Effects of Halide Ions on Micelle-Enhanced Chemiluminescence Reaction of Lucigenin with Adrenaline

Tamio KAMIDATE,* Tetsutoshi KANEYASU, Tadashi SEGAWA, and Hiroto WATANABE
Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo 060

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Synopsis. A remarkable lowering of chemiluminescence (CL) emitted from the CL reaction of lucigenin (Luc) with adrenaline (AD) was observed in cationic micellar assemblies containing halide ions, when their concentrations were above 5×10^{-3} mol dm^{-3}. These results could be explained in terms of the quenching of the Luc CL reaction by halide ions. The quenching by chloride ions was dependent on the carbon number in the alkyl group of surfactant reagents.

The use of appropriate aqueous micellar solutions has been shown to enhance the chemiluminescence (CL) intensity from CL reaction systems involving lucigenin (10,10′-dimethyl-9,9′-biacridinium dinitrate, Luc). Micelle-enhanced Luc CL reactions have been employed in order to improve the sensitivity of the determination of hydrogen peroxide and biological reductants.[1,2)]

We previously proposed the Luc CL method for the determination of such catecholamines (CAs) as dopamine, noradrenaline and adrenaline (AD).[3)] In addition, we have shown that cationic surfactant micelles are superior to nonionic and anionic surfactant micelles with respect to the enhancement effect on the CL intensity.[4)] In this paper we describe the effects of such halide ions as bromide and chloride on the CL intensity emitted from the Luc CL reaction with AD in cationic micellar solutions.

Experimental

Reagents. Hexadecyltrimethylammonium hydroxide (CTAOH), hexadecyltrimethylammonium chloride (CTAC), hexadecyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium chloride(TTAC) and dodecyltrimethylammonium chloride (DTAC) were used without further purification. All of the solutions used were prepared as described previously.[4)]

Apparatus. All CL measurements were performed by use of a fluorometer (Farrand Optical Co., Type Ratio-2) equipped with an automatic injector which had two flow lines (Ohtsuka Denshi Co., Type MX-7). A strip-chart recorder was used to record the CL intensity–time profiles.

Procedure. A 250 µl portion of surfactant solution and a 250 µl portion of a 0.2 M (1 M=1 mol dm^{-3}) NaOH solution were added using an Eppendorf pipet into a 1-cm glass cell in the fluorometer. Next, a 250 µl portion of 6.0×10^{-5} M Luc solution and a 250 µl portion of 1.0×10^{-4} M AD solution were injected simultaneously through Teflon tubing into the cell by using an automatic injector. Thus, the CL reaction was initiated and light emission was detected by a photomultiplier tube. The resultant photocurrent was converted to a voltage and displayed on a chart recorder. The maximum light emission was corrected using the light emission of a blank containing no AD. These background-corrected CL values were referred to as the CL intensities.

Results and Discussion

The CL measurements were carried out using different counterion-types of such cationic surfactants as CTAOH, CTAC, and CTAB. Figure 1 shows the CL intensity-surfactant concentration profiles. When the surfactant concentrations were well below the critical micelle concentrations (cmc) (results not shown), the CL intensity was about the same as that in water. The increase in the CL intensity commenced at surfactant concentrations near cmc, which were 9×10^{-4} M for CTAOH, 1.3×10^{-3} M for CTAC and 9.2×10^{-4} M for CTAB, respectively.[5)] The CL intensities were maximal at 5×10^{-3} M and were about the same, regardless of the cationic micellar assemblies used. However, the CL intensities were dependent on the counterion types and concentrations of cationic surfactants used, when their concentrations were above 5×10^{-3} M. The relative effectiveness of these cationic micelles at enhancing the CL intensity followed the order CTAOH>CTAC>CTAB, thus indicating that the micelle-enhanced Luc CL reaction was affected by the concentrations of halide ions.

In order to elucidate the effect of halide ions on the Luc CL reaction, a 250 µl portion of NaCl solution or that of NaBr solution was added to the reaction mixture instead of surfactant micellar solutions. The results

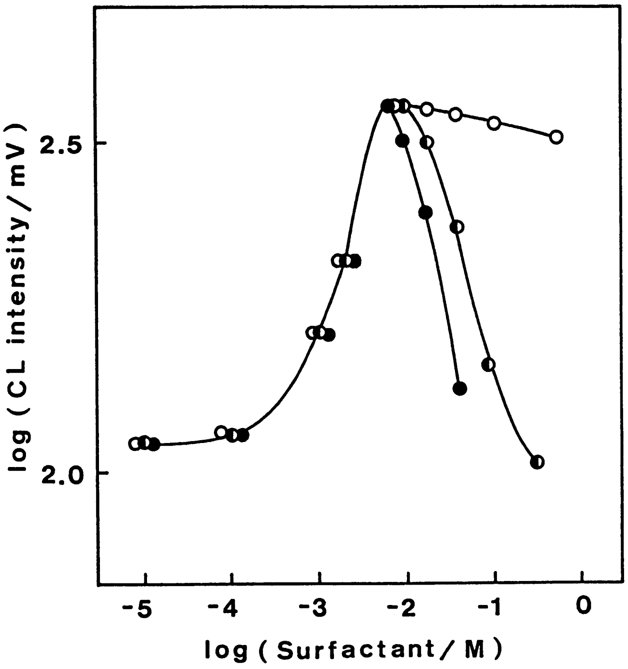

Fig. 1. Variation in the chemiluminescence intensity with surfactant concentration.
○: CTAOH, ◐: CTAC, and ●: CTAB.
Conditions: 9.0×10^{-4} M AD, 6.0×10^{-5} M Luc, and 0.2 M NaOH.

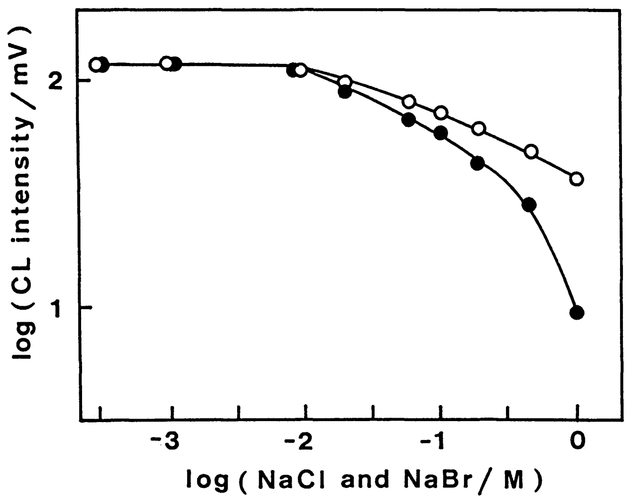

Fig. 2. Effect of halide concentration on the chemiluminescence intensity.
○: NaCl and ●: NaBr.
Conditions: 9.0×10^{-4} M AD, 6.0×10^{-5} M Luc, and 0.2 M NaOH.

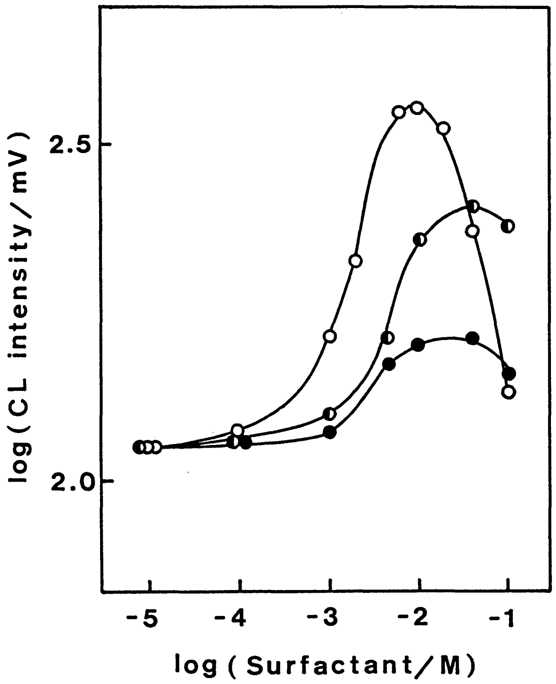

Fig. 3. Variation in the chemiluminescence intensity with surfactant concentration.
○: CTAC, ◐: TTAC, and ●: DTAC.
Conditions: 9.0×10^{-4} M AD, 6.0×10^{-5} M Luc, and 0.2 M NaOH.

shown in Fig. 2 indicate that halide ions play the roll as a quencher for the Luc CL reaction with AD when their concentration are above 1×10^{-2} M. Quenching by bromide ions was greater than that by chloride ions. Therefore, the remarkable decrease of the CL intensity in the micellar assemblies containing halide ions is probably attributable to quenching of the Luc CL reaction by halide ions. However, the degree of lowering the CL intensity in micellar assemblies was greater than that in water alone at the same concentration of haliden ions. These results may be interpreted as follows. Halide ions interact electrostatically with and bind to a cationic micelle pseudophase. Consequently, the local halide concentration on the micelle surface is greater than the stoichiometric concentration in bulk water alone. Thus, quenching by halide ions is greater in micellar assemblies compared to that in water alone.

We then examined the effect of chloride ions on the micelle-enhanced CL using DTAC, TTAC, and CTAC with different carbon numbers in an alkyl group of surfactant reagents. Figure 3 shows the CL intensity–surfactant concentration profiles for the respective surfactants. The CL intensity increased with an increase in the carbon number of the alkyl group. The degree of quenching by chloride ions was dependent on the carbon number in the alkyl group of the surfactant reagents used. This is ascribable to their cmc, which are 1.3×10^{-3} M for CTAC, 4.5×10^{-3} M for TTAC,[6] and 2.0×10^{-2} M for DTAC,[7] respectively. Along with a decrease in the carbon number of the alkyl group, the cmc, and thus the concentration of surfactant micelles, increased, resulting in an effective enhancement of the CL intensity in micellar assemblies. The concentration of chloride ions increases simultaneously under these conditions.

Consequently, the degree of the quenching by chloride ions may increase with a decrease in the carbon number of the alkyl group of surfactant reagents. On the other hand, the maximum CL intensities in such C_{16} surfactants as CTAOH, CTAC, and CTAB, were not affected by the counterions of the surfactant reagents. This result may be interpreted by taking into acount their cmc. That is, the CL intensity reached a maximum value without suffering from the quenching effect of halide ions on the CL intensity, since the cmc for CTAC and CTAB are well below the concentrations required for quenching by halide ions.

As described above, CTAOH is very useful as a micellar medium for enhancing the CL intensity of Luc CL with AD. On the other hand, the optimum concentrations of CTAC and CTAB are within a very limited range, thus precluding their use.

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