Comparative Study of Chemiluminescence of Luminol and Lucigenin in Some Aliphatic Amines

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ABSTRACT
Effect of temperature on the chemiluminescence (CL) of Luminol and Lucigenin in some aqueous aliphatic amines such as ethyl amine (EA), diethyl amine (DEA), and triethyl amine (TEA), have been studied and reported. On the basis of experimental results, it is found that the chemiluminescence intensity initially increased with temperature, attains an optimum value of particular temperature and then decrease on further increase in temperature. It is also found that maximum CL intensity (I max) of chemiluminescence of Luminol founds in diethyl amine. While in case of Lucigenin it is independent of pH of amine above 11.

Keywords- Luminol, Lucigenin, Chemiluminescence, Aqueous, Amines.

1. INTRODUCTION
An enormous interest in the studies on the effect of temperature on luminescence properties have been emerged in past few years as it provides important information concerning the nature of luminescent material. Several reviews have been published relating to applications of chemiluminescence in analysis[1-3]. It is also proved to be useful for analytical applications and increasing investigations resulted in highly sensitive and selective detection methods[4-7]. In case of many substances which are not luminescent at room temperature shows luminescence at higher temperature[8]. Ettinger et. Al[9] have observed pronounced effect on light yield with change in solvent temperature. Recently Kher et. Al[10] reported the effect of temperature on the chemiluminescence of alcohols and aldehydes. Obviously the dependence of luminescence intensity on temperature is extremely interesting from experimental and theoretical point of view as it helps in understanding the basic mechanism of Chemiluminescence (CL) excitation in chemical components. The CL of Luminol has been studied either in aqueous alkaline solution of sodium hydroxide[11] or carbonates[12]. Very little work on chemiluminescence of Luminol in aqueous aliphatic
amines at different temperatures have been reported. The pH dependence of luminol[11] showed maximum CL intensity at pH 12. It is observed that aqueous solution of aliphatic amines has pH of 10 to 12. The present paper reports the studies on the effect of temperature on the chemiluminescence of Luminol-H₂O₂+ K₃[Fe(CN)₆] and Lucigenin-H₂O₂ in some aliphatic aqueous amines such as ethyl amine(EA), diethyl amine(DEA) and triethyl amine(TEA) in presence of potassium ferricyanide and the result have been discussed on the basis of present theories.

2. EXPERIMENTAL

All the chemicals used in the present investigation were taken in solution and prepared by using AR grade material adopting standard method. Solutions of all chemical compound was prepared in double distill water. Commercially available Luminol and Lucigenin were used without further purification. The alkaline solutions of Luminol and Lucigenin were prepared by adding aqueous solution of amines such as ethyl amine(EA), diethyl amine(DEA) and triethyl amine(TEA). It is observed that aqueous solution of aliphatic amines has pH of 10 to 12. All solutions used were freshly prepared. Luminol in aqueous alkaline medium showed a self-glow. Therefore, it is necessary to prepare these solutions whenever required. Solutions of known concentrations of different amines are prepared in double distill water. An exact concentration of Luminol and Lucigenin were prepared by dissolving a known weight of the substance in one litre of aqueous amine solution. Binary mixtures of oxidants as hydrogen peroxide and potassium ferricyanide is used to study their effects on CL of Luminol while only H₂O₂ as an oxidant in case of Lucigenin at different temperatures.

All the experiments were performed on a chemiluminometer setup which essentially consists of chemiluminescent cell, high voltage supply and light detector with a recorder. The chemiluminescence cell is a double walled cubical box and inner part of the cell is cylindrical. A heater coil is wound round the cylinder, which may be connected to a variac. Two circular holes were made in the top surface of the box. One for placing syringe to inject H₂O₂ solution in the cuvate and other for placing thermocouple in the CL cell. The cuvate is fitted inside the top surface of the light tight box and it rests just below the circular hole in which the syringe is placed. The cuvate was highly transparent glass tube of 1.0 cm diameter and 5 cm length. The box was covered with black cloths and syringe was placed on the hole. The light emitted during the reaction was detected by photomultiplier tube. All the measurement was carried out in dark. As mentioned earlier the CL cell has the heating arrangement in it. The heater was connected to the variac. The temperature of the cell was varied by changing voltage by the variac. The temperature of the CL cell was measured by inserting a thermocouple in the cell through the hole made at the top surface of the light tight box. To avoid the heating of the photomultiplier tube, a thick rubber sheet with a hole at its center was placed between the CL cell and PMT housing.
3. RESULT AND DISCUSSION

The optimum CL intensity at different temperatures of CL of Luminol and Lucigenin in ethyl amine(EA), diethyl amine(DEA) and triethyl amine(TEA) have been summarized in Table 1 and Table 2. The time dependence of CL intensities of chemiluminescence of Luminol H$_2$O$_2$ at different temperatures in ethyl amine, diethyl amine and triethyl amine in presence of potassium ferricyanide are as shown in Graph 1, 2 and 3. The time dependence of CL intensities of chemiluminescence of Lucigenin H$_2$O$_2$ at different temperatures in ethyl amine, diethyl amine and triethyl amine are as shown in Graph 4, 5 and 6. It was observed that there is only one peak in the CL intensity versus time curve and the shape of the glow curve is almost same at all the temperatures. It is further observed that CL intensity initially increases with increase in time, attains an optimum value and then with further increase in time it decreases. We found that the peak CL intensity of chemiluminescence of Luminol and Lucigenin in EA, DEA and TEA attains an optimum value at 60$^0$C, then decreases with further increase in temperature and finally disappears. It is also observed that the time corresponding to attain the optimum CL peak decreases with increase in temperature.

Table 1: Optimum CL intensity of Luminol in Aqueous EA, DEA and TEA.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Temperature (0C)</th>
<th>Ethyl Amine (EA) I max (Arb. Unit)</th>
<th>Diethyl Amine (DEA) I max (Arb. Unit)</th>
<th>Triethyl Amine (TEA) I max (Arb. Unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>38.9</td>
<td>48.2</td>
<td>40.1</td>
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<td>2</td>
<td>40</td>
<td>45.4</td>
<td>60.4</td>
<td>47.5</td>
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<tr>
<td>3</td>
<td>50</td>
<td>59.2</td>
<td>88.2</td>
<td>64.3</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>78.5</td>
<td>104.4</td>
<td>90.2</td>
</tr>
<tr>
<td>5</td>
<td>70</td>
<td>32.4</td>
<td>44.6</td>
<td>36.5</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>24.5</td>
<td>38.1</td>
<td>34.1</td>
</tr>
</tbody>
</table>

Table 2: Optimum CL intensity of Lucigenin in Aqueous EA, DEA and TEA.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Temperature (0C)</th>
<th>Ethyl Amine (EA) I max (Arb. Unit)</th>
<th>Diethyl Amine (DEA) I max (Arb. Unit)</th>
<th>Triethyl Amine (TEA) I max (Arb. Unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>34.7</td>
<td>31.5</td>
<td>20.4</td>
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<td>2</td>
<td>40</td>
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<td>44.6</td>
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<tr>
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<td>80</td>
<td>18.7</td>
<td>11.5</td>
<td>9.6</td>
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</table>
Fig. 1, 2, 3 and 4, 5, 6 show the effect of temperature on the chemiluminescence intensity of Luminol and Lucigenin in ethyl amine (EA), diethyl amine (DEA) and triethyl amine (TEA). It is clear from the figure that chemiluminescence intensities of Luminol initially increase with time attains a maximum value and then it decreases and finally disappears. It is also clear from the Fig. 1, 2, 3 and 4, 5, 6 shows that the chemiluminescence intensity initially increases with temperature, attains a maximum value at a certain temperature and then decreases. It is seen that chemiluminescence has a tendency to decrease beyond a particular temperature of the solution.
The chemiluminescence of Luminol shows intense chemiluminescence only in presence of binary mixture of oxidants while Lucigenin shows intense chemiluminescence only in presence of hydrogen peroxide as an oxidant. Table 1 and 2 show the observed chemiluminescence intensities of CL of Luminol and Lucigenin in various amines. The representative graphs are as given in Fig. 7(a), (b) and (c). In the present investigation we have found that the CL intensity initially increases with increase in temperature attains an optimum value then decreases with further increase in temperature. Rate of reaction increases with increase in temperature and probability of radiative process may decrease with further increase in temperature. Thus we expect that the CL intensity should be optimum at a particular temperature. From this study on effect of temperature on the chemiluminescence of Luminol and Lucigenin in aliphatic amines shows CL and CL intensity initially increases with increase in temperature attains an optimum value then decreases with further increase in temperature. It is also conclude that the CL intensity of CL of Luminol and Lucigenin shows highest optimum CL intensity at 60°C.

**CONCLUSIONS**

Ethyl amine, diethyl amine and triethyl amine have different basic pH. The Luminol and Lucigenin both give chemiluminescence in the presence of these amines. The optimum intensity (Arb. Unit) of Luminol in these amines is in order –

![Fig. 8: Comparative graph showing Imax For Luminol and Lucigenin in a) EA, b) DEA and c) TEA](image)
Diethyl amine > Triethyl amine > Ethyl amine

While, the order of optimum intensity in case of Lucigenin is-

Diethyl amine ≈ Triethyl amine > Ethyl amine

Hence, it can be concluded that chemiluminescence intensity of Luminol is dependent of amines pH. Whereas, the Chemiluminescence intensity of Lucigenin is independent of pH of these amines above pH 11.

5. ACKNOWLEDGEMENT

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REFERENCES


