A CTTS BAND IN THE SPECTRUM OF $Ru(CN)_6^{4-}$ ION IN AQUEOUS SOLUTION

CLAUDINE GUTTEL and MIRIAM SHIROM

Department of Physical Chemistry, The Hebrew University, Jerusalem (Israel)
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SUMMARY

Environmental and temperature effects on the absorption spectrum of $Ru(CN)_6^{4-}$ ion in solution were used to detect the existence of a charge transfer to solvent (CTTS) band. The salt and solvent effects were related to the theory dealing with the environmental effects on CTTS bands of polyvalent ions. The formation of hydrated electrons from the photoexcitation of the $Ru(CN)_6^{4-}$ in aqueous solutions was attributed to the involvement of the CTTS excited state.

INTRODUCTION

The existence of charge transfer to solvent (CTTS) bands in the spectra of $Fe(CN)_6^{4-}$ [1] and $Mo(CN)_8^{4-}$ [2] ions has been established from the study of environmental effects on the absorption spectra of ions in aqueous and other polar solutions. In both these cases, the CTTS bands are overlapped by intraionic transitions[3,4].

The formation of hydrated electrons from the photoexcited $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$ ions in aqueous solutions[5-8] is attributed to the dissociation of CTTS excited states[9,10]. As suggested[9,10], the CTTS excited states can be reached either by direct excitation, or through internal conversion from other excited states.

The photochemical production of hydrated electrons from other transition metal cyanide complexes, such as $Ru(CN)_6^{4-}$ and $W(CN)_8^{4-}$, in aqueous solutions was also reported[8]. As the existence of CTTS transitions seems to be connected with the electron formation process from photoexcited $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$ ions, we have decided to look for a CTTS band also in the spectrum of the $Ru(CN)_6^{4-}$ ion.

EXPERIMENTAL

Materials

K$_4$ [Ru(CN)$_6$].3H$_2$O was obtained commercially (Alfa Inorganics Inc.) and used as pure substance. D$_2$O (99.7%, Fluka, Puriss) was used without further purification. The water used was triply distilled. All other materials were analytical grade. The ethylene glycol was dried over MgSO$_4$ during 24 hours.

Measurements of absorption spectra

These were carried out with a Cary Recording spectrophotometer Model 14R. The temperature of solutions in the cell compartment was kept constant within $\pm$ 1°C in the range 9–51°C.

RESULTS

All solutions were found to obey Beer's law in the range of 2×10^{-5}–2×10^{-3} M. Figure 1 shows the spectrum of 4×10^{-5} M K$_4$[Ru(CN)$_6$] in various media at

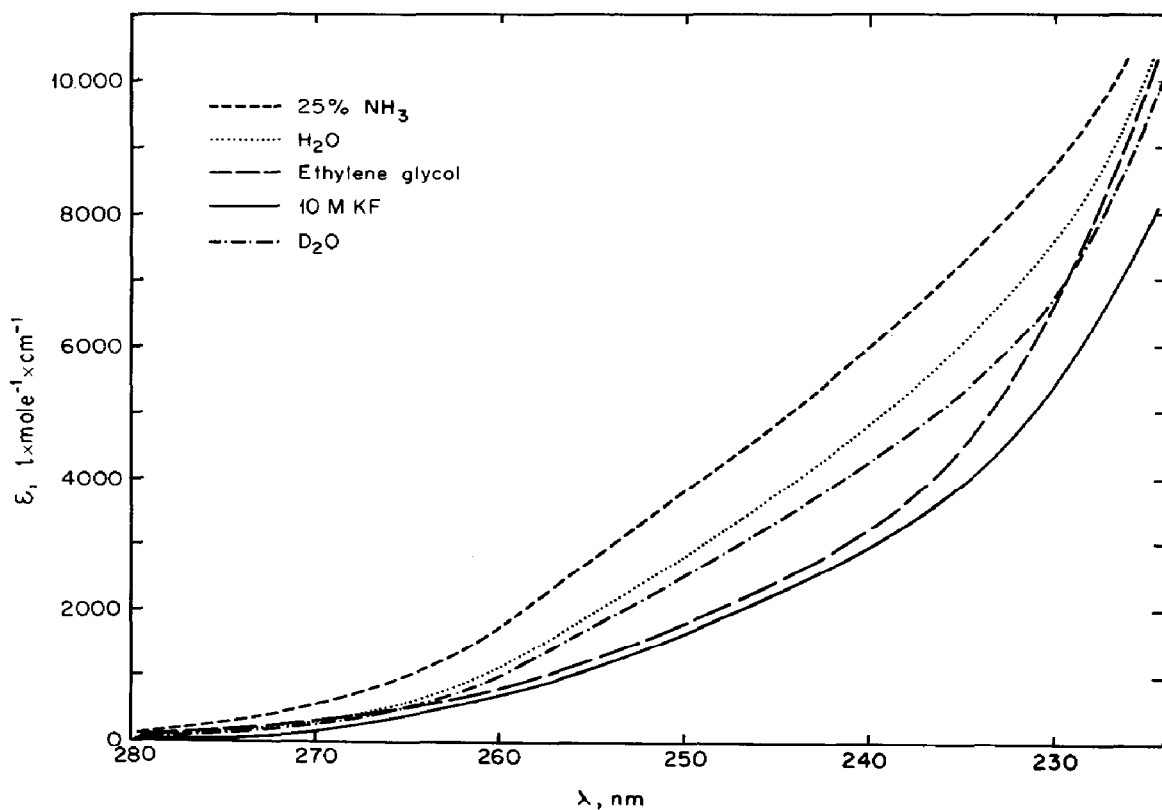Fig. 1. The salt and solvent effects on the absorption spectra of 4×10^{-5} M K$_4$[Ru(CN)$_6$].
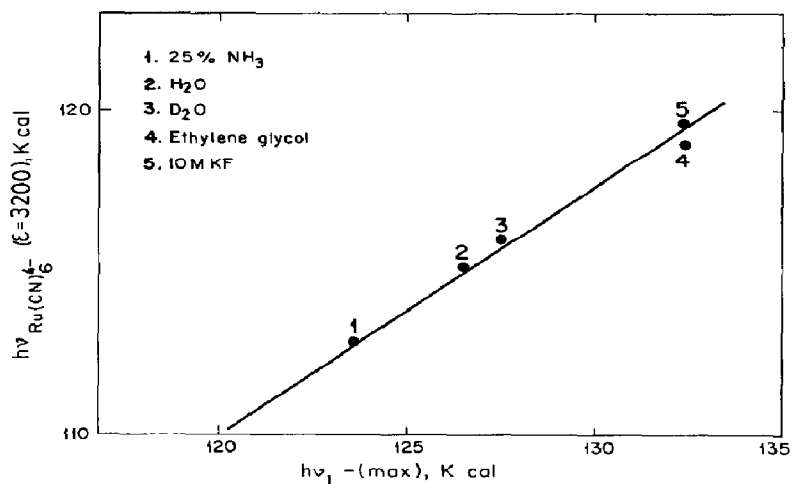
Fig. 2. $h\nu(Ru(CN)_6^{4-})$ at $\varepsilon = 3200$ l mole^{-1} cm^{-1} against $h\nu(I^-)$ (max).
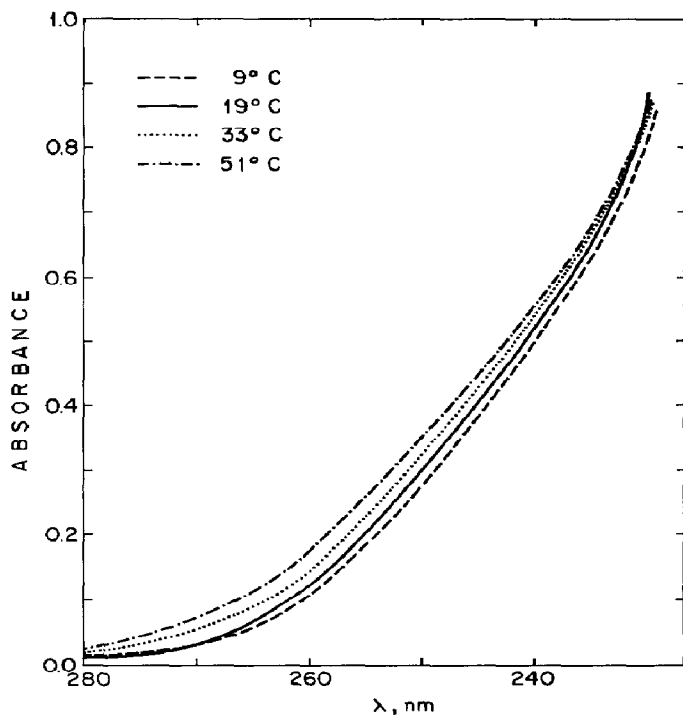

Fig. 3. The effect of temperature on the spectrum of 1×10^{-4} M Ru(CN)$_6^{4-}$ in water.

25° C. As shown, shifts typical for CTTS spectra[11] appear in the region 230–270 nm: $h\nu_{max}$ increases in the order: 25% NH$_3$ < H$_2$O < D$_2$O < ethylene glycol < 10 M KF. Using Burak and Treinin's solvent scale for CTTS transitions[12], the transition energy in various solvents was plotted against $h\nu_{max}$ of I$^-$ in the same solvents at

several absorptivity ε values (between 3200 1 mole^{-1} cm^{-1} and 4200 1 mole^{-1} cm^{-1}) for which the biggest shifts of λ were obtained. The plot of $h\nu(Ru(CN)_6^{4-})$ at $\varepsilon = 3200$ 1 mole^{-1} cm^{-1} against $h\nu(I-)$ (max) is shown in Fig. 2. A linear relation is obtained.

Figure 3 shows the effect of temperature on the spectrum of a 1×10^{-4} M $K_4[Ru(CN)_6]$ in water. The spectrum in the 230–270 nm region undergoes changes which are typical of CTTS transitions[11].

DISCUSSION

Our results give evidence for the existence of a CTTS transition in the 230–270 nm region of the $Ru(CN)_6^{4-}$ spectrum. The CTTS band is overlapped by intramolecular transitions[4].

Treinin's theory for polyvalent ions[13], relating $h\nu_{(max)}$ with the crystallographic radius and the ionic charge Z, was checked in the case of the $Ru(CN)_6^{4-}$ ion. Introducing a value of $R = 4.6$ Å for the crystallographic radius of the $Ru(CN)_6^{4-}$ ion into the equation expressing the slope of the line[13] in Fig. 2, we obtain a value of $Z = -1.5$ for the charge of the $Ru(CN)_6^{4-}$ ion. (The crystallographic radius of the $Ru(CN)_6^{4-}$ ion was calculated using a value of 1.15 Å for the C–N distance, 1.57 Å for the nitrogen van der Waals radius and an estimated value of 1.9 Å for the Ru–C distance[14].)

The relation of the charge and radius of the ion, according to Treinin's theory[13], led to similar values of $Z = -1.85$ for the $Mo(CN)_8^{4-}$ ion [2] and $Z = -2$ in the case of the ferrocyanide ion[1].

Although an error is introduced by the fact that the CTTS bands in the spectrum of the three cyano-complex ions are overlapped by other bands (due to intramolecular transitions), the values derived for the charge of the ions, are lower by a factor of $\geqslant 2$ than their formal charges of -4. As it has been suggested by Stein for the ferrocyanide ion[1,15] it seems to be more reasonable to speak of an operative effective charge $\geqslant 2$ on the surrounding solvent molecules, possibly because of the distribution of the ionic charge over larger volumes, rather than to assume a radius smaller than the crystallographic one. The effective charge acting on the solvent appears to be less than the formal charge.

We suggest that, as in the case of the $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$ ions, the formation of hydrated electrons from $Ru(CN)_6^{4-}$ ions by illumination at 254 nm[8] is due to the involvement of a CTTS state.

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