Importance of a role of $(EuN_3)^{2+}$ complex generated in the $Eu^{3+}/N_3^-/H_2O_2$ system studied by the chemiluminescent method

K. Staninski, M. Kaczmarek, S. Lis, and M. Elbanowski†

Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, Poznań, 60-780, Poland

ABSTRACT. Chemiluminescence has been studied in the systems containing hydrogen peroxide H_2O_2 and Eu^{3+} and N_3^- ions. Ultraweak emission lasting for a few tens of hours has been observed. The dominant bands in the spectral distribution of the chemiluminescence are those of $\lambda = 594$ and 620 nm, which proves that excited Eu^{3+} ions are the only emitters in the system. As follows from measurements of chemiluminescence intensity for different pH of the solution and concentration of F^- ions, introduced as ligands competitive to N_3^-, it is in direct proportion to the concentration of the $(EuN_3)^{2+}$ complex forming in the solution.

1. INTRODUCTION

In earlier works on the role of lanthanide ions in the processes of chemiluminescence [1–3] it has been proved that exited Eu^{3+} ions can appear in the system containing hydrogen peroxide. Excited europium ions have been obtained in the reaction of Eu^{2+} oxidation by hydrogen peroxide [4, 5], and in the process of energy transfer from the excited reaction products generated in the decomposition reaction of hydrogen peroxide to complexed europium ions [6].

Weak complex-forming properties of azide ions towards lanthanide ions are known [7]. As far as trivalent lanthanide ions are concern, as yet only the occurrence of $(LnN_3)^{2+}$ type complex has been confirmed.

The aim of this study was to explain the important role of the $(EuN_3)^{2+}$ complex for generation and course of chemiluminescence in the $Eu^{3+}/N_3^-/H_2O_2$ system.

2. EXPERIMENTAL

Chemiluminescence was recorded by special instruments recording an ultraweak emission (Figure 1).

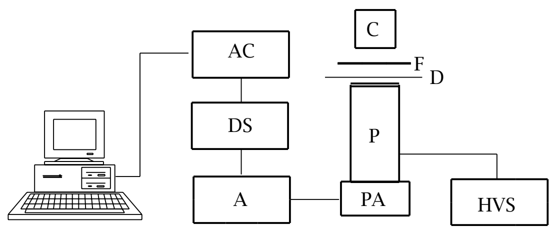

Figure 1. *Apparatus for measurement of chemiluminescence: AC - automatic counter C570; F - filters; HVS - high voltage supplier; DS.- discriminator; D - diaphragm; A - amplifier; P - photomultiplier M12 FQC51; C - measurement cell; PA - preamplifier.*

The spectrum of chemiluminescence was recorded by the method of cut-off filters. All solutions were made in doubly distilled water. Measurements were conducted in solutions of constant ionic strenght $\mu = 0.05$ achieved with the aid of KCl. Europium (III) chloride was obtained by dissolving Eu_2O_3 (99.99%, Aldrich) in hydrochloric acid. The other reagents were sodium azide (99.99%, Aldrich), sodium fluoride NaF (extra pure, Merck) and hydrogen peroxide H_2O_2 (30% water solution, pure for analysis).

3. RESULTS AND DISCUSSION

Introduction of H_2O_2 into a solution containing Eu^{3+} and N_3^- ions resulted in the appearance of a long-lasting and intense chemiluminescence (Figure 2) with the maximum emission in the red part of the spectrum (595 and 620 nm).

As follows from the kinetic curve of this chemiluminescence (Figure 2), it is long-lasting–up to a few tens of hours till reaching the background level–and shows high intensity.

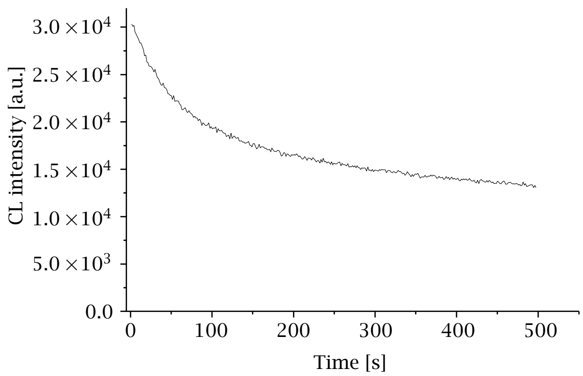

Figure 2. *Kinetic curve of chemiluminescence of* $Eu^{3+}/N_3^-/H_2O_2$ *system, for initial* 500 *s of the reaction.*

†Author to whom correspondence should be sent

No chemiluminescence was observed when studying the Eu^{3+}/H_2O_2 system. Excitation of the europium ions in the $Eu^{3+}/N_3^-/H_2O_2$ system is a result of oxidation of Eu^{2+} by hydrogen peroxide and the products generated in the decomposition reaction of hydrogen peroxide [4–6]. In view of the reducing properties of N_3^- ions, as observed in the case of Mn^{3+} [8] and Ce^{4+} [9], the Eu^{2+} ions also appear in solutions containing the $(EuN_3)^{2+}$ complex [10, 11]. Based on spectra analysis of Eu^{3+} in the Eu^{3+}/N_3^- system the formation of Eu^{2+} ions was evidenced. Since only the Eu^{3+} ions bound in the azide complex undergo the reduction to Eu^{2+} ions, the intensity of the chemiluminescence observed should be proportional to the concentration of the $(EuN_3)^{2+}$ complex.

Given the known values of the stability constant of the $(EuN_3)^{2+}$ complex ($\beta = 3.75$), dissociation constant of the hydrazoic acid HN_3 ($pK_a = 4.38$) [7, 12] and total concentration of the Eu^{3+} and N_3^- ions, the values of the equilibrium concentrations of the $(EuN_3)^{2+}$ complex were calculated as a function of pH of the solution (curve 1, Figure 3). The other curve in Figure 3

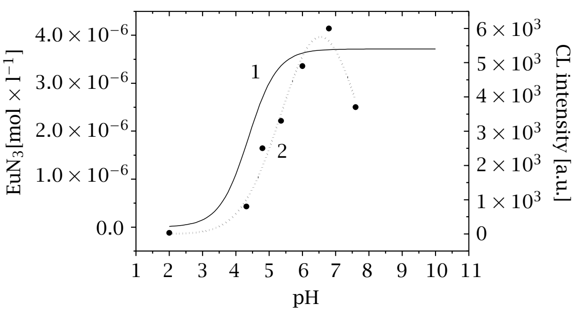

Figure 3. *Dependence of a calculated equilibrium concentration of the* $(EuN_3)^{2+}$ *complex on* pH *of the solution (curve* 1*). In calculation of the* $(EuN_3)^{2+}$ *complex concentration, the values of stability constant of the* $(EuN_3)^{2+}$ *complex (*$\beta = 3.75$*), dissociation constant of the hydrazoic acid* HN_3 *(*$pK_a = 4.38$*) and the total concentrations of the* Eu^{3+} *and* N_3^- *ions (*$c_{Eu} = 5 \cdot 10^{-4}$ *mol* $\cdot$ l^{-1} $c_{N_3} = 2 \cdot 10^{-3}$ *mol* $\cdot$ l^{-1}*) were taken into account. Changes of chemiluminescence intensity of* $Eu^{3+}/N_3^-/H_2O_2$ *system vs.* pH *of the solution (curve* 2*).*

(curve 2) illustrates the chemiluminescence intensity of the $Eu^{3+}/N_3^-/H_2O_2$ system versus pH of the solution. As shown, increasing pH of the solution caused an increase in the chemiluminescence intensity, which reached a maximum for pH ~ 7. Further increase in the system's pH led to a decomposition of the complex, the solution turbidity and precipitation of europium hydroxide at a simultaneous decrease of the chemiluminescence intensity. As follows from Figure 3, the increase of the chemiluminescence intensity in the pH range 3.5–6 is proportional to increasing of the $(EuN_3)^{2+}$ complex concentration.

In order to confirm the role of the $(EuN_3)^{2+}$ complex in the course of chemiluminescence, the influence of fluoride ions F^-, pushing off the N_3^- ions from the coordination sphere of europium, on the chemiluminescence intensity was studied.

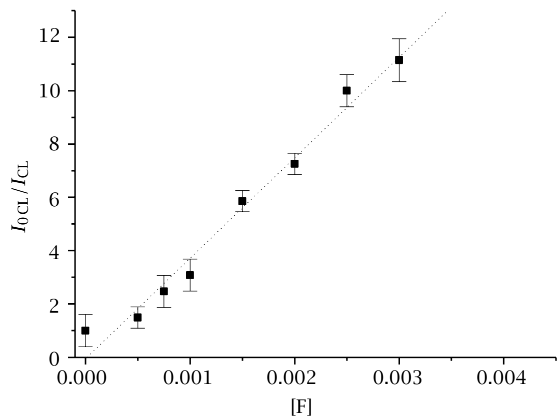

Figure 4. *Influence of the* F^- *ions concentration on chemiluminescence intensity of the* $Eu^{3+}/N_3^-/H_2O_2$ *system;* $I_{0\,CL}$ *- chemiluminescence of the system without the* F^- *ions.*

Figure 4 presents dependence of chemiluminescence intensity of the $Eu^{3+}/N_3^-/H_2O_2$ system on the concentration of fluoride ions. As can be shown, the quenching effect caused by the fluoride ions is proportional to their concentration in the studied system.

According to the equation of equilibrium of the system, after addition of fluoride ions:

$$(EuN_3)^{2+} + F^- \rightleftarrows (EuF)^{2+} + N_3^-$$

the concentration of the $(EuN_3)^{2+}$ complex is inversely proportional to the concentration of the introduced F^- ions and hence, the intensity of chemiluminescence is directly proportional to the concentration of the $(EuN_3)^{2+}$ complex.

It should be emphasised that the $(EuN_3)^{2+}$ complex, responsible for emission in the studied system, reveals a relatively low concentration of about 10^{-6} mol $\cdot$ l^{-1}.

In view of the above, a study of the yield of the emitter (europium ions) excitation and total quantum yield of chemiluminescence of the $Eu^{3+}/N_3^-/H_2O_2$ system [13] seems particularly interesting.

ACKNOWLEDGEMENTS

This work was supported by the Polish State Commitee for Scientific Research, Grant No 3 T09A 105 19.

References

[1] M. Elbanowski, K. Staninski, M. Kaczmarek, and S. Lis, Acta. Phys. Pol. A **90** (1996), 101.

[2] K. Staninski, M. Kaczmarek, G. Schroeder, and M. Elbanowski, Monatsh. Chem. **130** (1999), 1311.

[3] M. Elbanowski, B. Makowska, K. Staninski, and M. Kaczmarek, J. Photochem. Photobiol., A Chem. **130** (2000), 75.

[4] M. Elbanowski, J. Wierzchowski, M. Paetz, and J. Sławiński, Z. Naturforsch. **38a** (1983), 808.

[5] M. Elbanowski, K. Staninski, and M. Kaczmarek, Spectrochim. Acta, Part A **54** (1998), 2223.

[6] M. Kaczmarek, K. Staninski, and M. Elbanowski, Monatsh. Chem. **130** (1999), 1443.

[7] G. R. Choppin and D. W. Barber, J. Less-Comm. Met. **149** (1989), 231.

[8] G. Davies, L. J. Kirschenbaum, and K. Kustin, Inorg. Chem. **8** (1969), 663.

[9] C. F. Wells and M. Hussain, J. Chem. Soc. A (1969), 2981.

[10] M. Elbanowski, K. Staninski, M. Kaczmarek, and S. Lis, J. All. Comp. (2001).

[11] S. Lis, T. Kimura, and Z. Yoshida, J. All. Comp. (2001).

[12] R. M. Smith and A. E. Martell, *Critical Stability Constans*, in Inorganic Complexes, Vol. **4**, Plenum Press, New York, 1979.

[13] M. Elbanowski, K. Staninski, and M. Kaczmarek, in press.