Short Communication

Interaction of Fe^{2+}/Fe^{3+} and Ti^{3+}/Ti^{2+} with Chromotropic Acid: Conductometric and Spectrophotometric Studies

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Summary

This paper reports the results of investigations into photo-chemical oxidation and reduction of Fe^{2+}/Fe^{3+} and Ti^{3+}/Ti^{2+} redox systems, that are used to constitute a redox cell. The investigations have been carried out with the object of developing a suitable photo activator to charge redox cells by photochemical means. The present work investigates the photo-oxidation of Fe^{2+}/Fe^{3+} and the photo-reduction of Ti^{3+}/Ti^{2+} in presence of chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid).

Introduction

Redox cells have been examined as rechargeable battery systems for more than two decades [1]. In recent times NASA has developed a Ti–Fe redox battery system for load-levelling applications [2]. It has been considered that the charging of redox batteries be carried out by the conventional method of using electricity. Redox systems can, however, be used for another important purpose, namely, the storage of solar energy. If this goal is achieved successfully, redox battery systems may emerge as a useful source of primary energy for utility applications.

Charge-transfer complexes are substances that allow transfer of electrons between metal ions and ligands. The charge transfer causes splitting of the energy levels of the interacting species [3]. The complexes are formed when the ionisation potential of the donor is sufficiently low, and the electron affinity of the acceptor is sufficiently high, to permit the transfer of an electron from the donor to the acceptor. The complex compounds can be grouped broadly into anionic and cationic species. The anionic species exhibit intense absorption bands in the u.v. range; this is due to charge

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transfer from a hydrated ion that leads to the formation of a free radical with the electron remaining in association with the hydration sphere. The absorption bands observed with cationic species are also due to charge transfer that occurs in conjunction with internal d-d or f-f transitions. The formation of charge-transfer complexes can be followed by conductometric titration [4, 5].

Photon-induced oxidation/reduction reactions are being extensively studied in respect of the photochemical conversion of solar energy [6, 7]. For example, cells based on the thionine–Fe^{2+} system have been investigated [8, 9]. Recently, Rajadurai and Regis [10] examined the photochemistry of Co(II) complexes with dithiocarbamate ligands, and their use in photogalvanic cells. Yamase and Ikawa [11] studied the photogalvanic effect in alkylammonium molybdate, based on photo-reduction of Mo^{6+} to Mo^{5+}. This effect was also studied by Goldstein [12] for a system based on rubidium ions in THF solution.

An attempt has been made to develop a photon-trapping agent (*i.e.*, a charge-transfer complex) that will be suitable for the photo-oxidation of Fe^{2+} to Fe^{3+} and the photoreduction of Ti^{3+} to Ti^{2+}. The objective is ultimately to use solar energy for charging redox batteries in place of mains electricity. The investigations are, at present, confined to the study of the formation of charge-transfer complexes with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) using the techniques of absorption spectroscopy and conductometric titration against solution pH.

Experimental

Ferrous chloride solution (0.1 M) was prepared by dissolving $FeCl_2 \cdot 4H_2O$ (Fluka guaranteed reagent) in the minimum quantity of hydrochloric acid (Analytical Reagent) and then diluting to the required volume with double-distilled water. Solutions of titanium(III) chloride (0.1 M) and chromotropic acid (0.05 M) were prepared by using $TiCl_3$ (VEB Laborchemie, Apolda guaranteed reagent) and BDH grade reagent, respectively, in double-distilled water. The pH of the solution was maintained at 5.0.

An Elico digital pH meter was employed for pH measurement. A 1 ml sample of the stock chromotropic acid solution was diluted to 50 ml with double-distilled water and then titrated with the $FeCl_2$ solution at room temperature. The change in conductivity of the acid solution as a function of the dropwise addition of $FeCl_2$ was recorded using a Toshniwal digital conductivity meter.

An Elico spectrophotometer (Model GS 886C) was used for the spectrophotometric studies. Optical density *versus* time curves were obtained for a 5 ml chromotropic acid + 15 ml $FeCl_2$ solution, both at room temperature (in the dark) and under exposure to a u.v. lamp (Ultraviolet Products Inc) of wavelength 254 nm. This experimental procedure was repeated for $TiCl_3$ solutions.

Results and discussion
Fe^{2+}/Fe^{3+} system

Figure 1 shows the variation in the conductivity of the chromotropic acid solution with regular addition (dropwise) of $FeCl_2$ solution. The de-
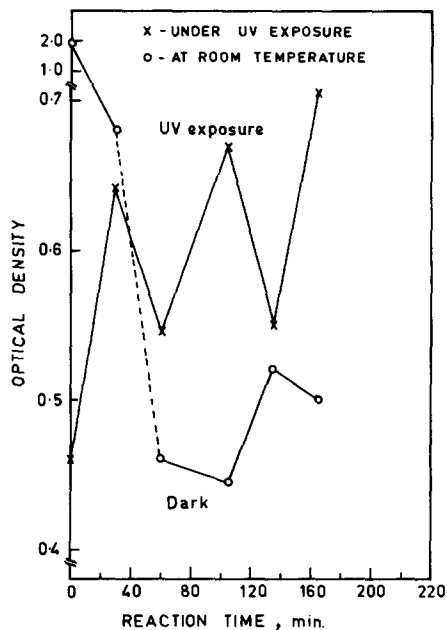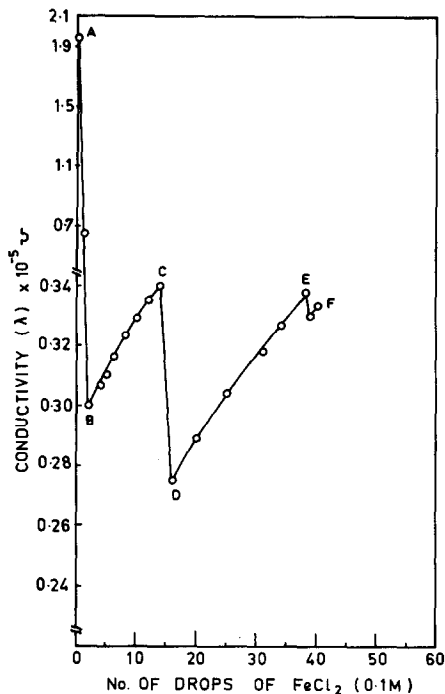

Fig. 1. Conductometric titration of chromotropic acid with ferrous chloride.

Fig. 2. Spectrophotometric studies of chromotropic acid/ferrous chloride solution.

crease in conductivity over the AB region of the curve indicates the addition of free protons from the $FeCl_2$ solution to the sulphonic groups of the chromotropic acid. The subsequent increase in the conductivity over the BC region is due to the release of H^+ ions from the hydroxyl groups of the chromotropic acid. No complex formation occurs at this stage. In this process, an electron transfer takes place that results in the oxidation of Fe^{2+} ions to Fe^{3+} ions. A sharp decrease in conductance is observed over the CD region which is attributed to the rapid formation of a complex between chromotropic acid and Fe^{3+} ions. With the further addition of Fe^{2+}, increasing amounts of Fe^{3+} are generated and an unstable Fe^{3+} complex is formed (component EF of the curve) with the immediate release of Fe^{3+} ions and the return of the organic complex molecule to the original state of chro-

motropic acid. These observations demonstrate clearly the reversibility of the complex formation.

Figure 2 gives the optical density *versus* time curves obtained at room temperature (in the dark) and under u.v. exposure. It is interesting to note the striking behaviour exhibited by chromotropic acid. The optical density at room temperature (dark) is the reciprocal of the obtained on exposure to u.v. radiation. The reaction under u.v. exposure is followed by unstable complexation between chromotropic acid and Fe^{3+} ions, thus making it reversible with no precipitation. On the other hand, the reaction in the dark is followed by the formation of a stable complex. The proposed reaction scheme is shown in Fig. 3.

A. ON UV EXPOSURE

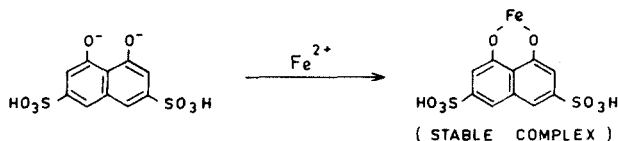$$\tfrac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2 OH^-$$

$$2 OH^- + 2H^+ \longrightarrow 2 H_2O$$
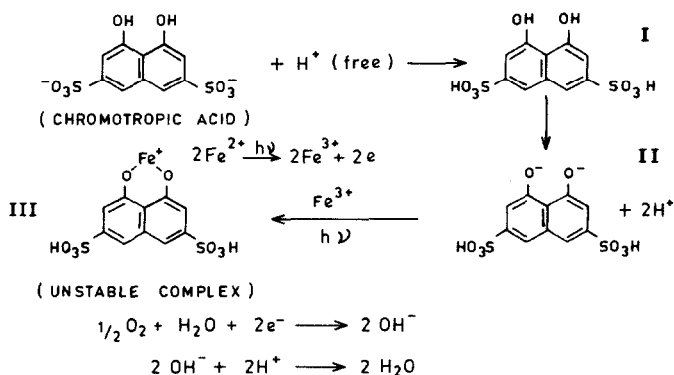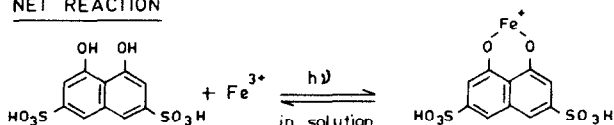
NET REACTION

B. IN DARK

FROM II

Fig. 3. Scheme for reaction between chromotropic acid and Fe^{2+}/Fe^{3+} system.

Ti^{3+}/Ti^{2+} system

The variation of the conductivity of chromotropic acid solution with the continuous addition (dropwise) of titanium(III) chloride is given in

Fig. 4. It can be seen that there is an almost linear increase in conductance to a maximum value at which a short, but distinct, decrease in conductance is observed which is then followed by a sharp increase. The latter phenomena are due to rapid complex formation (complex ratio is 1:3) and instant removal of H^+ ions from the 1- and 8-hydroxyl groups of the chromotropic acid. Further increase in conductivity is small with the addition of Ti(III) ions.
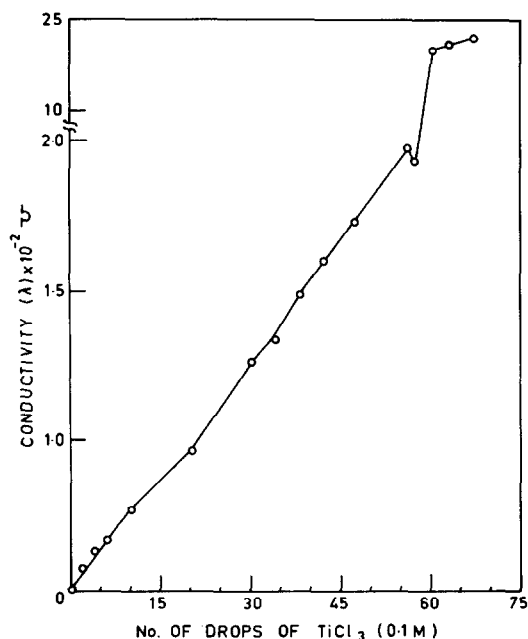

Fig. 4. Conductometric titration of chromotropic acid with titanium trichloride.

The optical density *versus* time curve recorded both under u.v. exposure (254 nm) and in the dark is presented in Fig. 5. As observed with the Fe^{2+}/Fe^{3+} system, the optical density under u.v. exposure is the reverse of that observed in the dark. This finding clearly shows that the reaction under u.v. exposure *is* reversible, and involves the formation of a stable, soluble complex of Ti(II) with chromotropic acid. This is further confirmed by the fact that no precipitation is observed. By contrast, the reaction in the dark at room temperature proceeds irreversibly. The proposed reaction mechanism is given in Fig. 6.

Conclusion

From the above results, it can be concluded that chromotropic acid can be used successfully as a photon-trapping agent for the photo-reduction
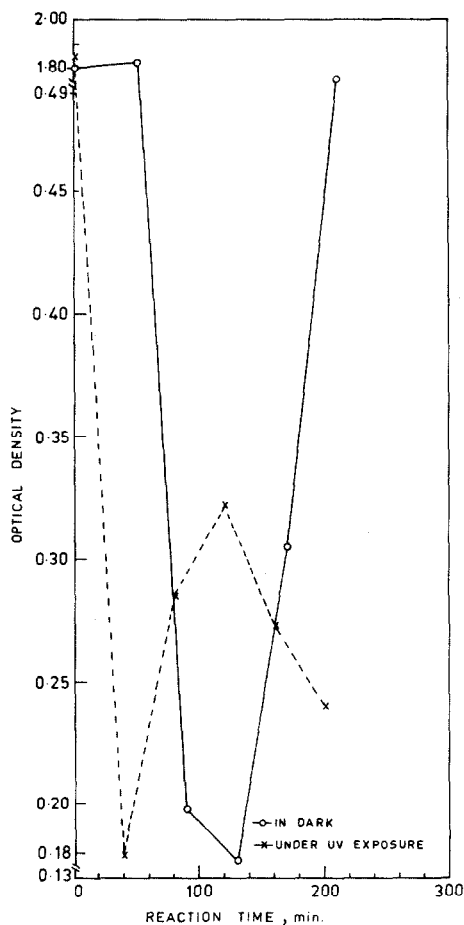
Fig. 5. Spectrophometric studies of chromotropic acid/titanium trichloride solution.

of Ti^{3+} to Ti^{2+} and the photo-oxidation of Fe^{2+} to Fe^{3+}. In other words, photochemical energy is transformed into chemical-bond energy, *i.e.*, the basic process for photogalvanic cells.

It is interesting to note that the Fe(III) forms a metastable soluble complex with chromotropic acid on exposure to light, while Ti(II) forms a stable soluble complex. This behaviour is extremely beneficial for Ti^{2+}/Fe^{3+} redox cells as the two desired conditions are met with by a single complexing agent. Fe(II) and Ti(III), on the other hand, form ordinary complexes.

ON UV EXPOSURE

$$2\ OH^- \xrightarrow{h\nu} \tfrac{1}{2}O_2 + H_2O + 2e$$

$$2\ Ti^{3+} + 2e \xrightarrow{h\nu} Ti^{2+}$$

(SOLUBLE COMPLEX)
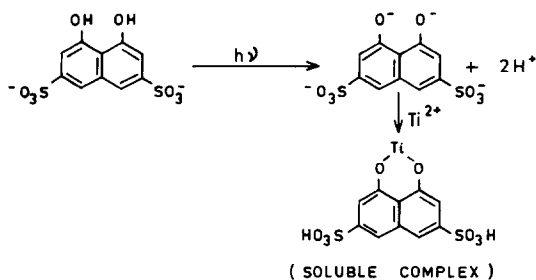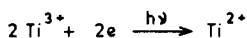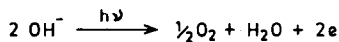
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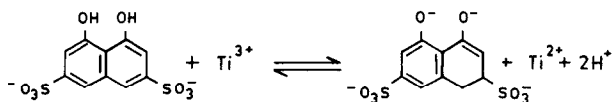

Fig. 6. Scheme for reaction between chromotropic acid and Ti^{2+}/Ti^{3+} system.

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