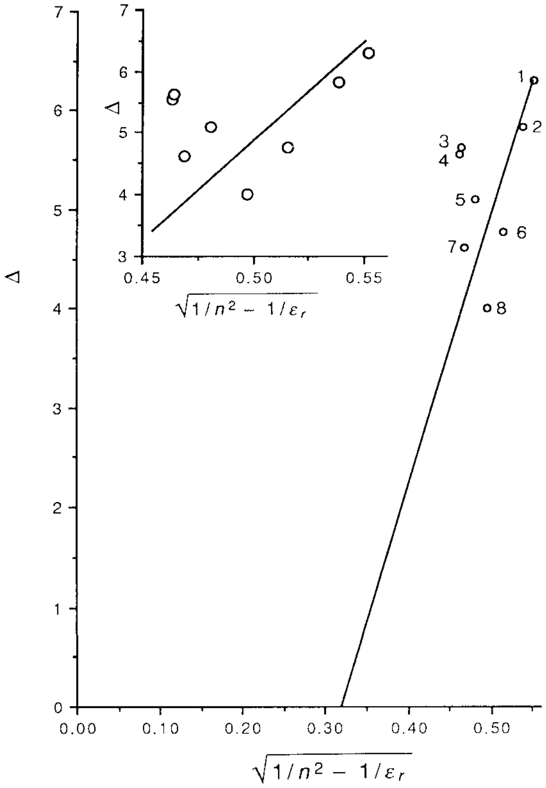

Fig 6. Plot of the width of a CT band at half peak height, Δ against $\sqrt{1/n^2 - 1/\varepsilon_r}$ for the BzV^{2+}–$[Fe(CN)_6]^{4-}$ CT system for a range of eight solvents: 1 = water; 2 = methanol; 3 = DMF; 4 = ethylene glycol; 5 = propylene carbonate; 6 = formic acid; 7 = formamide and 8 = nitromethane. Values of n and ε are from Ref. [30].

using computer molecular modelling that the ground state MV dication is skewed with a sizeable dihedral angle ϕ. This angle decreases (the molecule becomes more planar) on electron uptake to become the radical cation $MV^{+\bullet}$.

The plot in Fig. 6 for the BzV^{2+}-$[Fe(CN)_6]^{4-}$ couple is very similar to Ulstrup's, and is seen to be fairly linear and with a non-zero intercept. If Ulstrup's assignment is correct, then this non-zero intercept is further evidence for a non-Condon CT transition; whilst BzV^{2+} was used here rather than MV^{2+}, the electronic bipyridilium "core" of the two viologens is electronically very similar.

4. Conclusion

Optical and thermodynamic parameters of charge transfer complexation have been determined for methyl viologen in the presence of nine donor species. A simple model of competing equilibria is presented to account for the way the absorbance of an optical CT band decreases as a function of ionic strength. The energy of the CT transition (as determined from the wavelength maximum of the CT band) is a linear function of the ionization energy of the donor, except for donors of fluoride and ethylamine. The changes in Gibbs function on charge transfer correlates well with the change in transition dipole ($\bar{\mu}$), with the exceptions of ethylamine and hexacyanoferrate (II). In both cases, $\bar{\mu}$ is much larger than predicted from ΔG^o_{CT}. Graphs of spectral width at half peak height Δ against standard functions from classical electrostatics implies that the CT transition is a non-Condon process; it is postulated that the molecular motion involves changes in the dihedral angle ϕ between the two pyridinium rings of the viologen dication, with ϕ decreasing on excitation.

Acknowledgements

We thank Mr. Kevin Jones for measurements of spectra in different solvents (Fig. 6). We also thank the Faculty of Science and Engineering, Manchester Metropolitan University, for a research studentship for NMH and the EPSRC for a research studentship for RDP.

Appendix: Modelling of observed absorbance:ionic-strength dependence

Complexation changes the Gibbs function according to the isotherm $-RT \ln K$, where the equilibrium constant K relates to CT complexation, [Eq. (6)]:

$$K = \frac{a(\mathrm{A{:}D})}{a(\mathrm{A})a([\mathrm{D})} \tag{6}$$

If the activities a are rewritten as the product of respective concentrations c and activity coefficients g, then Eq. (6) becomes Eq. (7):

$$K = \frac{c(\mathrm{A{:}D})}{c(\mathrm{A})c(\mathrm{D})} \times \frac{\gamma(\mathrm{A{:}D})}{\gamma(\mathrm{A})\gamma(\mathrm{D})} \tag{7}$$

Eq. (7) is simplified by assuming the ionic activity coefficients to be equivalent, and using a mean ionic activity coefficient $\gamma_\pm$ [Eq. (8)]:

$$K = \frac{c(\mathrm{A{:}D})}{c(\mathrm{A})c(\mathrm{D})} \times \frac{1}{\gamma_{\pm(\mathrm{av})}} \tag{8}$$

So, from the van't Hoff isotherm [Eq. (9)]:

$$\Delta G = -RT\ln\left(\frac{c(\mathrm{A{:}D})}{c(\mathrm{A})c(\mathrm{D})} \times \frac{1}{\gamma_{\pm(\mathrm{av})}}\right) \tag{9}$$

and then converting to $\log_{10}$ and dissembling the K term, Eq. (10) is obtained:

$$\frac{-\Delta G}{2.303RT} = \log[\mathrm{A{:}D}] - \log[\mathrm{A}] - \log[\mathrm{D}] - \log\gamma_{\pm(\mathrm{av})} \tag{10}$$

When an inert electrolyte is added to the solution, the ionic strength I increases, causing the mean ionic activity coefficient ($\gamma_\pm$) to decrease, with a dependence described by the Debye–Hückel laws [33,34]. For consistency, the extended law will be used throughout, [Eq. (11)]:

$$-\log_{\gamma\pm} = \frac{A|z^+z^-|\sqrt{I}}{1+\sqrt{I}} \tag{11}$$

where [34,35] A = 0.5115 for aqueous solutions at 25°C. Substitution of Eq. (11) into Eq. (10) yields Eq. (12):

$$\frac{-\Delta G}{2.303RT} = \log[\mathrm{A{:}D}] - \log[\mathrm{A}] - \log[\mathrm{D}] + \frac{A|z^+z^-|\sqrt{I}}{1+\sqrt{I}} \tag{12}$$

In this study, the absorbance of the CT optical band of the complex is used to monitor its concentration, [A:D]. Provided the complex is the only species to absorb at the wavelength of observation, its concentration is described by the Beer–Lambert law [Eq. (13)]:

$$Abs = c\varepsilon l \tag{13}$$

where all terms have their usual meanings. Substitution for $c = [\mathrm{A{:}D}]$, and with rearrangement, yields Eq. (14):

$$\frac{-\Delta G}{2.303RT} = \log(Abs) - \log(e) - \log(l) - \log[\mathrm{A}] - \log[\mathrm{D}] + \frac{A|z^+z^-|\sqrt{I}}{1+\sqrt{I}} \tag{14}$$

Now, the acceptor species in this study is a relatively weak electrolyte (e.g. see Ref [36] concerning heptyl viologen dibromide) and is involved in separate ion-association equilibria with further ions X [Eq. 15]:

$$A + n\mathrm{X} = \mathrm{AX}_n \tag{15}$$

where n is almost certainly unity. If the equilibrium constant of association is K' [Eq (16)],

$$K' = \frac{[\mathrm{AX}_n]}{[\mathrm{X}]^n[\mathrm{A}]}\left(\frac{1}{\gamma_{\pm(\mathrm{av})}}\right)^n \tag{16}$$

rearranging Eq. (16) and substituting for [A], gives Eq. (17):

$$\frac{-\Delta G}{2{\cdot}303RT} = \log(Abs) - \log(e) - \log(l) - \log\left(\frac{[\mathrm{AX}_n]}{K'[\mathrm{X}]^n}\right) - \log[\mathrm{D}] + (n+1) + \frac{A|z^+z^-|\sqrt{I}}{1+\sqrt{I}} \tag{17}$$

Eq. (17) therefore becomes Eq. (18):

$$\frac{-\Delta G}{2{\cdot}303RT} + \log(\varepsilon) + \log(l) - \log K' + \log[AX_n] = \log(Abs) + \log[\mathrm{X}]^n - \log[\mathrm{D}] + (n+1)\frac{A|z^+z^-|\sqrt{I}}{1+\sqrt{I}} \tag{18}$$

in which $\Delta G, \varepsilon, l, K'$ are all constants at fixed temperature and, since the concentration of acceptor involved in ion association $[\mathrm{AX}_n]$ is always rather small (and can therefore be assumed constant), Eq. (18) simplifies to Eq. (19):

$$k = \log(Abs) + n\log[\mathrm{X}] - \log[\mathrm{D}] + k'\sqrt{I} \tag{19}$$

where k and k' here are simply collections of constants. The extent of complexation is always low, so log[D] will also be effectively constant. So, particularly when the concentration of the inert electrolyte is slight, plots of log(Abs) vs log[X] will be more or less linear for an appreciable concentration range [see Fig. 2 and Eq. (19)]. Furthermore, since the ionic strength I of 1:1 electrolytes is the same as the concentration c, plots of log(Abs) against log(I) will be linear also, again particularly at low [X].

The assumptions inherent in the treatment advanced above are as follows:

1. mean ionic activities are used throughout;
2. molarity and molality have been used interchangeably;
3. only one competing ionic-associative reaction is considered to occur, although others are known to exist; and
4. only the extended form of the Debye-Hückel law is used.

This latter simplification will only affect the exact form of the $\sqrt{I}$ term.

It is also noted that only when I is small [and therefore $\log(I)$ is large and negative] will the Debye–Hückel term become negligible with respect to $\log(I)$. This, together with the assumptions above, causes the non-linearity observed when I is large.

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