Fluorometric Determination of the 2nd Critical Micelle Concentration of Sodium Dodecyl Sulfate

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The determination of the critical micelle concentration (CMC) of various surfactants has been intensively investigated by several different techniques, *i.e.*, electric conductivity, light scattering, surface tension and viscosity methods.

Nonetheless, most of these techniques are only concerned with the determination of the 1st CMC of them[1,2]. Those methods are usually failed to obtain a cloar 2nd CMC, most probably, due to the low sensitivity to detect.

Spectro-fluorometric method with fluorescence probe anilino-naphthalene sulfonate (ANS) has been employed to determine the 1st CMC of sodium dodecyl sulfate (SDS)[3].

Since the fluorescence parameters such as quantum yield, polarization and lifetime are very sensitive to the microenvironmental changes of the fluorophores, the change of those properties of fluorescence probe has been frequently employed to study the hydrophobic interactions in protein and membrane bilolgy.

A drastic enhancement of fluorsecence quantum yield, when the probes(ANS and Pyrene) interact with the hydrophobic interior of the micelle, makes us attempt to determine the 2nd CMC of SDS with this method. The representative physical property changing at its 2nd CMC is known to be the shape of micelle . Consequently, a certain microenvironmental change can be expected to occur and there must be a change of the fluorescence properties.

In this communication, we present the results on the determination of the 2nd CMC of SDS by the fluorometric method using ANS and pyrene as an extrinsic fluorescence probe.

Fluorescence intensities monitored by the Aminco-Bowman spectro-fluorometer are corrected through the normalization with the PM tube response-curve presented at the manual. Optical density correction is also P performed by multiplying the factor of $(1-10^{-O.D})$ to each fluorescence intensities.

Figure 1 shows the plot of fluoresence intensities of ANS at its concentration of 3.2×10^{-4} M vs. SDS concentrations.

Two distinct breaking points at 8 mM and 70 mM concentration of SDS are demonstrated. These two values coincide well with the 1st and 2nd CMC of SDS determined with other method[5].

Pyrene, which has fairly long fluorescence lifetime, is used as an another probe. Pyrene-SDS solution has been prepared to be [pyrene]/[SDS]$=1/100$ and solubilize it completely by boiling[6].
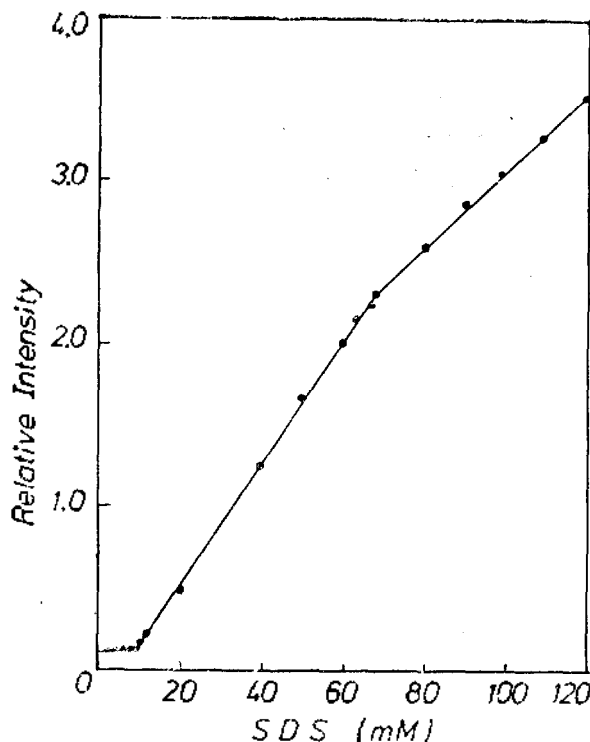

Figure 1. Relative fluorescence intensities of ANS $(3.2 \times 10^{-4}M)$ are plotted as a fucntion of SDS concentration. Fluorescence emission spectra were monitored exciting at 425nm.
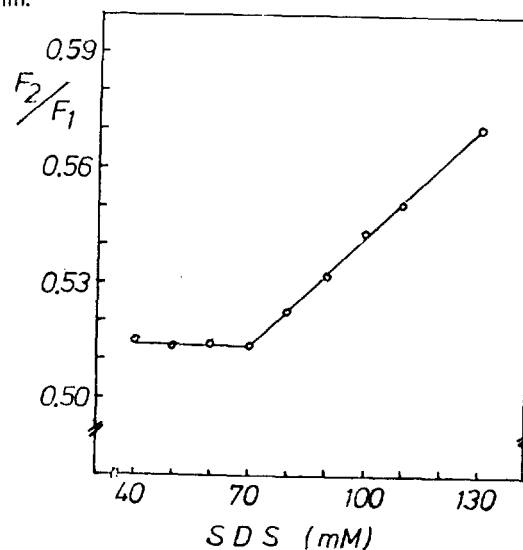

Figure 2. The ratios (F_2/F_1) of fluorescence intensities of excimer (F_2) and monomer (F_1) are plotted as a function of SDS concentration. Fluorescence emission spectra were monitored exciting at 360 nm.

Fluorescence measurements are carried out after 2 days of equilibrium at 25 °C.

This compound forms a face-to-face excimer[7] and gives excimer emission (F_2) at 470 nm and monomer emission (F_1) at 390 nm.

In this experiment, we plotted the value of F_2/F_1 as a function of SDS concentration and also found a sharp break at 70 mM of SDS in good agreement with the one determined by using ANS (Figure 2).

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Thermal Unimolecular Decomposition Reactions of Ethyl Bromide at 724.5-755.1°K

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The thermal decomposition reaction of ethyl bromide was studied in the temperature range of 724.5-755.1°K. Pressure dependence of the reaction was observed in its fall-off region. A theoretical evaluation of the rate constants was carried out adopting RRKM formulation in the region and was compared with the experimental observation. The validity of theory was also reevaluated by using the observed results. The observed activation energy in this study and Arrhenius A-factor were 51.7 kcal/mole and $10^{12.5}$, respectively. The small A-factor in the study was discussed in terms of the formation of a tight activated complex and the molecular elimination as a prevalent reaction mode.

Introduction

The kinetics for the decomposition of ethyl bromide is known to be first-order and mechanism consisted of simple homogeneous molecular stplitting and radical chain reaction which can be inhibited by various inhibitors. However, the detailed mechanism of radical reaction is not well established[1-4].

Fugassi and Daniels[1] have proposed the non-chain radical reaction as the primary decomposition in which ethyl bromide is splitted into ethyl radical and bromine atom. But this suggestion was not fully supported by other workers[2]. It has been also suggested by Goldberg and Daniels[3] that the decomposition is composed of two different types of reactions. They have found the radical chain reaction was catalyzed by the wall and unimolecular splitting was occurred during the induction period which was not detected at temperatures above 400°C. And the overall decomposition exhibited the first-order behavior by the inhibitor even after the induction period. Nevertheless, the disagreements between workers and difficulties of precise product analyses in earlier works are greater than would normally be expected and thus a reinvestigation of this system, coupled with a theoretical treatment, would appear in order. Since spectroscopic data on this system are available the dissociation of ethyl bromide lends itself to a fairly detailed analysis in terms of the quantum statistical RRKM theory[5] of unimolecular reactions and this forms the objective of the present study.

Experimental

Materials. Ethyl bromide, obtained from Eastmann Kodak Co., was purified several times by fractional distillation and low boiling trap-to-trap distillation until zero detection of impurities by GC. Ethylene stated purity of 99.5%, product of Matheson Co., was purified by the same technique as ethyl bromide. Carbon dioxide state purity of 99.995%, Matheson research gade, was used as a filling gas in the high pressure region without further purification.

Apparatus.. The reaction system in this study was a static system connected to a standard vacuum line for gas handling and pressure measurement. The reaction vessel was constructed from a total volume 43.5 ml silica tubing with 2.5×6 cm dimension and was heated in an air furnace. The temperature gradient of the reaction section was maximum $\pm 2°C$ over entire temperature range, *i.e.*, 200-700°C, and was calibrated against Leeds and Northrup 8686 potentiometer. Feedback temperature control was carried out by use of Love controller Model 51 on-off type with chromel-alumel K type thermocouple as a detection