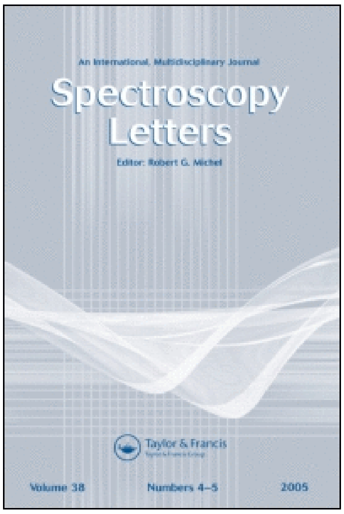

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Inverted Micellar Enhanced Organic Peroxyoxalate Chemiluminescence

Zhengliang Zhi[a]; Xuejie Yang[a]; Lude Lu[a]; Xin Wang[a]
[a] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, China

To cite this Article Zhi, Zhengliang , Yang, Xuejie , Lu, Lude and Wang, Xin(1999) 'Inverted Micellar Enhanced Organic Peroxyoxalate Chemiluminescence', Spectroscopy Letters, 32: 2, 273 — 279
To link to this Article: DOI: 10.1080/00387019909349982
URL: http://dx.doi.org/10.1080/00387019909349982

SPECTROSCOPY LETTERS, 32(2), 273-279 (1999)

INVERTED MICELLAR ENHANCED ORGANIC PEROXYOXALATE CHEMILUMINESCENCE

Keywords: Chemiluminescence; Surfactant; Inverted micelle; Bis(2-butoxycarbonyl-3,4,6-trichlorophenyl) oxalate; 9,10-Diphenylanthracene.

Zhengliang Zhi, Xuejie Yang, Lude Lu and Xin Wang

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

Abstract

The use of neutral surfactant polyoxyethylene (9) dodecyl ether (AEO9) and polyoxyethylene (10) hexylphenol ether (TX-10) as an additive to enhance the chemiluminescence of peroxyoxalate reaction using bis(2-butoxycarbonyl-3,4,6-trichlorophenyl) oxalate (BBTPO) and hydrogen peroxide as the energy source in organic media with 9,10-diphenylanthracene as a fluorophore had been investigated. The oxidation of BBTPO in both AEO9 and TX-10 inverted micelles produced significantly improved intensity and efficiency of the chemiluminescence relative to that in normal organic media. It was found that in AEO9 and TX-10 inverted micellar media the enhancement of chemiluminescence was mainly due to the improvement of the reaction excitation efficiencies, but only slightly contributed by the increase of the fluorescence efficiency.

 www.dekker.com

1. Introduction

The chemiluminescence generated from the reaction of a diaryl oxalate ester and hydrogen peroxide in an organic dilutent in the presence of a fluorophore had been used to produce light emission of sufficiently high intensity and efficiency, being very useful for many practical illuminating purposes[1]. Much effort, since its first invention in 1967[2], had been devoted to find the strategies for greater intensity and longer duration of the reaction. Thus, catalysts including sodium salicylate[3] magnesium salicylate[4] to mention but a few, and other additives such as polymers[5,6] were used to increase the light output and/or duration of the chemiluminescence systems.

The use of surfactants in aqueous medium which formed micellar systems to enhance the peroxyoxalate chemiluminescence for analytical applications had been studied as reported in the literature[7-9]. The main features of the aqueous micelles were to increase the solubility of the oxalate, improve the microenvironment, and as a result, enhance the chemiluminescence intensity and quantum efficiency in some cases[7]. Here, we report the improvement of the illuminating performance of the peroxyoxalate chemiluminescence of bis(2-butoxycarbonyl-3,4,6-trichlorophenyl) oxalate (BBTPO) with the inverted micelles formed by the selected surfactants in nonaqueous media.

2. Experimental

2.1 Instrumentation

All chemiluminescence measurements were performed in a tip-fitted quartz cuvette (10-cm path length) placed in the sample holder of a 930-fluorometer (Shanghai). The fluorometer was operated at an emission wavelength of 410 nm without external excitation. The sensitivity of the instrument was set at minimal in order to reduce the output to a measurable level. The intensity readings were obtained in arbitrary units. The emitting spectra for fluorescence intensity were measured with a Hitachi 204-A fluorescence spectrophotometer fitted with a XWT-164 flat-bed recorder (Shanghai) for output recording.

2.2 Chemicals and solutions

BBTPO was prepared by the established procedure[3]. 9,10-Diphenylanthracene was purchased from Sigma (St. Louis, MO). Concentrated

H_2O_2 (>90%, w/v) was prepared as described previously[10]. Other chemicals used in this study were of commercially available products and of analytical reagent grade or better, being purchased from a local chemical reagent company in China. The neutral surfactant polyoxyethylene (9) dodecyl ether (AEO9) and polyoxyethylene (10) hexylphenol ether (TX-10) were supplied by Sinopec Jinling Petrochemical Corporation, Lab Plant (Nanjing, China). A 2-component system was adopted for the chemiluminescence test. Component 1 contained 2.0 g of BBTPO and 20 mg of 9,10-diphenylanthrance, being added 20 ml of dibutylphthalate; the mixture was heated in a water bath to provide a complete dissolution of the solids. Component 2 was made by 1.5 ml of concentrated H_2O_2 and 8.5 ml dimethylphthalate/ tertiary butanol (4/1, v/v).

2.3 Procedure

A typical testing procedure was as follows: a solution of 1 (2.0 ml) was pipetted into the cuvette, and an appropriate volume of the surfactant was added. After the sample had been mixed, the chemiluminescence reaction was initiated by adding a 1.0-ml aliquot of Component 2 and, if necessary, adding a few drops of dibutylphthalate to the cuvette to make up the volume of 3.5 ml (as shown by a marker), shaking the closed cuvette to provide rapid mixing. The variation of the intensity with time was measured at 5 min, intervals during 3 h. All chemiluminescence data were measured at 25 ℃.

The sample solutions for fluorescence spectra determination were similar to that for chemiluminescence reaction but in the absence of BBTPO. Fluorescence spectra were measured at $\lambda ex = 350$ nm and the emission spectra were scanned from 380-550 nm.

3. Results and Discussion

In our previous study[10], the effects of stoichimetric and other variables including solvent system, catalyst, inhibitor etc. on the light emission were examined and an optimal component formulation was obtained. These variables thus remained constant throughout this study. The efficiency of the chemiluminescence reaction is studied in two different inverted micellar systems and compared with the reaction in normal organic medium. A comparison of the intensity-time decay curves is indicative of relative chemiluminescence efficiency, which is further divided into the excitation efficiency of the reaction and fluorescence efficiency of the emitting species.

The enhancement of intensity depends on the type and concentration of surfactant. AEO9 and TX-10 are chosen in this study because, in a preliminary experiment in search for the best additives within a range of surfactants, these two surfactants have been found to provide the most promising results. All the concentrations of the surfactants studied in this study are above the respective critical micellar concentration[11].

Fig. 1 shows the effect of concentration of AEO9 on the chemiluminescence capacity and duration. The results obviously suggest that as the concentration of the surfactant increases, the chemiluminescence intensity, especially the peak intensity, increases significantly, and the effect duration also increases to some extent, indicating the overall light capacity has been improved. However, a concentration of AEO9 above 0.09 ml/ml increases the intensity, but compromises the effect duration of the light. Therefore, the addition of a concentration of 0.06 ml/ml of the surfactant was recommended as the optimal in this study. With TX-10, as shown in Fig. 2, the increase in chemiluminescence capacity was also observed, but less significant than that in AEO9 inverted micelles.

The fluorescence spectra of 9,10-diphenylanthrance in the inverted micelles and in mixing solvents of dibutylphthalate/dimethylphthalate/tertiary butanol were measured to be essentially similar. Both have one emission peak with the same maximum emission wavelength at 427 nm. However, the fluorescent intensity, measured by the peakheight at the maximal excitation wavelength, as shown in Fig. 3, was increased only to some extend or remained unchanged as the increase of the concentration of the surfactants, indicating the fluorescence emission efficiency was enhanced slightly in inverted micellar media. It can therefore be concluded that the observed enhancement in chemiluminescence is not only due to the improvement of the fluorescence efficiency, but also to the change of excitation and reaction rate.

In inverted micelles, the aggregates have an aqueous core with the hydrophobic portion of the surfactant in contact with the bulk organic solvent. Therefore, H_2O_2, the main hydrophilic component in the chemiluminescence system, is expected to be found in the aqueous core of the inverted micelles. This might increase the local concentration of H_2O_2 contacting the bulk organic hydrophobic phase, which in turn makes it more effective and feasible to react with BBTPO. The reaction intermediate 1,2-dioxetanedione, a polar compound,

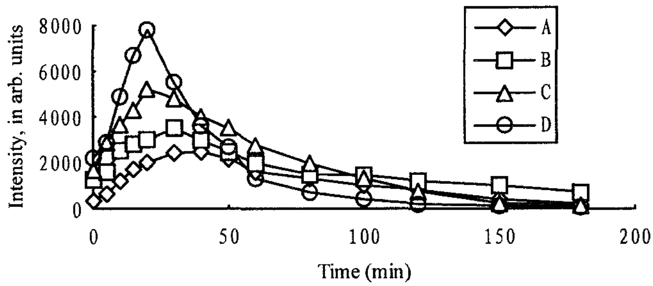

Fig. 1 Effect of AEO9 concentration on the chemiluminescence enhancement. AEO9 added: (A) 0; (B) 0.03 ml/ml; (C) 0.06 ml/ml; (D) 0.09 ml/ml. General conditions: 0.1 M BBTPO, 2×10^{-3} M diphenylanthrance and 1.35 M H_2O_2 in mixing solvents of dibutylphthalate/ dimethylphthalate/tertiary butanol (2:0.68:0.17,v/v/v).

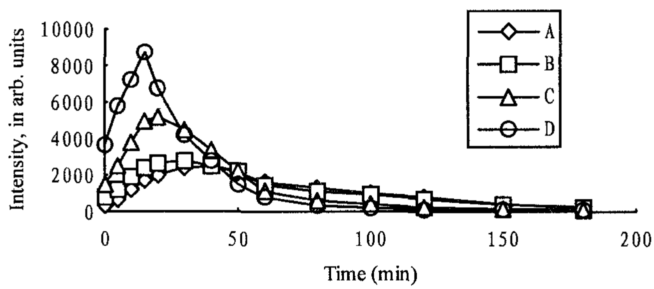

Fig. 2 Effect of TX-10 concentration on the chemiluminescence enhancement. TX-10 added: (A) 0; (B) 0.03 ml/ml; (C) 0.06 ml/ml; (D) 0.09 ml/ml. General conditions were same as that in Fig. 1.

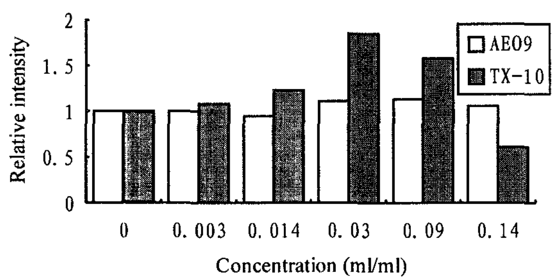

Fig. 3 Effect of surfactants on the fluorescence intensity. General conditions: 2×10^{-3} M diphenylanthrance and 1.35 M H_2O_2 in mixing solvents of dibutylphthalate/ dimethylphthalate/tertiary butanol (2:0.68:0.17,v/v/v).

will also be mainly present in the aqueous core. Therefore, it is also possible that the inverted micelles stabilize the reaction intermediates of the peroxyoxalate reaction, or enhance the energy transferring efficiency from the intermediate to the fluorophor.

4. Conclusions

The significantly enhanced light capacity and efficiency by use of the AEO9 and TX-10 inverted micellar systems has a great potential in the further improvement of lighting performance of the currently available peroxyoxalate chemiluminescence systems. For the present study which used the high-intensity light emitting energy source, i.e., BBTPO, the inverted micelles were found to enhance the light intensity more significantly than the efficient illuminating duration. From this point of view, it would be very interesting if the inverted micellar system is applied to the low intensity peroxyoxalate chemiluminescence system using bis(6-alkoxycarbonyl-2,4-dichlorophenyl)oxalate as the energy source[3]. Further research on this respect is in progress in our laboratory and will be published in our later reports.

Acknowledgment

This research was supported by the Fundamentally Applied Science Fund, administered by the Science & Technology Committee of the Jiangsu Province (CHINA).

References

1. Hanhela P.J., Paul D.B., Aust. J. Chem., 1981; 34: 1669; 1701.

2. Rauhut M.M., Bollyky L.J., Roberts B.G., Loy M., Whitman R.H., Iannota A.V., Semsel A.M., Clarke R.A., J. Am. Chem. Soc., 1967; 89: 6516.

3. Dowd C.D., Paul D.B., Aust. J. Chem., 1984; 37: 73.

4. Schleck J.R., Keyko G.J., Chopdekar V.M., US Pa tent 5281367 (1994).

5. Maulding D.R., Rauhut M.M., US Patent 3994820 (1976).

6. Maulding D.R., Rauhut, M.M., S. African Patent 7302681 (1974).

7. Dan N., Lau M.L., Grayeski M.L., Anal. Chem., 1991; 63: 1766.

8. Abdel-Latif M.S., Guilgault G.G., Anal. Chem., 1988; 60: 2671.

9. Steijger O.M., Van Mastbergen H.M., Holthuis J.J.M., Anal. Chim. Acta, 1989; 217: 229.

10. Zhi Z.L., Yang X.J., Lu L.D., Wang X., Spectrochim. Acta Part A, in press.

11. Becher P. *Non-ionic Surfactants*. In: Schick M.J. and Fowkes F.M. (Eds.), Surfactant Science Series, Vol. 1, Marcel Dekker: New York, 1967.

Date Received: September 2, 1998
Date Accepted: December 16, 1998