Salt effects on charge-transfer transitions

María Luisa Moyá*, Amalia Rodriguez and Francisco Sánchez
Departamento de Química Física, Universidad de Sevilla, C/ Profesor García González s/n, 41012 Seville (Spain)

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Abstract

Charge-transfer transitions of $Fe(CN)_5(3\text{-}pzCO_2)^{4-}$ ($pzCO_2$ = pyrazinecarboxylate) and $Fe(CN)_6^{3-}$ are studied in different electrolyte solutions. The applicability of the dielectric continuum theory has been investigated. Results indicate that the electrolyte present in the medium may affect the optical transition energies in two different ways: indirectly, changing the polarity and polarizability of the medium, and directly through ion-pair formation.

Introduction

Medium effects on the energy of charge-transfer absorption bands have been studied by several authors [1–8]. Most of these studies have been made in different pure solvents or in binary solvent mixtures. In the latter media, the observed solvent dependence has been used as an indicator of preferential solvation of solutes by solvent molecules [8b]. This information can be used to account for specific medium effects in binary mixtures on reactivity [9]. The properties of the medium can also be changed by adding a salt, making it possible to study salt effects on charge-transfer transition energies [10–14].

In the present work salt effects on the metal-to-ligand charge-transfer (MLCT) transition energy of $Fe(CN)_5(3\text{-}pzCO_2)^{4-}$ ($pzCO_2$ = pyrazinecarboxylate) and on the ligand-to-metal charge-transfer (LMCT) transition energy of ferricyanide are studied in different electrolyte solutions at 298 K. In a previous work [15] we studied the optical energy shifts of the complexes $Fe(CN)_4(bpy)^{2-}$ and $Fe(CN)_2(bpy)_2$ in different electrolyte solutions. The results did not show clearly the possible participation of ion-pairs in the solvent effects observed. As other authors [11] have studied salt effects on LMCT transition energies of various $Fe^{III}(CN)_5L^{2+}$ complexes, providing valuable information, the choice of the species $Fe(CN)_5(3\text{-}pzCO_2)^{4-}$ to study the role of ion-pairing in the solvatochromic shifts of charge-transfer transitions in salt solutions seemed correct. We have also studied salt effects on the LMCT transition energy of $Fe(CN)_6^{3-}$. In contrast to the $Fe(CN)_5(3\text{-}pzCO_2)^{4-}$ complex, the ferricyanide ion does not have a permanent dipole moment in the ground state. At the beginning, the medium dependence of the LMCT transition would be expected to be quite small. However, in a medium rich in ions and taking into account the high negative charge of the complex, specific interactions (like ion-pairing) could be operative, causing greater changes in the spectral transition energy which could provide information about such interactions.

Experimental

Measurements

Absorption spectra were measured on a Hitachi 150-20 spectrophotometer at 298 K. The measurements were made versus an electrolyte solution blank using matched 1-cm quartz cells. Slow scan rates (0.25 nm s^{-1}) were used to maximize resolution.

Materials

$K_3Fe(CN)_6 \cdot 2H_2O$ was from Merck and was used without further purification. Sodium pentacyano(3-pyrazinecarboxylate)ferrate(II) was synthesized from pentacyanoaquoferrate(II) and the ligand pyrazinecarboxylate according to procedures described previously [16]. Alkali and alkaline earth nitrates and sodium perchlorate were from Merck P. A.; lithium nitrate was from Carlo Erba with similar purity.

All solutions were freshly prepared with deionized water (conductivity $< 10^{-6}$ S cm^{-1}).

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*Author to whom correspondence should be addressed.

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Results and discussion

Both electronic transitions studied appear in the visible region of the spectrum. In this region the absorption bands of the different electrolytes do not interfere. The maximum of the absorption bands could be determined to an accuracy of ±0.5 nm; however, the relative shifts were determined to an accuracy of ±0.3 nm. The assignment of the bands in the absorption spectra are well established [17, 18].

The MLCT transition energy of the complex $Fe(CN)_5(3\text{-}pzCO_2)^{4-}$ in the different media is given in Table 1. Table 2 shows the LMCT transition energy of the ferricyanide ion in the different electrolyte solutions.

An electronic charge-transfer transition involves excitation from a donor orbital in the ground state of a molecule to an acceptor orbital in a Franck–Condon (non-equilibrium) excited state. As stated before [6], following earlier authors [19–25] and considering the fact that the ionic charge of the complexes does not change as a consequence of the optical excitation, the expression for the total polar contribution to the spectral transition energy (ΔE_T) of a polar solute in a polar medium is given by the following equation:

$$\Delta E_T = \frac{\vec{\mu}_1 - \vec{\mu}_0}{b^3}\left[\frac{1-D_{op}}{2D_{op}+1}\right] + \frac{2\vec{\mu}_0(\vec{\mu}_1-\vec{\mu}_0)}{b^3}\left[\frac{1-D_s}{2D_s+1}\right] \qquad (1)$$

where the term $(\vec{\mu}_1 - \vec{\mu}_0)$ is the transition dipole, which is a measure of the change in the electron dipole distribution before and after the excitation and b is the radius of the species. D_s and D_{op} are the static dielectric constant and the optical dielectric constant (square of the refractive index) of the medium, respectively. More general expressions that include effects of apparent dielectric saturation on the solvation energies of ions and dipoles have been derived [26].

If the ground state does not possess a permanent dipole moment, it can be written:

$$\Delta E_T = \frac{\mu^2}{b^3}\left[\frac{1-D_{op}}{2D_{op}+1}\right] \qquad (2)$$

where μ is the dipole moment of the excited state. Since the complex $Fe(CN)_6{}^{3-}$ does not possess a permanent dipole moment in the ground state, eqn. (2) should be adequate to rationalize the salt effects observed in its absorption spectra. Table 2 shows a slight decrease in the LMCT transition energy when increasing the salt concentration present in the medium. This result would be in agreement with eqn. (2), given that an increase in the electrolyte concentration brings about a decrease of the factor $(1-D_{op})/(2D_{op}+1)$ [15] and the slope must be positive (slope $=\mu^2/b^3$). However, taking into account the small shifts observed, the test of eqn. (2) is a rather rough one and no clear conclusions can be obtained from the analysis of the data. In this case the changes in salt concentration affects in a similar way the ground and the excited states.

The complex $Fe(CN)_5(3\text{-}pzCO_2)^{4-}$ possesses a permanent ground state dipole moment, thus it would be expected that eqn. (1) could explain the salt effects observed on its MLCT transition energy. To apply eqn. (1) to the treatment of the data we need the D_s and D_{op} values corresponding to the different electrolyte solutions studied. The D_{op} values were taken from ref. 15, but we have found the static dielectric constant values for only some of the sodium, lithium and potassium nitrate solutions studied [27–29]. With the available D_s and D_{op} values and the optical energy data a dual-parameter relation of the form $E_{op}(\text{MLCT}) = a'(1-D_{op})/(2D_{op}+1) + b'(1-D_s)/(2D_s+1)$ was obtained. A poor correlation coefficient was found for the above relation.

TABLE 1. Values of the MLCT transition energy of the complex $Fe(CN)_5(3\text{-}pzCO_2)^{4-}$ at 298 K in different electrolyte solutions

[Salt] (mol dm^{-3})	$10^{-3}\times E_{op}$ (cm^{-1})											
	0.10	0.20	0.25	0.50	1.0	1.5	2.0	2.5	3.0	4.0	5.0	6.0
LiNo$_3$			21.13	21.16	21.18		21.20		21.24	21.25	21.27	21.32
NaNO$_3$			21.16	21.18	21.22		21.27		21.31	21.35	21.38	21.42
KNO$_3$		21.17		21.18	21.25	21.27	21.30	21.32				
Ca(NO$_3$)$_2$	20.74	20.63		20.54	20.54	20.57	20.61	20.64	20.67			
Sr(NO$_3$)$_2$	20.95	20.89		20.78	20.78	20.80	20.83	20.86	20.89			
NaClO$_4$			21.17	21.20	21.24		21.29		21.33	21.37	21.42	21.44

$10^{-3}\times E_{op}$ (pure water) $= 21.11$ cm^{-1}.

TABLE 2. Values of the LMCT transition energy of the complex $Fe(CN)_6^{3-}$ at 298 K in different electrolyte solutions

[Salt] (mol dm^{-3})	$10^{-3} \times E_{op}$ (cm^{-1})									
	0.25	0.50	1.0	1.5	2.0	2.5	3.0	4.0	5.0	6.0
$LiNO_3$	23.83	23.83	23.83		23.81		23.81	23.80	23.78	23.78
$NaNO_3$	23.83	23.83	23.83		23.83		23.83	23.81	23.80	23.78
KNO_3	23.83	23.83	23.83	23.81	23.81	23.81				
$Ca(NO_3)_2$	23.83	23.81	23.81	23.81	23.80	23.78	23.78			
$Sr(NO_3)_2$	23.83	23.81	23.81	23.81	23.81	23.80	23.78			
$NaClO_4$	23.83	23.83	23.83		23.83		23.83	23.81	23.81	23.81

$10^{-3} \times E_{op}$ (pure water) = 23.83 cm^{-1}.

Actually, for a better way of testing the validity of eqn. (1), more extensive data would be necessary; however, the a' factor found has a negative sign, which is inconsistent with eqn. (1) ($a' = (\bar{\mu}_1 - \bar{\mu}_0)/b^3$), showing the inadequacy of the dielectric continuum theory to explain the salt effects observed. It seems that specific medium effects play an important role in determining the optical energy shifts when changing the concentration of the different electrolytes.

In a previous work Warner *et al.* [11] studied the shifts of the LMCT transition energies of complexes of the type $Fe^{III}(CN)_5L^{2-}$ in different dilute and concentrated electrolyte solutions. They found that the presence of the salt produced a bathochromic shift, which increases with increasing salt concentration. These changes were explained on the basis of ion-pair formation between the iron(III) complex and the metallic cations present in the medium. The LMCT transition in these complexes occurs with an increase in dipole moment in the excited state [10]. Considering that the transition dipole moments should have opposite signs for LMCT and MLCT transitions, it is expected that the MLCT transition of the complex $Fe(CN)_5(3\text{-pzCO}_2)^{4-}$ occurs with a decrease in dipole moment in the excited state (see Fig. 1). Figure 2 shows the plots of E_{op} (MLCT) of the iron(II) complex studied against salt concentration. Three salient features emerge from this Figure: (i) in sodium, potassium and lithium nitrate, as well as in sodium perchlorate solutions, a hipsochromic shift of the transition is found; (ii) for strontium and calcium nitrate solutions the same trend is found in the case of the more concentrated solutions, showing a bathochromic shift for the more dilute ones; (iii) a linear correlation between E_{op} (MLCT) and salt concentration is found when the electrolyte concentration is high ([salt] ⩾ 1 mol dm^{-3}).

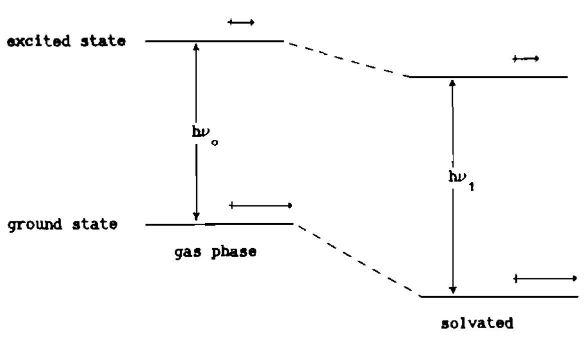

Fig. 1. Influence of a solvation cage on a transition having a decreased dipole moment.

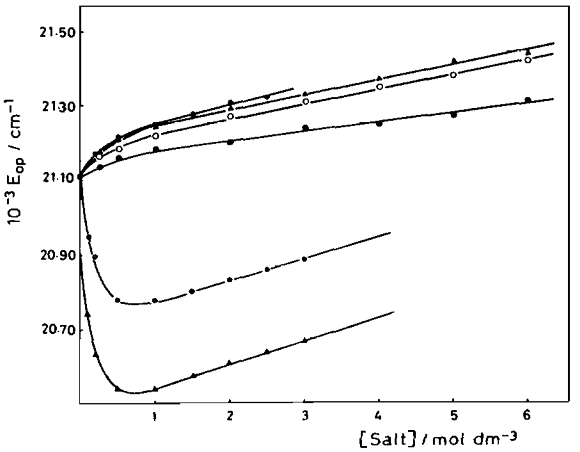

Fig. 2. Plots of the MLCT transition energy of the complex $Fe(CN)_5(3\text{-pzCO}_2)^{4-}$ against electrolyte molar concentration, at 298 K. Salt: (●) $LiNO_3$; (○) $NaNO_3$; (*) KNO_3; (△) $NaClO_4$; (▲) $Ca(NO_3)_2$; (**o**) $Sr(NO_3)_2$.

The presence of an ion in the medium can influence the electronic transition energy of a charge-transfer band directly, that is, forming an ion-pair, or indirectly, through the solvent by producing changes in the solvation of the complexes. Considering that the MLCT transition studied occurs with a decrease in dipole moment in the excited state, the more polar the medium, the more destabilized the excited state species will be, relative to the ground state. Taking into account that the polarity and polarizability of the medium (measured through the static and optical dielectric constants) decreases with increasing electrolyte concentration, the indirect electrolyte influence through the solvent would cause a higher destabilization of the ground state in relation to the excited state, that is, a bathochromic shift with increasing salt concentration would be expected. The experimental data (see Fig. 2) show the opposite trend except in the case of the more dilute alkali earth solutions indicating that other effects must contribute to the observed salt effects.

If the electrolyte influence is through ion-pair formation and taking into account that the complex studied has a high negative charge, it would be expected that the solvatochromic shifts are mainly due to the cation of the salt. In fact, the changes in the optical energy are very similar for sodium perchlorate and sodium nitrate and the sensitivity of the transition energy per mole of cation for both salts is nearly the same. The small differences observed could be related to a higher dissociation grade of the perchlorate salt [30], which would cause a greater effective concentration of sodium ions in these media than in sodium nitrate ones. Nevertheless, a possible specific effect of anions cannot be excluded. Considering a cation influence through ion-pair formation, the site of the aqua-metal cation interaction may be conceivably at either the lone pairs of the coordinated cyanide ligands or the non-coordinated lone pair of the pyrazine π donor ligand and of course at the negative charged carboxylate substituent of the pyrazine ligand. Taking into account that the transition studied is metal-to-ligand, the optical electron transfer would cause a decrease in the electronic density at the cyanide ligands and an increase at the π donor ligand in the excited state in relation to the ground state. Since the solvent molecules cannot change their orientation during the electronic transition, a greater cation-binding at the cyanide ligands for the ground state than the excited state in $Fe(CN)_5(3\text{-}pzCO_2)^{4-}$ is expected and thus a MLCT blue shift upon ion-pairing with salt concentration, as in fact is observed for most of the electrolyte solutions. The aquo-cation interaction at the pyrazine ligand is not expected to change substantially given that the ion-pair formation would be mainly at the carboxylate substituent. On the other hand, the slopes of the linear fraction plots of the optical energy against salt concentration, that is, the sensitivity of the energy shift per mole of M^{n+} follows the order $Ca^{2+} > Sr^{2+} > K^+ > Na^+ > Li^+$, which also suggests a cation influence via ion-pair formation [11]. The bathochromic shift observed for the solutions with low strontium and calcium nitrate concentrations could be related to an indirect influence of the cations. Both of them have a strong polarization power (proportional to q/r) [11] and produce a substantial change in the electric properties of the medium which would cause a decrease in the electronic transition energy. This effect would also be present in the monovalent cation solutions as well as in concentrated bivalent cation solutions, but in these cases the hipsochromic shifts caused by ion-pair formation would prevail determining the experimental trends observed. The fact that the MLCT transition energy in concentrated $Ca(NO_3)_2$ and $Sr(NO_3)_2$ solutions remains below that in pure water, in spite of the hipsochromic shift observed, could also be explained on the basis of this hypothesis.

In conclusion, the salt dependence of the MLCT transition energy of the complex $Fe(CN)_5(3\text{-}pzCO_2)^{4-}$ seems to be the result of two effects: (i) a hipsochromic shift caused by a greater cation-binding for the ground state than the excited state when increasing salt concentration; (ii) a bathochromic shift caused as a consequence of a decrease in the polarity and polarizability of the medium by increasing salt concentration.

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