

# Effect of some surfactants on the chemiluminescent reactions of bis(2,4,6-trichlorophenyl)oxalate and bis(2-nitrophenyl)oxalate with hydrogen peroxide

Patrícia Dantoni, Ana Clara B. Rodrigues, Margareth Mie N. Matsuda, and Nina Coichev

**Abstract:** The chemiluminescent reactions of bis(2,4,6-trichlorophenyl)oxalate (TCPO) and bis(2-nitrophenyl)oxalate (2-NPO) with hydrogen peroxide in acetonitrile/water micellar systems (anionic, cationic, and non-ionic) and  $\gamma$ -cyclodextrin were studied in the presence of fluoranthene or 9,10-diphenylanthracene, imidazole, and two buffer solutions, HTRIS<sup>+</sup>/TRIS and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup>. The relative chemiluminescence (CL) intensity is higher in the presence of the cationic (DDAB, CTAC, DODAC, and OTAC), anionic (SDS), and non-ionic (Tween 80) surfactants. In the presence of some non-ionic surfactants (Brij 35, Brij 76, and Tween 20), the CL intensity was partially quenched compared with the reaction with no surfactant. The sensitivity for hydrogen peroxide determination in the range  $0.01 \times 10^{-4}$  to  $1.0 \times 10^{-4}$  mol L<sup>-1</sup>, considering the slope of the calibration curves (maximum peak height of CL vs. concentration), improved with the introduction of DDAH, CTAB, and SDS in HTRIS<sup>+</sup>/TRIS buffer.

**Key words:** TCPO, 2-NPO, surfactant, chemiluminescence, hydrogen peroxide.

**Résumé :** On a étudié les réactions chimiluminescentes de l'oxalate de bis(2,4,6-trichlorophényle) (OTCP) et de l'oxalate de bis(2-nitrophényle) (O-2NP) avec le peroxyde d'hydrogène dans des systèmes micellaires d'acéonitrile/eau (anionique, cationique et non-ionique) et de  $\gamma$ -cyclodextrine, en présence de fluoranthène et de 9,10-diphénylanthracène, d'imidazole et de deux solutions tampons, HTRIS<sup>+</sup>/TRIS et H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup>. L'intensité relative de la chimiluminescence (CL) est plus élevée en présence des agents de surface cationiques (DDAB, CTAC, DODAC et OTAC), anionique (SDS) et non-ionique (Tween 80). En présence de quelques agents de surface non-ioniques (Brij 35, Brij 76 et Tween 20), l'intensité de CL est partiellement piégée par rapport à la réaction sans agent de surface. Si on se base sur la pente des courbes de calibration (hauteur maximale du pic de la CL vs. concentration), la sensibilité de la détermination du peroxyde d'hydrogène dans la plage de concentration allant de  $0,1 \times 10^{-4}$  à  $1,0 \times 10^{-4}$  mol L<sup>-1</sup> augmente avec l'introduction de DDAH, de CTAB et de SDS dans le tampon HTRIS<sup>+</sup>/TRIS.

**Mots-clés :** oxalate de bis(2,4,6-trichlorophényle) (OTCP), oxalate de bis(2-nitrophényle) (O-2NP), agent de surface, chimiluminescence, peroxyde d'hydrogène.

[Traduit par la Rédaction]

## Introduction

The chemiluminescent reactions of bis(2,4,6-trichlorophenyl)oxalate (TCPO) and bis(2,4-dinitrophenyl)oxalate (DNPO) in the presence of hydrogen peroxide have been widely used for the detection of fluorescent compounds (fluorophores) at fmol levels. Most of the analytical applications of these systems refer to indirect methods for the determination of species, which generates hydrogen peroxide in a parallel reaction (for instance enzymes) or derivatization reaction using fluorophores as a label.<sup>1-22</sup>

Applications of the peroxyoxalate system, as a post-column reagent in chemiluminescence (CL) detection, in liquid chromatography,<sup>23</sup> and electrophoresis,<sup>24</sup> for clinical, pharmaceutical, environmental, and food analyses, combines the selectivity of the separation methods with the sensitivity of this detection technique.

A critical review of the influence of Cr<sup>III</sup>, Zn<sup>II</sup>, and Pb<sup>II</sup> on the chemiluminescent reactions of TCPO and bis(2-nitrophenyl)oxalate (2-NPO) with hydrogen peroxide in the presence of 3-aminofluoranthene, as fluorophore, and imidazole

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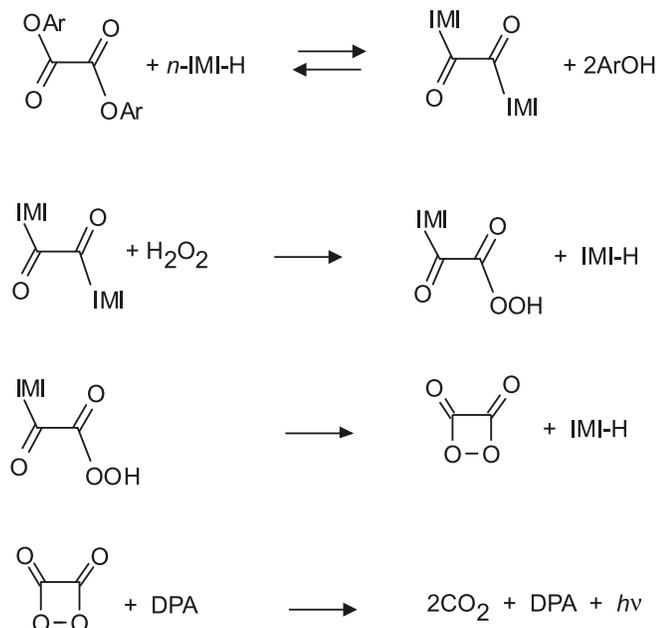
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**Scheme 1.** Simplified mechanism for the chemiluminescent reaction of bis(2,4,6-trichlorophenyl)oxalate (TCPO) with hydrogen peroxide, catalyzed by imidazole, in ethyl acetate anhydrous medium.<sup>31</sup> Ar = (2,4,6-trichlorophenyl) for TCPO and (2-nitrophenyl) for NPO.



(IMI), as catalyst, showed that the metal ions had no influence when the experiments were carried out in buffer solutions such as tris(hydroxymethyl)aminomethane (HTRIS<sup>+</sup>/TRIS, pH 6.9–8.0) or  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  (pH 7.0–8.0).<sup>25,26</sup>

According to Motoyoshiya and Maruyama,<sup>27</sup> zinc and copper ions markedly enhanced the CL efficiencies in the presence of the chelator *N*-phenyl-*N,N'*-bis(2-pyridinylmethyl)-1,2-ethanediamine, owing to the interaction of this ligand with the metal ion and the fluorophore.

A detailed study of several parameters such as acidity, water and acetonitrile (ACN) contents, and concentrations of TCPO, 2-NPO, IMI, hydrogen peroxide, and metal ions was reported by our group.<sup>25,26</sup> Among these factors, the catalytic effect of IMI depends very much on the unprotonated imidazole concentration and the acidity. The complex formation of these metal ions with IMI may change the acidity by disturbing the acid–base equilibrium of  $\text{HIMI}^+/\text{IMI}$ . As the CL efficiency sharply decreases at pH higher than 7.5, small variations of the acidity conditions can lead to several errors in the interpretation of the data. Some alternative methods described in the literature using flowing streams, such as continuous flow, flow injection<sup>28–30</sup> analysis, and liquid chromatography, require an appropriated optimization of the experimental parameters.

Some authors have intensively studied the possible mechanisms and intermediates for the chemiluminescent reaction of peroxyoxalate (PO-CL) catalyzed by IMI. The main reactions of the mechanism for the system TCPO, hydrogen peroxide, IMI, and 9,10-diphenylanthracene (DPA), in anhydrous ethyl acetate medium, involved the formation of an IMI-substituted peracid and an energy-rich intermediate (1,2-dioxetane-3,4-dione), which excited the fluorophore DPA, leading to light emission and  $\text{CO}_2$  formation (Scheme 1).<sup>31–34</sup>

The main disadvantage of these systems is the insolubility of these compounds in water and their instability towards

hydrolysis, which requires the use of organic solvents. The application of micelles has been studied to solve these problems, to use these systems for analytical purposes, decreasing the amount of organic solvents, or even avoiding IMI.

The results of the proposed CL systems in micellar media showed that enhancement on the CL intensity could arise by the solubilization of the reagents, the electrostatic effect of the ionic surfactant, and the alteration of the pH and the microenvironment of the CL reaction.<sup>35,36</sup>

There are some studies on analytical applications for the determination of fluorophores, proteins, and hydrogen peroxide in aqueous samples using the PO-CL reaction with the introduction of the micelles.<sup>28–30,37–44</sup>

Sodium dodecyl sulfate (SDS) micellar medium was used as a carrier to avoid the rapid degradation of TCPO in water in a flow-injection analysis,<sup>28–30,41</sup> allowing the use of TCPO in the absence of organic solvent.

Some groups have reported on the effect of micellar medium.<sup>40,42,45</sup> Steijger et al.<sup>42</sup> compared the stability of TCPO in ACN micellar systems and ACN/water phosphate buffer solution (80–20, v/v) with perylene as fluorophore. They investigated the effect of several types of surfactants, such as the anionic SDS and the cationic hexadecyltrimethylammonium bromide (CTAB). All analyzed micelles had a total or partial quencher effect compared with ACN buffer (no surfactant). The TCPO/ $\text{H}_2\text{O}_2$  chemiluminescent reaction did not occur in CTAB, which may be the result of the quenching of CL intensity by the bromide ion of CTAB, and the intensity in SDS anionic micelles was appreciably less than that in neutral micellar solutions.

Based on the enhancement of PO-CL CL intensity by some surfactants in  $\text{H}_2\text{O}_2/\text{TCPO}/\text{rhodamine}$ , Wada et al.<sup>43</sup> proposed a method to detect commercially available detergent. The enhancement may occur by a notable change of pH by adding surfactants, such as a buffer solution was used. The effect of the buffer cations can be important because of the interaction of the polar surface of micelles and the cations, which can provide an electrostatic attraction for the hydrogen peroxide anions that penetrate into non-ionic micelles.<sup>40</sup> Several surfactants might play a catalytic effect, and the fluorescent impurities of some surfactants may contribute to this enhancement.<sup>43</sup>

Liang et al.<sup>35</sup> studied the synergetic effect of SDS, CTAB, and gold nanoparticles on the system  $\text{H}_2\text{O}_2/\text{TCPO}/\text{sodium citrate}/\text{Au nanoparticles}$ . The CL intensity enhanced sharply with  $5 \times 10^{-3} \text{ mol L}^{-1}$  CTAB and became reasonably constant when the concentration of  $2.5 \times 10^{-2} \text{ mol L}^{-1}$  CTAB was used. However, a too high concentration of surfactant depressed the CL. According to the authors,<sup>35</sup> the CL of TCPO is enhanced by the cationic surfactant CTAB because the solubilities of TCPO and its excited intermediate in an aqueous micellar system are greater than that in pure ACN. The electrostatic effect of the ionic surfactant helps to concentrate the counterion, and the citrate anion was adsorbed onto the surface of the gold nanoparticles, which resulted in the stability of the Au colloid. In the presence of CTAB, Au nanoparticles are linked to CTAB by electrostatic attraction. The cage structure of the micelle is helpful for stabilizing the excited state and preventing it from quenching.

The present work reports the effect of different types of micelles (anionic, cationic, and non-ionic) and  $\gamma$ -cyclodextrin

( $\gamma$ -CD; as further discussed) on the reaction of TCPO or 2-NPO with hydrogen peroxide in the presence of fluoranthene (FA) or DPA, as fluorophores, and two buffer solutions HTRIS<sup>+</sup>/TRIS and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup>. We carried out the experiments in three different media, with 25%, 37%, and 62% (v/v) ACN, since the stock solutions of TCPO, DPA, and IMI must be prepared in ACN. The CL intensity–time (*t*) profile was examined by varying the water content, acidity, IMI, hydrogen peroxide concentration, and fluorophore. Our results are reported in terms of the maximum peak height (*I*<sub>max</sub>, relative light unit/second) and the area (*A*) under the curve of relative CL intensity (relative light unit) vs *t*. The total *t* refers to the time for the complete CL signal decay.

## Experimental

### Apparatus, reagents, and chemicals

All reagents were used as received without purification. Aqueous solutions were prepared with deionized water from the Milli-Q system (Millipore).

The buffers used were HTRIS<sup>+</sup>/TRIS (0.12 mol L<sup>-1</sup> tris(hydroxymethyl)aminomethane, pH 6.8, 8.3, and 8.7; (Kanto Chemical Co.) and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> (0.10 mol L<sup>-1</sup>, pH 6.6, 7.6, and 8.4; Kanto Chemical Co.). The pH of the buffers was adjusted with sodium hydroxide or nitric acid. The pH measurements were done with a pH meter (Metrohm, model 713) with a glass electrode (filled with saturated NaCl).

2-NPO was prepared according to the procedure in ref. 46.

Solutions of 4.5 × 10<sup>-4</sup> mol L<sup>-1</sup> TCPO (TCI Tokyo Kasei), 4.5 × 10<sup>-4</sup> mol L<sup>-1</sup> 2-NPO, 1.0 × 10<sup>-3</sup> mol L<sup>-1</sup> DPA (TCI Tokyo Kasei), 6.0 × 10<sup>-3</sup> and 1.2 × 10<sup>-2</sup> mol L<sup>-1</sup> IMI (Sigma-Aldrich), and 1.0 × 10<sup>-3</sup> mol L<sup>-1</sup> FA (Nakalai Chemicals Ltd.) were prepared in ACN (Mallinckrodt) every day.

Diluted hydrogen peroxide solutions were prepared every day in water from hydrogen peroxide stock solution (30%, *m/m*, Merck). The stock solution of 0.100 mol L<sup>-1</sup> hydrogen peroxide was standardized by titration with KMnO<sub>4</sub> standard solution in acid medium.

The surfactant (from Sigma-Aldrich, Kanto Chemical Co., and Merck) solutions were prepared in water or buffer solution (as indicated in the text): Brij 35 (polyoxyethylene(23) lauryl ether; critical micelle concentration (cmc) = 1 × 10<sup>-4</sup> mol L<sup>-1</sup>), Brij 76 (polyoxyethylene(10) stearyl ether; cmc = 3 × 10<sup>-3</sup> mol L<sup>-1</sup>), Tween 20 (polyoxyethylene (20) sorbitan monolaurate; cmc = 5 × 10<sup>-5</sup> mol L<sup>-1</sup>), Tween 80 (polyoxyethylene(20) sorbitan monooleate; cmc = 1.2 × 10<sup>-5</sup> mol L<sup>-1</sup>), TDTAB (tetradecyltrimethylammonium bromide; cmc = 3.5 × 10<sup>-3</sup> mol L<sup>-1</sup>), DDAB (dododecyltrimethylammonium bromide; cmc = 1.8 × 10<sup>-4</sup> mol L<sup>-1</sup>), CTAC (cetyltrimethylammonium chloride; cmc = 1.3 × 10<sup>-3</sup> mol L<sup>-1</sup>), DODAC (dioctadecyldimethylammonium chloride) and OTAC (octadecyltrimethylammonium chloride; cmc = 3.4 × 10<sup>-4</sup> mol L<sup>-1</sup>), CTAB (cmc = 9 × 10<sup>-4</sup> mol L<sup>-1</sup>), SDS (cmc = 8.1 × 10<sup>-3</sup> mol L<sup>-1</sup>), DDAH, (3-(dimethyldodecylammonio)-propane-1-sulfonate; cmc = 1.2 × 10<sup>-3</sup> mol L<sup>-1</sup>).<sup>47</sup>

$\gamma$ -CD (cyclooctaamylose, 0.01 mol L<sup>-1</sup>; Sigma-Aldrich) solution was prepared in buffer medium.

### Sample preparation

The experiments were done in the presence of two fluorophores, FA and DPA.

**Table 1.** Effect of some cationic surfactants on maximum emission intensity (*I*<sub>max</sub>) in the reactions of bis(2-nitrophenyl)oxalate (2-NPO) or bis(2,4,6-trichlorophenyl)oxalate (TCPO) with H<sub>2</sub>O<sub>2</sub>.

Surfactant	Oxalate			
	2-NPO		TCPO	
	<i>I</i> <sub>max</sub> /10 <sup>4</sup>	<i>t</i> (s)	<i>I</i> <sub>max</sub> /10 <sup>4</sup>	<i>t</i> (s)
None	3.5	30	0.036	40
TDTAB	1.8	30	0.047	45
DDAB	10	45	0.19	45
CTAC	14	60	0.72	45
DODAC	18	60	1.8	60
OTAC	21	60	1.2	45

**Note:** [2-NPO] = 5.6 × 10<sup>-5</sup> mol L<sup>-1</sup>, [TCPO] = 5.6 × 10<sup>-5</sup> mol L<sup>-1</sup>, [H<sub>2</sub>O<sub>2</sub>] = 1.6 × 10<sup>-3</sup> mol L<sup>-1</sup>, [FA] = 1.2 × 10<sup>-4</sup> mol L<sup>-1</sup>, % ACN = 25, [surfactant] = 10cmc; *t* refers to the time for the complete chemiluminescence (CL) signal decay. TDTAB, tetradecyltrimethylammonium bromide; DDAB, dododecyltrimethylammonium bromide; CTAC, cetyltrimethylammonium chloride; DODAC, dioctadecyldimethylammonium chloride; OTAC, octadecyltrimethylammonium chloride; FA, fluoranthene; ACN, acetonitrile.

**Table 2.** Effect of surfactant on maximum emission intensity (*I*<sub>max</sub>) in the reaction of bis(2-nitrophenyl)oxalate (2-NPO) with H<sub>2</sub>O<sub>2</sub>.

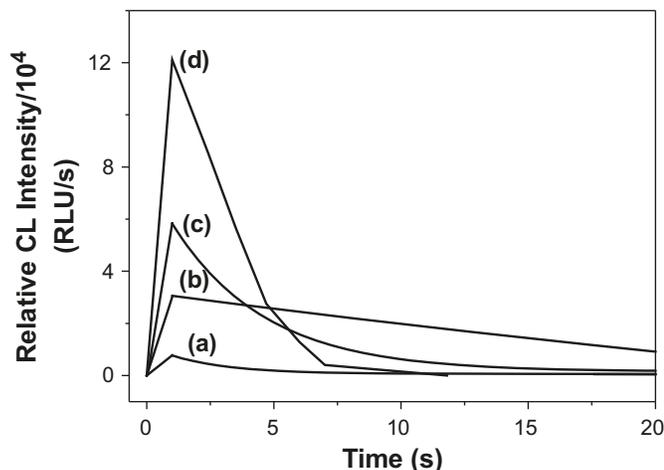
Surfactant	Peak height ( <i>I</i> <sub>max</sub> /10 <sup>4</sup> )	<i>t</i> (s)
None	3.5	30
Non-ionic		
Brij 35	2.2	60
Brij 76	1.9	75
Tween 20	1.6	60
Tween 80	4.6	75
Anionic		
SDS	4.5	75

**Note:** [2-NPO] = 5.6 × 10<sup>-5</sup> mol L<sup>-1</sup>, [H<sub>2</sub>O<sub>2</sub>] = 1.6 × 10<sup>-3</sup> mol L<sup>-1</sup>, [FA] = 1.2 × 10<sup>-4</sup> mol L<sup>-1</sup>, % ACN = 25, [surfactant] = 10cmc; *t* refers to the time for the complete chemiluminescence (CL) signal decay. FA, fluoranthene; ACN, acetonitrile.

In the experiments with FA, the CL intensity profile was obtained with a Lumicounter 1000 (Microtec Nichi-on) and the signal recorded with a Shimadzu 135 recorder. The emission began just after the addition of the oxalate solution. The emission intensity is represented as the peak height (*I*<sub>max</sub>) and the total emission time of reaction as (*t*). The sequence of the addition of the solutions was 0.1 mL of water, buffer, or surfactant solution (10 times the surfactant cmc), and 0.02 mL of 1.0 × 10<sup>-3</sup> mol L<sup>-1</sup> FA, 0.02 mL IMI (when used), 0.02 mL hydrogen peroxide, and 0.02 mL of 4.5 × 10<sup>-4</sup> mol L<sup>-1</sup> oxalate (2-NPO or TCPO). The sequence influences the emission intensity because the peroxyoxalates hydrolyze in aqueous solution. The concentrations of the final solutions (0.16 mL) are indicated in Tables 1 and 2.

In the experiments with DPA, the procedure for the CL intensity measurements involved mixing the reagents in a 3 mL glass flask placed in the luminometer (Lumat LB 9507, Berthold

**Fig. 1.** Relative chemiluminescence (CL) intensity in the presence of different surfactants in acetonitrile (ACN)/ water (25% ACN). [TCPO] =  $5.6 \times 10^{-5}$  mol L<sup>-1</sup>, [DPA] =  $1.2 \times 10^{-4}$  mol L<sup>-1</sup>; HTRIS<sup>+</sup>/TRIS pH 8.7; [H<sub>2</sub>O<sub>2</sub>] =  $5.0 \times 10^{-5}$  mol L<sup>-1</sup>. (a) No surfactant or [ $\gamma$ -CD] =  $6.2 \times 10^{-3}$  mol L<sup>-1</sup>. (b) Sodium dodecyl sulfate (SDS), 10cmc. (c) 3-(Dimethyldodecylammonio)-propane-1-sulfonate (DDAH), 10cmc. (d) Hexadecyltrimethylammonium bromide (CTAB), 10cmc. TCPO, bis(2,4,6-trichlorophenyl)oxalate; DPA, 9,10-diphenylanthracene;  $\gamma$ -CD,  $\gamma$ -cyclodextrin; cmc, critical micelle concentration; RLU, relative light unit.



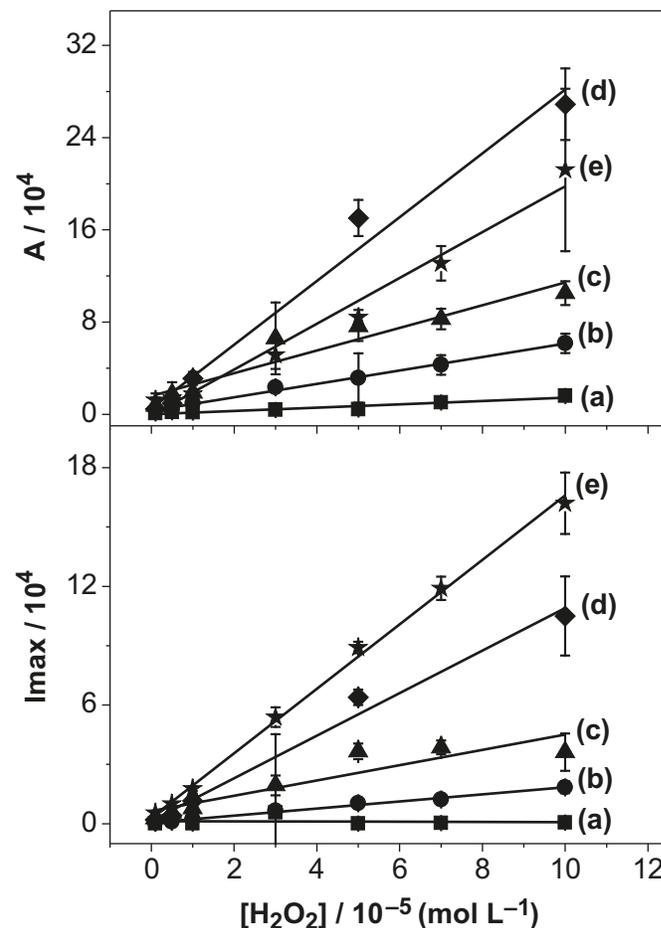
Technologies), positioned in front of the photomultiplier tube.

Because the peroxyoxalates hydrolyze in aqueous solution, the following mixing orders for the different reagents were used: 25% ACN (v/v): 50  $\mu$ L of water or H<sub>2</sub>O<sub>2</sub> ( $0.1 \times 10^{-5}$  to  $10 \times 10^{-5}$  mol L<sup>-1</sup>), 50  $\mu$ L of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> DPA, and 250  $\mu$ L of surfactant (in water or buffer) were introduced into the glass flask, followed by automatic jet-injection, after 10 s, of 50  $\mu$ L of  $4.5 \times 10^{-4}$  mol L<sup>-1</sup> TCPO. As the DPA and TCPO solutions were prepared in ACN, the final solutions after mixing were 25% ACN (v/v); 37% ACN (v/v): 50  $\mu$ L of water or H<sub>2</sub>O<sub>2</sub> ( $0.1 \times 10^{-5}$  to  $10 \times 10^{-5}$  mol L<sup>-1</sup>), 50  $\mu$ L of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> DPA, 50  $\mu$ L of  $6.0 \times 10^{-3}$  mol L<sup>-1</sup> IMI, and 200  $\mu$ L of water or surfactant (in water or buffer) were introduced into the glass flask, followed by automatic jet-injection, after 10 s, of 50  $\mu$ L of  $4.5 \times 10^{-4}$  mol L<sup>-1</sup> TCPO. As the DPA, TCPO, and IMI solutions were prepared in ACN, the final solutions after mixing were 37% ACN (v/v); 62% ACN (v/v): 50  $\mu$ L of water or H<sub>2</sub>O<sub>2</sub> ( $0.1 \times 10^{-5}$  to  $10 \times 10^{-5}$  mol L<sup>-1</sup>), 50  $\mu$ L of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> DPA, 100  $\mu$ L of  $1.2 \times 10^{-2}$  mol L<sup>-1</sup> IMI, 50  $\mu$ L of ACN, and 100  $\mu$ L of water or surfactant (in water or buffer) were introduced into the glass flask, followed by automatic jet-injection, after 10 s, of 50  $\mu$ L of  $4.5 \times 10^{-4}$  mol L<sup>-1</sup> TCPO. As the DPA, TCPO, and IMI solutions were prepared in ACN, the final solutions after mixing were 62% ACN (v/v). The concentrations of the final solutions (0.40 mL) are indicated in Figs. 1–4.

## Results and discussion

The effects on the  $I_{\max}$  and  $A$  values of different types of surfactants (anionic, cationic, and non-ionic), with different charged groups and hydrophobic chain lengths, were eval-

**Fig. 2.** Effect of pH and H<sub>2</sub>O<sub>2</sub> concentration on maximum emission intensity ( $I_{\max}$ ) and emission area ( $A$ ). Reaction of bis(2,4,6-trichlorophenyl)oxalate (TCPO) in acetonitrile (ACN)/ water (25% ACN), at different pH values in HTRIS<sup>+</sup>/TRIS and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> buffers. No surfactant. [TCPO] =  $5.6 \times 10^{-5}$  mol L<sup>-1</sup>, [DPA] =  $1.2 \times 10^{-4}$  mol L<sup>-1</sup>. (a) Unbuffered medium (■). (b) H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup>, pH 6.6 (●). (c) H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup>, pH 7.6 (▲). (d) HTRIS<sup>+</sup>/TRIS, pH 6.8 (◆). (e) HTRIS<sup>+</sup>/TRIS, pH 8.7 (★). DPA, 9,10-diphenylanthracene.



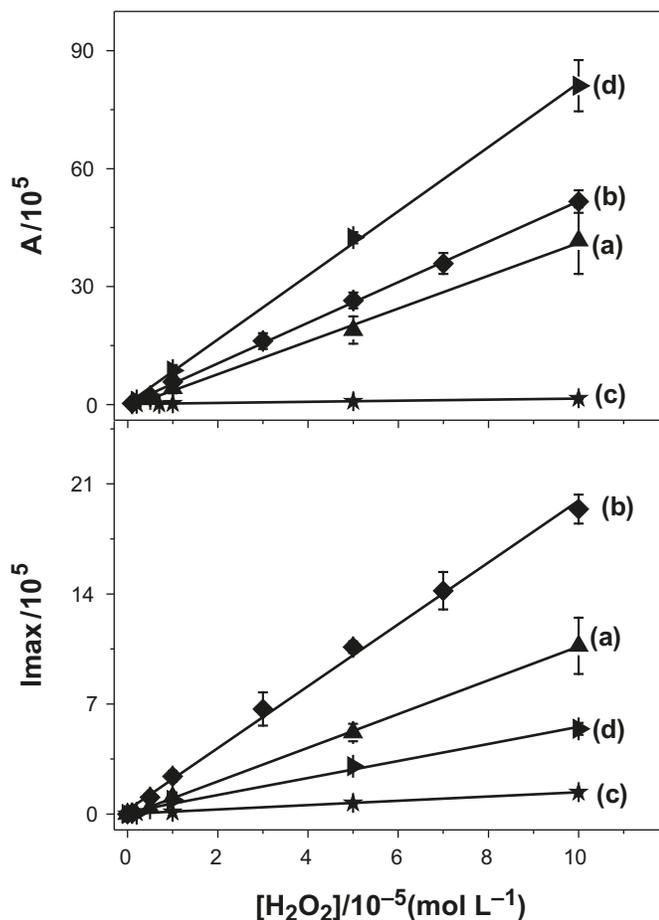
uated. We conducted experiments in the presence of fluorophores (FA or DPA) and oxalates (2-NPO or TCPO), as they were used in previous research<sup>22</sup> and showed different CL intensity–time profiles.

### Experiments in the presence of FA

The data for the 2-NPO reaction are reported in Tables 1 and 2. In the presence of the cationic surfactants (DDAB, CTAC, DODAC, and OTAC; Table 1)  $I_{\max}$  and  $t$  increased. TDTAB and DDAB have bromide ions (reactive counterion), which can react with hydrogen peroxide in solution; even so, DDAB (with a larger hydrophobic chain length) had a positive effect on the CL intensity. The non-ionic Tween 80 and anionic SDS surfactants (Table 2) also showed higher  $I_{\max}$ , whereas Brij 35, Brij 76, and Tween 20 had one partial quencher effect compared with the ACN/water systems with no surfactant.

The 2-NPO/H<sub>2</sub>O<sub>2</sub> reaction was very much affected by the medium acidity and the buffer nature. Some experiments

**Fig. 3.** Effect of different surfactants and  $\text{H}_2\text{O}_2$  concentration on maximum emission intensity ( $I_{\text{max}}$ ) and emission area ( $A$ ). Reaction of bis(2,4,6-trichlorophenyl)oxalate (TCPO) in acetonitrile (ACN)/water (25% ACN) in HTRIS<sup>+</sup>/TRIS pH 8.7 buffer. [TCPO] =  $5.6 \times 10^{-5}$  mol L<sup>-1</sup>, [DPA] =  $1.2 \times 10^{-4}$  mol L<sup>-1</sup>. (a) DDAH 10cmc (▲). (b) CTAB, 10cmc (◆). (c)  $\gamma$ -CD,  $6.2 \times 10^{-3}$  mol L<sup>-1</sup> (★). (d) SDS, 10cmc (▶). DPA, 9,10-diphenylanthracene; DDAH, 3-(dimethyldodecylammonio)-propane-1-sulfonate; CTAB, hexadecyltrimethylammonium bromide;  $\gamma$ -CD,  $\gamma$ -cyclodextrin; SDS, sodium dodecyl sulfate; cmc, critical micelle concentration.

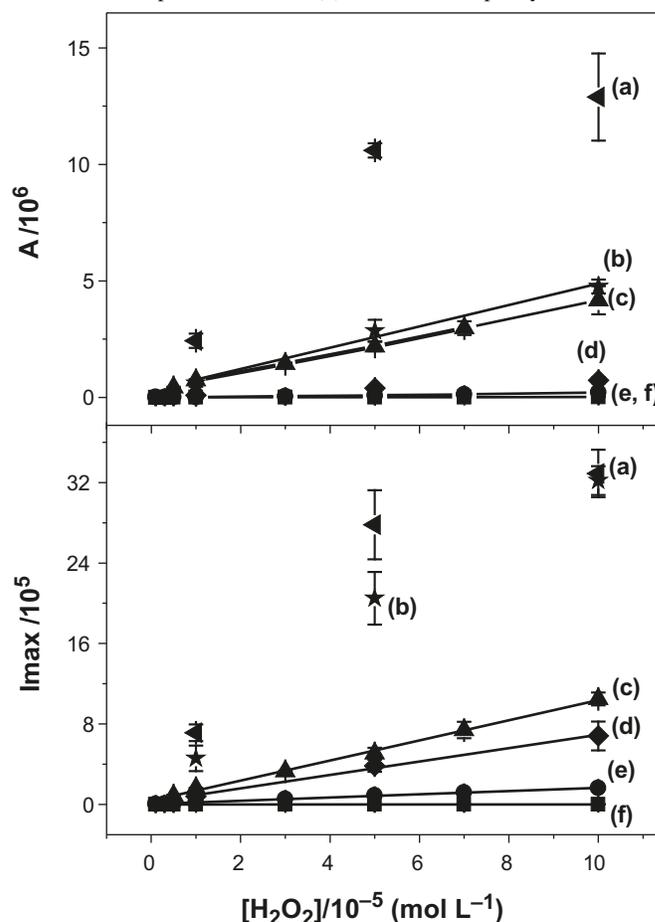


(data not shown) were carried out with  $3.5 \times 10^{-5}$  mol L<sup>-1</sup> 2-NPO,  $7.7 \times 10^{-4}$  mol L<sup>-1</sup>  $\text{H}_2\text{O}_2$ , and  $7.7 \times 10^{-5}$  mol L<sup>-1</sup> FA in the presence of Brij 76 (10cmc) and HTRIS<sup>+</sup>/TRIS (pH 8.3) or  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  (pH 8.5) medium. In the presence of Brij 76 and HTRIS<sup>+</sup>/TRIS buffer, the  $I_{\text{max}}$  value was twice the value of the one obtained in  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  buffer.

The data reported in Table 1 show that, for the same experimental conditions, the reaction with 2-NPO has a higher  $I_{\text{max}}$  than the reaction with TCPO, in the presence or absence of cationic surfactants. In the cationic surfactants (especially CTAC, DODAC, and OTAC) intense peaks were observed for 2-NPO/ $\text{H}_2\text{O}_2$  and TCPO/ $\text{H}_2\text{O}_2$  reactions, which had very low signals in the absence of surfactant.

Comparing the effect of the cationic micelles (CTAC and OTAC) (Table 1), CTAC, which has the smallest hydrophobic chain, showed a lower  $I_{\text{max}}$  value than OTAC. However, in DODAC medium, which forms vesicle micelles, the  $I_{\text{max}}$  value was in between CTAC and OTAC with a higher  $t$ . The

**Fig. 4.** Effect of imidazole (IMI) and  $\text{H}_2\text{O}_2$  concentration on maximum emission intensity ( $I_{\text{max}}$ ) and emission area ( $A$ ). Reaction of bis(2,4,6-trichlorophenyl)oxalate (TCPO) in acetonitrile (ACN)/water and HTRIS<sup>+</sup>/TRIS pH 8.7 buffer. No surfactant. [TCPO] =  $5.6 \times 10^{-5}$  mol L<sup>-1</sup>, [DPA] =  $1.2 \times 10^{-4}$  mol L<sup>-1</sup>. (a) 62% ACN, unbuffered medium, [IMI] =  $3.0 \times 10^{-3}$  mol L<sup>-1</sup> (▲). (b) 62% ACN; HTRIS<sup>+</sup>/TRIS, pH 8.7; [IMI] =  $3.0 \times 10^{-3}$  mol L<sup>-1</sup> (★). (c) 37% ACN, unbuffered medium, [IMI] =  $7.5 \times 10^{-4}$  mol L<sup>-1</sup> (▲). (d) 37% ACN; HTRIS<sup>+</sup>/TRIS, pH 8.7; [IMI] =  $7.5 \times 10^{-4}$  mol L<sup>-1</sup> (◆). (e) 25% ACN, unbuffered medium, no IMI (●). (f) 25% ACN; HTRIS<sup>+</sup>/TRIS, pH 8.7; no IMI (■). DPA, 9,10-diphenylanthracene.



increase of the hydrocarbon chain length of the surfactant results in an increase of both  $A$  and  $I_{\text{max}}$ . The length of the hydrocarbon chain of the surfactant influences the size of the micelles and the depth of penetration is different. This process may be favored by longer chain surfactants, which form looser micelles.

#### Experiments with TCPO in the presence of DPA

Additional experiments were carried out with DPA replacing FA. The acidity and micelle effects on the TCPO chemiluminescent reaction with hydrogen peroxide were investigated by analyzing the values of  $I_{\text{max}}$  and  $A$ .

Some CL intensity-time profiles, in the absence of IMI, are represented in Fig. 1. The emission began just after the addition of TCPO. The presence of  $6.2 \times 10^{-3}$  mol L<sup>-1</sup>  $\gamma$ -CD had no effect. However SDS, DDAH, and CTAB increased the CL intensity. The results are shown in Figs. 2–5.

**Fig. 5.** Effect of  $\text{H}_2\text{O}_2$  concentration on maximum emission intensity ( $I_{\text{max}}$ ) and emission area ( $A$ ). Reaction of bis(2,4,6-trichlorophenyl) oxalate (TCPO) in acetonitrile (ACN)/water (62% ACN) in unbuffered medium with different surfactants.  $[\text{TCPO}] = 5.6 \times 10^{-5} \text{ mol L}^{-1}$ ,  $[\text{DPA}] = 1.2 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{IMI}] = 3.0 \times 10^{-3} \text{ mol L}^{-1}$ . (a)  $[\text{DDAH}] = 10 \text{ cmc}$  ( $\blacktriangle$ ). (b)  $[\text{CTAB}] = 10 \text{ cmc}$  ( $\blacklozenge$ ). (c)  $[\gamma\text{-CD}] = 2.5 \times 10^{-3} \text{ mol L}^{-1}$  ( $\blackstar$ ). (d)  $[\text{SDS}] = 10 \text{ cmc}$  ( $\blacktriangleright$ ). (e) No surfactant ( $\bullet$ ). DPA, 9,10-diphenylanthracene; IMI, imidazole; DDAH, 3-(dimethyldodecylammonio)-propane-1-sulfonate; CTAB, hexadecyltrimethylammonium bromide;  $\gamma\text{-CD}$ ,  $\gamma$ -cyclodextrin; SDS, sodium dodecyl sulfate; cmc, critical micelle concentration.

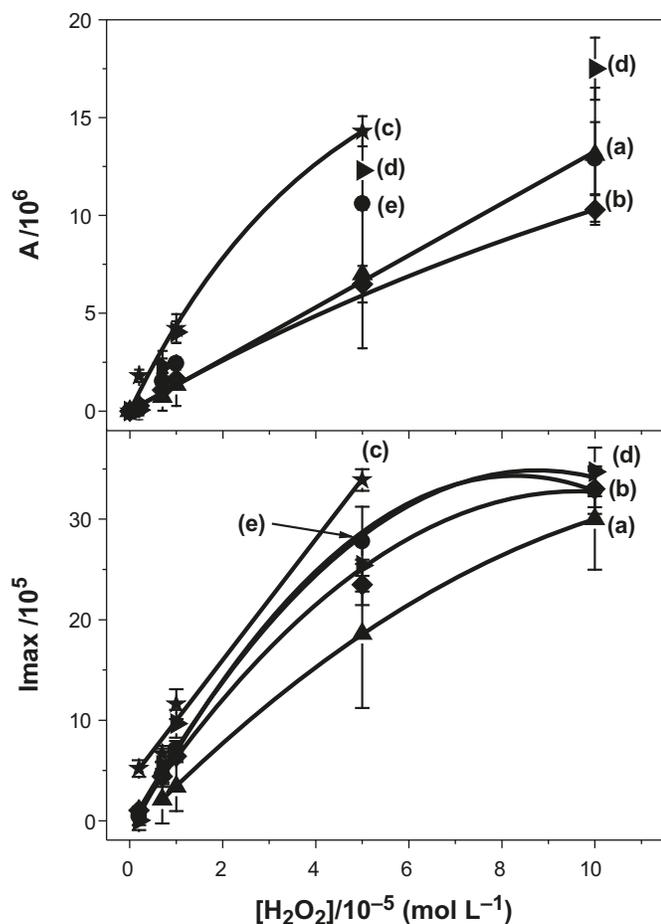


Figure 2 shows the effect of  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  and HTRIS<sup>+</sup>/TRIS buffers and the pH in the absence of surfactant. There was one smaller increase on the signals ( $I_{\text{max}}$  and  $A$ ) in  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  medium compared with the unbuffered medium. The considerable enhancement in HTRIS<sup>+</sup>/TRIS buffer might be due to the catalytic effect of TRIS, as reported by Hayakawa et al.<sup>37</sup>

Figure 3 shows the effect of some of the surfactants. SDS (anionic) and  $\gamma\text{-CD}$  ( $0.01 \text{ mol L}^{-1}$ ) completely suppressed the signal in unbuffered and  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  media (data not shown). However, as TRIS has some catalytic effect, a relatively high increase occurs on the  $A$  and  $I_{\text{max}}$  values in HTRIS<sup>+</sup>/TRIS buffer solution (pH 8.7) in the presence of these surfactants (compare Figs. 1 and 2). The special combination of TRIS and CTAB (cationic) showed the highest increase of the  $I_{\text{max}}$  value (Fig. 2b). The following is the order for the  $I_{\text{max}}$  values: CTAB (cationic) > DDAH (amphiprotic) > SDS (anionic) >  $\gamma\text{-CD}$ ; and the following is the

order for the area ( $A$ ): SDS (anionic) > CTAB (cationic) > DDAH (amphiprotic) >  $\gamma\text{-CD}$ .

Some relatively small signals were observed in the experiments in unbuffered medium in the presence of DDAH and CTAB (data not shown). When  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  (pH 7.6) was used, one relatively small signal was observed only in the presence of CTAB.

By comparing Figs. 2 (no surfactant) and 3,  $I_{\text{max}}$  and  $A$  were higher when the surfactants were present in HTRIS<sup>+</sup>/TRIS (pH 8.7), except when  $\gamma\text{-CD}$  was used (Fig. 2c). For the same hydrogen peroxide concentration, SDS had the most positive effect only on  $A$ , however, CTAB and DDAH also had good effects on  $I_{\text{max}}$  and  $A$  values, respectively.

1-Aroxalylimidazole and 1,1'-oxalylidiimidazole (Scheme 1) have been suggested as the relevant high-producing intermediates in aqueous ACN.<sup>31,32</sup> The catalytic effect of IMI on the TCPO/ $\text{H}_2\text{O}_2$  reaction can be seen from the data in Fig. 3, as a large increase in the signals was observed.

As TCPO is easily hydrolyzed,  $I_{\text{max}}$  and  $A$  increase in the medium with the higher percentage of ACN. There is no linearity of  $I_{\text{max}}$  and  $A$  with the concentration of hydrogen peroxide in 62% ACN and HTRIS<sup>+</sup>/TRIS (Figs. 4a and 4b). However, in the presence of 37% and 25% ACN a linear dependence was observed (Figs. 4c–4e).

In the presence of IMI and 62% ACN,  $\gamma\text{-CD}$  had the highest effect on the  $I_{\text{max}}$  and  $A$  values (compare Figs. 3c and 5c); at  $1 \times 10^{-4} \text{ mol L}^{-1}$  hydrogen peroxide, these values were so high that they could not be measured with the equipment that was used, showing one marked effect with the concentrations of hydrogen peroxide higher than  $5 \times 10^{-4} \text{ mol L}^{-1}$ . In the presence of IMI the effect of surfactants is not marked (compare Fig. 5e without surfactant and Figs. 5a and 5b with DDAH and CTAB), since the catalytic effect of IMI (better than TRIS) is the dominant influence. There is no linearity of  $I_{\text{max}}$  and  $A$  with hydrogen peroxide concentration, which would not be suitable for analytical purposes.

The use of  $\alpha\text{-CD}$ ,  $\gamma\text{-CD}$ , and  $\beta\text{-CD}$  was suggested by Kojó et al.<sup>38</sup> to obtain better sensitivity in the analytical method for the determination of dansyl acid and glucose based on the glucose oxidase/ $\text{H}_2\text{O}_2$  reaction in the presence of TCPO.  $\gamma\text{-CD}$  had better sensitivity in the phosphate buffer (pH 7.0), and the produced hydrogen peroxide was measured after 1 min with stirring at 37 °C. The detection limit corresponded to 1 pmol of hydrogen peroxide.

Inclusion in the CD cavity, which has a hydrophobic nature, is known to significantly affect the luminescent properties.<sup>39</sup> Woolf and Grayeski<sup>39</sup> reported the aqueous peroxyoxalate reactions of 4,4'-[oxalylbis[(trifluoromethylsulfonyl)imino]ethylene]bis[4-methylmorpholinium trifluoromethane sulfonate with hydrogen peroxide in the presence of several fluorophores and  $\alpha$ -,  $\gamma$ - and  $\beta$ -CD. The enhancement due to the CDs was attributed to the increase in reaction rate and excitation and fluorescence efficiencies of the emitting species.

In Table 3, analytical parameters for  $\text{H}_2\text{O}_2$  determination are represented for some selected experimental conditions. The detection limit is defined as three times the standard deviation of the linear coefficient divided by the angular coefficient value. The background signal and the standard deviation of the linear coefficient also increased, which restricts the improvement of the detection limits ( $10^{-6} \text{ mol L}^{-1}$ )

**Table 3.** Analytical parameters for H<sub>2</sub>O<sub>2</sub> determination.

Medium/%ACN	Surfactant	Slope/10 <sup>10</sup>		Detection limit/10 <sup>6</sup> (mol L <sup>-1</sup> )	
		I <sub>max</sub>	A	I <sub>max</sub>	A
HTRIS <sup>+</sup> /TRIS (pH 8.7)/25%	No	0.16	0.20	0.158	0.924
HTRIS <sup>+</sup> /TRIS (pH 8.7)/25%	DDAH	1.07	4.17	2.51	4.11
	CTAB	1.97	5.16	1.74	0.686
	γ-CD	0.14	0.14	2.09	7.80
	SDS	0.54	8.16	2.00	1.17
No buffer ([IMI] = 6.0×10 <sup>-3</sup> mol L <sup>-1</sup> )/37%	No	1.00	3.87	0.730	0.716
HTRIS <sup>+</sup> /TRIS (pH 8.7) ([IMI] = 6.0×10 <sup>-3</sup> mol L <sup>-1</sup> )/37%	No	0.66	0.71	12.6	12.8

**Note:** Linear range 0.01 × 10<sup>-4</sup> to 1.0 × 10<sup>-4</sup> mol L<sup>-1</sup>. IMI, imidazole; DDAH, 3-(dimethyldodecylammonio)-propane-1-sulfonate; CTAB, hexadecyltrimethylammonium bromide; γ-CD, γ-cyclodextrin; SDS, sodium dodecyl sulfate.

in the presence of the surfactants. In the presence of IMI, as a catalyst, the buffer HTRIS<sup>+</sup>/TRIS had a negative effect; however, one better detection limit was obtained in the absence of surfactant and HTRIS<sup>+</sup>/TRIS. The slopes of the calibration curves (*A* vs [H<sub>2</sub>O<sub>2</sub>] and *I*<sub>max</sub> vs [H<sub>2</sub>O<sub>2</sub>]), which represent the sensitivity, increase in the presence of DDAH, CTAB, and SDS in HTRIS<sup>+</sup>/TRIS buffer (pH 8.7, 25% ACN), whereas γ-CD had a small effect.

The analytical parameters reported by Dan et al.,<sup>40</sup> obtained for the chemiluminescent reaction of METQ with hydrogen peroxide in the presence of Brij 35 or CTAB, showed one detection limit of about 10<sup>-3</sup> mol L<sup>-1</sup>; so in the present work better results were obtained.

## Conclusion

Under the experimental conditions of the present work, the presence of some surfactants causes an increase in the *I*<sub>max</sub> and *A* signals. The effect on the increase is dependent on the nature of the fluorophore and hydrophobicity, charge differences, and concentration of the surfactant.

The effect of surfactants on the CL reaction is still unclear and depends on several parameters, and the comparison of different studies is not possible. The complexity of the system does not allow a definitive assignment of the species involved. However, based on the available literature and the data from Table 3, the sensitivity for hydrogen peroxide determination, considering the slope of the calibration curves (Table 3), improved with the introduction of some surfactants (DDAH, CTAB, and SDS) in HTRIS<sup>+</sup>/TRIS buffer.

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