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CHAPTER I

INTRODUCTION

A surfactant or a surface active agent is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system.

Surfactants can be used in a variety of fields, for example in detergency, wastewater treatment and purification, enhanced oil recovery and applications of novel separations methods in biotechnology. The study of thermodynamics of systems containing surfactant mixtures is also an area of fundamental interest.

A surfactant molecule has a characteristic structure, known as the amphipathic structure, which consists of a hydrophobic group (long chain hydrocarbon) and hydrophilic group (polar group). In a dilute solution, the surfactant exists as monomer species, then it starts to aggregate, forming micelles, at higher concentrations. The concentration at which the surfactant starts to form micelles is known as the critical micelle concentration (CMC). In an aqueous solution of a surfactant, the presence of hydrophobic groups causes distortion of the water structure, increasing the tendency of these groups to move out of the aqueous environment. Accordingly, the surfactant molecules tend to concentrate at the surface. On the other hand, the presence of the hydrophilic groups prevents the surfactant from being expelled completely from the solvent as a separate phase. This amphipathic structure of the surfactant causes not only accumulation of the surfactant at the surface, but also causes the molecules to orient at the surface, with their hydrophilic groups toward the bulk aqueous solution and the hydrophobic groups toward the interior of the micelle, thus forming a liquid hydrocarbon-like environment (1).

Although the question of the micellar shapes is *still* not completely settled, more information is available about micellar aggregation numbers. Light scattering is frequently used to determine aggregation numbers (2). They can also be obtained from sedimentation rates in the ultracentrifuge (3). As a rule, in aqueous medium, the greater the dissimilarity between the surfactant and solvent, the greater the aggregation number. Thus in aqueous solutions, increasing the hydrophobic character of the surfactant increases the aggregation number. This can be achieved by increasing the length of the hydrophobic group in ionics or nonionics, and increasing the binding of the counterions to the micelle in ionic surfactants. The addition of an electrolyte to the aqueous solution of ionic surfactant increases the aggregation number. The effect is not always in this direction in the case of nonionic surfactants. By increasing the temperature, there tends to be a small decrease in the aggregation number of ionic surfactants in aqueous medium. However, in the case of nonionic surfactants, an increase in temperature ordinarily causes a large increase in the aggregation number. The solution begins to show turbidity and then separates into two phases. This phase separation owes to the increase in micellar size (4). The lowest temperature at which clouding occurs is called the "cloud point".

The shape of the micelle depends on the total concentration of the surfactant solution (5). In dilute solutions, micelles can be considered to be roughly spherical. In concentrated solutions, micelles become larger with a reduced surface area per molecule. These structures are non-spherical, often becoming rod or disk shaped. In some cases, surfactant micelles take the form of parallel sheets, or long cylinders packed together and surrounded by solvent (6).

There are two main types of surfactants, ionic and nonionic. Ionic surfactants, which are more common, are divided into three classes depending on the nature of the hydrophilic group:

1. <u>anionic surfactants</u> with a negative charge on the hydrophilic head groups, e.g. sodium laurate (NaL) and sodium dodecylsulfate (SDS);

2. <u>cationic surfactants</u> having a positive charge at the hydrophilic head group, e.g. hexadecylpyridinium chloride (also known as cetyl

pyridinium chloride, CPC) and hexadecyltrimethylammonium bromide (CTAB); and

3. zwitterionic surfactants which possess both positive and negative charges on the same molecule and may behave as either cationic or anionic surfactants depending on the pH of the solution, e.g. long chain amino acids.

The nonionic surfactants are neutral molecules with polar hydrophilic groups, e.g. polydisperse nonylphenoxypolyoxyethylene ethanol (GAF CO-660).

Many factors affect the CMC in aqueous solutions: mainly the structure of the surfactant (1,5,7), the presence of an added electrolyte (8), and the temperature of the solution (9). Generally, anionic surfactants have relatively large CMC values compared with cationic surfactants. Nonionic surfactants usually have low CMC values.

Solubilization is one of the most important phenomena exhibited by surfactant solutions which form micelles. Solubilization may be defined as the spontaneous dissolving of a substance (solid, liquid or gas) by reversible interaction with the micelle of a surfactant in a solvent, to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized compound. These solubilized compounds are often solvent-insoluble or sparingly-soluble materials. Thus, the importance of the solubilization phenomenon is that it allows substances to dissolve in solvents in which they are normally insoluble or slightly soluble (10). The increased solubility