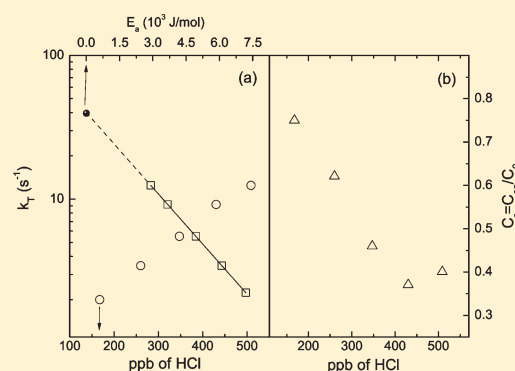


Laser-Induced Chemical Reaction Characterization in Photosensitive Aqueous Solutions

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ABSTRACT: A dual-wavelength on/off-excitation thermal lens technique was used to identify and quantify a laser-induced chemical reaction in ionic aqueous solutions of Fe(II)–TPTZ. On/off modeling was used to fit the TL experimental data, which provided the primary effect generated during laser-excitation. The addition of HCl in the solutions reduced the activation barrier; this behavior followed the Arrhenius correlation. The nature of the photo-oxidation of Fe(II)–TPTZ complex is discussed. The results suggest that this technique may contribute to the understanding of the dynamics of complex reactions, which may lead to a more precise determination of the physicochemical properties involved in a photochemical reaction.



INTRODUCTION

The accurate analysis of trace metals demanded in analytical chemistry requires continuous innovation in instrumental investigation. The determination of iron has been a particularly challenging task because it is of great economic importance to the materials industry and crucial for biological systems.^{1–4} The use of a variety of ferroin-type compounds has resulted in many developments. Fe(II) is often quantified using colorimetric methods.^{1–4} For example, it can be achieved by employing complexation with 2,4,6-tri(2'-pyridyl)-1,3,5-triazine (TPTZ).⁴ Although the complexation with TPTZ is a well-known and established method for iron determination, its chemical reaction under photoexcitation is not well understood. A broader understanding of the photoreactive characteristics of a complex system such as this will ensure advances in quantifying iron.

The thermal lens (TL) technique is used extensively as a precise spectroscopic tool for material characterization.^{5–23} This method has already been used in a wide range of applications such as trace^{7–12} and flow injection¹³ analysis, characterization of chemical reactions,^{14–16,20–23} and determination of fluorescence quantum efficiency.^{17,18} TL is particularly relevant for chemical characterization,^{9–12,20–23} and it has been used to investigate photoinduced chemical reaction (PCR) in aqueous solutions and hydrocarbon fuels.^{20–22} In a conventional TL measurement, a refractive index distribution is generated within a sample from the temperature increase produced by absorbance of a laser beam. This refractive index distribution is probed by another laser by measuring its far-field beam-center intensity. In a photoreacting substance, the absorbed light energy may induce a chemical reaction, and the concentration of absorbing species is modified in the excited volume, generating a mass (species) gradient. This phenomenon

creates a time-dependent absorption coefficient, which alters the TL signal accordingly.²⁰

In this work, we used the TL technique to investigate thermo-optical and PCR properties of aqueous solutions of Fe(II)–TPTZ with different concentrations of HCl. To verify the PCR effect, we performed TL experiments using dual-wavelength excitation at 514.5 nm within the absorption band of Fe(II) complex and at 875 nm outside the band. The on/off-excitation theoretical model was used to fit the TL experimental data. This model allowed us to identify the primary effect generated during laser-excitation in the sample. We showed that the addition of HCl reduced the activation barrier. This behavior followed the Arrhenius correlation. We developed a possible simplified scheme for the photo-oxidation of the Fe(II)–TPTZ complex.

THERMAL LENS EXPERIMENT

An aqueous solution of 6.1 mg/L TPTZ was prepared. The compound was dissolved in 1.4 $\mu\text{g/L}$ of hydrochloric acid (HCl) and diluted with Milli-Q water (Millipore Water Purification System). The required amount of ferrous sulfate hepta-hydrated complex was dissolved to add 200 mg/L Fe(II). In the final working solutions of Fe(II)–TPTZ, HCl was added up to 510 $\mu\text{g/L}$ (510 ppb); the final concentration was 1.4 to 510 ppb of HCl. The solutions were prepared immediately before each experiment. The liquid samples were contained in quartz cuvettes (thickness $L = 0.765$ cm at 300 K).

A schematic description of the TL experiment is given in Figure 1. The excitation lasers are TEM₀₀ cw Gaussian beams

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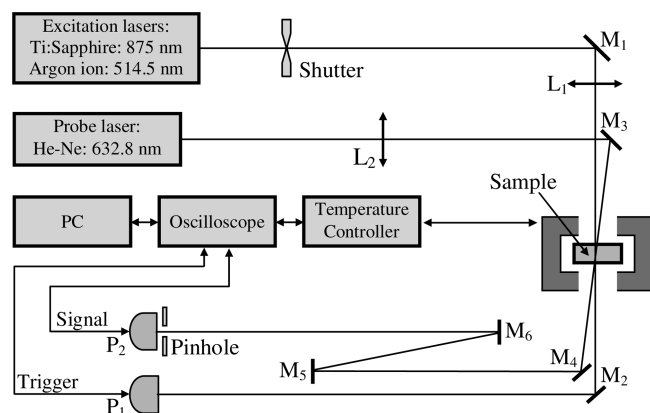


Figure 1. Schematic diagrams of the time-resolved TL experimental apparatuses. M_i , L_i , and P_i denote mirrors, lenses, and photodiodes, respectively.

from either an Ar^+ laser at $\lambda_{\text{ex}} = 514.5$ nm or a Ti/sapphire laser at $\lambda_{\text{ex}} = 875$ nm. The probe beam was a cw TEM₀₀ Gaussian He–Ne laser at 632.8 nm, focused by a lens ($f = 20$ cm) and almost collinear to the excitation beam. A converging lens ($f = 30$ cm) focused the excitation beams. The sample was placed at its focal plane and positioned near the confocal plane of the probe beam. A mechanical shutter controlled the sample's exposure to the excitation laser. A pinhole-photodiode (P_2) assembly captured the probe beam transmission through the TL to detect the TL signal. The signal from the P_2 assembly was sent to a digital oscilloscope, which was triggered by a photodiode P_1 to record the TL transients. A detailed description of the experimental apparatus is given in refs 20, 21, and 23.

THERMAL LENS THEORY

Assuming that the sample exhibits a PCR in the cw excitation regime, we calculate the TL probe beam intensity at the detector plane as²³

$$I(t) = \left| C \int_0^\infty e^{(1+iV)g} \exp \left\{ \frac{-i\theta_{\text{th}}}{t_c} \left[c_r \int_{t_0}^t \frac{1 - e^{-2mg/(1+2\tau/t_c)}}{1 + 2\tau/t_c} d\tau \right. \right. \right. \\ \left. \left. \left. + \frac{(1-c_r)}{e^{k_T t}} \int_{t_0}^t \frac{1 - e^{-2mg/(1+2\tau/t_c)}}{1 + 2\tau/t_c} e^{k_T \tau} d\tau \right] \right\} dg \right|^2 \quad (1)$$

Equation 1 represents laser-on ($0 < t \leq \xi$) and laser-off ($t > \xi$) excitations, with $t_0 = 0$ for $t \leq \xi$ and $t_0 = t - \xi$ for $t > \xi$. It has been shown that the laser-off TL transient is necessary when identifying whether PCR or another diffusion process is the leading mechanism during a TL experiment.²³ In eq 1, C is a constant,²³ $g = r^2/\omega_{1P}^2$, $m = (\omega_{1P}/\omega)^2$, and $c_r = C_{\text{eq}}/C_0$. C_0 denotes the initial concentration, and C_{eq} is the average equilibrium concentration in the illuminated area. The total reaction rate constant is k_T . In the sample, the radius of the excitation beam is ω and the radius of the probe beam is ω_{1P} .

The characteristic heat diffusion time constant is $t_c = \omega^2/(4D)$, where $D = k/(\rho c)$ is the thermal diffusivity, k is the thermal conductivity, ρ is the mass density, and c is the specific heat of the sample. θ_{th} is a dimensionless parameter measuring the strength of the TL effect, which is given by

$$\theta_{\text{th}} = -\frac{P_e A_e L}{k \lambda_p} \frac{dn}{dT} \varphi \quad (2)$$

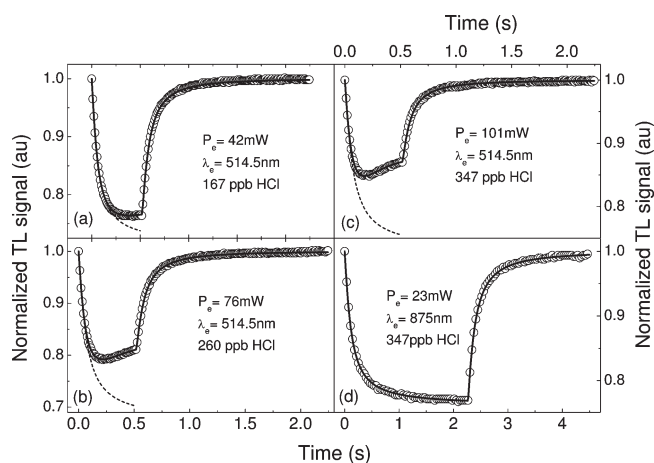


Figure 2. Normalized TL signals $I(t)/I(0)$ for the Fe-TPTZ solutions with (a) 167, (b) 260, and (c) 347 ppb HCl excited at 514.5 nm. (d) Same samples as part c excited at 875 nm. Solid lines represent least squares curve fits using eq 1 for parts a–c and eq 1 with $k_T = 0$ for part d, that is, no PCR effect. Dashed lines represent the TL signal without considering the PCR effect (eq 1 using $k_T = 0$).

A_e is the optical absorption coefficient at the excitation wavelength, λ_{ex} , dn/dT is the temperature coefficient of the refractive index at the probe beam wavelength λ_p . P_e is the power of the excitation laser in the sample. $\varphi = 1$ represents the fraction of the absorbed energy available that is totally converted to heat. As a special case, pure thermal effect is obtained in this model (eq 1) by taking $k_T = 0$. Equation 1 is used to fit the experimental TL transients, and t_c , θ_{th} , c_r , and k_T are free adjustable parameters. The experimental parameters for the excitations are: $\omega = 79.5 \mu\text{m}$, $m = 45.1$, and $V = 6.8$ (514.5 nm) and $\omega = 151 \mu\text{m}$, $m = 35.6$ and $V = 11.9$ (875 nm).

RESULTS AND DISCUSSION

Figure 2a–c clearly shows the effect of the PCR on the TL transients under 514.5 nm excitation for the (HCl)/Fe-TPTZ solutions. On exposing the sample to cw laser radiation, the PCR suppressed the generated TL, reducing the beam-center intensity at the detector. This was likely to be due to a reduction of the absorbing species from the interaction volume of the excitation laser with the sample.²⁰ The PCR behavior also changed as the HCl concentration increased. For 167 ppb HCl, the TL transient signal reached the steady state on a time scale shorter than that for higher concentrations of HCl. When excited at 875 nm, no PCR effect was observed in any sample. This is depicted in Figure 2d for the 347 ppb HCl sample. The transient followed a pure TL effect even for $t > 2$ s. A possible simplified scheme for the photo-oxidation of an aqueous solution of Fe(II)–TPTZ is discussed below.

TPTZ is very sensitive to iron; it acts as a tridentate ligand with two pyridyl nitrogens and one ring nitrogen attached to the iron atom; the third pyridyl group is free. In this ion, the two TPTZ ligands must lie at right angles to each other.⁴ The binding of Fe(II) to this ligand creates a very intense navy blue color centered at 593 nm. This absorbance can be measured using spectrophotometric methods.⁴ The nature of the photoreaction under visible cw-excitation has not yet been described. Under 514.5 nm excitation, it is possible that the ion Fe(II) in TPTZ complex could have been formulated as a metal charge-transfer state resulting

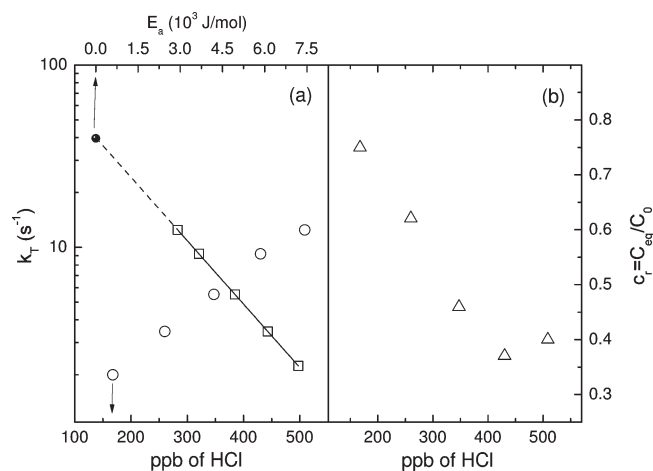


Figure 3. (a) Logarithm plot of rate constant k_T as a function of both the HCl concentration (O) and activation energy E_a (□). (b) c_r as a function of HCl concentration.

from an internal electron transfer to the ligand. Such transitions are found where a metal is easily oxidized and the ligand is easily reduced.²⁵ The photo-oxidation of Fe(II) to Fe(III) complex under laser excitation leads to a slightly lower absorbance in the visible region of the electromagnetic spectrum, which results from the elimination of the chromophoric properties of the molecule. From this point of view, it is possible that the addition of HCl might have facilitated the process of charge-transfer when its concentration increased. This will be discussed in more detail later in this work.

It has been demonstrated²³ that it is possible to distinguish between the PCR and other diffusion phenomena that accompany laser excitation of fluid mixtures. Both mass diffusion and PCR effects were shown to present similar trends in the TL on-transient signal. However, the laser-off behavior was very different. The parameters obtained here using only the PCR model provided very good agreement between the calculated curve and the experimental on/off-transient data, as shown by the continuous lines in Figure 2a–c. The data showed that the primary mechanism during laser excitation was the PCR. Dashed lines in Figure 2a–c represent the TL signal without considering the PCR effect; eq 1 using $k_T = 0$ was used to simulate these curves.

The PCR became clearly evident when both excitation wavelengths were used; the excitation at 514.5 nm was within the known absorption band for the Fe(II)–TPTZ aqueous solutions.² At 875 nm, only hydroxyl groups absorb the light energy, and no PCR effect was expected to occur. We used the 875 nm excited transients to obtain the thermal diffusivity of the solutions by using eq 1 with $k_T = 0$ for the 347 ppb HCl sample, as seen in Figure 2d. This parameter was later fixed and used when fitting the transients excited at 514.5 nm. In the absence of PCR, the thermal diffusivity of the samples was measured as $(1.40 \pm 0.05) \times 10^{-3}$ cm²/s, which is the expected value for pure water.²⁶ These values were calculated from the relationship $D = \omega^2/4t_c$ using the TL time constants from the fitted data; $t_c = (11.2 \pm 0.5)$ ms for this example.

The PCR rate constants obtained by fitting the transients excited at 514.5 nm are plotted on a logarithmic scale against the HCl concentration in Figure 3a. The PCR time constant, $\tau_T = 1/k_T$, varied from $\tau_T = (0.45 \pm 0.04)$ s for the 167 ppb HCl sample to $\tau_T = (0.080 \pm 0.008)$ s for the 508 ppb HCl sample. These

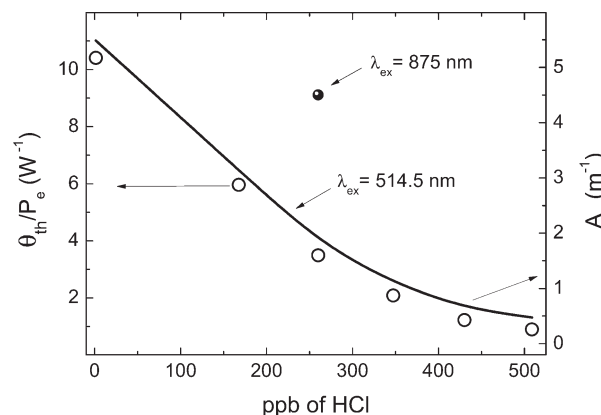


Figure 4. (Open circles) HCl dependence of θ_{th}/P_e and (continuous line) A_e for the aqueous Fe-TPTZ solutions for laser excitation at 514.5 nm. The solid circle represents the absorption coefficient at 875 nm laser excitation.

values fell within a range of 7 to 40 times greater than the characteristic TL time constants.

Because of its ionic characteristics, the addition of HCl to Fe(II)–TPTZ solutions was expected to reduce the barrier (activation energy, E_a) for the reaction to take place. This was expected to follow the Arrhenius theory, $k_T = k_0 e^{-E_a/RT}$, in which k_0 is the total frequency of molecular collisions²⁴ and R is the ideal gas constant.²⁴ k_T can be represented as the frequency of the collisions that result in a reaction, and the exponential factor is the probability that any particular collision will result in a reaction. Using this correlation together with the fact that the activation energy could be considered inversely proportional to the HCl concentration in the solutions, the value of k_0 was calculated to be ~ 40 s⁻¹ by extrapolation of the Arrhenius equation to the value of $E_a \rightarrow 0$. With k_0 , E_a was then calculated. Figure 3a shows k_T against E_a .

The parameters θ_{th}/P_e and c_r are also dependent on the HCl concentration (Figures 3b and 4). The c_r behavior shows that only a percentage of the initial concentration of species contributed to the TL-formed signal at low HCl concentration. As the HCl content increased, more species were created in the illuminated area, and a tendency to saturation was observed around 400 ppb HCl, as shown in Figure 3b.

As the thermal diffusivity results showed, properties of the solutions such as thermal conductivity and the temperature coefficient of the refractive index can be approximated by the values for pure water. Using $dn/dT = -0.95 \times 10^{-4}$ K⁻¹, $k_{\text{water}} = 0.605$ W/mK,²⁶ and eq 2, the optical absorption coefficients for the samples were also determined at 514.5 and 875 nm (Figure 4, right side scale). The addition of HCl reduced the absorption band of the Fe(II)–TPTZ complex around 593 nm, which accordingly decreased the θ_{th}/P_e amplitude. The addition of HCl did not affect the optical absorption coefficient at 875 nm (solid circle in Figure 4). We found $A_e = (4.5 \pm 0.5)$ m⁻¹ at 875 nm, which agrees with the literature value for the absorption coefficient of pure water.²⁶

CONCLUSIONS

We have presented thermo-optical and photochemical properties of Fe-TPTZ aqueous solutions. These properties were determined using a generalized theoretical model for the TL

effect caused by PCR using on/off laser excitations. In this PCR, the photo-oxidation of Fe(II) to Fe(III) complex under 514.5 nm excitation eliminated the chromophoric properties of the molecule. The metal charge-transfer nature of the TPTZ complex was strongly influenced by the HCl content. The addition of HCl in the solutions facilitated the charge-transfer processes, and it was found to reduce the activation barrier, which then modified the reaction rate according to the Arrhenius correlation. In addition, the thermo-optical (θ_{th}) and PCR (c_r and k_T) parameters correlated to the HCl content. The technique presented here appears to be applicable for the study of complex reactions. However, the complexity of Fe(II)–TPTZ solution requires additional chemical investigation for a complete understanding of the chemical reaction path involved in this process. The results obtained using the TL technique provide a general picture of the dynamics of the photoreaction taking place during the laser excitation in (HCl)/Fe(II)–TPTZ aqueous solutions.

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