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Tris(2,2′-bipyridyl)ruthenium(III)-based electrochemiluminescence detector with indium/tin oxide working electrode for capillary electrophoresis

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Abstract

A novel tris(2,2′-bipyridyl)ruthenium(III) [$Ru(bpy)_3^{3+}$]-based electrochemiluminescence (ECL) detector for capillary electrophoresis (CE) has been developed. The detector was of the wall-jet configuration and an indium/tin oxide (ITO)-coated glass plate was used as the working electrode for end-column detection. Potential control of the ITO electrode was provided using a DC battery, without decoupling the detector from the CE field. Electrochemical behavior of $Ru(bpy)_3^{2+}$ at the ITO electrode was found to be analogous to that at a Pt electrode. In the presence of tertiary or some secondary amines, ECL emission due to reaction between in situ generated $Ru(bpy)_3^{3+}$ and analytes can be observed at the ITO surface. With 15 m*M* sodium borate (pH 9.5) plus 1 m*M* $Ru(bpy)_3^{2+}$ present in the detection cell and the ITO electrode biased at 1.5 V (vs. Pt wire reference), a detection limit of 1 μ*M* proline with a theoretical plate number of 4000 was obtained using the developed CE–ECL detection system. The detector response was found to be analyte-dependent, e.g. tryptophan gives no response, and the response for histidine is about 13-fold lower than that of proline.

Keywords: Electrochemiluminescence detection; Chemiluminescence detection; Detection, electrophoresis; Tris-(bipyridyl)ruthenium (III); Alkylamines; Amines; Amino acids

1. Introduction

Electrochemiluminescence (ECL) is the chemiluminescence (CL) process produced directly or indirectly as a result of electrochemical reactions. In general, reactive species formed electrochemically, diffuse from the electrode surface and react either with each other or with chemicals in the bulk solution to produce light in the vicinity of the electrode. Among the various ECL reagents, luminol and tris(2,2′-bipyridyl)ruthenium(III) [$Ru(bpy)_3^{3+}$] have been the most studied and exploited [1]. Analytical applications of ECL have recently been reviewed in detail [2,3].

ECL has long been employed as a sensitive detection method for flow injection analysis (FIA) and high-performance liquid chromatography (HPLC). Recently, ECL detection coupled to capillary electrophoresis (CE) also has been demonstrated [4–9]. However, it is difficult to couple ECL directly

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to CE as is done with FIA or HPLC, considering that the injection volume in CE is in nanoliters compared to microliters for FIA or HPLC. Special design of an ECL detector for CE is generally required. Gilman et al. [4] first reported a post-column luminol-based ECL detector for CE. In the cathodic buffer reservoir, a 10-μm carbon or platinum fiber electrode was aligned with the outlet of a 25-μm I.D. separation capillary. The light emitted from the luminol–ECL reaction on the microelectrode was collected with two optic fibers and monitored with a photomultiplier tube (PMT). Similar design was adopted by Dickson et al. [5], Forbes et al. [6] and Bobbitt et al. [7,8] in their respective CE works with $Ru(bpy)_3^{3+}$-based ECL detection. The precursor $Ru(bpy)_3^{2+}$ can be added to a post-capillary reservoir [5,7], incorporated into the CE buffer eluent [6], or continuously delivered to the capillary end using a syringe pump and a mixing tee [8]. A microwire electrode either precisely aligned with the capillary tip or directly inserted into the capillary end performs in situ oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$, followed by ECL reaction with the analyte. In order to overcome the high field interference, ECL detection was often carried out in an off-column mode where a field decoupler was created near the capillary outlet to isolate the detector from the CE field. However, the procedures of electrode alignment and decoupler fabrication are always tedious and time-consuming. Active $Ru(bpy)_3^{3+}$ can also be generated off-line by external oxidation of $Ru(bpy)_3^{2+}$ with a potentiogalvanostat in a separate cell, followed by mixing the electrogenerated $Ru(bpy)_3^{3+}$ with the CE eluate using a syringe pump and a mixing tee [9]. This design is similar to the conventional CE–CL detection scheme [10], and ECL emits from the solution at the mixing point inside the detection capillary, not from the electrode surface.

In this paper, we describe a simple and novel $Ru(bpy)_3^{3+}$-based ECL detector for CE. $Ru(bpy)_3^{2+}$ was included in the CE cathodic buffer reservoir. An indium/tin oxide (ITO)-coated glass plate, positioned at the capillary outlet, was used as the working electrode for in situ generation of active $Ru(bpy)_3^{3+}$. The detection cell was of the wall-jet configuration; that is, the CE effluent directly impinges on the ITO surface. Potential control of the ITO electrode was provided using a DC battery, which eliminates the need for an on-column field decoupler. The emitted ECL was collected with an optic fiber attached to the back of the ITO electrode plate. Performance of this ECL detector was evaluated with trialkylamines and some amino acids as the test analytes.

2. Experimental

2.1. Apparatus

Cyclic voltammetry was carried out with the BAS CV-27 voltammetric controller (Bioanalytical System, West Lafayette, IN, USA). A Pt-disk electrode (1.6 mm diameter) was polished with 0.05 μm alumina to obtain a mirror surface and then was throughly rinsed with distilled water. An ITO-coated glass slide with a sheet resistance (R_s)<20 Ω/sq was purchased from Delta Technologies (Stillwater, MN, USA). The ITO electrode with an area of ~1 cm^2 was cut from the glass slide. Electrical conduction was made by gluing a short piece of Cu wire onto the ITO electrode with silver epoxy (EPO-TEK H20E; Epoxy Technology, Billerica, MA, USA). Before use, the ITO electrodes were cleaned with detergent, rinsed, and then sonicated in 2-propanol for 15 min followed by 15 min sonication in water [11]. The reference electrode was an Ag/AgCl/3 *M* KCl electrode. A Pt wire was used as the auxiliary electrode. Before each experiment, the electrode was subjected to repeated cycling in the potential range 0~+1.8 V (vs. Ag/AgCl) in 0.1 *M* phosphate buffers (pH 7.5) until a reproducible voltammogram was obtained. The voltammograms were recorded with an x–y recorder (model F-3F; Riken Denshi, Tokyo, Japan).

The CE system was assembled in the laboratory. A 0–30 kV power supply (Glassman High Voltage, Whitehouse Station, NJ, USA) provided the separation voltage. The capillary used for separation was 50 cm×50 μm I.D.×360 μm O.D., (Polymicro Technologies, Phoenix, AZ, USA).

A schematic diagram of the ECL detection cell is shown in Fig. 1. The cell body was made of PTFE and the volume was about 8 ml. This cell also functioned as a cathodic buffer reservoir for CE. The separation capillary and a grounded Pt wire were

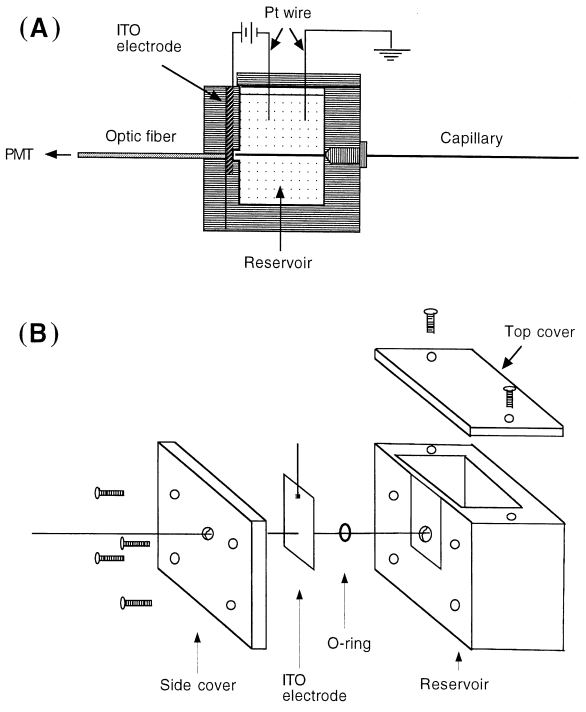

Fig. 1. Schematic diagram of the ECL detection cell: (A) overview; (B) exploded view.

fixed to the cell. A 2-mm diameter tunnel was drilled on the wall opposite to the capillary end. A 1.5 cm×1 cm×0.6 mm slide of an ITO electrode was attached to the other side of the tunnel facing the capillary outlet via a 2-mm diameter O-ring. The ITO electrode was held in position by another piece of Teflon plate and four screws. Before use, each ITO electrode was activated by repeated cycling in the potential range 0~+1.6 V (vs. Ag/AgCl) at a scan rate of 0.2 V/s for 5 min in a phosphate buffer (pH 7.5). During CE analysis, two 1.5-V d.c. batteries connected in series and a homemade voltage divider provided the potential of the ITO electrode. A Pt wire was used as a pseudo-reference electrode.

The ECL emitted on the ITO surface was collected using an optic fiber with a 600-μm core diameter (FO-600-SMA; World Precision Instruments, Sarasota, FL, USA) and was monitored with a photomultiplier tube (PMT; Model R928, Hamamatsu, Hamamatsu City, Japan). The photocurrent was amplified by a picoammeter (model 485; Keithley Instruments, Cleveland, OH, USA), converted to voltage and recorded using a personal computer equipped with a data acquisition interface. The whole CE–ECL detection system was held in a large light-tight box constructed from black Plexiglas to exclude stray light.

2.2. Chemicals

Tris(2,2′-bipyridyl)ruthenium(II) chloride (98%), tripropylamine (99+%), and triethylamine (99.5%) were purchased from Aldrich (Milwaukee, WI, USA). L-Proline (99%) and L-hydroxyproline were obtained from Merck (Darmstadt, Germany). All other chemicals were of analytical-reagent grade. Distilled water was further purified by passing it through a Nanopure II deionization system (Barnstead/Thermolyne, Dubuque, IA, USA). The CE buffer was 15 m*M* aqueous sodium tetraborate (pH 9.5). All solutions were filtered through a 0.45-μm pore-size membrane filter before use.

3. Results and discussion

3.1. Electrochemistry of $Ru(bpy)_3^{2+}$ at an ITO electrode

Electrochemical behavior of $Ru(bpy)_3^{2+}$ at various solid electrodes (e.g. Pt, Au and glassy carbon) has been described in detail [3,12]. However, few reports relevant to the electrochemistry of $Ru(bpy)_3^{2+}$ at an ITO electrode have appeared in the literature [13]. Electrochemical characterization was therefore performed using both an ITO electrode and a Pt electrode for comparison. Fig. 2 shows the cyclic voltammograms (C.V.s) obtained in 0.1 *M* phosphate buffer (pH 7.5) containing 1 m*M* $Ru(bpy)_3^{2+}$. The general shape of the two voltammograms is similar. At a Pt electrode (Fig. 2A), the well-known reversible C.V. wave of the reaction, $Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e^-$, was observed with an E_{pa}=1.12 V (vs. Ag/AgCl), which agrees with the published result [14]. In the absence of $Ru(bpy)_3^{2+}$, a rapid rise of the anodic current was observed as the potential was scanned to >1.2 V (Fig. 2A, dashed curve), which can be attributed mainly to the oxidation of H_2O. At an ITO electrode (Fig. 2B), the redox behavior of $Ru(bpy)_3^{2+}$ was quasi-reversible with an

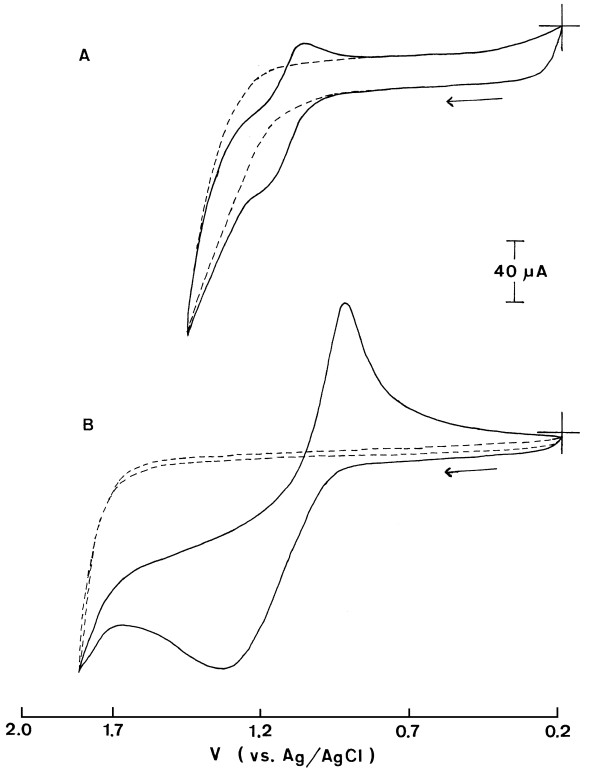

Fig. 2. Cyclic voltammograms of 1 m*M* $Ru(bpy)_3^{2+}$ at (A) a Pt electrode and (B) an ITO electrode. The dashed line represents data in the absence of $Ru(bpy)_3^{2+}$. Background electrolyte, 0.1 *M* aqueous phosphate buffer (pH 7.5); potential scan rate, 0.1 V/s.

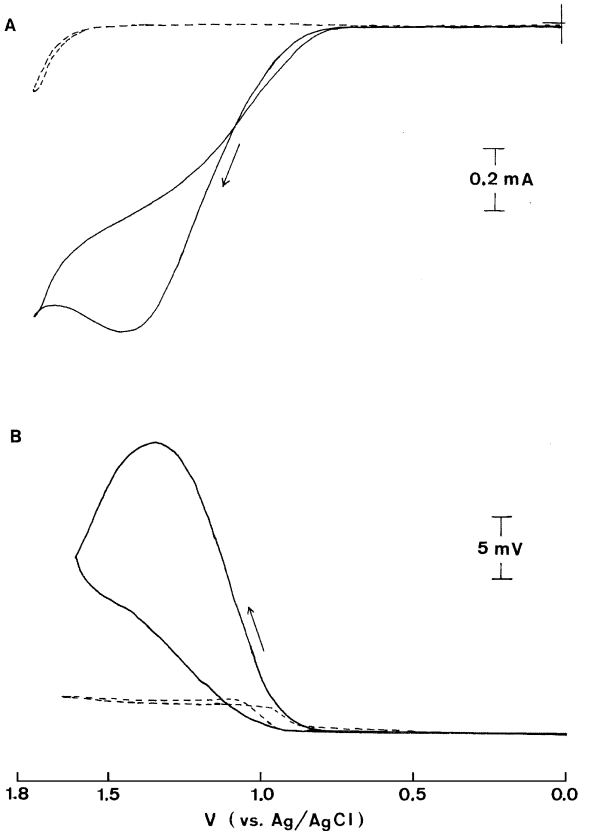

Fig. 3. (A) Cyclic voltammogram of 10 m*M* TPrA and 1 m*M* $Ru(bpy)_3^{2+}$ in 0.1 *M* phosphate buffer solution (pH 7.5) at an ITO electrode. (B) ECL curve recorded during the C.V. of (A). The dashed line represents data in the absence of TPrA. Potential scan rate, 0.1 V/s.

E_{pa}=1.30 V (vs. Ag/AgCl), approximately 180 mV more positive than that obtained with Pt. In the absence of $Ru(bpy)_3^{2+}$, a potential scan between 0.2 and +1.8 V is featureless, with the current increase beginning at ~+1.7 V signaling the onset of electrode surface oxidation (Fig. 2B, dashed curve). In comparison with the Pt electrode, one obvious advantage of the ITO electrode is its higher limit of anodic background potential in aqueous solution, which enables a wider potential control in anodic region. A similar advantage was also observed for ITO in various nonaqueous solvents [15].

In the presence of a trialkylamine, the ECL reaction between $Ru(bpy)_3^{3+}$ and trialkylamine can be observed. Fig. 3A shows the C.V. at an ITO electrode in a 0.1 *M* phosphate buffer (pH 7.5) containing 1 m*M* $Ru(bpy)_3^{2+}$ and 10 m*M* tripropylamine (TPrA) while Fig. 3B shows the observed ECL wave. In Fig. 3A, the rather broad irreversible anodic wave was due to the oxidation of both $Ru(bpy)_3^{2+}$ and TPrA, and the reduction wave was totally disappear. The completely irreversible anodic oxidation behavior of TPrA is similar to that on a glassy carbon electrode [12], and the disappearance of the $Ru(bpy)_3^{3+}$ reduction wave agrees with the reported catalytic reaction scheme at a Pt electrode (see below) [16,17]. In Fig. 3B, when the electrode potential was scanned positively beyond 0.9 V, upon the oxidation of $Ru(bpy)_3^{2+}$, an ECL signal was observed and its intensity increased rapidly to a maximum of ~1.35 V. The shape of the C.V. and ECL curves at an ITO electrode is similar to those at a Pt electrode, except a shift of relative

redox potentials. This observation implies a similar ECL reaction mechanism occurred at both electrodes. The reaction of the $Ru(bpy)_3^{2+}$+TPrA system at a Pt electrode can be expressed by [16,17]:

$$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e^- \quad (1)$$

$$Ru(bpy)_3^{3+} + TPrA \rightarrow Ru(bpy)_3^{2+} + TPrA\cdot \quad (2a)$$

$$TPrA \rightarrow TPrA\cdot + e^- \quad (2b)$$

$$Ru(bpy)_3^{3+} + TPrA\cdot \rightarrow [Ru(bpy)_3^{2+}]^* \quad (3)$$

$$[Ru(bpy)_3^{2+}]^* \rightarrow Ru(bpy)_3^{2+} + h\upsilon(610\ nm) \quad (4)$$

The excited state $[Ru(bpy)_3^{2+}]^*$ is generated by reaction 3 where the highly reducing radical species, TPrA·, reacts with $Ru(bpy)_3^{3+}$. In this path, the oxidation of TPrA occurs mainly by reaction with electrogenerated $Ru(bpy)_3^{3+}$ (reaction 2a) and direct oxidation of TPrA at the Pt electrode (reaction 2b) is inhibited.

3.2. Performance of the battery-powered ECL detector

An ECL detector for CE using ITO as the working electrode was constructed in the lab. The detail of the detector design has been depicted in the Experimental section. During our initial CE–ECL experiments, a BAS LC-4C amperometric controller was used to control the potential of the ITO electrode. However, without decoupling the ECL detector from the high CE field, significant interference with the ITO's potential control was observed. This problem is also common in CE with electrochemical detection (ED) [18]. It is well known that high-performance CE–ED generally demands that steps be taken to prevent the electrophoretic current from returning to ground via the detector, which causes baseline noise and detector instability. Although there have been many reported methods which may be employed to create an on-column field decoupler, the fabrication procedures are always tedious and often require special skill. Unlike CE–ED, in CE–ECL detection the only function of the potentiostat is to provide the working electrode with a fixed d.c. voltage. Since it is not necessary to monitor the current response of the working electrode during ECL detection, a simple d.c. battery should fulfill the same object as a potentiostat. Therefore, we replaced the BAS LC-4C amperometric controller with two 1.5-V d.c. batteries connected in series and a homemade voltage divider in our latter experiments.

In order to examine the applicability of the battery-powered ECL cell for detection in CE, preliminary experiments were carried out in a 20-ml quartz beaker containing 50 μ*M* $Ru(bpy)_3^{2+}$ and 0.5 m*M* of each test analyte (viz., tripropylamine (TPrA), triethylamine (TEA), proline and hydroxyproline) in 5 m*M* phosphate buffer (pH 7.5). An ITO working electrode and a Pt wire pseudo-reference electrode were connected to the positive and negative terminals of the d.c. battery pack, respectively. By changing the applied voltage step by step, the ECL emitted from the ITO electrode was monitored with a PMT positioned in front of the electrochemical cell. The solution was stirred briefly before each potential step to keep the solution homogeneous. Fig. 4 shows the obtained curves of ECL output intensity versus applied voltage for the four test analytes. These curves resemble the hydrodynamic voltammograms often found in HPLC– or CE–ED [19,20]. It is noted that in conventional hydrodynamic voltammograms, the current response is due to direct redox reaction of analytes at the working electrode under varied potentials. Since different analytes often show differ-

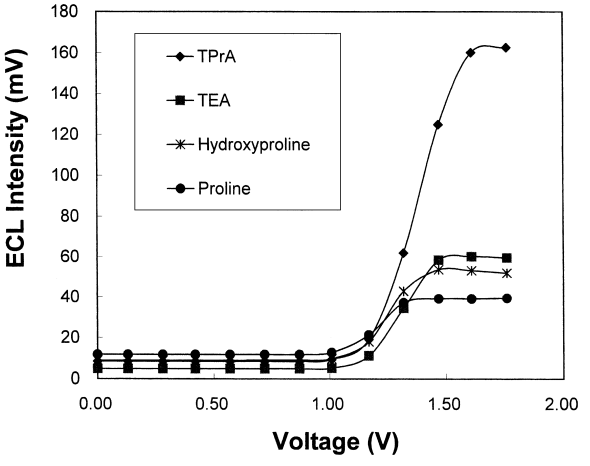

Fig. 4. ECL emission intensity of tripropylamine (TPrA), triethylamine (TEA), hydroxyproline and proline as a function of applied voltage. Experimental details see text.

ent electrochemical behavior at a solid electrode, each analyte will have its characteristic hydrodynamic current response curve. However, the mechanism is different in the present case. In Fig. 4, the ECL emission is mainly due to the reaction between electrogenerated $Ru(bpy)_3^{3+}$ and analyte, not from the analyte itself. Besides, ECL intensity is directly proportional to the amount of excited state $[Ru(bpy)_3^{2+}]^*$, which in turn is related to the extent of $Ru(bpy)_3^{2+}$ oxidation as well as the analyte concentration. Therefore, different analytes would have similar appearances of the ECL intensity vs. voltage curve. Indeed, the general shape of the four curves is very much alike, indicating a similar ECL reaction mechanism at the ITO electrode. There is another point in Fig. 4 that should be clarified. Since the purpose of constructing Fig. 4 was to investigate the ECL behavior of each analyte vs. applied voltage, the four curves were obtained individually using different ITO electrodes with varied surface areas and under irreproducible electrode location in the electrolytic cell. Therefore, the magnitude of the unnormalized steady-state ECL current of each analyte found in Fig. 4 is irrelevant to their relative luminescence efficiency at the ITO surface. The difference in luminescence efficiency will be discussed in the next section.

In Fig. 4, all four ECL curves begin to increase at an electrode voltage about 1.2 V and reach a plateau at ~1.5 V, which is in agreement with the electrooxidation behavior of $Ru(bpy)_3^{2+}$ at the ITO electrode (see Fig. 2B). From Fig. 4, a detection voltage of 1.5 V was selected as the optimal for all test analytes in the following CE analyses.

3.3. CE–ECL detection of trialkylamines and amino acids

End-column ECL detection was performed in a two-electrode mode. With the ITO electrode biased at 1.5 V (vs. Pt wire reference), we did not observe any adverse effect on the ECL signal by varied CE field strength. An on-column field decoupler was therefore unnecessary. The anodic buffer reservoir contained a solution of 15 m*M* sodium borate (pH 9.5) as the background electrolyte (BGE). In the cathodic buffer reservoir (which is also the ECL detection cell), 1 m*M* $Ru(bpy)_3^{2+}$ was incorporated into the BGE as the ECL reagent. Fig. 5 illustrates the electropherogram of triethylamine, proline and hydroxyproline obtained with the developed ECL detector, which clearly demonstrates the feasibility of ECL detection based on an ITO electrode. Baseline separation of the three analytes was achieved in 8 min and no attempt was made to further improve the separation performance.

It is known that tertiary and some secondary

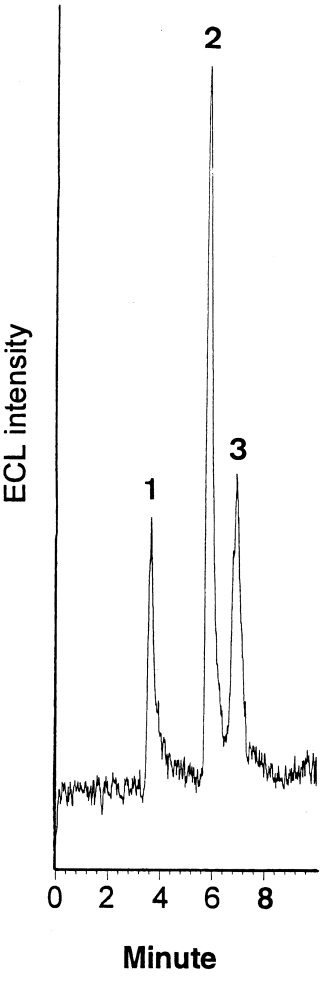

Fig. 5. Electropherogram of (1) triethylamine, (2) proline, and (3) hydroxyproline with ECL detection. Separation capillary, 50 cm × 50 μm I.D. × 360 μm O.D.; background electrolyte in anodic reservoir, 15 m*M* sodium borate (pH 9.5); BGE in detection cell, 15 m*M* borate + 1 m*M* $Ru(bpy)_3^{2+}$; separation voltage, 12 kV; electrokinetic injection, 3 s; ITO electrode potential, 1.5 V; photomultiplier tube voltage, −950 V; analyte concentration, 10 μ*M*; injected amount, 0.12 pmol of each compound.

amines can be determined by utilizing their ECL reaction with $Ru(bpy)_3^{3+}$ without prior derivatization [21]. We have tested several tertiary amines and amino acids, which include TPrA, TEA, proline, histidine, hydroxyproline and tryptophan, by CE–ECL detection with an ITO electrode. Using the most efficient TPrA as a standard, the order of ECL signal strength observed for the test analytes can be arranged as TPrA (1.00)>proline (0.38)>TEA (0.18)≈hydroxyproline (0.16)>histidine (0.03)> tryptophan (0.00). Difference in luminescence efficiency has been reported by other workers [6,7,22] and attributed to both the molecular characteristics of the reacting species [23], and the kinetics of the reaction [24].

3.4. Analytical figures of merit

With repeated injections of 10 μ*M* proline, a secondary amine and the most efficient amino acid for $Ru(bpy)_3^{3+}$-ECL reaction [25], the relative standard deviation of peak area was 6.4% ($n=12$). The linear range of the calibration curve was 2–500 μ*M* ($r=0.998$). Limit of detection ($S/N=3$) for proline was about 1 μ*M*, corresponding to an amount of 12 fmol. This value is about 10 times lower than that reported by Dickson et al. [5], but about 5-fold higher than that of Wang and Bobbit's work [8].

The number of theoretical plates for proline in Fig. 5 was calculated to be approximately 4000 using the width at half-height, which is about 4- to 10-times smaller than those reported in the literature. This relatively poor efficiency may be attributed to two reasons. First, the effective area of the ITO working electrode during ECL detection was determined by the diameter of the O-ring, which is 2 mm in the present work (see Fig. 1B). Since the capillary end is only 50 μm I.D., it is possible that the reaction/luminescence zone continues past the impinging point of CE effluent to some extent leading to a broadened peak. Because an O-ring with 2 mm I.D. is the smallest that we can find locally, we need to pursue other strategies to limit the effective electrode area in the future study. Second, the wall-jet electrode configuration of the detector might create more turbulence at the capillary outlet region. Lower efficiency was also observed in CE–ED using wall-jet system with larger diameter disk electrodes [26].

4. Conclusion

The feasibility of a $Ru(bpy)_3^{3+}$-based ECL detector using an ITO electrode for CE has been demonstrated. End-column ECL detection was carried out in a two-electrode mode with an ITO working electrode and a Pt wire pseudo-reference. The wall-jet electrode configuration simplifies the coupling procedure between CE and ECL detection. Potential control of the ITO electrode was provided using a d.c. battery, which eliminates the need for an on-column field decoupler. The developed system has been successfully employed to the CE–ECL detection of two trialkylamines and two favorable amino acids (proline and hydroxyproline) at μ*M* concentration level. In comparison with other reported ECL detectors for CE, this detector has several advantages, which include simple cell fabrication, economic apparatus used, easy ECL light collection, no need of field decoupler, and μ*M* level detection sensitivity. On the other hand, the major drawback of the present design is its relatively large void volume at the detection region, which creates a low count of theoretical plate number. Ongoing research is directed toward the improvement in efficiency and sensitivity, which should be realized by minimizing the effective electrode area and enhancing the light collection capability of the system.

Acknowledgements

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