

## CHAPTER II

### BACKGROUND

#### 2.1 Molecular Sieves MCM-41

In the broadest sense, any materials that can exclude molecular species by size can be considered a molecular sieve. The term molecular sieve is restricted to inorganic materials that possess uniform pores with diameters in either the micro-(<2 nm) or meso-(2-20 nm) size range. The most technologically important molecular sieves are zeolites, crystalline silicate or aluminosilicate framework structures with channels of diameters <1.2 nm (Breck, 1974). The technological applications of molecular sieves are as varied as their chemical makeup. Heterogeneous catalysis and adsorption processes make extensive use of molecular sieves. The utility of the latter materials lies in their microstructures, which allow access to large internal surfaces and cavities that enhance catalytic activity and adsorptive capacity.

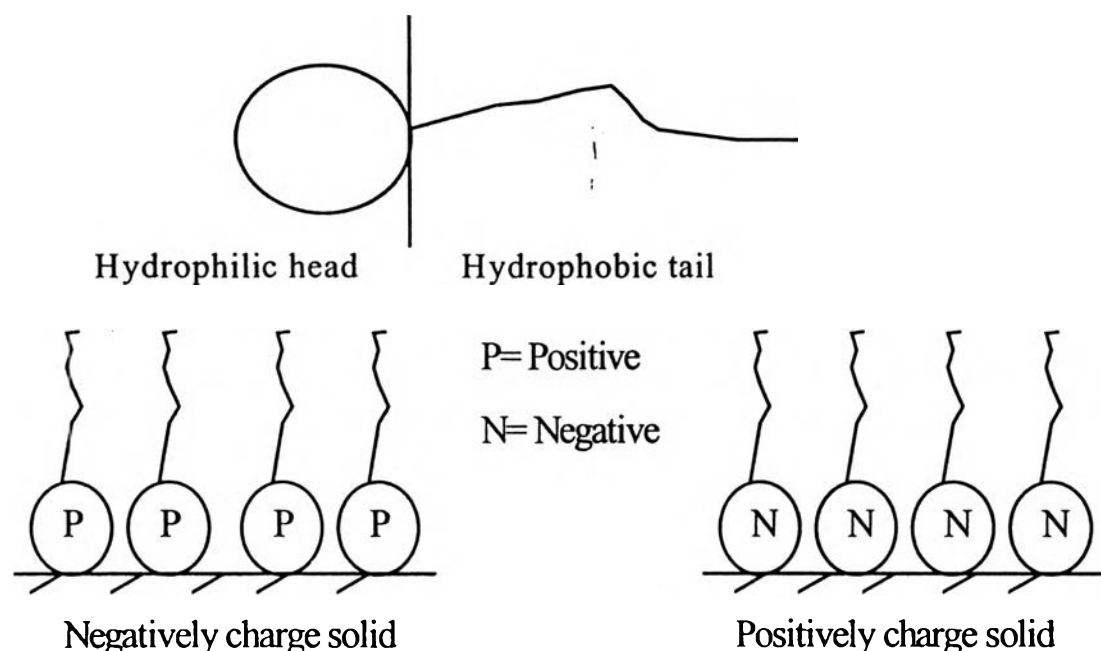
Typical microporous materials are the crystalline framework solids, such as zeolites, but the largest pore dimensions found so far are 10-12 Å for some metallophosphates and 14 Å for the mineral caxenite (Moore and Shen, 1983; Davis et al., 1988; Dessau et al., 1990; and Estermann et al., 1991). Examples of mesoporous solids include silicas and modified layered materials, but the pores of these materials are irregularly spaced and broadly distributed in size (Pinnavaia, 1983).

Mobil Composition of Matter number 41 (MCM-41) which is a member of a new family of mesoporous molecular sieves designated as M41S has been

discovered and developed by Mobil Oil researchers. MCM-41 has been synthesized with uniform channels varying from approximately 15 Å to greater than 100 Å in diameter, the dimension of which can be tailored through the choice of surfactant, auxiliary chemical and reaction conditions.

## 2.2 Adsorption of Surfactant at the Solid-Liquid Interface

A surface active agent or surfactant is a substance that, when presents at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system depending on the charges of the surfactant and the solid substrate. A surfactant has an amphipathic structure which consists of hydrophobic and hydrophilic parts (Figure 2-1),(Rosen, 1990).

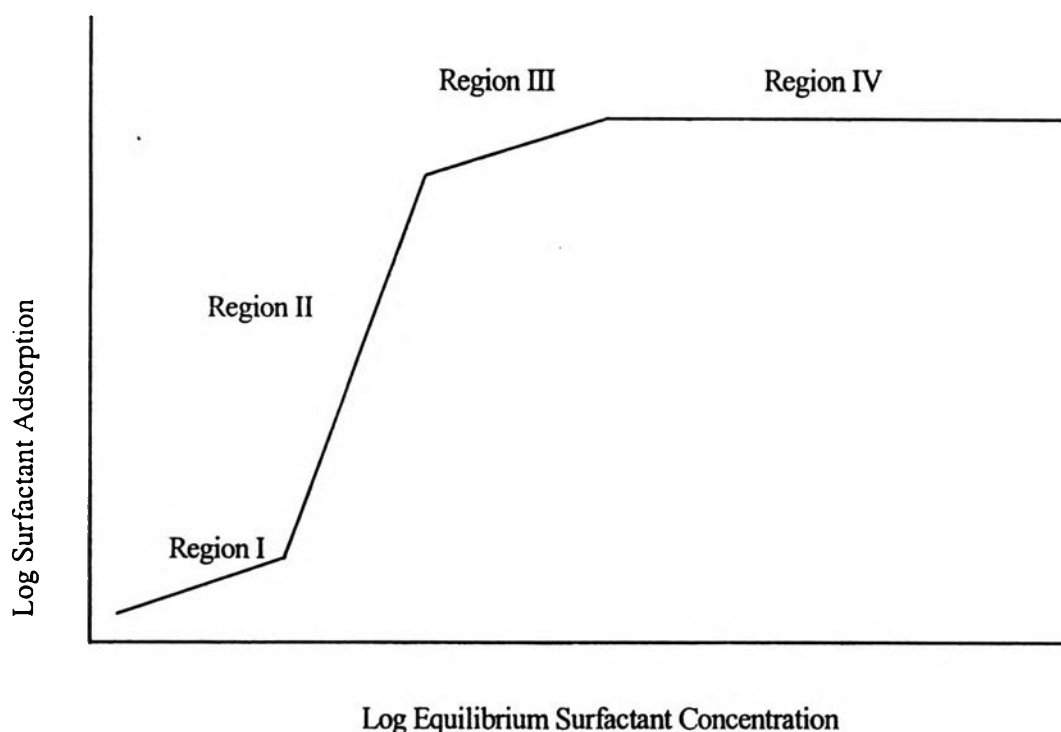


**Figure 2.1** Amphipathic structure of surfactant and adsorption pattern on solid substrate surface.

The group which has strong attraction for the solvent is called the hydrophilic group or lyophilic group and the group which has little attraction for the solvent is called the hydrophobic group or lyophobic group, depending on whether the solution is aqueous or nonaqueous, respectively.

### **2.3 Adsorption Isotherm of Ionic Surfactant on Solid Oxide Surface**

For a dilute solution containing a surfactant, the number of moles of surfactant adsorbed per unit mass of the adsorbate (the solid substrate) can be obtained from the calculation of the surfactant concentration in the liquid phase before and after the solution is mixed with the solid substrate. The curve of the number of moles of the surfactant adsorbed and the equilibrium concentration of surfactant is plotted in log/log scale to produce the adsorption isotherm. The typical surfactant adsorption isotherm of an ionic surfactant on an oppositely charged oxide surface is an 'S'-shaped curve when plotted in the log of adsorbed surfactant versus the log equilibrium concentration of surfactant (Scamehorn et al., 1982)(Figure 2-2). Generally, this 'S'-shaped adsorption isotherm can be separated into four regions (Rosen, 1990; Valsaraj, 1992). Region I is the Henry's law region because the adsorbed surfactant is considered to be infinite dilution in the surface phase due to very low concentration and low adsorption of surfactant (monomer adsorption). The change density in this area remains almost constant and, thus, the interaction between molecules of surfactants is negligible. Adsorbed surfactants in this region are viewed as being adsorbed alone and forming no aggregates.



**Figure 2.2** Typical adsorption isotherm of surfactants on solid oxide surfaces (Rosen,1990).

Region II is eminent by a dramatically increase in adsorption and is known to be an effect of the cooperative interaction between hydrocarbon tails of the adsorbed surfactant molecules, which results in the formation of surfactant aggregates on the most energetic patches (Scamehorn et al., 1982). The slope of the isotherm increases drastically in this region. These adsorbed surfactant aggregates are called admicelles (Harwell et al., 1985) or hemimicelles (Somasundarun and Fuerstenau, 1966), depending on whether the aggregates are considered as bilayer or monolayer. The admicelle is considered as local bilayer structure with a lower layer of head groups adsorbed on the substrate surface and an upper layer of head groups in contact with the solution. The hemimicelle is a monolayer structure having the head group adsorbed on the surface whereas the tail group is in contact with the aqueous phase.

In region III, adsorption increases slowly because of competition between admicelle so that the slope of the isotherm decreases. This is thought to be caused by repulsion between the like-charged head groups on the surface. The adsorption now must overcome this electrostatic repulsion between the oncoming ions and the similarly charged solid (Rosen, 1990). Region IV is the plateau region in which the surface is completely covered with a monolayer or bilayer of the surfactants. The surfactant adsorption is almost constant with increasing surfactant concentration. Typically, the equilibrium surfactant concentration at the transition point from region III to IV is approximately at the Critical Micelle Concentration (CMC).

The adsorption of surfactant on solid substrates is influenced by several parameters including the pH of the solution, the electro-chemical nature of the substrate, and the type of surfactant molecule. The charge on the solid oxide surface can be handled to be either negative or positive by adjusting the pH of the contacting aqueous solution. As the pH of the aqueous phase is lowered, a solid surface will usually become more positive, or less negative because of adsorption onto charged sites of the protons from the solution (Conner, 1971). The reverse is true when the pH of the aqueous phase is raised. The pH that makes the charge on the surface equal zero is called the Point of Zero Charge (PZC). When the pH of the contacting aqueous solution is below the PZC of the solid surface, the surface will be protonated and become more positive. Vice versa, the solid surface will be negatively charged at a pH over the PZC. For example, silica having  $2 < \text{PZC} < 3$  will be negatively charged if the pH of the aqueous phase exceeds 3 (Iler, 1979). As a result, cationic surfactants such as octyltrimethylammonium bromide or any quaternary ammonium surfactants adsorb readily on the surface of silica and MCM-41 which is a siliceous solid when the pH of the contacting aqueous phase is greater than 3.

Adsorption is the term used to describe the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid or adsorbent. This is a fundamental property of matter, having its origin in the attractive forces between molecules (Ruthven, 1991).

The adsorption of surfactant at the solid-liquid interface is strongly influenced by several factors such as the nature of the structural groups on the solid surface whether the surface contains highly charged sites or not, the molecular structure of the surfactant being adsorbed (the adsorbate) and the environment of the aqueous phase (Lyklema, 1983).