Effect of supporting electrolytes on the positions of outer-sphere charge-transfer bands in electronic absorption spectra

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The positions of the outer-sphere charge-transfer bands in the electronic absorption spectra of the EV^{2+}–$[Fe(CN)_6]^{4-}$ system depend on the nature and concentration of supporting-electrolyte cations.

Aromatic N-heterocyclic cations are convenient objects for studying electron-transfer processes.[1–5] The simultaneous presence of these cations and electron-donor anions in aqueous solutions results in the appearance of charge-transfer bands in electronic absorption spectra (EAS). The *N,N'*-dialkyl-4,4'-bipyridinium (alkyl viologen)–hexacyanoferrate(II) systems are most informative for studying electron-transfer processes. A band due to the outer-sphere charge transfer (OSCT) from the $[Fe(CN)_6]^{4-}$ ion to an aromatic cation is observed[1,3] at 18000–20000 cm^{-1}, where the self-absorption of ions is practically absent. A change in the supporting-electrolyte composition affects the positions of bands. The observed shift of band maxima was assumed[1,3] to result from the fact that, in addition to the ion pairs MV^{2+}, $[Fe(CN)_6]^{4-}$ (MV^{2+} is methylviologen), associates in which two $[Fe(CN)_6]^{4-}$ ions are accounted for one MV^{2+} cation or *vice versa* can be formed in this system. In this work, we studied the effect of supporting electrolytes on the position of OSCT bands in associates that include the $[Fe(CN)_6]^{4-}$ ion and a homologue of MV^{2+}, the *N,N'*-diethyl-4,4'-bipyridinium cation (ethylviologen, EV^{2+}).

The compound $EV_{1.5}K[Fe(CN)_6]\cdot 12.5H_2O$ was isolated by the isothermal evaporation ($T = 277$ K) of a solution of potassium hexacyanoferrate (analytical grade) and *N,N'*-diethyl-4,4'-bipyridinium iodide (Aldrich) in the 1:1 molar ratio.

The EAS of freshly prepared solutions in twice-distilled water were measured on a Specord M400 spectrophotometer (Germany) in 1 cm quartz cuvettes at 298 K.

Cyclic voltammograms were recorded on a PARC 273 potentiostat using a glassy carbon electrode at the potential scan rate $v = 5$–100 mV s^{-1}. A saturated calomel electrode was used as the reference electrode. From –0.92 to +0.60 V, the heights of current peaks were proportional to $v^{1/2}$. This fact allowed us to attribute these currents to redox processes uncomplicated by adsorption and chemical stages. Therefore, the half-wave potential ($E_{1/2}$) was determined by averaging the potentials of anodic and cathodic peaks. The potentials were given with reference to a normal hydrogen electrode.

The absorption band in the test system appears in the same spectral range as the bands observed previously.[1–3]

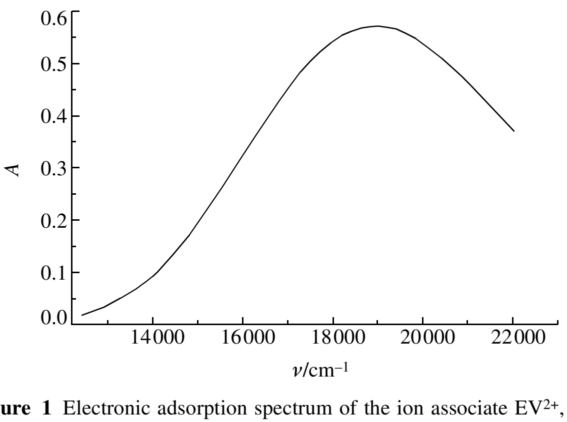

Figure 1 Electronic adsorption spectrum of the ion associate EV^{2+}, nK^+, $[Fe(CN)_6]^{4-}$ in an aqueous solution at 298 K, $C_{[Fe(CN)_6]} = 0.109$ mol dm^{-3}, $C_{EV} = 0.01$ mol dm^{-3}.

Table 1 Half-wave potentials of $[Fe(CN)_6]^{3-/4-}$ and $EV^{2+/+}$ pairs, reorganization energies and OSCT band energies for $EV_{1.5}K[Fe(CN)_6]$ (0.02 mol dm^{-3}) in the presence of supporting electrolytes (1 mol dm^{-3}).

Supporting electrolyte	$E_{1/2}$ $(EV^{2+/+})$/V	$E_{1/2}$ $\{[Fe(CN)_6]^{3-/4-}\}$/V	$\Delta E_{1/2}$/V	$E_{h\nu}$/eV	χ/eV
no electrolyte			0.80[a]	2.30	1.56
Et_4NBr	–0.41	0.30	0.71	2.22	1.55
Me_4NCl	–0.42	0.38	0.80	2.28	1.52
$EtNH_3Cl$	–0.41	0.45	0.86	2.34	1.52
Me_2NH_2Cl	–0.41	0.45	0.86	2.36	1.54
NaCl	–0.42	0.46	0.88	2.37	1.53
$MeNH_3Cl$	–0.42	0.46	0.88	2.39	1.55
KBr	–0.42	0.47	0.89	2.39	1.54
KCl	–0.43	0.47	0.90	2.39	1.53
NH_4Cl	–0.43	0.47	0.90	2.40	1.54

[a] The value corresponds to the standard-potential difference.

In the visible range, the EAS of $EV_{1.5}K[Fe(CN)_6]$ (0.02 mol dm^{-3}) has a band at 18520 cm^{-1}:

$$EV^{2+}, [Fe(CN)_6]^{4-} \xrightarrow{h\nu} EV^{+}, [Fe(CN)_6]^{3-}.$$

The position of the band maximum remained unchanged when the solution was diluted to a concentration of 0.0028 mol dm^{-3}. When supporting electrolytes were added to the system, the position of the band maximum changed. Thus, the EAS of an aqueous solution containing 0.01 mol dm^{-3} EVI_2 and 0.109 mol dm^{-3} $K_4[Fe(CN)_6]$ (Figure 1) has an OSCT band at 19060 cm^{-1}. The addition of KCl or NaCl to this solution resulted in a greater shift of the band to the high-frequency region of the spectrum (Figure 2). The addition of Me_4NCl to the system shifted the band in the opposite direction (Figure 2). As a result, in solutions of equal ionic strength, the positions of OSCT bands differed by 1400 cm^{-1} (~0.2 eV). The tendency illustrated by Figure 2 is similar to the dependence of the formal redox potential of a hexacyanoferrate system on the nature and concentration of supporting cations.[6,7]

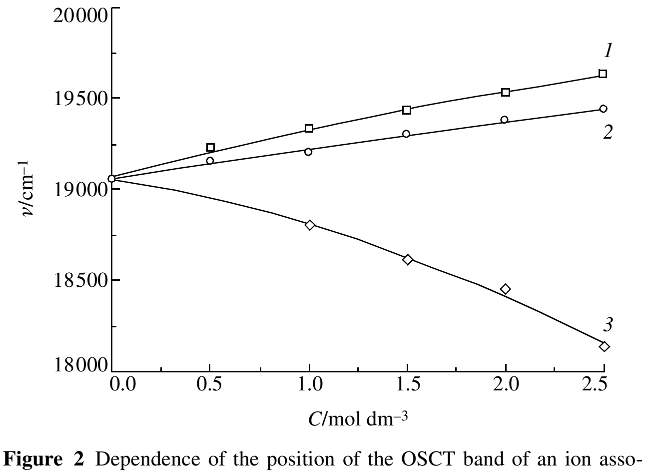

Figure 2 Dependence of the position of the OSCT band of an ion associate in an aqueous solution on the supporting-electrolyte concentration. The conditions are specified in Figure 1. (*1*) KCl, (*2*) NaCl and (*3*) Me_4NCl.

Table 2 The difference between half-wave potentials of redox processes, reorganization energies and the optical transition energy for the ion pair $EV^{2+},[Fe(CN)_6]^{4-}$ in an aqueous solution as functions of the concentration of potassium chloride (Figure 2).

KCl concentration/ mol dm^{-3}	$\Delta E_{1/2}$/V	$E_{h\nu}$/eV	χ/eV
0.0	0.87	2.36	1.53
0.5	0.89	2.38	1.53
1.0	0.90	2.40	1.53
1.5	0.91	2.41	1.53
2.0	0.92	2.42	1.53
2.5	0.92	2.43	1.54

We determined the $E_{1/2}$ of the pairs $[Fe(CN)_6]^{3-/4-}$ and $EV^{2+/+}$ in solutions containing simultaneously both reactants and different supporting electrolytes by voltammetry (Figure 3; Table 1, columns 2–4). The difference of $E_{1/2}$ for two redox systems demonstrated the same dependence on the cation nature as reported earlier for hexacyanoferrate.[6,7] It results from the fact that for $EV^{2+/+}$, the $E_{1/2}$ are practically independent of the nature of supporting-electrolyte cations and amount to –0.42±0.01 V. Table 1 also compares the difference in $E_{1/2}$ with the energies of OSCT bands in the same solutions. An increase in the $E_{1/2}$ difference in the system leads to a corresponding increase in $E_{h\nu}$. The relationship between the redox-pair potential[7] and the $E_{h\nu}$ was also observed when we varied the supporting-electrolyte concentration (Table 2).

Within the framework of the classical Marcus–Hush theory, we can write the following expression for the optical transition energy:[8,9]

$$E_{h\nu} = \Delta E^0 + U_p - U_r + \chi_i + \chi_O + F_\chi.$$

Here, ΔE^0 is the free energy of the reaction; U_p and U_r are the electrostatic work terms for products and reactants, respectively; χ_i, χ_O and F_χ are the components of reorganization energy corresponding to the intramolecular degrees of freedom, the solvent, and the ionic atmosphere, respectively.

A constant half-width of bands (5700 cm^{-1}) gives evidence for the same reorganization energy ($\chi = \chi_i + \chi_O + F_\chi$) for all test systems. The value of ($U_p - U_r$) calculated for the studied range of supporting-electrolyte concentrations is low (0.02–0.04 eV) and independent of the nature of cations. Thus, ΔE^0 makes the main contribution to the change in $E_{h\nu}$. This result can be explained, if we assume that this ionic associate includes the supporting-electrolyte cations, for example:

$$EV^{2+}, K^+, [Fe(CN)_6]^{4-} \xrightarrow{h\nu} EV^+, K^+, [Fe(CN)_6]^{3-}.$$

It also agrees with the data of X-ray diffraction analysis of $EV_{1.5}K[Fe(CN)_6]\cdot 12.5H_2O$.[10] The standard redox potential of the hexacyanoferrate pair is equal to 0.355 V.[6] For the pair $K^+,[Fe(CN)_6]^{4-}/K^+,[Fe(CN)_6]^{3-}$, the potential is 0.41 V, if we take into account data from refs. 6, 11. To explain the dependence of the energy of OSCT band maximum on the supporting-electrolyte concentration (Figure 2), it should be taken into account that a solution with a high alkali-metal concentration can contain associates with several cations in the periphery of $[Fe(CN)_6]^{4-}$ ion,[6,7,11] for example:

$$EV^{2+}, nK^+, [Fe(CN)_6]^{4-} \xrightarrow{h\nu} EV^+, nK^+, [Fe(CN)_6]^{3-}.$$

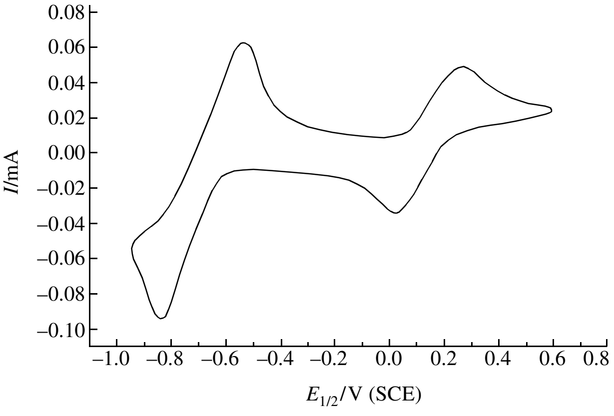

Figure 3 Cyclic voltammogram of a solution of $EV_{1.5}K[Fe(CN)_6]$ (0.02 mol dm^{-3}) in Me_4NCl (1 mol dm^{-3}); the potential scan rate is 5 mV s^{-1}.

In conclusion, a number of factors (solvent,[4] pressure[12] and temperature[1]) affects the position of the OSCT band maximum of the EV^{2+}–$[Fe(CN)_6]^{4-}$ system, and a shift of the redox potential was responsible for all these effects. The nature and concentration of supporting-electrolyte cations were also found to affect the band maximum positions.

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