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CHEMILUMINESCENCE IN MODEL MEMBRANE STRUCTURES. CHEMILUMINESCENCE OF LUCIGENIN IN DDAB AGGREGATES IN THE PRESENCE OF CHOLESTEROL

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Abstract In the present study we report the chemiluminescence of Lucigenin (L) in DDAB (didodecyldimethylammonium bromide) aggregates as a function of cholesterol concentration in the range of 10^{-7} to $5x10^{-4}$ M. The DDAB aggregates employed were 10^{-2} M, both lamellar (unsonicated) and vesicular (sonicated). The effect of cholesterol at the concentration employed was expressed as a ratio of quantum yields in the presence and absence of cholesterol. Taking into account the effect in the two systems above, it appears that cholesterol affects the smecticity of the bilayer lamellar aggregate.

INTRODUCTION

We have shown earlier that factors affecting the fluidity of biological membranes, such as hormones, vitamins, ions and cholesterol itself at a concenration of 10^{-4} M, can also affect the fluidity of model membrane systems. In a typical membrane mimetic agent, DDAB aggregates, the effect is followed and is illustrated by differentiation of the quantum yields as well as the chemiluminescence spectra of the Lucigenin (L) light reaction carried out in the said media.

DISCUSSION

Chemiluminescence in organized media is associated with differentiation in both quantum yields and emission spectra as compared with the same in homogeneous media.[1,2,3] Furthermore, factors affecting the rigidity and fluidity of biological membranes can also affect the chemiluminescence of Lucigenin (L) in membrane mimetic

agents such as the (DDAB) aggregates of the present work[4]. Indeed, cholesterol at concentrations of 10^{-4} M in DDAB lamellar aggregates gives rise to increased quantum yields of the (L) light reaction in this medium.[5] In a more thorough examination of the latter, we now report the effect of the cholesterol concentration, in both lamellar (unsonicated) and vesicular (sonicated) DDAB aggregates, on the (L) light reaction, together with the effect of temperature on this system.

The cholesterol concentration effect on the light reaction's quantum yield (expressed as Q_{ch}/Q where Q_{ch} is the quantum yield in the presence of cholesterol and Q the quantum yield without cholesterol added) is shown in Fig. 1. It is interesting to notice the difference between

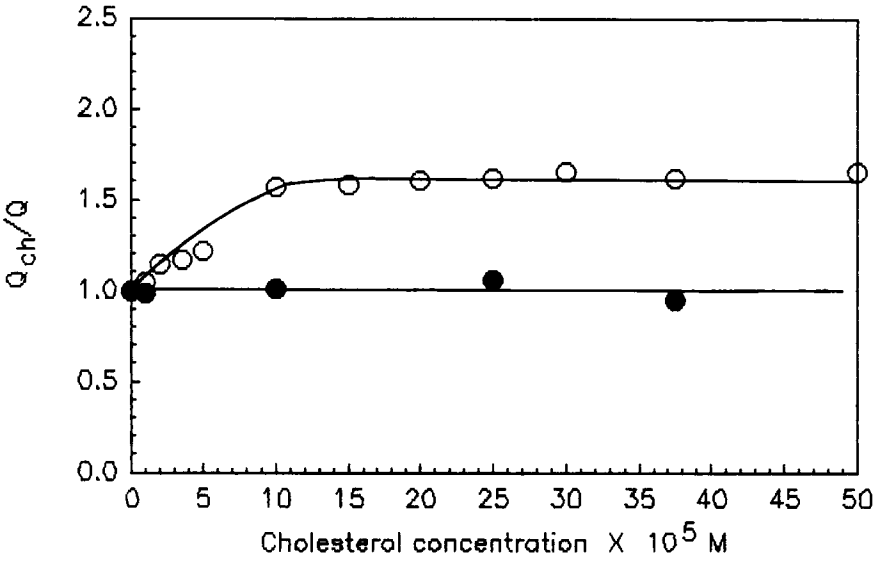

FIGURE 1. Variation of the light reaction quantum yield as a function of Cholesterol concentration. [DDAB] = 10^{-2} M, o=lamellar and ●=sonicated preparations.

lamellar and vesicular systems; the insignificant effect in the vesicular systems becomes very pronounced in the lamellar system. Apparently, the effect of cholesterol is more drastic on a system of superimposed lamellae than on

the outer surface of a vesicle. Indeed, progressive addition of cholesterol to the lamellar system increases the opacity of the solution indicating smecticity differentiations which affect the polarity of the region in which the critical chemiexcitation step of the light reaction takes place. No such effect was observed in the vesicular system.

The effect of temperature on the lamellar system containing $2x10^{-4}$ M cholesterol was rather insignificant. On going from 12° to 16° C, a 0.04 decrease in Q_{ch}/Q was observed which became 0.08 while at 20° C and 0.1 at 25° C.

In conclusion, the above results offer further evidence in support of our earlier suggestions that chemiluminescence can be a tool in the study of the structure of membrane mimetic agents.

EXPERIMENTAL

Didodecyldimethylammonium bromide (DDAB) and Lucigenin (L) were used was received. Cholesterol was recrystallized twice from ethanol.

Stirred solutions of DDAB aggregates (10^{-2} M) with or without cholesterol were prepared at least 24 hours prior to use. Solutions of cholesterol below 10^{-5} M were made from stock solutions of 10^{-3} M.

Sonication times were 20 min on a MSE sonicator. Chemiluminescence and UV measurements were taken at the constant assigned temperature on a LKB 1250 Luminometer and a UVIDEL-340 specrophotometer respectively.

Sample used: Lucigenin (to reach 10^{-5} M) was dissolved and stirred in the medium 15 min prior to light reaction and absorption was measured at λ 500 nm. 500 µl samples were taken and the light reactions were followed upon addition of 20 µl 5 N NaOH and 20 µl 10% H_2O_2. All reactions were terminated in about 2.5 hours. Upon termination, absorption was measured again. The ratio's of quantum yields were corrected for self absorption [8] and found for each individual concentration measured.

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