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Decrease in the yield of photoionization of hexacyanoferrate(II) ions condensed onto partially protonated poly(ethylene imine)

Devidas B. Naik [1], Wolfram Schnabel

Hahn-Meitner-Institut Berlin GmbH, Glienicker Strasse 100, D-14109 Berlin, Germany

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Abstract

The yield of the photoionization of hexacyanoferrate(II) ions is reduced by a factor of about 2.9 provided that the $[Fe(CN)_6]^{4-}$ complexes are bound to partially protonated poly(ethylene imine). This was evidenced by flash photolysis (λ_{inc} = 266 nm) of $K_4[Fe(CN)_6]$ in aqueous solutions containing partially protonated poly(ethylene imine) (PEI). The extent of the decrease in the yield of hydrated electrons becomes larger with increasing polycation concentration and eventually levels off. The reduced ionization efficiency is thought to be related to ion condensation, i.e. to rather strong electrostatic interaction (ion binding) between $[Fe(CN)_6]^{4-}$ and ethylene iminio ions. This is substantiated by the following facts. Upon addition of LiCl the ionization yield increases again (owing to the replacement of bound $[Fe(CN)_6]^{4-}$ ions by chloride ions). Moreover, $[Fe(CN)_6]^{4-}$ ions are less reactive towards O_2 in the presence of partially protonated PEI, and radiolytically generated hydrated electrons react in the presence of $K_4[Fe(CN)_6]$ more slowly with ethylene iminio ions than in its absence. It is tentatively suggested that, in the present case, ion binding to protonated PEI results in an increase in the oxidation potential of the hexacyanoferrate(II) ion.

Keywords: Polyelectrolytes; Complex compounds; Ion condensation; Photoionization

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1. Introduction

Recently, we have found that the biphotonic photoionization of tris(2,2′-bipyridyl) ruthenium(II) complexes is enhanced when the complexes are bound to polyanions such as poly(vinyl sulfate) and poly(methacrylate) or to negatively charged colloidal silica particles [1]. Moreover, it turned out that Ru(II) complexes bound to colloidal silica or poly(vinyl sulfate), in contrast with unbound complexes, are capable of reducing azide radicals [2]. This led to the conclusion that, in these cases, ion binding results in a decrease in the oxidation potential of the complexed metal ions. Being aware of the strong effects resulting from the binding of positively charged metal complexes to polyanions, we have started to investigate inverse systems consisting of negatively charged metal complexes bound to polycations. In this paper we report the photoionization of (negatively charged) hexacyanoferrate(II) ions bound to iminio ethylene groups formed by the protonation of poly(ethylene imine) (PEI):

$$\text{-NH-CH}_2\text{-CH}_2\text{-} + H^+ \longrightarrow \text{-NH}_2{}^+\text{-CH}_2\text{-CH}_2\text{-} \qquad (1)$$

It is known that hexacyanoferrate(II) ions eject electrons upon irradiation in aqueous solution at $\lambda \leqslant 313$ nm via a CTTS process [3]:

$$[Fe(CN)_6]^{4-} + h\nu \longrightarrow ([Fe(CN)_6]^{4-})^* \longrightarrow [Fe(CN)_6]^{3-} + e_{aq}^- \qquad (2)$$

and that the quantum yield of the generation of hydrated electrons $\Phi(e_{aq}^-)$ increases with decreasing wavelength, at $\lambda_{inc} = 266$ nm: $\Phi(e_{aq}^-) = 0.52$ [3]. Therefore we were interested to study whether $\Phi(e_{aq}^-)$ is influenced when hexacyanoferrate(II) ions are condensed onto protonated PEI.

In this connection it should be recalled that protonated PEI readily binds with appropriate polyanions and therefore has been frequently employed as positively charged polyelectrolyte (polycation) in the preparation of polyelectrolyte complexes [4].

2. Experimental details

2.1. Materials

Potassium hexacyanoferrate(II) ($K_4[Fe(CN)_6]$) and PEI (aqueous solution containing 50% PEI; average molar mass, about 5×10^4 g mol^{-1}) were obtained from Aldrich Chemie

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[1] On leave from Bhabha Atomic Research Centre, Applied Chemistry Division, Trombay, Bombay, India.

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and from Sigma-Aldrich Chemie respectively. According to the supplier's information the PEI sample contains, apart from secondary nitrogen atoms corresponding to the structure $-CH_2-CH_2-NH-$ (50%), also primary and tertiary nitrogen atoms (25% each). This is not considered an obstacle in the present work because all these nitrogen atoms are prone to protonation.

2.2. Flash photolysis experiments

Solutions purged with pure argon were irradiated in rectangular quartz cells (1 × 1 cm) with 15 ns flashes of 266 nm light generated by a Nd-doped yttrium aluminum garnet laser system operated in conjunction with two frequency doublers. The optical absorption of hydrated electrons was measured at $\lambda_{obs} = 720$ nm. In aqueous solution containing only $K_4[Fe(CN)_6]$ and no other additive the quantum yield of hydrated electrons is $\Phi(e_{aq}^-) = 0.52$ [3]. On this basis the absorbed dose per flash was calculated from the optical density (OD) measured at 720 nm at the end of the flash.

2.3. Pulse radiolysis experiments

Solutions purged with pure argon were irradiated in rectangular quartz cells (1 × 1 cm) with single 50 ns pulses of 16 MeV electrons generated by a L-band linear accelerator (Vickers). Also here, the optical absorption detection method was applied to measure the formation and decay of hydrated electrons.

2.4. Preparation of solutions

The commercially obtained PEI solution was diluted with water purified by a Millipore system. The pH value of the PEI solutions was adjusted by the addition of aqueous HCl solution. Afterwards, $K_4[Fe(CN)_6]$ was added. Its concentration was kept constant in all experiments: $[K_4[Fe(CN)_6]] = 1 \times 10^{-4}$ mol dm^{-3}. In the text, PEI concentrations are given in terms of base mol per cubic decimeter, i.e. mols of structural repeating units per cubic decimeter. Notably, transparent solutions of both PEI and $K_4[Fe(CN)_6]$ were obtained only at PEI concentrations larger than 1×10^{-3} base mol dm^{-3}. At lower PEI concentrations, complexes of $[Fe(CN)_6]^{4-}$ ions and polycations precipitated. Many of the experiments described below were performed at pH 8.2. On the basis of the amount of HCl added to the PEI solution in this case the resulting degree of protonation is $\alpha_H = 0.03$, i.e. only relatively few repeating units of the polymer carry positive charges. Experiments at higher α_H values could not be performed because the addition of larger amounts of HCl results in a decrease in pH. At the rather high $[H^+]$ concentration corresponding to low pH values, protons react with hydrated electrons with the consequence that hydrated electron lifetimes become shorter than the time resolution of the flash photolysis set-up used in these experiments.

3. Results and discussion

3.1. Photoionization of hexacyanoferrate(II) ions in the presence of partially protonated poly(ethylene imine)

3.1.1. The yield of hydrated electrons as a function of the poly(ethylene imine) concentration and the pH value

Upon irradiation of an argon-saturated solution of $K_4[Fe(CN)_6]$ (1×10^{-4} mol dm^{-3}) the characteristic optical absorption spectrum of hydrated electrons was observed. The transient OD at 720 nm measured at the end of the 15 ns flash was 0.175. When PEI was added, the hydrated electron yield decreased as can be seen from Fig. 1 where the OD at 720 nm is plotted vs. the PEI concentration. Notably, the OD levels off at about 0.06. The observed effect of PEI on the hydrated electron yield can be interpreted on the basis of binding of negatively charged $[Fe(CN)_6]^{4-}$ ions to positively charged iminio ethylene sites of PEI. Consequently, the extent of the decrease in the hydrated electron yield should depend on α_H, the degree of protonation of PEI. α_H increases with decreasing pH value. As can be seen from Fig. 2, where the OD at 720 nm measured at the end of the flash is plotted vs. pH, the extent of the decrease in the hydrated electron yield increases with decreasing pH. In these experiments the

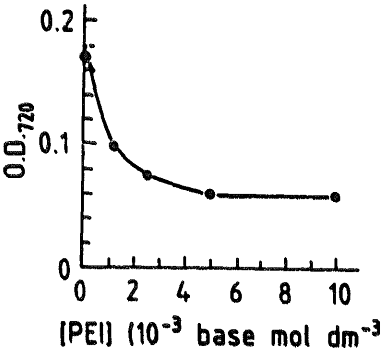

Fig. 1. Effect of partially protonated PEI on the yield of hydrated electrons: the OD at 720 nm measured at the end of the 15 ns flash as a function of the PEI concentration (argon-saturated solutions containing $K_4[Fe(CN)_6]$ (1×10^{-4} mol dm^{-3}); pH 8.2; absorbed dose per flash, 1×10^{-5} einstein dm^{-3}).

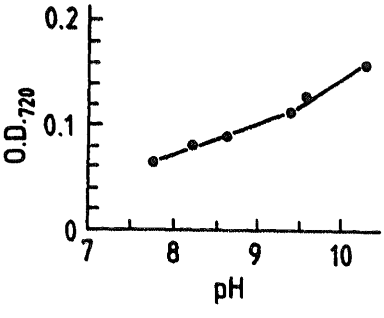

Fig. 2. Effect of PEI on the yield of hydrated electrons: the OD at 720 nm measured at the end of the 15 ns flash as a function of pH (argon-saturated solutions containing $K_4[Fe(CN)_6]$ (1×10^{-4} mol dm^{-3}) and [PEI] (1×10^{-2} base mol dm^{-3}); absorbed dose per flash, 1×10^{-5} einstein dm^{-3}).

PEI concentration was kept constant at $[PEI] = 1 \times 10^{-2}$ base mol dm^{-3}.

Principally, hydrated electrons and hexacyanoferrate(III) ions are generated simultaneously (vide reaction (2)). The absorption spectrum of the hexacyanoferrate(III) ion contains bands at about 300 and 420 nm. Its detection at these wavelengths was nevertheless impossible in the present case because of the rather strong absorptivity of the hydrated electron in this wavelength range.

3.1.2. The lifetime of hydrated electrons as a function of the poly(ethylene imine) concentration and the pH value

Fig. 3 shows a plot of the half-lifetime $\tau_{1/2}(e_{aq}^-)$ of the hydrated electrons as a function of the PEI concentration. During these experiments the $K_4[Fe(CN)_6]$ concentration and the pH value were kept constant. At relatively low PEI concentration (1×10^{-3} base mol dm^{-3}), $\tau_{1/2}(e_{aq}^-)$ is of the same order as in the absence of PEI. However, at higher PEI concentration, $\tau_{1/2}(e_{aq}^-)$ decreases drastically with increasing PEI concentration. Notably, at pH 8.2 and $[PEI] = 1 \times 10^{-3}$ base mol dm^{-3} the concentration of positive charges located at the polymer chains is $\alpha_i[PEI] = 3 \times 10^{-5}$ mol dm^{-3}. Therefore it appears that, at $[K_4[Fe(CN)_6]] = 1 \times 10^{-4}$ mol dm^{-3} and at low PEI concentrations, most of the iminio ethylene groups are protected by condensed $[Fe(CN)_6]^{4-}$ ions and, consequently, are unreactive towards hydrated electrons. At higher PEI concentrations, however, iminio ethylene groups become available, i.e. they can react with hydrated electrons:

$$e_{aq}^- + -NH_2^+-CH_2-CH_2- \longrightarrow -NH-CH_2-CH_2- + H \qquad (3)$$

In fact, the decrease in $\tau_{1/2}(e_{aq}^-)$ observed at $[PEI] \geqslant 1 \times 10^{-3}$ base mol dm^{-3} is thought to reflect the occurrence of reaction (3).

3.1.3. The influence of LiCl on the yield of hydrated electrons

When LiCl was added to a solution of $K_4[Fe(CN)_6]$ (1×10^{-4} mol dm^{-3}) containing PEI (5×10^{-3} base mol dm^{-3}) at pH 8.2 the yield of hydrated electrons increased. As can be seen from Fig. 4 the OD at 720 nm measured at the end of the flash increases upon the addition of LiCl to the solution and levels off at a value about twice that measured in the absence of LiCl. This result is thought to indicate that $Fe(CN)_6^{4-}$ ions attached to ethylene iminio groups are replaced by chloride ions.

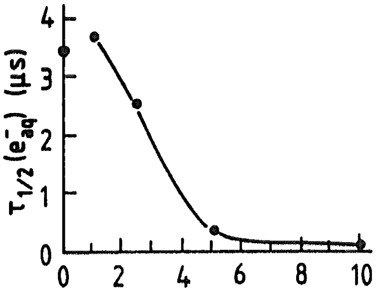

Fig. 3. Effect of PEI on the half-lifetime of hydrated electrons: $\tau_{1/2}(e_{aq}^-)$ as a function of the PEI concentration (argon-saturated solutions containing $K_4[Fe(CN)_6]$ (1×10^{-4} mol dm^{-3}); pH 8.2; absorbed dose per flash, 1×10^{-5} einstein dm^{-3}).

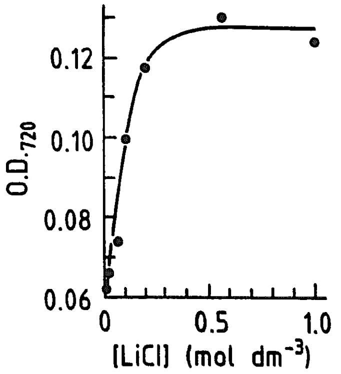

Fig. 4. Effect of LiCl on the yield of hydrated electrons: OD at 720 nm measured at the end of the 15 ns flash as a function of LiCl concentration (argon-saturated solutions containing $K_4[Fe(CN)_6]$ (1×10^{-4} mol dm^{-3}) and [PEI] (5×10^{-3} base mol dm^{-3}); pH 8.2; absorbed dose per flash, 1×10^{-5} einstein dm^{-3}).

3.2. Reaction of hydrated electrons with unprotonated and protonated poly(ethylene imine)

Irradiation of water with high energy radiation results in the formation of hydroxyl and hydrogen radicals and hydrated electrons at the *G* value ratio 2.6:0.6:2.6. The hydroxyl radicals can be converted into much less reactive carbon-centered radicals by the addition of *tert*-butanol. In this work, aqueous solutions containing PEI and *tert*-butanol (0.1 mol dm^{-3}) were irradiated with 50 ns pulses of fast electrons and the absorption of hydrated electrons generated during the pulse was monitored at 720 nm. At $[PEI] = 5 \times 10^{3}$ base mol dm^{-3} and pH 10.3, where PEI is unprotonated, the same value of $\tau_{1/2}(e_{aq}^-)$ was measured as in the case of a solution not containing PEI at pH 7. Therefore it is concluded that unprotonated PEI does not react with e_{aq}^- ($k < 10^5$ dm^3 mol^{-1} s^{-1}). However, when PEI was partially protonated by decreasing the pH value to 8.2, $\tau_{1/2}(e_{aq}^-)$ substantially decreased, indicating that ethylene iminio groups react with hydrated electrons. When solutions containing, in addition to PEI, also $K_4[Fe(CN)_6]$ were irradiated, $\tau_{1/2}(e_{aq}^-)$ increased significantly with increasing $K_4[Fe(CN)_6]$ concentration and leveled off at $[K_4[Fe(CN)_6]] > 2.5 \times 10^{-4}$ mol dm^{-3}, as can be seen from Fig. 5. Obviously, the reactivity of ethylene iminio ions towards hydrated electrons is diminished in the presence of $K_4[Fe(CN)_6]$. Notably, the $K_4[Fe(CN)_6]$ concentration at which $\tau_{1/2}(e_{aq}^-)$ levels off is not very much higher than the concentration of ethylene iminio ions: $\alpha_H[PEI] = 3 \times 10^{-2} \times 5 \times 10^{-3} = 1.5 \times 10^{-4}$ mol dm^{-3}. Therefore these results suggest that $Fe(CN)_6^{4-}$ ions added to PEI solutions are rather strongly attached to the positively charged sites of the polymer and thus reduce its reactivity towards hydrated electrons.

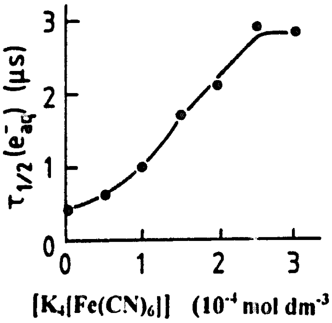

Fig. 5. Pulse radiolysis of Ar-saturated aqueous solutions (pH 8.2) containing PEI (5×10^{-3} base mol dm^{-3}), *tert*-butanol (0.1 mol dm^{-3}) and $K_4[Fe(CN)_6]$. $\tau_{1/2}(e_{aq}^-)$ as a function of the $K_4[Fe(CN)_6]$ concentration.

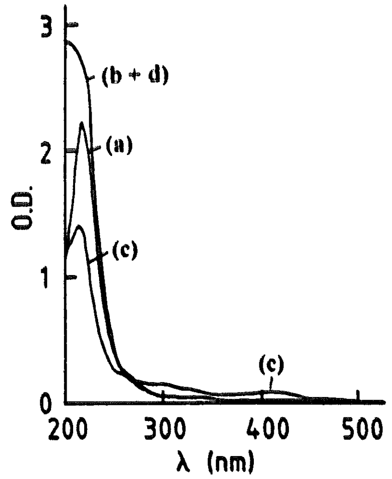

Fig. 6. Photo-oxidation of $[Fe(CN)_6]^{4-}$ ions in aerated aqueous solution at pH 8.2: optical absorption spectra recorded with $K_4[Fe(CN)_6]$ solutions before (curves (a) and (b)) and after (curves (c) and (d)) a 48 h exposure to daylight in the absence (curves (a) and (c)) and the presence (curves (b) and (d)) of partially protonated PEI (1×10^{-3} base mol dm^{-3}) ($[K_4[Fe(CN)_6]]=1\times10^{-4}$ mol dm^{-3}).

3.3. The oxidation of hexacyanoferrate(II) complexes

Hexacyanoferrate(II) slowly oxidizes to hexacyanoferrate(III) in O_2-containing aqueous solution at pH 8.2 which causes a decrease in the absorption band at 218 nm and the formation of new absorption bands at about 300 and 420 nm. The oxidation is strongly retarded when partially protonated PEI ($\alpha_H = 0.03$) is present in the solution. This can be seen from Fig. 6 where optical absorption spectra recorded with potassium hexacyanoferrate(II) solutions exposed for 48 h to daylight in the absence and presence of PEI are presented. The daylight exposure does not bring about any change in the absorption spectrum of the PEI containing solutions. This result suggests that $Fe(CN)_6^{4-}$ ions are condensed onto partially protonated PEI and that, thereby, the oxidation potential of the complex is increased. This could explain why the oxidation of the hexacyanoferrate(II) ion is strongly retarded or inhibited.

4. Conclusions

This paper shows that the yield of photoionization of hexacyanoferrate(II) ions in aqueous solution is reduced by the presence of partially protonated PEI. Moreover, the spontaneous oxidation of hexacyanoferrate(II) ions is strongly retarded by partially protonated PEI. These effects are explained on the basis of ion condensation, i.e. strong electrostatic interaction between positively charged ethylene iminio sites in the polymer chain and negatively charged hexacyanoferrate(II) ions. Evidence that ion condensation is responsible for the observed effects comes from two observations.

(a) The reduction in the ionization yield is counteracted by the addition of another low molecular electrolyte (LiCl) to the solution. This is in accordance with the replacement of $Fe(CN)_6^{4-}$ ions bound to ethylene iminio sites by chloride ions.

(b) The rate of the reaction of hydrated electrons with ethylene iminio sites is slowed down when $K_4[Fe(CN)_6]$ is added to the solution. Also this effect is in accordance with electrostatic binding of hexacyanoferrate(II) ions to the positively charged sites of the polymer.

A possible explanation of the observed effects might be that in the present case ion binding results in an increase in the oxidation potential of the metal complex. It has been pointed out by a reviewer that photogenerated electrons would recombine rapidly with hexacyanoferrate(III) ions when the latter are condensed onto PEI. In this case the yield and lifetime of hydrated electrons should decrease simultaneously with increasing PEI concentration. However, a comparison of the data presented in Figs. 1 and 3 reveals that this is not the case. The yield of hydrated electrons drops off much faster than the half-life. In fact, at low PEI concentrations the half-life is not affected (within the error limit). On the contrary, at high PEI concentrations, where the product α[PEI] exceeds the hexacyanoferrate(II) concentration, $\tau_{1/2}(e_{aq}^-)$ drops off significantly. Here, hydrated electrons react with ethylene iminio ion sites, preferentially with those not shielded by condensed hexacyanoferrate(II) ions.

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