

A New Enhanced Oscillating Chemiluminescence System with Increased Chemiluminescence Intensity and Oscillation Time

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Received: 24 September 2007 / Accepted: 12 November 2007 / Published online: 13 December 2007
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Abstract Oscillating chemical reactions are complex systems, involving a large number of chemical species. In an oscillating chemical reaction, some species, usually a reaction intermediate, exhibit fluctuation in its concentration. In this report, oscillating chemiluminescence produced by the addition of thiosemicarbazide (TSC) to the oscillating system H_2O_2 –KSCN– CuSO_4 –NaOH was investigated using luminometry method. The effects of complexing agents, triethylenetetramine (TETA) and D-penicillamine, on the behavior of the oscillating system were investigated. Moreover, the influence of non-aqueous solvents, dimethyl sulfoxide (DMSO), nitromethane and acetonitrile, was studied. In the presence of solvents with high protophilicity, the chemiluminescence (CL) intensity was increased (sevenfold), the light emitting and oscillating time was enhanced by threefold. In addition, the effect of presence of non-ionic, cationic, and anionic surfactants was investigated. Non-ionic surfactant increased the intensity of the oscillating CL reaction by 4.5-fold.

Keywords Oscillating chemiluminescence · Thiosemicarbazide · Chelating agent · Non-aqueous solvent · Surfactant effect

Introduction

Oscillating chemical systems have been the focus of many researchers for the past two decades because of the wealth

of dynamic behavior in these far-from-equilibrium complex systems [1, 2]. Basically, an oscillating chemical reaction is the one where some species (usually a reaction intermediate) exhibit fluctuations in their concentrations; such fluctuations are periodic or non-periodic under specific reaction conditions. For a chemical reaction to be the source of an auto-oscillating system, at least the following requirements must be met (a) the system should be far from thermodynamic equilibrium, i.e., its Gibbs free energy difference (ΔG) should be large and negative; (b) there should be at least one autocatalytic step or, alternatively, cross-catalysis between two steps of the reaction mechanism; and (c) the system should possess at least two steady states under the initial conditions [3–4]. Several methods, such as pH metry, potentiometry [5–8] and chemiluminescence [9–12], have been applied in the investigation of oscillating reactions. Copper (II) takes part as a catalyst in a major group of oscillating systems. The most widely studied among Cu (II) oscillators is the reaction developed by Orban [13] based on the oxidation of KSCN by H_2O_2 in a strongly alkaline medium, which is catalyzed by traces of copper. The reaction takes place in both open and closed systems; in the latter, however, oscillations are gradually damped and eventually disappear altogether. While a substantial number of chemical oscillators are known [8], relatively few oscillating chemiluminescent reactions in the liquid phase have been described [10]. A new chemiluminescence (CL) reagent, thiosemicarbazide (TSC) has been already proposed for the first time by our research group [14] and based on the catalytic activity of copper (II) on thiosemicarbazide (TSC)- H_2O_2 CL system, a novel method for the determination of nanogram per milliliter amounts of copper (II) in human hair [14] and micro molar amounts of EDTA in ophthalmic drugs has been established [15]. In our

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previous work oscillating chemiluminescence produced by the addition of thiosemicarbazide (TSC) to the oscillating system $\text{H}_2\text{O}_2\text{-KSCN-CuSO}_4\text{-NaOH}$ was reported and the dependence of the induction time and the oscillation period on the reagent concentrations was investigated [16]. Typical oscillation attributes such as the oscillation period and amplitude were recently used to evaluate their use in chemical analysis [17, 18]. In this report, using luminometry technique, the effects of complexing agents such as TETA and D-Penicillamine on TSC- $\text{H}_2\text{O}_2\text{-KSCN-CuSO}_4\text{-NaOH}$ system were investigated. The influence of non-aqueous solvents DMSO, nitromethane and acetonitrile was also examined. Furthermore, the behavior of the oscillating system and chemiluminescence intensity in the presence of different surfactants was studied.

Experimental

Reagents

Stock solutions were prepared from commercially available reagent-grade (Merck) potassium thiocyanate, 30% hydrogen peroxide, sodium hydroxide, copper sulphate pentahydrate, DMSO, nitromethane, acetonitrile, sodium dodecyl sulfate (SDS), Triton-X-100, *N*-cetyl-*N,N,N*-trimethyl-ammonium bromide (CTMAB), TSC without further purification and D-Penicillamine was purchased from Sigma. Doubly distilled water was used throughout.

Apparatus

The oscillating reaction was monitored by a Junior LB 9509 luminometer (Berthold Technologies, Germany). Data were collected and excel program was used for plotting graphs (intensity vs time). Experiments were carried out with magnetic stirring at ambient temperature ca. 21 °C. The time resolution of the apparatus is 0.6 s and CL intensity is reported in relative units.

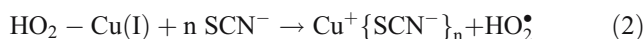
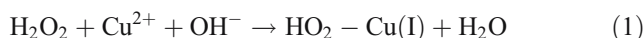
Procedure

Oscillating light producing reactions were carried out in a 12 × 47 mm test tube placed in the luminometer sample holder. A 2.0 ml portion of the solution containing $5.0 \times 10^{-2} \text{ mol l}^{-1}$ NaOH, $4.0 \times 10^{-2} \text{ mol l}^{-1}$ KSCN, $7.0 \times 10^{-4} \text{ mol l}^{-1}$ CuSO_4 and $1.0 \times 10^{-3} \text{ mol l}^{-1}$ TSC (reagent 1) was added into the test tube. Then 1 ml of 1 mol l^{-1} H_2O_2 (reagent 2) was injected to initiate oscillating CL reaction. The cover was closed and the progress of oscillating CL was continuously monitored on the computer connected to luminometer.

Results and discussion

Mechanism of oscillating chemiluminescence system

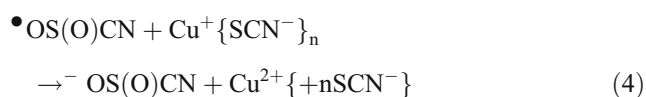
In TSC CL reaction, upon injection of H_2O_2 into the mixed solution of Cu (II)-TSC in basic media, CL occurred and emission intensity was dependent on Cu (II) concentration. In this reaction, Cu (II) catalyzes the radical decomposition of H_2O_2 to produce superoxide ion. The superoxide ion reacts with TSC to form an intermediate product, which emits light by fragmenting into two parts [14]. Based on similarity of ingredients participated in CL [Cu(II)- $\text{H}_2\text{O}_2\text{-NaOH-TSC}$] and the oscillating system [Cu(II)- $\text{H}_2\text{O}_2\text{-NaOH-KSCN}$], it was proposed that TSC can act as a chemiluminescence indicator for Cu(II) in oscillating system. The $\text{H}_2\text{O}_2\text{-KSCN-CuSO}_4$ system is the slowly damped oscillating system under batch conditions. Such batch oscillations are quite rare, even among the much larger group of halogen-based chemical oscillators. As stated by Orban et al. [19] the mechanism for the oscillatory $\text{H}_2\text{O}_2\text{-KSCN-CuSO}_4$ system is composed of 30 kinetic reactions involving 26 independent variables. Briefly, in this oscillatory system, Copper(II) catalyzes alkaline H_2O_2 decomposition in the mixed reaction and provides two essential intermediates, HO_2^\bullet and $\text{Cu}^+ \{\text{SCN}^-\}_n$ for the core part of the oscillation. Meanwhile by changing Cu (II) to $\text{Cu}^+ \{\text{SCN}^-\}_n$, chemiluminescence intensity decreases.



where n may be 2, 3, or 4.

Orban *et al.* [13] postulated that SCN^- strongly complexes Cu^+ after it is formed from the decomposition of $\text{HO}_2\text{-Cu(I)}$, preventing copper from immediate reoxidation by O_2 or H_2O_2 . In the reaction between H_2O_2 and KSCN some intermediates such as cyanosulfite, $^-\text{OS(O)CN}$, and peroxocyanosulfite, $^-\text{OOS(O)CN}$, are produced (the oxygen in parentheses is double bonded to sulfur). The intermediate $^-\text{OS(O)CN}$ is produced very slowly in reaction, and it initially has a very low concentration. When the concentrations of $^-\text{OS(O)CN}$ and $\text{Cu}^+ \{\text{SCN}^-\}_n$ become high enough to make this pathway (Eqs. 3 and 4) significant, the Cu (I) is simultaneously oxidized to Cu (II). Thus light emission is started again. The sharp increase in the light emission stops when most of the $\text{Cu}^+ \{\text{SCN}^-\}_n$ is consumed.





Therefore oscillating chemical system exhibits periodic changes in the concentration of Cu (II). Since CL is dependent on the concentration of Cu (II) the oscillation of Cu(II) concentration is reflected in cyclic changes in the intensity of light emission ($\lambda_{\text{max}}=440 \text{ nm}$).

Solvent effect

To investigate the effect of non-aqueous solvents on the behavior of the oscillating chemiluminescence, we have examined DMSO (protophilic solvent), Nitromethane and Acetonitrile (protophobic solvents) [20]. In these studies, during the oscillating reaction, the emitted light was monitored using the luminometry technique. Factors such as the number of pulses, period of oscillating, total time of oscillating chemiluminescence and intensity of emitted light was studied. The effect of DMSO on TSC–H₂O₂–KSCN–CuSO₄–NaOH oscillating system was studied in a series of experiments at different concentrations of DMSO, 0.0, 5.0, 10, 20% (v/v) but constant concentrations of NaOH, KSCN, CuSO₄, H₂O₂ and TSC, 5.0×10^{-2} , 4.0×10^{-2} , 7.0×10^{-4} , 1.0, and $1.0 \times 10^{-3} \text{ mol l}^{-1}$ respectively. Results obtained from this experiment (Fig. 1) reveal that by increasing the DMSO concentration, a significant increase of light intensity as well as total time of oscillating CL occurs. Radical and anion radical species play a critical role in the oscillating CL system [1, 2]. Clearly, the reactivity of chemical species in solvents is inversally proportional to solvation of the species in solvent. DMSO is an example of protophilic solvents and solvation of radical and anion radical species such as OS(O)CN and O₂^{•-} are much weaker in DMSO than in water [20] therefore it seems that their lifetime and reactivity in DMSO is higher than in water. With increasing the concentration of DMSO, the life time and reactivity of the unstable intermediate and consequently the light intensity, number of pulses and oscillation duration increased. However, the induction time and period remained fairly constant. In protophobic solvents, nitromethane and acetonitrile, solvation of radical and anion radical species are much stronger than in water therefore, their reactivity in nitromethane and acetonitrile is lower than in water and in our experiments in the presence of only 5% (v/v) of any of these solvents no light was observed.

Chelating agent effect

Copper plays a critical role as a catalyst in the oscillating and CL system [13–16]. In the our previous experiments [16] it

was observed that copper has a significant effect on the oscillating period, therefore, it is worthwhile to examine the effect of chelating agents in this system. By addition of chelating agent copper ion tends to react with it and consequently the behavior of the oscillating system is affected. In this study, triethylenetetramine (TETA) and D-penicillamine were used as Chelating agents in the oscillation system of TSC–H₂O₂–KSCN–CuSO₄–NaOH. The luminescence spectra of the TSC–H₂O₂–KSCN–CuSO₄–NaOH oscillating system were obtained at different concentrations of TETA, 5.0×10^{-7} , 1.0×10^{-6} , 5.0×10^{-6} and $1.0 \times 10^{-5} \text{ mol l}^{-1}$, and constant concentrations of TSC, H₂O₂, KSCN, Cu(II), and NaOH, 1×10^{-3} , 1.0, 4.0×10^{-2} , 5.0×10^{-4} and $5.0 \times 10^{-2} \text{ mol l}^{-1}$, respectively. Figure 2 represents luminescence spectra of the TSC–H₂O₂–KSCN–CuSO₄–NaOH oscillating system in the presence of TETA. Results obtained from this experiment reveal that by increasing the concentration of TETA, the period of oscillations and amplitude is decreased. The effect of D-Penicillamine was studied with different concentrations of 5.0×10^{-7} , 1.0×10^{-6} , 5.0×10^{-6} and $1.0 \times 10^{-5} \text{ mol l}^{-1}$, but constant concentrations of TSC, H₂O₂, KSCN, Cu(II), and NaOH, 1×10^{-3} , 1.0, 4.0×10^{-2} , 5.0×10^{-4} and $5.0 \times 10^{-2} \text{ mol l}^{-1}$ respectively. Figure 3 illustrates that by increasing the concentration of D-Penicillamine, the period of oscillations slightly decreased. Influence of chelating agent on oscillating CL may arise in the following possible ways: (1) By increasing the concentration of chelating agent, the amount of Cu (II) involved in the reaction of oscillating system is reduced and consequently the oscillating frequency is decreased. (2) Indeed the more tendency of chelating agent to copper(II) influences the redox potential of Cu (II)/Cu (I) couple and consequently time delay in Cu²⁺ reduction to Cu⁺ {SCN⁻}_n is affected and the oscillating frequency is varied. Reports in the literature indicate that decreasing Cu (II) concentration causes an increase in the oscillation period [7, 16, 26]. Therefore the first possibility is not likely the case. Second explanation seems reasonable since Cu⁺ is stabilized by SCN⁻ as a complex Cu⁺ {SCN⁻}_n, resulting in a time delay in its reoxidation to Cu²⁺ [19]. Therefore variation in the Cu (II)/Cu (I) couple redox potential influences the time delay and consequently the period of oscillation.

Surfactant effect

The utilization of surfactants in CL reaction systems offered many advantages [21, 25]. In order to investigate whether surfactant media function effectively in the present oscillating CL system, some organized systems, including a non-ionic surfactant (Triton X-100), a cationic surfactant (CTMAB) and an anionic surfactant (SDS) were added to the present system. By adding CTMAB, it entered into an interaction with SCN⁻. The solution became turbid, and

Fig. 1 Effect of DMSO on the oscillating chemiluminescence system of TSC–H₂O₂–KSCN–CuSO₄–NaOH in a batch reactor with different concentrations of DMSO (**a** 0.0, **b** 5.0, **c** 10, **d** 20% (v/v); with constant concentrations of TSC, $1.0 \times 10^{-3} \text{ mol l}^{-1}$, H₂O₂, 1.0 mol l^{-1} ; KSCN, $4 \times 10^{-2} \text{ mol l}^{-1}$; CuSO₄, $7 \times 10^{-4} \text{ mol l}^{-1}$ and NaOH, $5 \times 10^{-2} \text{ mol l}^{-1}$)

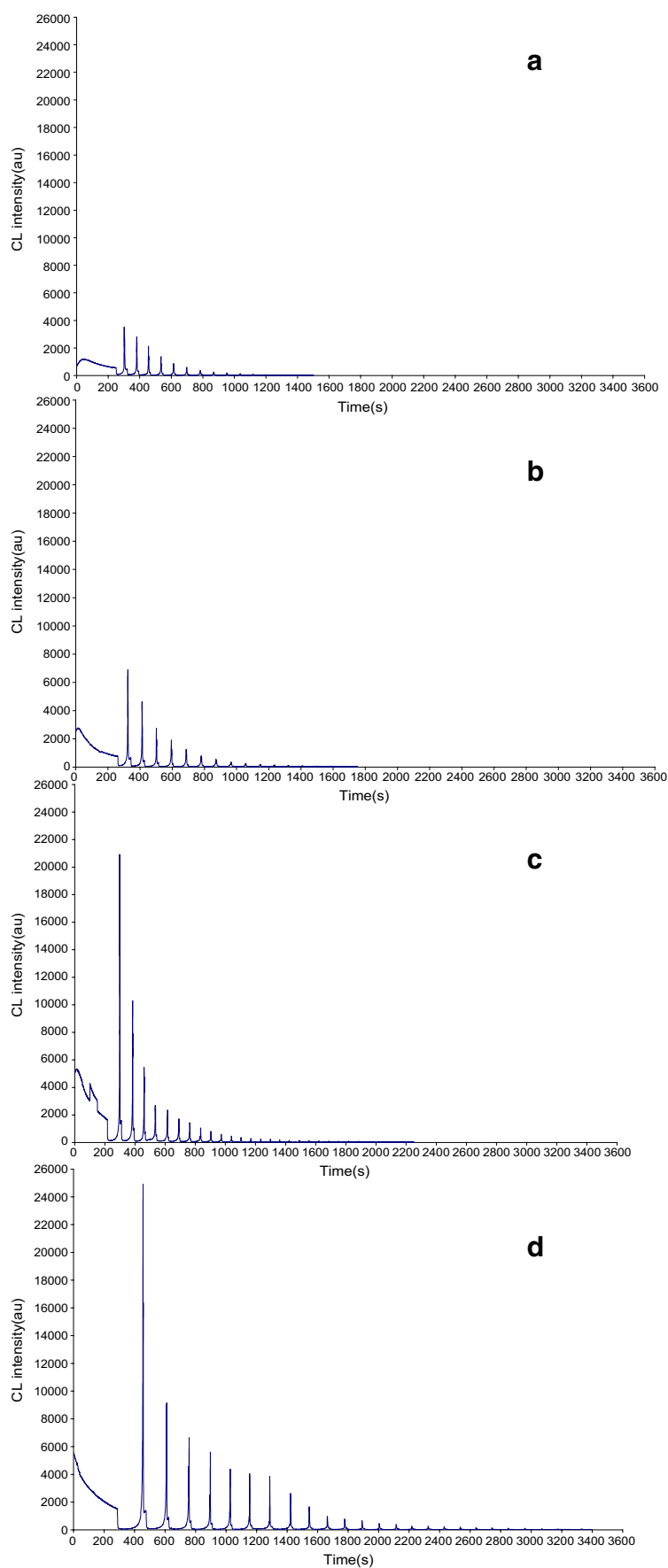
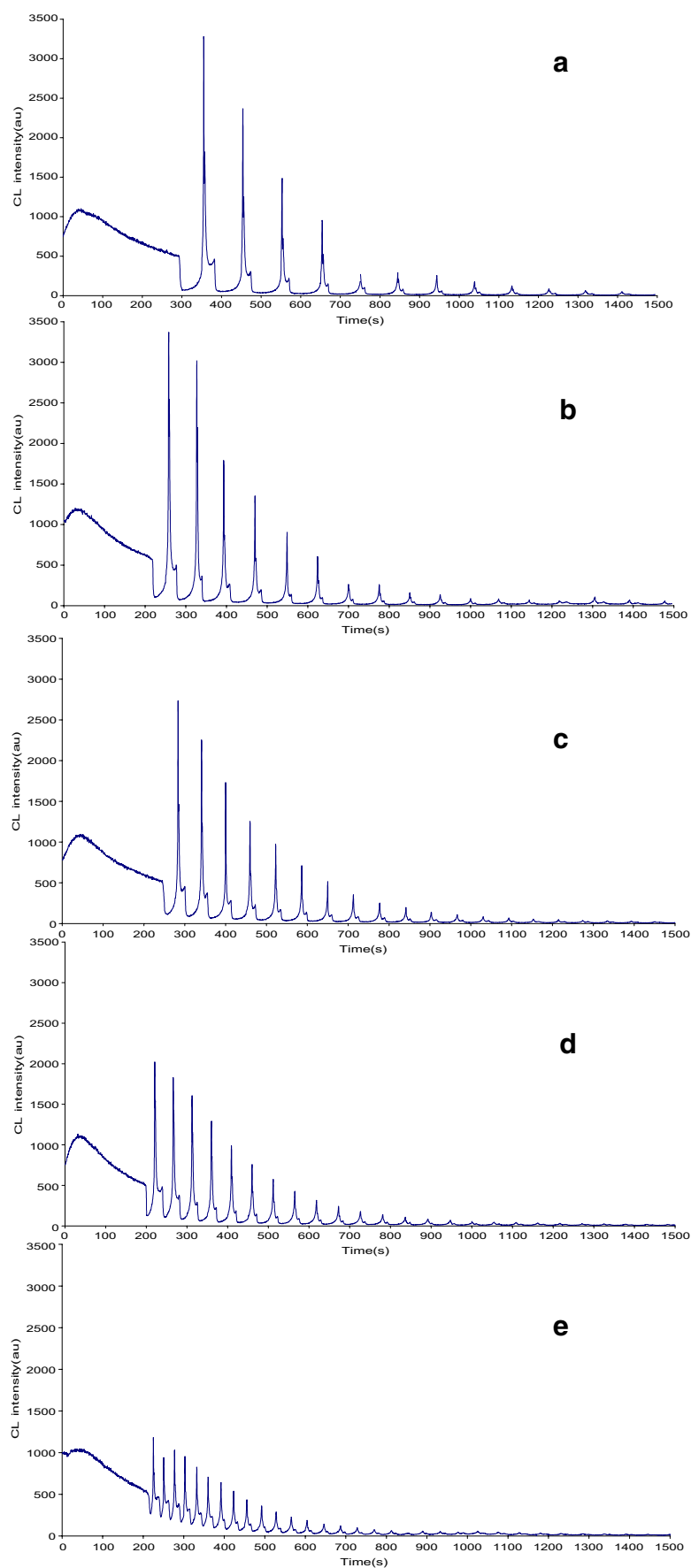


Fig. 2 Effect of TETA on the oscillating chemiluminescence system of TSC–H₂O₂–KSCN–CuSO₄–NaOH in a batch reactor with different concentrations of TETA (**a** 0.0, **b** 5.0×10^{-7} , **c** 1.0×10^{-6} , **d** 5.0×10^{-6} , **e** 1.0×10^{-5} mol l⁻¹ and constant concentrations of TSC, 1.0×10^{-3} mol l⁻¹, H₂O₂, 1.0 mol l⁻¹; KSCN, 4×10^{-2} mol l⁻¹; CuSO₄, 7×10^{-4} mol l⁻¹ and NaOH, 5×10^{-2} mol l⁻¹)



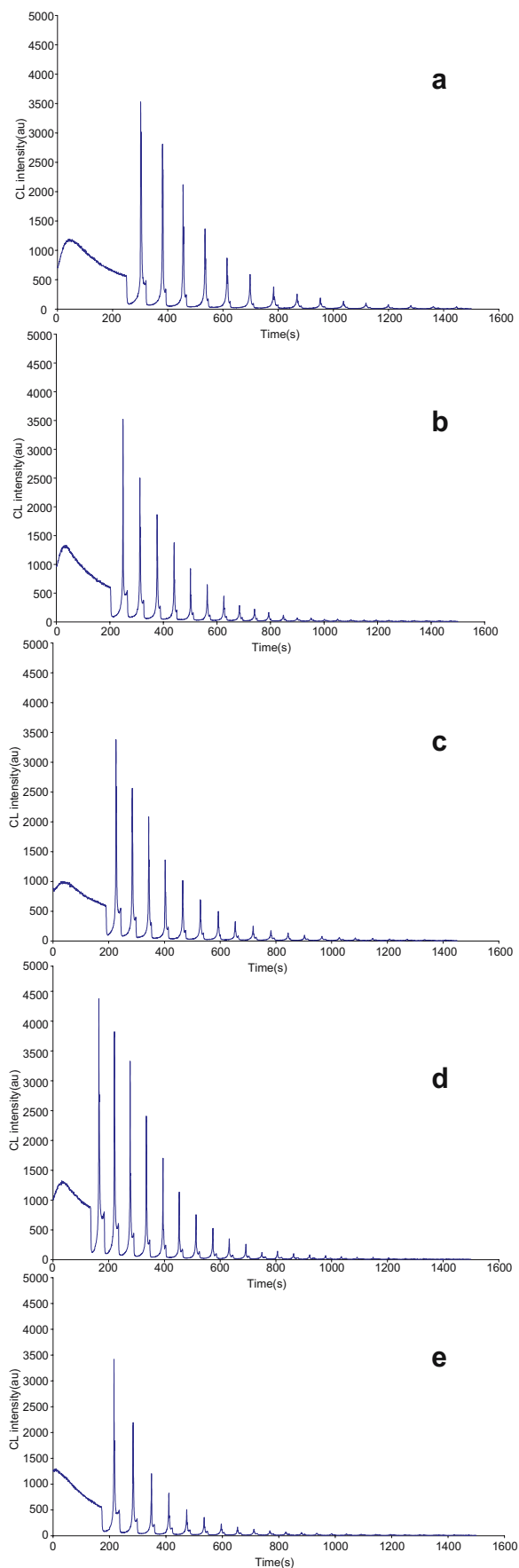


Fig. 3 Effect of D-Penicillamine on the oscillating chemiluminescence system of TSC–H₂O₂–KSCN–CuSO₄–NaOH in a batch reactor with different concentrations of D-penicillamine (**a** 0.0, **b** 5.0×10^{-7} , **c** 1.0×10^{-6} , **d** 5.0×10^{-6} , **e** 1.0×10^{-5} mol l⁻¹ and constant concentrations of TSC, 1.0×10^{-3} mol l⁻¹, H₂O₂, 1.0 mol l⁻¹; KSCN, 4×10^{-2} mol l⁻¹; CuSO₄, 7×10^{-4} mol l⁻¹ and NaOH, 5×10^{-2} mol l⁻¹]

white precipitate formed and no light was observed. The effect of Triton X-100 on relative CL intensity was studied at concentrations of 0.0, 0.5, 1.0, 1.5% (v/v; Fig. 4). The CL intensity was found to increase with increasing Triton X-100 concentration and the induction time and period was remained fairly constant. SDS gave somewhat enhanced signals with decreased induction times (Fig. 5) but the enhancing effect of Triton X-100 was higher than that of SDS. CL reaction in micellar media showed that sensitized CL could arise in the following possible ways: (1) Solubilization. The CL of lucigenin was enhanced by non-ionic surfactant Triton-X 100 micelles because the insoluble lucigenin and excited intermediate become more soluble in the micellar medium [21]. (2) Electrostatic effect. The electrostatic effect of the ionic surfactant helps to concentrate the counter ion reactant [22]. (3) Altering the microenvironment of the CL reaction. The cage structure of the micelle is helpful for stabilizing the excited state and prevents it from quenching [23, 24]. (4) Altering the pH of the microenvironment [25], as pH is an important parameter for most CL reactions. In the studied oscillating CL system, all the above possible explanations seem to be reasonable except the first one, since there is no insoluble CL reagent in the system. Based on explanation (II) and our previous experiences [14, 15], the cationic surfactants should enhance CL much more than the anionic surfactants, since [•]O₂ could be concentrated in the Stern zone of the cationic micelle. However, opposite result was obtained to the reaction between SCN⁻ and CTMAB where the solution became turbid, and a white precipitate formed.

Conclusions

This work presents luminometry studies of oscillating chemiluminescence in the system of H₂O₂–KSCN–CuSO₄–NaOH. By using non-aqueous solvent and micellar systems as the medium for oscillating CL systems, the unstable free radical or singlet oxygen generated in oscillating CL reaction could be protected from quenching, which is especially important for the oscillating CL emitted by free radicals or singlet oxygen molecules. The amplitude and the overall oscillating time is increased since the life time of the unstable intermediate or product of the reaction in such a medium is prolonged. The behavior of the oscillating reaction is considerably affected by TETA but the influence of D-Penicillamine was not remarkable.

Fig. 4 Effect of non-ionic surfactant (Triton-X-100) on the oscillating chemiluminescence system of TSC–H₂O₂–KSCN–CuSO₄–NaOH in a batch reactor with different concentrations of Triton-X-100 (**a** 0.0, **b** 0.5, **c** 1.0, **d** 1.5% (v/v) and constant concentrations of TSC, $1.0 \times 10^{-3} \text{ mol l}^{-1}$, H₂O₂, 1.0 mol l^{-1} ; KSCN, $4 \times 10^{-2} \text{ mol l}^{-1}$; CuSO₄, $7 \times 10^{-4} \text{ mol l}^{-1}$ and NaOH, $5 \times 10^{-2} \text{ mol l}^{-1}$)

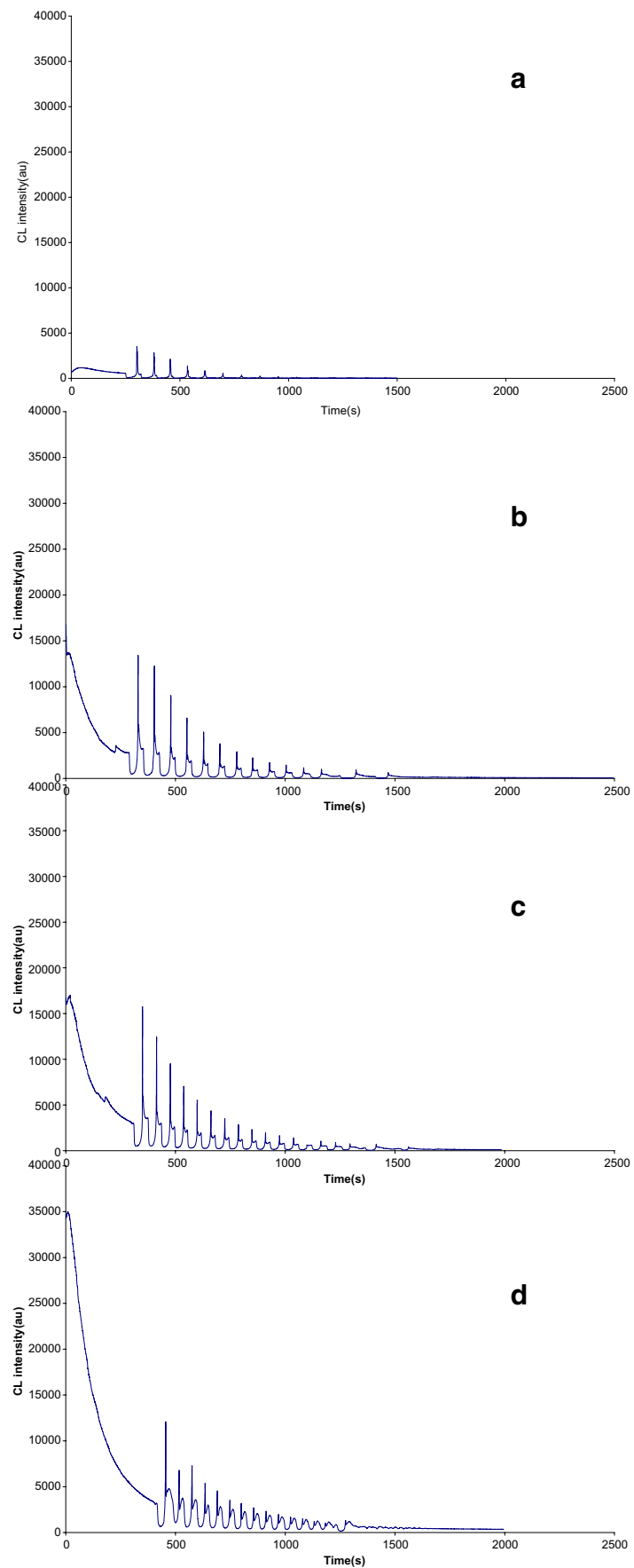
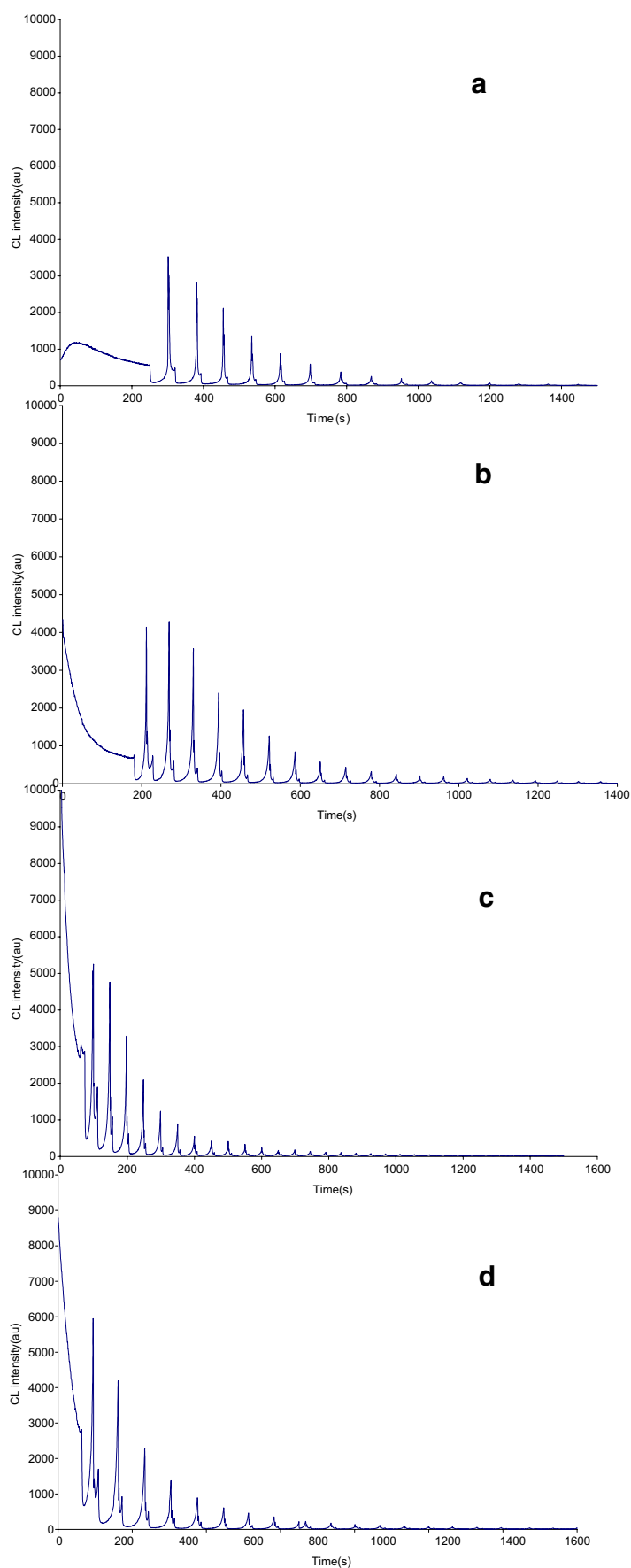


Fig. 5 Effect of anionic surfactant (*SDS*) on the oscillating chemiluminescence system of TSC–H₂O₂–KSCN–CuSO₄–NaOH in a batch reactor with different concentrations of SDS (**a** 0.0, **b** 0.5, **c** 1.0, **d** 1.5% (*m/v*)) and constant concentrations of TSC, 1.0×10^{-3} mol l⁻¹, H₂O₂, 1.0 mol l⁻¹; KSCN, 4×10^{-2} mol l⁻¹; CuSO₄, 7×10^{-4} mol l⁻¹ and NaOH, 5×10^{-2} mol l⁻¹)



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