E2-33: Similarities between charge transfer to solvent transition of solved iodide ion and intervalence transition of Berlin Green

R H Wijayanayake, M A D N Perera
(*Dept. of Chemistry, Univ. of Ruhuna, Matara*)

When a spectrum shows sensitivity to variations such as solvent, temperature, pressure and salt effects, such spectra are assigned as Charge transfer to solvent transition (CTTS).

This is a study to test the above criteria for the spectrum involving intervalence transition in Berlin Green.

Although the 2 theories pertaining to the 2 transitions are different, they are essentially based on F-centre like environment. The sensitivity of these transitions to external stimuli has been explained for the CTTS transition as due to changes in the radius of the potential well, described by the solvent molecules around the iodide ion, while the intervalence transition of Berlin

Green could be explained on the changes in the coulombic destabilization energy expended on transferring an electron from a "C hole" to "N hole" in Berlin Green.

All materials used were of Analar grade. Berlin Green was prepared by adding a saturated solution of ferric oxide dissolved in 4 molar nitric acid to a solution of potassium ferricyanide and the precipitate was boiled with deionized water several times until it was free of K^+ ions.

Perkin Elmer 272 atomic absorption spectrophotometer was used for the determination of Fe, while for C,N & H a Carlo Erba-1186 elemental analyser was used. The composition of Berlin Green (BG) sample was found to be Fe (23%), C (13.9%), N (17.5%), H (4.85%). The composition indicated a formula for Berlin Green as $Fe_4\,[Fe(CN)_6]_3.12H_20$ with 4.9% by weight of water.

UV/Vis spectra were recorded on a Hitachi U3200 and on Carry 14H spectrophotometer. With Carry 14H a special cell was used to hold the solid samples which were heated over a temperature range 20 -210°C in a furnace. The powdered BG was held in a thin (usually 1.0 mm thick) potassium halide disk, which was prepared in a manner similar to that of the KBr disks for IR studies.

The following colours were imparted to KX (X=F,Cl,Br,I) disks on treatment with BG: KF(pale green), KCl dark green, KBr (blue) and KI (dark blue or violet). With the increase of the polarizability (or increase in ionic radii) of the anion in KX the intervalency band shifts from 13000 cm^{-1} in KCl, to 12600 cm^{-1} in KI.

The spectrum of Berlin Green in KI shows clearly a second band around 10200 cm^{-1}. This second band was ascribed to preferential coordination of Fe^{2+} to yield $[FeI_6]^{4-}$. On increasing temperature the intervalency band of Berlin Green in KX shifted to lower wavelength.

KX disks subjected to different pressures yielded different peak positions but their reproducibility was found to be inconsistent. CTTS transition (E_{max}) of I^{-1} ion in various solvents (whose dielectric constant vary from 80 to 25) change from 44208 cm^{-1} to 37037 cm^{-1}. In aqueous alkali chloride solutions E_{max} shifts to higher energies with increase of salt concentrations. On increasing the temperature of an iodide solution. CTTS band was found to shift linearly to longer wavelength. The pressure studies also showed a shift to higher wavelength with increase of pressure.

According to confined model, the CTTS band (E_{max}) of the iodide ion is given by

$$E_{max} = I + h^2/8mr^2_0$$

Where I is the ionization potential of iodide ion and r_0 the radius of the solvation shell. The changes in E_{max} of iodide ion in different media and varying temperatures and pressures have been attributed to corresponding changes in r_0. The intervalence transition of Berlin Green according to Braterman is given by,

$$E'_{max} = 12280 + \frac{e^2}{Ed}\left[\frac{1}{3}\alpha_1 + \frac{1}{3}\alpha_2 - 1\right]$$

Where e-electronic charge. E-relative permittivity of the medium d-distance between Fe^{3+}-Fe^{2-} and α_1 and α_2 are Madullung numbers. Changes in E'_{max} due to KX and at varying temperatures are explained on the basis of accompanying changes in relative permittivity.

This study reveals that the assignment of spectra to CTTS by mere observations of sensitivity to external stimuli does not uniquely define the spectrum as CTTS, since the behaviour of the spectrum of Berlin Green is identical to that of the CTTS spectrum.