A quantitative treatment of the dynamics of micelles in aqueous solutions was given in 1974 by Aniansson and Wall. The validity of this treatment has been checked in a large number of studies from which a wealth of information concerning the dynamics of micellar systems has been obtained. After briefly recalling the main features of the theory of Aniansson and Wall, this paper reviews (i) the results concerning the kinetics of the exchange of the surfactant between micelles and the bulk, and of the micelle formation-breakdown in aqueous solution; (ii) the kinetics of similar processes in mixed alcohol + surfactant micellar solutions, and microemulsions; (iii) the kinetics of the exchange of solubilizates between micelles (and other organized assemblies) and the bulk; and (iv) the available evidence for the exchange of compounds between microemulsion droplets occurring through micelle collisions or partial micellar breakdown and the results concerning their kinetics.

INTRODUCTION

This review deals with the dynamics of organized assemblies such as micelles, microemulsions and bilayers (vesicles, liposomes). The word dynamics may include many different processes: (i) intramolecular motions (rotations around C-C bonds of the surfactant and cosurfactant alkyl chains); (ii) exchange of counterions and water between the assembly surface and the bulk; (iii) exchange of surfactant, cosurfactant and solubilizate between the assembly and the bulk; (iv) assembly formation and breakdown; (v) exchange of matter between assemblies through processes which do not involve the continuous phase about the assemblies. This review, however, deals only with processes (iii) to (v).

* In memory of the late Dr. E. A. G. Aniansson.
In addition to providing information on the assemblies per se, the study of the dynamics of organized assemblies may help in understanding three widely differing phenomena.

1. The kinetics of solubilization of otherwise water-insoluble compounds by micellar solutions. This process may involve the micelle formation-breakdown equilibrium.

2. The interactions between micelles or microemulsion droplets. Indeed the exchange of matter by processes (iii) and (v) between assemblies gives rise to interactions between these assemblies. Exchange interactions may be responsible for the existence of a lower consolute critical temperature in some micellar systems and microemulsions.

3. The effect of organized assemblies on the rate and mechanism of chemical reactions. Indeed the reactants must reside a sufficient time within or on the surface of the organized assembly for the reaction to occur. Thus their residence time in the assembly has some bearing on the kinetics of the reaction. Also the reactants must be in a favorable configuration and remain in this configuration for the reaction to occur. This involves the diffusion of the reactants on the assembly surface (lateral diffusion) or in the bulk of the assembly. Finally the assembly must be sufficiently long-lived and, thus, its lifetime which is determined by the kinetics of process (iv) is also of importance.

We shall successively consider micellar solutions, solubilized systems and bilayers or vesicles with solubilized molecules, mixed alcohol + surfactant micellar solutions, and, finally, microemulsions.

DYNAMIC OF MICELLES

The extensive use of chemical relaxation methods for the study of the dynamics of micelles in aqueous solutions has shown that the response of these systems to a sudden perturbation involves two characteristic times. These relaxation processes were assigned on the basis of the dependence of the corresponding relaxation times on various parameters: concentration, surfactant nature and chain length, nature of the counterion, and temperature. Thus the fast process was attributed to the exchange of surfactants between micelles and the bulk solution. The slow process was attributed to the micelle formation-breakdown equilibrium, a process which is thought to be equivalent to a nucleation. Until 1975, however, the considerable amount of experimental results which had accumulated could not be quantitatively interpreted because of the lack of a comprehensive theory of the dynamics of micellar solutions. This gap was filled by Aniansson and Wall in two papers reported in 1974 and 1975. The basis of this theory can be most easily understood by considering the size distribution curve of the aggregates present in a micellar solution, that is, at a concentration above the critical micelle concentration or the CMC (see Figure 1). An aggregate containing s surfactants is referred to as A, with N being the experimentally determined aggregation number. The shape of the size distribution curve in Figure 1 is that predicted by numerous thermodynamic treatments of micellization. The very deep minimum between the micelles proper and the oligomers in the size distribution curve is responsible for the observed dynamic behavior of micellar solutions. Indeed, upon a sudden perturbation, the system first responds by a fast re-equilibration