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INFLUENCE OF N_3^- IONS ON CHEMILUMINESCENCE OF THE Eu(II)/Eu(III)–H_2O_2 SYSTEM

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The basic system of chemiluminescence investigations of relevant biological and inorganic compounds consists of Eu(II)/Eu(III)–H_2O_2. In these studies the increase in Eu(III) ion emission intensity usually results from an effective complexation reaction. In the present study, the N_3^- ions are used as a ligand. The increase in the chemiluminescence intensity of the Eu(III) ion, the *pH* influence (in the range of 4.5–7.5) on the chemiluminescence intensity of the Eu(III) ion, as well as the quenching of the $^5D_0$ excited state of the Eu(III) ion are observed due to N_3^- complexation. Taking into account the well-known Fenton system [Fe(II)/Fe(III)–H_2O_2], containing additionally the N_3^-, Eu(III) or Sm(III) ions, we found that the Eu(III) or Sm(III) ions were excited as a result of energy transfer process. A mechanism of the studied reactions is proposed.

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1. Introduction

A chemiluminescence (CL) method is used to study both biological and inorganic compounds in systems containing lanthanide ions, mainly europium [1–3]. The basic reaction of the method is oxidation of Eu(II) to Eu(III) ions, occurring in complexes with ligand, through hydrogen peroxide and excitation of these ions, which then come down to the ground state emitting characteristic radiation [3]. Products of simultaneous reactions of H_2O_2 decomposition and radicals recombination are excited dimoles of a singlet state $^1O_2$ [4, 5], whose influence on the level of CL may by determined using quenchers [6]. In literature the often reported quencher of an excited state $^1O_2$ are azide ions N_3^-. So far, the mechanism of $^1O_2$ emission quenching by N_3^- ions has not been well recognized. While Harbour' and Issler claim that the process of $^1O_2$ quenching proceeds through formation of charge–transfer complex [7], Haag and Mill prove that the dominant reaction in this process is typical physical quenching [8].

In our studies incorporation of azide ions, N_3^-, into the Eu(II)/Eu(III)–H_2O_2 system, brings about a strong increase in chemiluminescence emission characteristic of Eu(III) ions. On the basis of both chemiluminescence and fluorescence studies, where particular emphasis was paid to the measurements of a lifetime of $^5D_0$ Eu(III) ions, a mechanism of chemiluminescence process was proposed.

2. Experimental

A solution of $EuCl_2$ applied in the studies was obtained via a reduction of $EuCl_3$ according to the McCoy's method [9]. Solutions of $EuCl_3$ and other salts of lanthanides were prepared by dissolving appropriate oxides (spec. pure, prepared in our laboratory) in HCl (analar grade, POCh – Gliwice). To produce NaN_3 solutions with an appropriate *pH*, NaOH was added portion-wisely to a solution of HN_3. The hydrazoic acid was obtained by distillation of NaN_3 (analar grade, POCh – Gliwice) and diluted H_2SO_4 (analar grade, POCh – Gliwice) mixture. Moreover, in the studies the following compounds were used: $FeCl_2$ (analar grade, Merck), H_2O_2 (35% aqueous solution, analar grade, Merck) and NaOH (analar grade, POCh – Gliwice).

2.1. The procedure used in chemiluminescence measurements

To a solution containing Eu(II) ions, HN_3 of an appropriate *pH* was added and by using NaOH *pH* was established. Then, H_2O_2 at equimolar amounts relative to the Eu(II) was injected.

In the studies with the Fenton system (Fe(II) + H_2O_2), solutions of Fe(II) and a given lanthanide (Eu(III), Sm(III) or Tb(III)) with HN_3 were mixed, and then *pH* was determined. The final stage of the process was an addition of hydrogen peroxide. Each time the reaction solution was mixed using argon (99.99%) by passing it through the system.

To measure the lifetime, an apparatus built in our laboratory and described in Ref. [10] was used. Kinetic curves and chemiluminescence spectra were recorded using the apparatus shown in Fig. 1. Spectral distribution was obtained using the cut-off filters method.

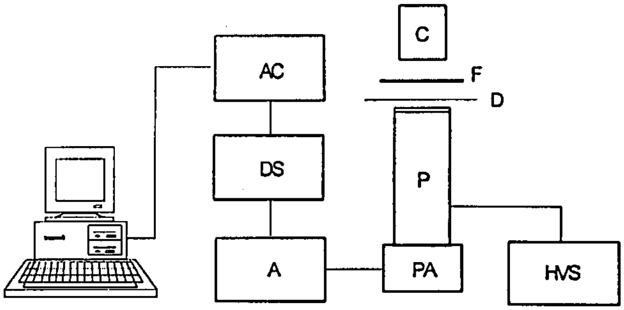

Fig. 1. Scheme of the apparatus for chemiluminescence measurements:
AC — automatic counter C570, DS — discriminator, A — amplifier, C — measurement cell, F — filters, D — diaphragm, P — photomultiplier M12 FQC51, PA — preamplifier, HVS — high voltage supplier.

3. Results and discussion

Chemiluminescence emitted from solutions containing Eu(II)/Eu(III) ions, N_3^- and H_2O_2 was studied. A strong and relatively long (a few hours) emission was observed. Figure 2 shows kinetic curves of CL emitted from the Eu(II)/Eu(III)-N_3^--H_2O_2 system for different pH values. Curve 1 in Fig. 2 presents an azide-free solution, while other curves correspond to solutions containing N_3^- at an equimolar amount relative to the Eu(II) ions.

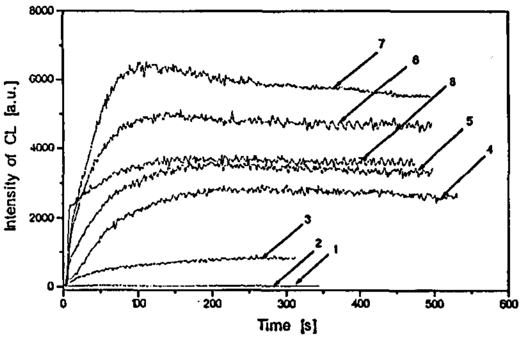

Fig. 2. Kinetic curves of chemiluminescence of the Eu(II)/Eu(III)-N_3^--H_2O_2 system for different pH: curve 1 — (without N_3^-; pH 4.0), 2 — (pH 4.0), 3 — (pH 4.8). 4 — (pH 5.3), 5 — (pH 5.8), 6 — (pH 6.5), 7 — (pH 7.2), 8 — (pH 8.0). Concentration of europium ions was equal to 2×10^{-3} mol×l^{-1}, molar ratio of Eu(II) : N_3^- was 1 : 1.

Changes in pH for solutions containing N_3^- ions strongly affect the intensity of chemiluminescence. An increase in the basicity of solution led to an increase in CL intensity (curves 3–7, Fig. 2). For pH above 7.2 a decrease in emission intensity was observed (curve 8, Fig. 2). Chemiluminescence measurements in solutions with $pH < 4.7$ revealed a similar intensity and the course to those observed for systems free of azide ions.

Figure 3 shows CL spectrum (spectral distribution) of a solution containing Eu(II)/Eu(III), N_3^- and H_2O_2. As can be seen the maximum at ca. 600 nm is dominant, which testifies to the fact that the only emitter in the studied systems are exited Eu(III) ions. The observed band is a result of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions. The width of spectral region, obtained using the cut-off filters method, is equal to 10–20 nm. A precise resolution of the two bands in the presented spectrum is not possible then.

So far, for most lanthanides, a presence of azide complexes of the $Ln(N_3)^{2+}$-type in solution has been found [11]. The fact that CL intensity increases in solutions with pH higher than 4.7 (pK_a of hydrazoic acid is equal to 4.7) testifies to a considerable contribution of the forming complex in the processes. A decrease in CL intensity in solutions with pH higher than 7.5 is a result of hydrolysis of europium ions.

The Eu(II)/Eu(III)-H_2O_2 system is a source of $HO^\bullet$ radicals formed during

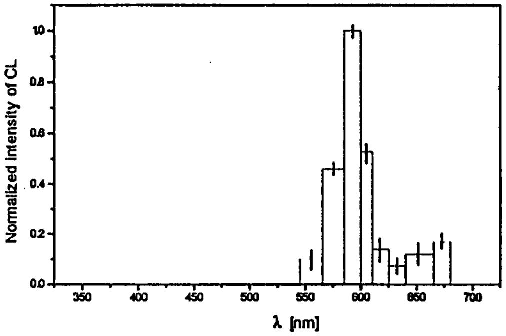

Fig. 3. Spectral distribution of chemiluminescence of the Eu(II)/Eu(III)-N_3^--H_2O_2 system. Concentration of europium ions was equal to 2×10^{-3} mol$\times$l^{-1}, molar ratio of Eu(II) : N_3^- was 1 : 1, *pH* of solution was equal to 7.2.

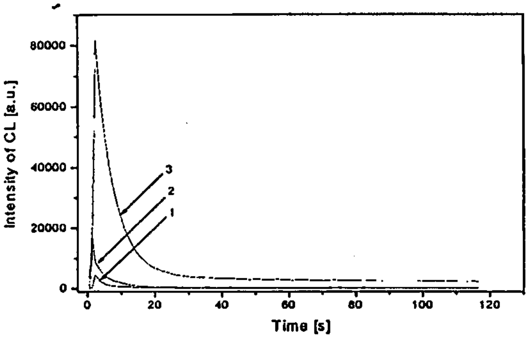

Fig. 4. Kinetic curves of chemiluminescence of the systems: Fe(II)/Fe(III)-H_2O_2 (1), Fe(II)/Fe(III)-Sm(III)-N_3^--H_2O_2 (2), Fe(II)/Fe(III)-Eu(III)-N_3^--H_2O_2 (3). Concentration of europium, samarium and ions was equal to 2×10^{-3} mol$\times$l^{-1}, molar ratio Eu(II) or Sm(II) : Fe(II) : N_3^- = 1 : 1 : 2, *pH* 5.3.

a decomposition of hydrogen peroxide

$$\mathrm{Eu(II)} + H_2O_2 \rightarrow \mathrm{Eu(III)} + HO^{\bullet} + HO^{-}. \qquad (1)$$

An analogous system that undergoes similar transformations is the Fenton system, (Fe(II)/Fe(III)-H_2O_2). In the two systems, radical reactions of a similar character take place, yielding, among others, excited molecules of singlet oxygen [12]. Addition of azide ions and separately the trivalent lanthanide ions (Eu(III), Sm(III), Tb(III)) to the Fenton system led to a development of a medium in which the forming azide complexes are affected by the radicals and singlet oxygen (Fig. 4).

Curve 1 in Fig. 4 characterizes the course of chemiluminescence for the Fenton system: low intensity of emission and its fast disappearance. Introduction of azide ions to the studied system leads to a complete quenching of CL. A presence of Eu(III) or Sm(III) and N_3^- ions in the Fenton system causes a significant increase in the emission of CL (curves 2, 3 in Fig. 4), unlike a presence of Tb(III) ions which do not exert such an effect.

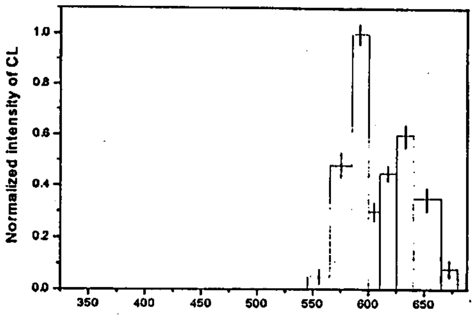

Fig.5

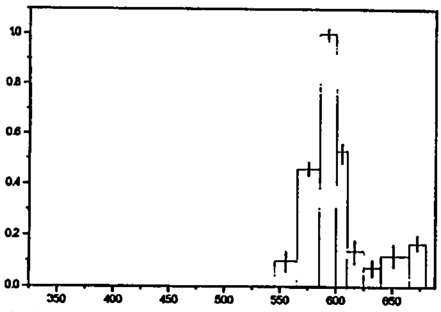

Fig.6

Fig. 5. Spectral distribution of CL of the Fe(II)/Fe(III)-Sm(III)-N_3^--H_2O_2 system. Concentration of samarium ions was equal to 2×10^{-3} mol×l^{-1}, molar ratio of Fe(II):Sm(III):N_3^- was 1:1:2, *pH* 5.3.

Fig. 6 Spectral distribution of CL of the Fe(II)/Fe(III)-Eu(III)-N_3^--H_2O_2 system. Concentration of europium ions was equal to 2×10^{-3} mol×l^{-1}, molar ratio of Fe(II):Fe(III):N_3^- was 1:1:2, *pH* 5.3.

Spectral distribution of the systems: Fe(II)/Fe(III)-Sm(III)-N_3^--H_2O_2 (Fig. 5) and Fe(II)/Fe(III)-Eu(III)-N_3^--H_2O_2 (Fig. 6) were also analyzed. A presence of maxima in the two spectra enables us to conclude that lanthanide ions present in the solution play the sole role of emitters in the systems.

So far, azide ions have been applied, for instance, as quenchers of singlet oxygen [6] and excited triplet states of some organic compounds. It could be anticipated therefore that the energy required to excite lanthanide ions is transferred through the complexing azides. The analysis of the energy levels of singlet oxygen and exited Ln(III) ions provides grounds for a supposition that the factor responsible for excitation of lanthanide ions are dimoles $^1O_2$ (Fig. 7).

The fact that Tb(III) ions in the system under study are not subjected to excitation allows us to suppose that singlet oxygen, at a high-energy state $^1\Sigma_g^+$, either did not occur in the studied system or did not take part in the energy transfer process due to its markedly shorter lifetime than the $^1\Sigma_g^+$ state. The emission intensity of the complexed Sm(III) ions, relative to that of complexed Eu(III) ions, is lower among others due to the fact that the former ions may be excited only by singlet oxygen at 2 $^1\Sigma_g^+(2, 0)$ state, while the latter ions may be excited both by singlet oxygen at the 2 $^1\Sigma_g^+(1, 0)$ and in the 2 $^1\Sigma_g^+(2, 0)$ states (Fig. 7).

In order to obtain more data about the character of N_3^- ligand, in a complex with europium ions, measurements of the lifetime of the $^5D_0$ excited state of these ions were taken. Results of the measurements are compiled in Table.

Azide ions proved to be a strong quencher of the $^5D_0$ state of europium ions. The quenching effect by N_3^- ions increases with an increase in concentration of these ions.

On the basis of the hitherto observations, it can be concluded that in systems containing Eu(III), N_3^- and the excitation factor ($^1O_2$), two competitive processes occur:

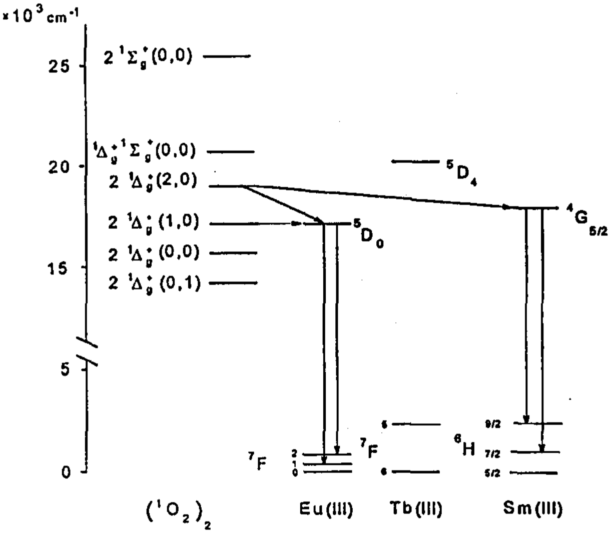

Fig. 7. Energy level diagram presenting the intramolecular energy transfer process from $^1O_2$ to $Ln(N_3)^{2+}$.

TABLE
Lifetime of the excited state of Eu(III) ions complexed by N_3^-, $c_{Eu(III)} = 0.01$ mol × l^{-1}.

Concentration of N_3^- [mol×l⁻¹]	Lifetime of Eu(III) [μs]
0.00	110.0 ± 3.3
0.01	87.3 ± 2.6
0.05	37.3 ± 1.1
0.10	29.5 ± 0.9
0.20	17.6 ± 0.5
0.30	12.4 ± 0.4

1. energy transfer of the singlet oxygen through the complexing N_3^- ions to the metal ions,

2. quenching of the excited state of Eu(III) by complexing N_3^- ions.

It follows from the obtained results that in chemiluminescence of the Eu(II)/Eu(III)-N_3^--H_2O_2 system, the energy transfer process is dominant. The mechanism of quenching of $^1O_2$ dimoles by the N_3^- ions has not been exactly recognized yet. It is only assumed that this process involves radiationless quenching, yielding a charge transfer complex [7, 8] (Scheme 1).

$$ {}^1O_2 + N_3^- \rightarrow [O_2^{\bullet-} \cdots N_3^{\bullet}] \begin{array}{l} \nearrow \; O_2^{\bullet-} + N_3^{\bullet} \\ \searrow \; O_2 + N_3^- \end{array} $$

The phenomenon of “trivial” energy transfer should be rejected due to a specific character of azide ions whose spectra do not reveal the bands of emission or absorption in the visible and near UV range.

For the system under consideration the mechanism of Eu(III) ions excitation may be explained by the energy transfer process (Scheme 2).

$$ ({}^1O_2)_2 + [Eu(III)N_3]^{2+} \rightarrow [Eu(III)N_3]^{2+} \cdots ({}^1O_2)_2 \rightarrow \begin{array}{c} [Eu(III))^{*}N_3]^{2+} + 2\,{}^3O_2 \\ \downarrow \\ h\nu \text{ (600 nm)} \end{array} $$

The charge-transfer complex formation permits energy transfer through Coulomb or exchangeable interactions.

Oxygen ion-radicals generated in the reaction with the N_3^- ions (Scheme 1) may take part in a number of subsequent radical reactions [5], partly reproducing the singlet oxygen in solution

$$ O_2^{-\bullet} + HO^{\bullet} \rightarrow {}^1O_2 + HO^-, \tag{2} $$

$$ O_2^{-\bullet} + HO^{\bullet} + H^+ \rightarrow {}^1O_2 + H_2O, \tag{3} $$

$$ O_2^{-\bullet} + H^+ \rightarrow HO_2^{\bullet}, \tag{4} $$

$$ HO_2^{\bullet} + HO_2^{\bullet} \rightarrow {}^1O_2 + H_2O_2. \tag{5} $$

A progressive increase in CL intensity in the Eu(II)/Eu(III)–N_3^-–H_2O_2 is a result of an increase in Eu(III) ions concentration, which is due to the effect of Eu(II) ions oxidation (Reaction 1).

The increase in Eu(III) ions concentration in the system enhances the probability of formation of the active-complex with the singlet oxygen, as well as the energy transfer from the singlet oxygen to the Eu(III) ions (Scheme 2). In the case of the Fe(II)/Fe(III)–Eu(III)–N_3^-–H_2O_2 system, a very short lived and intensive chemiluminescence of a fast decay is observed.

Given the fact that the course of hydrogen peroxide decomposition is very similar for these two systems, it can be stated that the differences in the course of kinetic curves results from a different quantity of the Eu(III) ions in the initial stage of the reaction.

The relatively fast decay of CL in the Fe(II)/Fe(III)–Eu(III)–N_3^-–H_2O_2 system, as well as in the Fe(II)/Fe(III)–Sm(III)–N_3^-–H_2O_2 system is also a result of the singlet oxygen quenching by the iron–azide complex [13].

By applying the chemiluminescence method, for the first time, to study the azide–lanthanide ions complexes, it was possible to reveal significant differences in the kinetics and to explain the course of the reaction mechanism.

Acknowledgments

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