PRE-MICELLAR MAXIMUM IN THE LIGHT SCATTERING FROM CETYLTRIMETHYL-
AMMONIUM BROMIDE AND CHLORIDE*

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Polarized light scattering measurements at a scattering angle of 90° on aqueous solutions of cetyltrimethylammonium bromide (CTAB) and chloride (CTAC) each exhibit a pre-micellar maximum as a function of concentration at 20°C. Further evidence from angular light scattering and correlation spectroscopy suggests the existence of a low concentration of large anisotropic structures both above and below the cmc. Interpretations are formulated in terms of thermodynamic and geometrical packing considerations.

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INTRODUCTION

Consideration of geometrical and thermodynamical aspects of the aggregation of amphiphiles into micelles is essential for understanding the process of their spontaneous formation. The distribution function of molecular aggregates changes drastically around the cmc. Prior to this event the constant level of most physical properties lends credence to the model of mostly unassociated amphiphiles with some low concentration of n-mers. This is borne out for most surface active systems.

Light scattering has been routinely used to determine the cmc in aqueous surfactant systems. In addition to the break in the light scattering at the cmc, many systems exhibit a sharp maximum just prior to the cmc. The phenomena appears to have been first reported and studied in some detail by Mysels who showed that the peak was due to traces of alcohol impurities in the surfactant, i.e. lauryl alcohol in sodium lauryl sulfate. The peak was thought to be a new finely divided phase consisting of an alcohol-surfactant complex. The prevailing view in subsequent studies has been that the peak was due to spherical droplets although the composition of the droplets has not been established. In this work we report new studies showing that the structures responsible for the peak are not spherical and are much larger than the normal micelles. Our size estimates are consistent with recent independent determinations by Corti and Degiorgio although their analysis was based on the assumption of spherical droplets as discussed below.

In this work we present light scattering evidence in two systems that suggests the existence of large structures prior to as well as above the cmc. These aggregates appear to undergo a dissociation before the true cmc is reached and are present in a very low concentration. Packing constraints based on the double layer properties and molecular geometry may help in partially explaining the result.

EXPERIMENTAL

Cetyltrimethylammonium bromide (CTAB) obtained from the Aldrich Chemical Company was purified by recrystallization from 95% ethanol, and in control experiments was used without purification.

Cetyltrimethylammonium chloride (CTAC) obtained from Pfaltz and Bauer Company, Inc., was used as received.

Aqueous solutions were prepared with twice distilled water filtered through a 0.2 μm Nuclepore filter. Further filtering did not improve the depolarization ratio ($\rho_v = H_v/V_v$) at 90°,