

# The Photogalvanic Effect of Fe(II)- $\beta$ -Diketonate/Thionine Systems in Aqueous Acetonitrile

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**Summary.** The photogalvanic effect of ferrous *bis*-(acetylacetonate) (Fe(II)(*acac*)<sub>2</sub>) and ferrous *bis*-(trifluoroacetylacetonate) (Fe(II)(*tfac*)<sub>2</sub>) complexes in aqueous acetonitrile thionine dye solutions has been studied in a photogalvanic cell of 70 cm<sup>3</sup> capacity with identical platinum electrodes (area: 0.25 cm<sup>2</sup>) using visible light (80 mW/cm<sup>2</sup>) at 25 °C. The theoretical Sunlight Engineering Efficiency (SEE) was determined for both complexes and it was found that the best SEE was obtained when Fe(II)(*tfac*)<sub>2</sub> was used at a concentration of  $1.5 \times 10^{-4}$  mol/dm<sup>3</sup> with a thionine concentration of  $1 \times 10^{-4}$  mol/dm<sup>3</sup> at *pH* = 4 in 40% aqueous acetonitrile. Effects of incident light intensity and temperature on the photogalvanic performance and the action spectrum of the present system were also investigated. A mechanism of the photoredox reaction between the Fe(II)-complex and the dye molecule is proposed.

**Keywords.** Photogalvanic effect; Ferrous *bis*-( $\beta$ -diketonate); Thionine.

## Der photogalvanische Effekt von Fe(II)- $\beta$ -Diketonat/Thionin-Systemen in wäßrigem Acetonitril

**Zusammenfassung.** Der photogalvanische Effekt von Eisen(II)-*bis*-(acetonylacetonat) (Fe(II)(*acac*)<sub>2</sub>) und Eisen(II)-*bis*-(trifluoracetylacetonat) (Fe(II)(*tfac*)<sub>2</sub>) in wäßriger acetonitrilischer Thioninlösung wurde in einer photogalvanischen Zelle (70 cm<sup>3</sup>) mit identischen Platinelektroden (Fläche: 0.25 cm<sup>2</sup>) mit sichtbarem Licht (80 mW/cm<sup>2</sup>) bei 25 °C untersucht. Für beide Komplexe wurde die theoretische Sunlight Engineering Efficiency (SEE) bestimmt; der beste SEE-Wert wurde für Fe(II)(*tfac*)<sub>2</sub> bei einer Konzentration von  $1.5 \times 10^{-4}$  mol/dm<sup>3</sup> bei *pH* = 4 in 40%igem Acetonitril gefunden (Thioninkonzentration:  $1.0 \times 10^{-4}$  mol/dm<sup>3</sup>). Effekte, die durch Änderung der Lichtintensität und der Temperatur hervorgerufen werden, werden diskutiert. Ein Mechanismus für die Photoredoxreaktion zwischen dem Fe(II)-Komplex und dem Farbstoffmolekül wird vorgeschlagen.

## Introduction

The photogalvanic effect relies on the excitation of a dye molecule by light to induce a redox reaction with a reduced metal ion yielding high energy products. Such products can loose their energy electrochemically like an ordinary battery. Photo oxidation-reduction reactions are often studied in connection with the photochemical

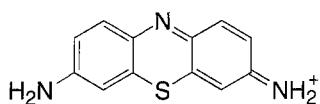


Fig. 1. The oxidized form of thionine ( $Th^+$ ).

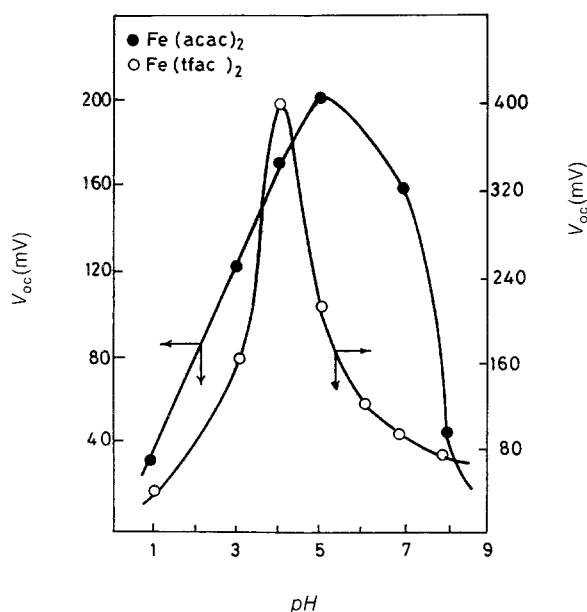
conversion of solar energy [1,2]. The thionine-ferrous sulfate system provides a well-known example of the photogalvanic effect [3–6]. Cells based on this system have been extensively studied [7].

The main thrust of these studies has been to provide an understanding of the various factors governing the performance and efficiency of these systems. It has been demonstrated [8–11] that the optimum performance of the photogalvanic cell (highest power efficiency) may be achieved by careful choice of  $pH$ , temperature, concentrations of the dye and the reducing agent (*e.g.* metal chelate complex), and the conductivity of the electrolyte medium. It has been shown that for the methylene blue/vanadium *tris*-( $\beta$ -diketonate) photogalvanic system the voltage efficiency is strongly dependent on the type of the  $\beta$ -diketone used [9]. Introduction of an electron donating group drastically reduces the photovoltage, whereas an electron withdrawing group substantially enhances the photovoltage efficiency of the photogalvanic cell. It has also been demonstrated that using aqueous-polar organic solvents instead of pure water greatly improves the performance of a photogalvanic system [7, 8, 11, 12, 13].

In this paper, we describe the photogalvanic effect of a photo redox system based on the Fe(II)-*bis*-(acetylacetonate) and Fe(II)-*bis*-(trifluoroacetylacetonate)/thionine redox couples in aqueous acetonitrile solutions. The structure of the oxidized form of thionine ( $Th^+$ ) is shown in Fig. 1.

## Results and Discussion

The main objective of the present work was to investigate the effect of structural changes in the  $\beta$ -diketonate ligand on the photoredox characteristics of Fe(II)-*bis*-( $\beta$ -diketonate) complexes in conjunction with thionine dye in aqueous acetonitrile solution. It is well established that the performance of photogalvanic systems is very sensitive to variations in the  $pH$  of the electrolyte [7]. In order to investigate the effect of  $pH$  in the present system, we have varied the  $pH$  of the aqueous acetonitrile solution (using citrate buffer) from 1 to 9. The results shown in Fig. 2 indicate that the highest photo voltage of the photogalvanic cell was produced at a  $pH$  of 4 for Fe(II)(*tfac*)<sub>2</sub>/thionine and of 4–5 for Fe(II)(*acac*)<sub>2</sub>/thionine. Other parameters, such as the concentrations of the photosensitizing dye (thionine) and that of the metal complex, the light intensity, and the composition of the aqueous acetonitrile medium, were also studied in connection with the photogalvanic cell performance. The results presented in Table 1 summarize optimum conditions required to achieve a maximum power output for both Fe(*acac*)<sub>2</sub> and Fe(*tfac*)<sub>2</sub>/thionine systems. These results clearly show the strong dependence of the efficiency of the photogalvanic cell upon the electronic structure of the Fe(II)-*bis*-( $\beta$ -diketonate) complex. The presence of an electron withdrawing substituent such as the trifluoromethyl group greatly enhances the photo oxidation of the metal species in these complexes by the photochemically excited thionine dye molecules. The same effect was reported by



**Fig. 2.** The variation of the photo potential of  $\text{Fe}(\text{acac})_2$  (●) and  $\text{Fe}(\text{tfac})_2$  (○) with  $pH$  (citrate buffer); thionine concentration:  $1.0 \times 10^{-4} \text{ mol/dm}^3$ ,  $[\text{Fe}(\text{acac})_2] = 1.1 \times 10^{-4} \text{ mol/dm}^3$ ,  $[\text{Fe}(\text{tfac})_2] = 1.5 \times 10^{-4} \text{ mol/dm}^3$ , 40% aqueous acetonitrile solution, temperature:  $25^\circ\text{C}$

**Table 1.** Conditions for optimum photogalvanic cell performance of ferrous bis-( $\beta$ -diketonate)/thionine in aqueous acetonitrile medium; concentration of thionine;  $1.0 \times 10^{-4} \text{ mol/dm}^3$ ,  $I_0 = 80 \text{ mW/cm}^2$

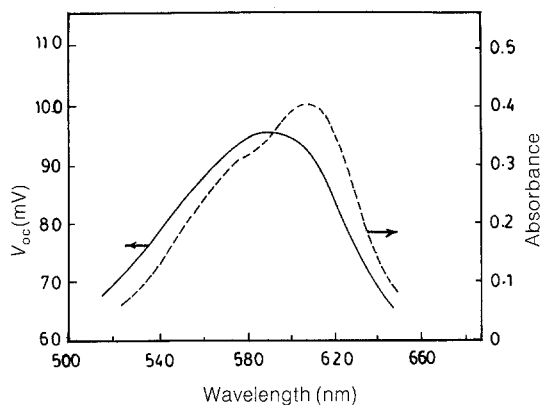
Complex	$[\text{Fe}(\beta\text{-diketonate})_2]$ ( $\times 10^4 \text{ mol/dm}^3$ )	% Acetonitrile	$pH$	$i_{ph}^a$ ( $10^6 \text{ A/cm}^2$ )	$V_{oc}^a$ (mV)	SEE <sup>b</sup> ( $\times 10^4 \%$ )
$\text{Fe}(\text{acac})_2$	1.1	40	4–5	0.017	205	0.043
$\text{Fe}(\text{tfac})_2$	1.5	40	4	1.14	407	5.8

<sup>a</sup> Average of three measurements;

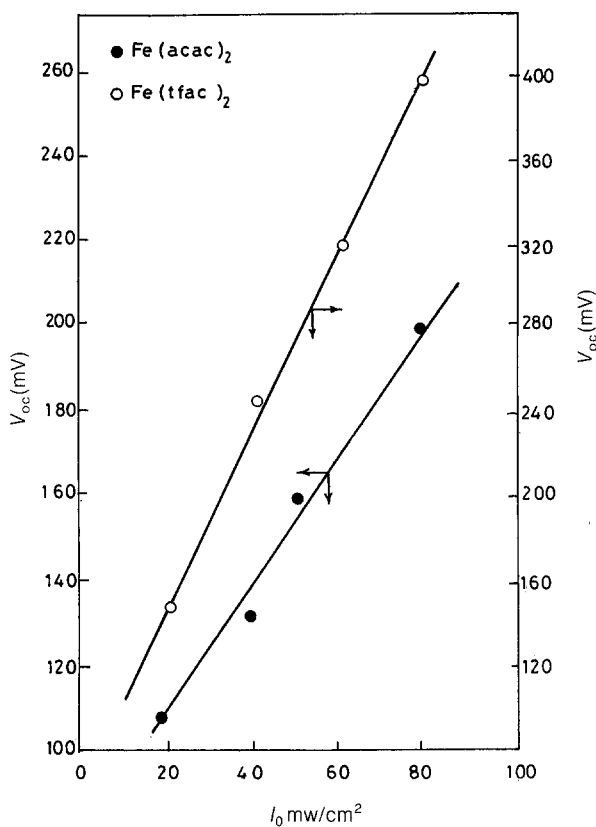
<sup>b</sup> theoretical Sunlight Engineering Efficiency,  $SEE = \frac{V_{oc}(\text{mV}) \times i_{ph}(\text{A/cm}^2)}{I_0(\text{mW/cm}^2)}$

*Hamdi and Aliwi* [9] for the Vanadium(III)-tris-( $\beta$ -diketonate) / new methylene blue photogalvanic system. This is also supported by the findings of *Butler et al.* [16] and *Denti et al.* [17] on the effects of ligands on the redox potential of transition metal organometallic complexes. Thus, the presence of electron withdrawing fluorine atoms in these complexes may result in an increase in the redox potential  $E_0$  of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  couple, thereby enhancing the power efficiency of the present photogalvanic system. Additionally, the power output of the present ferrous bis-( $\beta$ -diketonate)/thionine systems (Table 1) is higher than that of comparable vanadium(III) tris-( $\beta$ -diketonate) / new methylene blue systems [9] with the same  $\beta$ -diketonate moiety.

The open circuit photo potential  $V_{oc}$  of the  $\text{Fe}(\text{acac})_2$  and the  $\text{Fe}(\text{tfac})_2$  / thionine systems was monitored as a function of the wavelength of incident light. A typical action spectrum of the photopotential (mV) in the  $\text{Fe}(\text{acac})_2$  / thionine system is displayed in Fig. 3 together with the visible absorption spectrum of thionine. The observed  $V_{oc}$  profile follows closely the absorption spectrum of the dye. Thus, it



**Fig. 3.** Comparison of the photo potential (mV) in the  $\text{Fe}(\text{acac})_2$  / thionine system with the visible absorption spectrum of thionine in 20% aqueous acetonitrile;  $I_0 \sim 20 \text{ mW/cm}^2$



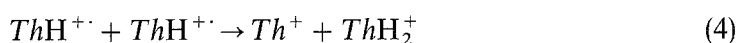
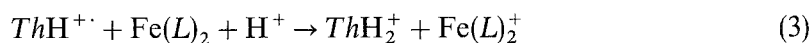
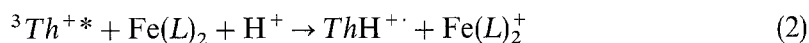
**Fig. 4.** Variation of the photo potential with incident light intensity for  $\text{Fe}(\text{acac})_2$  (●) and  $\text{Fe}(\text{tfac})_2$  (○); other experimental parameters are the same as in Fig. 1

seemed reasonable to conclude that the photo excitation of thionine dye is basically responsible for the initiation of the photogalvanic effect in the present system.

Figure 4 shows that the photogalvanic cell potential increases as the incident light intensity ( $I_0$ ) increases, indicating that the concentration of the dye's reduced form increases accordingly. It is also evident from Fig. 4 that both  $\text{Fe}(\text{acac})_2$  and  $\text{Fe}(\text{tfac})_2$  show a dark cell potential. This might be attributed to the redox behavior of these chelates and the type of the ionic species near the Pt electrodes. Based on the present experimental results and by analogy with similar systems, we propose the

following mechanism for the photoreduction of the thionine dye molecule by Fe-( $\beta$ -diketonate)<sub>2</sub> complexes.

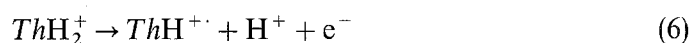
#### Reactions in solution



(dismutation reaction)

#### Reactions at the electrodes

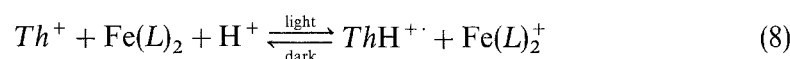
At the illuminated electrode (anode):



At the dark electrode (cathode):



#### Overall reaction



In Eqs. (1) to (8),  $Th^+$ ,  $ThH^{+\cdot}$ , and  $ThH_2^+$  represent the oxidized, semi-reduced, and leuco-thionine cations, respectively.  ${}^1Th^{+*}$  and  ${}^3Th^{+*}$  represent the singlet and triplet excited electronic states of thionine, and *ISC* denotes intersystem crossing. *L* is the  $\beta$ -diketonate ligand.

It is of interest to note that in the ferrous sulfate / thionone system electron transfer processes involved in the initial photoreduction of the oxidized form of thionine and in the quenching of the reduced thionine by ferrous ions are believed to proceed within a ferrous-thionine complex, especially at higher ferrous ion concentrations [18–21]. In the present photoredox system, however, the tendency of the ferrous *bis*-( $\beta$ -diketonate) chelates to form complexes with thionine is much less pronounced due to electronic and steric factors. Thus, a more plausible route for the initial photoreduction step in these systems may involve an electron transfer from the ferrous *bis*-( $\beta$ -diketonate) chelate to the lowest triplet excited state of thionine. This is in accordance with our previous work on the vanadium(III) *tris*-( $\beta$ -diketonate) / new methylene blue photoredox system [9].

The effect of temperature on the present system was also studied by following the change in  $V_{oc}$  at different temperatures. The drop in the photo potential caused by an increase in temperature may be attributed to the increasing rate of the back reaction and the consequent decrease in the concentration of the leuco-thionine [22, 23]. The decrease of  $V_{oc}$  by  $-1.80 \text{ mV}/^\circ\text{C}$  clearly demonstrates the importance of the

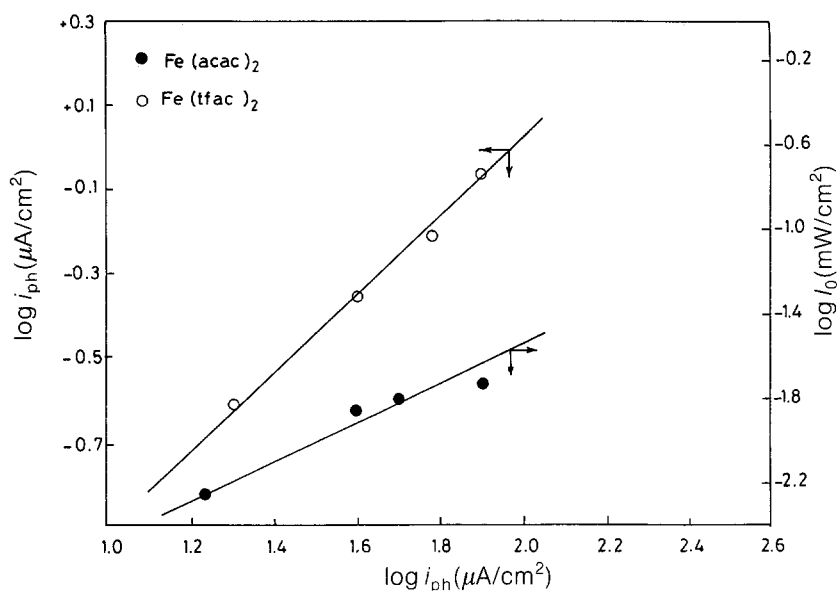


Fig. 5. Relationship between photo current and incident light intensity for  $\text{Fe}(\text{acac})_2$  (●) and  $\text{Fe}(\text{tfac})_2$  (○); other experimental parameters are the same as in Fig. 1

concentration of the photoexcited dye molecules for the promotion of the photo-redox reaction in the illuminated half-cell. The change in  $V_{oc}$  in the present photoredox system is higher than that reported for  $\text{VCl}_3$  / thionine ( $-1.3 \text{ mV}/^\circ\text{C}$ ) and  $\text{VOSO}_4$  / thionine ( $-0.9 \text{ mV}/^\circ\text{C}$ ) [11, 15]. However, the potential gradient  $dV_{oc}/dt$  for the present photogalvanic system is less negative than that of the photo-electrochemical cell using a semiconductor electrode on a solid p-n junction ( $-2.6$  to  $-3.6 \text{ mV}/^\circ\text{C}$ ) [24].

To examine which reduced form of thionine ( $\text{ThH}^+$  or  $\text{ThH}_2^+$ ) is responsible for the production of the photo current, an experiment was carried out to measure the photo current ( $i_{ph}$ ) at various light intensities keeping other parameter constant. Figure 5 shows the linear relationship between  $\log(i_{ph})$  and  $\log I_0$  with a slope approaching unity for both  $\text{Fe}(\text{acac})_2$  and the  $\text{Fe}(\text{tfac})_2$  / thionine systems. It is therefore concluded that the responsible anodic reaction is represented by Eq. 5 and not by Eq. 6 in the above reaction scheme, since the concentration of the semi-reduced thionine species ( $\text{ThH}^+$ ) is proportional to  $I_0$ , whereas the concentration of the leuco-form ( $\text{ThH}_2^+$ ) is proportional to  $(I_0)^2$  [25]. Therefore, the main electrode reaction is 5 at the anode and 7 at the cathode.

Finally, we may conclude that the photogalvanic effect in a metal chelate / thiazine dye photoredox system is highly sensitive to variations in the electronic structure of the metal chelate, particularly the electron withdrawing ability of the ligand. The present work has established that the presence of electron withdrawing groups like fluorine in the  $\beta$ -diketonate moiety of a ferrous bis-( $\beta$ -diketonate) chelate substantially enhances the photo current, the photo potential, and the power output of the photogalvanic cell. Thus, it seems instructive to extend this investigation to other transition metal chelates with ligands of a wider range of electron-acceptor capabilities.

## Experimental

### Materials

Both ferrous *bis*-(acetylacetonate) and ferrous *bis*-(trifluoroacetylacetonate) were prepared according to the method reported by *Chalmers* and *Umar* [14]. Complexes were purified by vacuum sublimation at 80 °C; melting points: 150–152 °C and 108–109 °C, respectively.

Thionine dye was supplied by Fluka A.G. (Switzerland) and was used without further purification. Ammonium iron(II) sulfate hexahydrate (AR grade) and acetonitrile (distilled before use) were supplied by BDH (UK). Sodium citrate was supplied by Ridel-deHaen (Germany). Argon gas of 99.99% purity was used during the photogalvanic effect measurements. Bidistilled water was used throughout all experiments.

### Apparatus and Technique

The measurements of the photo current ( $i_{ph}$ ) and the open-circuit photo potential ( $V_{oc}$ ) were performed in a Pyrex cell described previously [15]. Two platinum electrodes of 0.25 cm<sup>2</sup> area from Ingold were used as illuminated and dark electrodes (preconditioned by keeping immersed in 0.5 M HCl solution). The volume of each half-cell was 35 cm<sup>3</sup>.

An illuminated half-cell with a quartz window of 0.5 cm diameter facing the optical beam of a Xenon lamp (1000 W) supplied by Kratos (Germany) and equipped with an UV cut-off filter was used. The intensity of the incident light was 80 mW/cm<sup>2</sup> as measured by a solar meter (model 770 KBE / Germany). The photo currents and photo potentials were measured by a PM-2521 digital multimeter from Philips and by a pH-M85 digital Radiometer *pH*-mV meter, respectively. UV and visible spectra were recorded using a Pye-Unicam SP8-200 spectrophotometer. A Kratos GM 252 high intensity grating monochromator with a 1000 W Xenon lamp was used for monochromatic irradiation experiments.

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