

A CONTRIBUTION TO THE ELECTROCHEMILUMINESCENCE DETERMINATION OF COBALT WITH LUMINOL

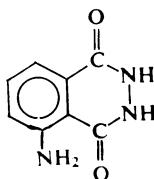
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The effect was studied of experimental conditions (pH, ionic strength, supply voltage, and type of electrodes) and of the presence of some cations and anions on the luminescence of aqueous solutions of luminol generated by alternating current. Of the ions studied, Co^{2+} and Br^- affected the electrochemiluminescence (ECL) of luminol to the highest extent. Co^{2+} ions increase the ECL of luminol in alkaline solutions in concentrations $c_{\text{Co}^{2+}} = 10^{-3} - 6 \cdot 10^{-6} \text{ mol l}^{-1}$, the limit of determination of cobalt is $0.13 \mu\text{g ml}^{-1}$. In the presence of bromide in concentrations higher than 0.2 mol l^{-1} , however, Co^{2+} lowers the ECL intensity over the concentration region of $c_{\text{Co}^{2+}} = 10^{-2} - 2 \cdot 10^{-4} \text{ mol l}^{-1}$. Alkali metal and alkaline earth cations as well as small amount of Pb^{2+} , Zn^{2+} , Cu^{2+} , Cr^{3+} , and Fe^{3+} have no appreciable effect on the ECL of luminol.

Electrochemiluminescence (ECL) has been utilized for the determination of metal ions in aqueous solutions only rarely¹. The effect of metal ions on the ECL of luminol (I) has been the concern of Haapakka and Kankare², who made use of the influence



I

of Cu^{2+} ions on the shape of the emitted light pulse generated by alternating rectangular voltage of 1 160 mV for the determination of copper within the concentration region of $0.1 - 6 \mu\text{mol l}^{-1}$. Trace quantities of cobalt ($0.01 - 3 \mu\text{mol l}^{-1}$) have been determined likewise³.

In the present work, the effect is studied of the experimental conditions and of the presence of some metal ions on the ECL of luminol generated by alternating line current. In contrast to the works cited^{2,3}, a significant effect is established of Co^{2+} and Br^- ions on the ECL intensity of luminol in alkaline solutions.

EXPERIMENTAL

Chemicals

Solution of luminol, in a concentration of 10 mmol l^{-1} , was prepared by dissolving the G.R. chemical (Chempol, Prague) in warm 0.02M -NaOH; if stored in darkness, it was steady for several days. Glycine buffer⁴ was prepared in a concentration of 0.1 mol l^{-1} . The ionic strength was adjusted with the use of NaF, NaCl, NaBr, NaI, NaNO₃, or NaClO₄. The metal salts solutions were made up using reagent grade chemicals and deionized water.

Apparatus

An adapter to the Spekol spectrophotometer (Carl Zeiss, Jena) was set up for the ECL measurements (Fig. 1). To the aluminium body 1 is attached a flange 4 allowing for fixing the cell of the Spekol photocells. Into the fixture is inserted a polystyrene stand 6 with the cell 7, provided with a Teflon stopper with the electrodes 5 (Fig. 2). The electrodes are made up of a glass tube 4 mm in diameter into which a platinum wire 0.4 mm in diameter is sealed up so that 15 mm of wire protrudes. The end of the wire is shaped into a helix, the other end is connected to an insulated wire fitted with a mini-plug. The whole adapter is painted black and is equipped with a lid for closing.

The measuring apparatus is shown diagrammatically in Fig. 3. For measurements of very low ECL intensities, an auxiliary amplifier SP 1 was linked to the basic unit SP 2 via an interface P (Fig. 4) allowing for recording the voltage brought from the attached amplifier. This voltage is amplified, in the ZES amplifier, first by a differential amplifier ($R = 63k\Omega$) followed by an inverting amplifier ($R' = 3k3\Omega$, $nR' = 20k$). The output from the inverting amplifier is brought to the ZAP recorder (one-scale compensating TZ 213-S recorder, manufactured by Laboratorní přístroje, Prague; full scale deflection 10 mV). The recorder pen deflection was 100% when the SP 2 instrument displayed about 8 scale divisions (at the highest gain).

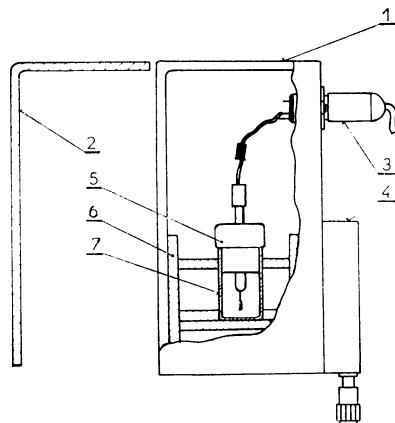


FIG. 1

Adapter to the Spekol instrument. 1 body, 2 cover, 3 voltage supply, 4 flange for the photocells, 5 electrode holder, 6 stand, 7 cell

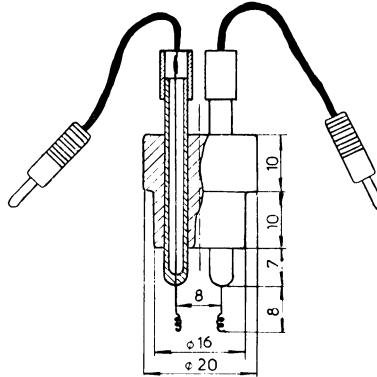


FIG. 2

Electrode holder

Procedure

The ECL measurements were carried out with solutions prepared by adding 5 ml of buffer solution, 1 ml of the solution of the substance under study, and 1 ml of luminol solution into a 10 ml volumetric flask and diluting to volume with water. The sample cell was rinsed and filled with this solution, closed with the stopper holding the electrodes, and inserted into the measuring

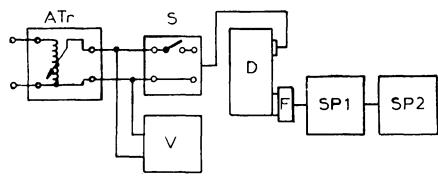


FIG. 3

Measuring apparatus layout. ATr auto-transformer, S switch, V voltmeter, D device, F photocells, SP1 attached amplifier (Spekol!), SP2 basic unit (Spekol)

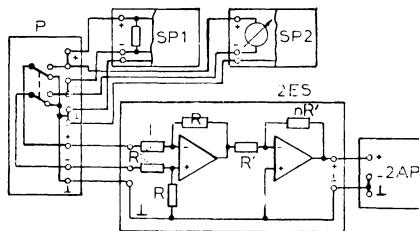


FIG. 4

Recorder-Spekol interfacing. P interface unit, ZES amplifier, ZAP recorder

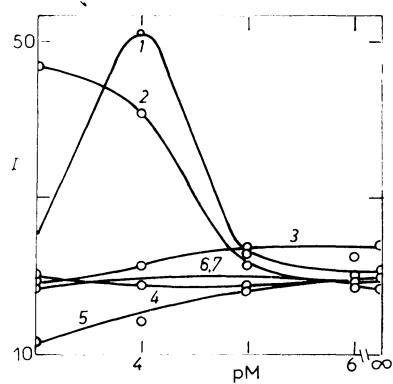


FIG. 5

Effect of some metal ions on the ECL intensity of luminol. I relative ECL intensity (Spekol scale reading at gain 1000); pM negative logarithm of the metal ion concentration (in mol l^{-1}); pH 10.5, $c_{\text{NaCl}} = 0.1 \text{ mol l}^{-1}$, $U_{\text{sup}} = 50 \text{ V}$. Metal ion: 1 Co^{2+} , 2 Ni^{2+} , 3 Cu^{2+} , 4 Hg^{2+} , 5 Mn^{2+} , 6 Cr^{3+} , 7 Fe^{3+}

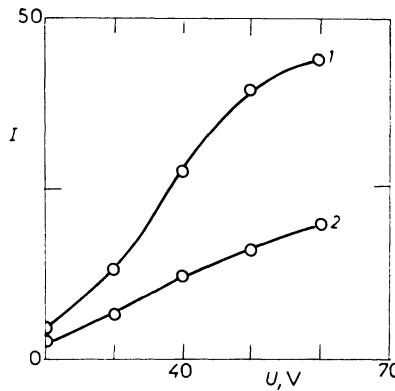


FIG. 6

Effect of the supply voltage on the ECL intensity of luminol in the presence of Co^{2+} ions (pCo 4) 1 and in the absence of cobalt 2. Conditions as in Fig. 5.

device. The gain on the amplifier SP 1 was adjusted, and the zero of the indicator instrument SP 2 was set by means of potentiometer "O". After reaching the steady state, the desired alternating voltage supply was activated by switching on the VYP switch (Fig. 3). The maximum of the blue ECL was read either on the SP 2 instrument at gain 1 000 (or at some other gain to be related to gain 1 000) or on the recorder trace. After the experiment, the electrodes were rinsed and dried with filter paper. The ECL intensities reported are averages of duplicate measurements.

RESULTS AND DISCUSSION

The effect of some selected metal ions on the ECL intensity of luminol is documented by Fig. 5. While the effect of Cu^{2+} , Hg^{2+} , Fe^{3+} , Cr^{3+} , CrO_4^{2-} , alkali metal and alkaline earth ions is negligible and Mn^{2+} ions lower the ECL intensity only slightly, Co^{2+} and Ni^{2+} ions affect it to an appreciable extent.

The effects of the supply voltage U_{sup} , pH, and ionic strength are demonstrated in Figs 6–8, respectively. The highest $(I_{\text{Co}} - I_0)/I_0$ intensity ratios where the subscripts Co and O refer to cobalt-containing and blank solutions, respectively, are attained with a supply voltage of 50 V and at pH 10.5. The requisite time is here about 8 s, and extends to several minutes if the voltage is lowered. As the ionic strength is increased, the ECL intensity rises and the time necessary for its establishment shortens, the solution, however, is heated more intensively and the platinum electrodes are subject to corrosion owing to the formation of chloroplatinate(IV) or of a grey haze of oxides of platinum in the presence and in the absence of cobalt,

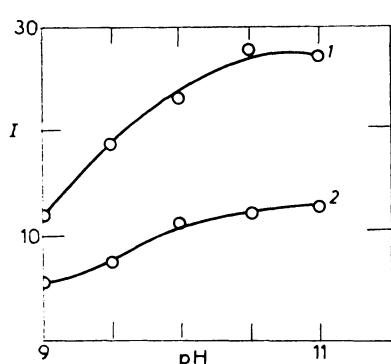


FIG. 7

Effect of pH on the ECL intensity of luminol in the presence of cobalt (pCo 4) 1 and in the absence of cobalt 2. Conditions as in Fig. 5

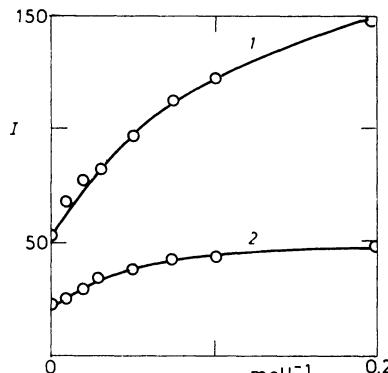


FIG. 8

Effect of ionic strength on the ECL intensity of luminol in the presence of cobalt (pCo 4) 1 and in the absence of cobalt 2. Ionic strength is regarded identical with $c(\text{NaClO}_4)$. Conditions as in Fig. 5

respectively. A very weak ECL is observed when using graphite electrodes, and no ECL appears at all if platinum electrodes coated with platinum black are employed. If the luminol concentration is lowered to be below 10 mmol l^{-1} , the ECL intensity drops appreciably. Solutions stored for a day afford virtually the same results as fresh solutions.

Masking agents (Chelaton 3, cyanide) and tensides (cetylpyridinium bromide, sodium lauryl sulphate, polyvinylpyrrolidone) lower the ECL intensity of solutions containing Co^{2+} ions in concentrations above approximately 0.1 mmol l^{-1} . Preliminary saturation of the solutions with oxygen has practically no effect on the ECL intensity.

The effect of some anions on the ECL intensity of luminol is shown in Fig. 9. Of the anions tested, bromide enhances the intensity most.

The dependences of the ECL intensity on the Co^{2+} ion concentration in the presence and in the absence of bromide were subjected to polynomial regression analysis. In the absence of bromide, the best fit was obtained with a straight line dependence of the logarithm of the ECL intensity on pCo (with a negative slope), whereas in the presence of bromide in a concentration of 1 mol l^{-1} , the intensity itself was linearly dependent on pCo (with a positive slope); the parameters are given in Table I. In the presence of bromide in a concentration of 0.1 mol l^{-1} the ECL intensity was too low and the $I = f(\text{pCo})$ dependence was of no practical utility.

The limit of determination of cobalt was calculated by using the adapted relation⁶

$$\log I_{\min} = \log (I_0 + 10s_{I_0}),$$

TABLE I

Parameters of the regression straight line equations for the dependence of the ECL intensity of luminol on the concentration of Co^{2+} ions. A in the absence of bromide, $\text{pCo} 3-6$, equation: $\log I = \alpha + \beta \text{pCo}$ (I recorder pen deflection in mm). B in the presence of bromide ($c_{\text{Br}^-} = 1 \text{ mol l}^{-1}$), $\text{pCo} 2-4$, equation: $I = \alpha + \beta \text{pCo}$ (I is the Spekol scale reading at gain 1 000). $c_{\text{NaClO}_4} = 0.1 \text{ mol l}^{-1}$

Case	α	β	s_{α}^a	s_{β}^b	r^c
A	3.474	-0.3856	0.103	0.0236	-0.955
B	-223.2	143.71	6.98	2.28	0.997

^a Standard deviation estimate for α ; ^b standard deviation estimate for β ; ^c correlation coefficient; all calculated from 24 points of the dependence.

where I_0 , the average ECL intensity of the blank (five replicate measurements), was 8.8, and its standard deviation, s_{I_0} , was 1.08. Inserted into the calibration curve equation in the absence of bromide, these values give the limit of determination of pCo 5.65, hence, the minimum concentration of cobalt in sample $0.13 \mu\text{g ml}^{-1}$.

The effect of selected metal ions on the ECL intensity of luminol in bromide-containing solutions is shown in Fig. 10. The metal ions lower the ECL intensity in order $\text{Co}^{2+} > \text{Mn}^{2+} > \text{UO}_2^{2+} > \text{Ni}^{2+}, \text{CrO}_4^{2-} > \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Cr}^{3+}, \text{Pb}^{2+}, \text{Zn}^{2+}, \text{Ca}^{2+}$.

The different dependences of the ECL intensity of luminol on the cobalt ion concentration in the absence and in the presence of bromide can be accounted for by the complex effect of conditions on the intricate mechanism of the electrochemical oxidation of luminol, which involves the formation of a number of intermediates, including free radicals in the presence of atmospheric oxygen. Several pathways of this process, leading to emission of light, have been suggested^{7,8}.

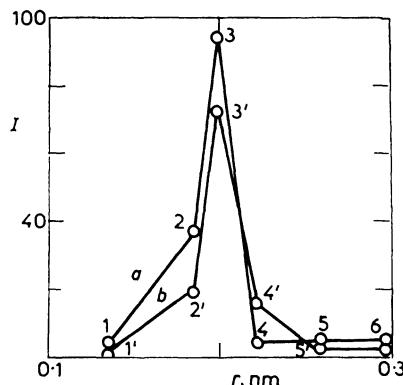


FIG. 9

Effect of some anions on the ECL intensity of luminol. I relative ECL intensity, r anion radius⁵; pH 10.5, $c(\text{Na}^+) = 0.1 \text{ mol l}^{-1}$, $U_{\text{sup}} = 50 \text{ V}$, pCo: a 4, $b \propto$ (blank solution); anion: 1, 1' fluoride, 2, 2' chloride, 3, 3' bromide, 4, 4' iodide, 5, 5' nitrate, 6, 6' sulphate

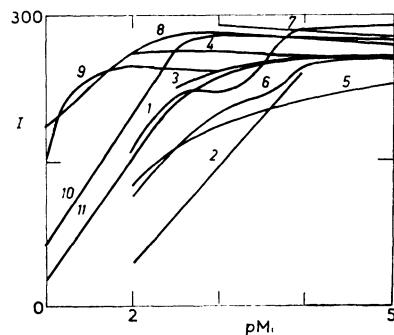


FIG. 10

Effect of some metal ions on the ECL intensity of luminol in the presence of bromide ($c_{\text{Br}^-} = 1 \text{ mol l}^{-1}$). I relative ECL intensity, pM negative logarithm of metal ion concentration; $U_{\text{sup}} = 50 \text{ V}$, pH 10.5, $c(\text{NaClO}_4) = 0.1 \text{ mol l}^{-1}$. Metal ion: 1 Ni^{2+} , 2 Co^{2+} , 3 Fe^{3+} , 4 Cr^{3+} , 5 UO_2^{2+} , 6 Mn^{2+} , 7 Pb^{2+} , 8 Ca^{2+} , 9 Zn^{2+} , 10 Cu^{2+} , 11 CrO_4^{2-}

Very low signals were measured in halide-free solutions; also, the solutions were heated and the electrodes corroded to a small extent only. In contrast, in halide-containing solutions the ECL intensities were considerably higher and various corrosion products appeared (oxides of platinum or haloplatinates(IV)) in dependence on the Co^{2+} content. The effect on the ECL mechanism then is clearly different. In the presence of chloride the ECL intensity increases over the region of pCo 3–4, followed by a decrease (Fig. 5); in the absence of chloride the intensity decreases constantly over the region of pCo 3–6 (Table I), the absolute values, however, are substantially lower. As to the effect of bromide, cobalt ions lower the ECL intensity if the bromide concentration is above 0.2 mol l^{-1} and raise it if the bromide concentration is lower. Catalytic effects of polyvalent ions of cobalt and platinum or their complexes with the anions present, as well as other counteracting effects associated with the nature of the electrode surface, changing during the electrolysis in a different manner according to the actual composition of solution, seem to play a role. We are so far unable to offer a detailed interpretation of these phenomena based on the ion size, stability constants, or kinetic properties of the complexes that may be involved.

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