

CHAPTER II

LITERATURE SURVEY

2.1 Blocking Agents

Complex oil reservoir water flooding is accompanied by early water breakthrough in production wells and a high water/oil ratio. In reducing this water/oil ratio, it can be basically achieved by blocking the high-permeability channels. Cross-linking polymer treatments show the good blocking in the injection well and producing well. In this process, polymer molecules are bound together into a gel structure by a metal or an organic cross-linking agent. To obtain significant amounts of incremental oil, while avoiding very large pressure build-up, the polymer gel system should have the correct combination of long gelation time and good permeable-reducing properties. No commercial polymer system has sufficiently long gel times that required to obtain deep emplacement in a large reservoir (Seright, 1988).

Bulk chemical gels, such as polyacrylamide, xanthan gum, and silica gel have been widely used for long-term profile modification treatments. Their slow gelation rates give deep placement in high permeability zones (Lockhart *et al.*, 1991). Although bulk gels create very stable, strong plugs suitable for diverting injected water, they are criticized because of high treatment cost.

Micro-organisms have been proposed as the blocking agent. The placement characteristics of micro-organisms are similar to the gelants because its placement is dictated by amounts of nutrients. A potential problem with the use of micro-organisms is their tendency to aggregate and adsorb onto the pore walls, limiting their depth of penetration (Seright, 1994).

The use of silica gels as the reactive water diverting agents to stop excess water production was investigated for selective diversion of aqueous fluids and brines from the production well (Thompson and Fogler, 1993). The advantage of this system was its ability to selectively react when contacting water within the formation. This work demonstrated the benefits of an oil-phase injection fluid as a water-displacing media prior to reaction. Thus no blocking should occur in high oil saturation. However, due to the highly reactive nature of the diverting agent, an injection procedure of delivery was necessary prior to shut-in.

The in-situ deposition of silica particles relies on selective placement of silica particles, not selective reaction within the formation. The suspension particles can penetrate into a high permeability zone containing large pores, but which will be removed by filtration on the formation faces of less permeability zones containing small pores. Therefore, the particle size distribution must be sufficiently narrow (Seright, 1994). The placement characteristics of particles are similar to those of gels, but should be able to penetrate deeper into a formation.

Silica particles synthesized in W/O nonionic microemulsions usually have a narrow size distribution with the average value between 25-70 nm (Osseo-Asare and Arriagada, 1990 and Chang and Fogler, 1996). These nanosized uniform particles are anticipated to be able to penetrate deeply into the formation. These particles will grow within the pores of the formation and subsequently will reduce the permeability.

2.2 Silica Particles Formation in W/O Microemulsions

Water-in-oil microemulsions provide particularly favorable reaction conditions for the preparation of monodisperse solid particles. At a suitable chosen composition, microemulsion systems will contain inverted micellar aggregates consisting of water pools surrounded by amphiphiles in a continuous nonpolar medium. By dissolving, for instance metal salts which undergo a dissociation inside the aqueous domain followed by a reduction step ($\text{Me}^{n+} \longrightarrow \text{Me}^0$), a subsequent precipitation can take place inside the water pools. The success of this procedure is most likely that particle nucleation can be initiated simultaneously at a very large number of locations in the microemulsion with the nucleation sites well isolated from each other and in close contact with surfactants that may act as stabilizers of the particles formed (Boutonnet *et al.*, 1982).

The synthesis of nanoparticles using reactions in microemulsions was first described by Boutonnet *et al.* (1982). They prepared platinum, palladium, rhodium and iridium particles in oil continuous microemulsions. Since then, there have been many reports on the use of microemulsions as a reaction media for the synthesis of a variety of inorganic particles such as gold, silver, titanium dioxide, calcium and barium carbonates and silica particles.

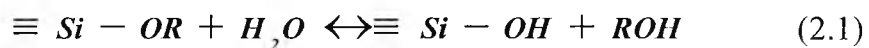
2.2.1 Kinetics of Silica Particles Formation in W/O Microemulsions

Osseo-Asare and Arriagada (1990) studied the preparation of silica particles by hydrolysis and condensation of tetra ethyl orthosilicate (TEOS) in reverse Igepal CO-520/cyclohexane/aqueous ammonia/water microemulsion. They demonstrated the ability of microemulsion media to produce monodisperse particles and stressed that microemulsion properties such as solubilization, structure and dynamics were relevant factors in the

formation of particles. All samples prepared exhibited a bluish white opalescence a few hours after addition of TEOS, indicating the presence of silica particles. The dispersion remained stable for months. The synthesized silica particles were monodisperse and spherical in shape. The mean particle diameter decreased as the water to surfactant molar ratio (r) increased.

The reactions involved in this silica synthesis include the hydrolysis of TEOS and the condensation (polymerization) of the hydrolyzed silica particles in the presence of base catalyst as shown below:

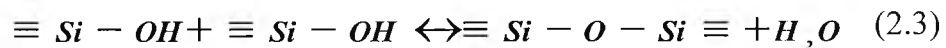
Hydrolysis



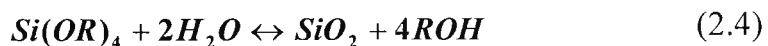
Alcohol condensation



Water condensation



Overall reaction



where R is C_2H_5

In the hydrolysis reaction, alkoxide groups (OR) are replaced by hydroxyl groups (OH). The condensation reactions produce siloxane bonds and either alcohol (ROH) or water (H_2O). In general the reactions are reversible (Osseo-Asare and Arriagada, 1990).

It is known that TEOS molecules are predominantly solubilized in the oil phase of microemulsions and then diffuse to the surfactant layer at oil-water interfaces and are hydrolyzed by water to form silanol groups (Si-O⁻ or Si-OH). Consequently, these hydrolyzed silica TEOS molecules are preferentially retained in the microemulsion droplets and condensed into polymeric species. After reaching the critical size these

polymeric species become nuclei that further grow into silica spheres by absorbing hydrolyzed TEOS molecules and small polymeric species.

Formation of colloidal particles in W/O microemulsions occurs not only through the polymerization of monomeric reactants into polymeric reacting species but also through the subsequent polymerization of polymeric species into even larger species (Chang and Fogler, 1997). The coagulation of hydrolyzed polymeric silica species through the mass exchange among W/O microemulsion droplets is shown in Figure 2.1.

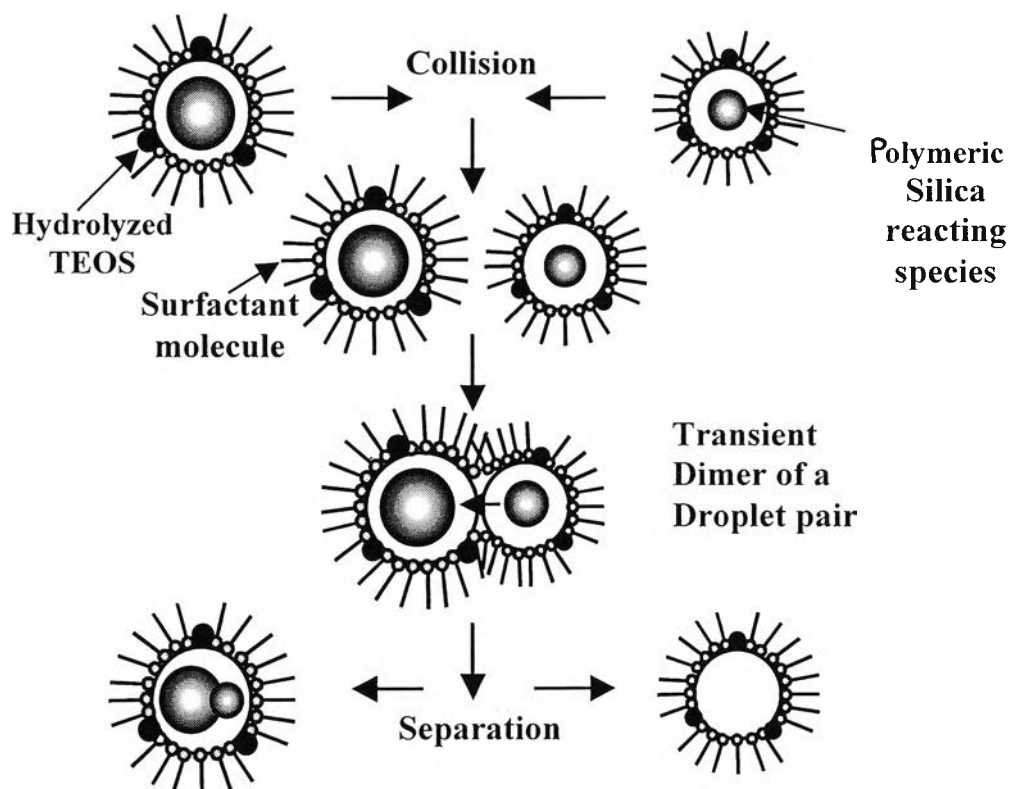


Figure 2.1 Schematic of the coagulation of hydrolyzed polymeric silica species through the mass exchange among W/O microemulsion droplets. (Chang and Fogler, 1997)

The kinetics and mechanism of silica particles growth have been studied extensively in alcohol media with the hydrolysis of TEOS via ammonia catalyst (Aelion *et al.*, 1950; Stober *et al.*, 1968; Brink and Scherer, 1989; and Burgna, 1994). These studies have provided the valuable insight of the formation of silica particles in microemulsion.

Aelion *et al.* (1950) investigated the kinetics of TEOS hydrolysis in methanol solutions under the catalysis of dilute sodium hydroxide (NaOH) by Karl-Fischer titration method. They suggested that the base-catalyzed hydrolysis of TEOS had a pseudo-first order reaction with respect to the concentration of both TEOS and hydroxyl ion (OH⁻), as shown below:

$$-\frac{d[TEOS]}{dt} = k[TEOS][OH^-] \quad (2.5)$$

In this study, the base catalyzed TEOS hydrolysis reaction was proposed as a nucleophilic (S_N2) substitution reaction involving with the displacement of the ethoxy (-OC₂H₅) group of TEOS by hydroxyl ion (OH⁻) through a pentacoordinate transition state. Nevertheless, the kinetics of TEOS hydrolysis in alcohol media with aqueous ammonia as a weak base catalyst appear to be more complicated. Based on the previous studied, it can be concluded that the rate of TEOS hydrolysis depends upon [H₂O] and [NH₃] which has reaction orders of 1.5 and 1, respectively (Byers *et al.*, 1987; Bogus and Zukoski, 1991; and Van Blaaderen *et al.*, 1992). Moreover, types of alcohol solvent also influence the rate of TEOS hydrolysis with 1-butanol > methanol > 1-propanol > ethanol > 2-propanol. This order may be induced from the hydrogen-bonding and steric hindrance effects of alcohol molecules (Harris *et al.*, 1990).

2.2.2 Control of Silica Particle Formation in W/O Microemulsions

Submicron silica particles (below 50 nm) can be prepared by the controlled hydrolysis of TEOS in the water pool of water in oil microemulsions. The particle size depends on the relative rates of the hydrolysis and condensation reaction. In general, the particle size is found to increase with increasing the concentrations of water and ammonia (Stober *et al.*, 1968). An increase in particle size obtained as the ammonia concentrations increased was attributed to the faster rate of condensation which, in turn, was the result of faster deprotonation of silanol groups. In the absence of ammonia, the irregularly shaped particles and no spheres could be observed under the electron microscope. Therefore, ammonia apparently influenced the morphology and created spherical particles whenever it was present during the reaction.

The question of bound or free water in the polar domain of a fluid medium is indeed relevant to the formation of particles in reverse micellar systems since the hydrolysis reaction is expected to facilitate when free water is present. The results of Osseo-Asare and Arriagada (1990) indicate that less than one water molecule per oxyethylene group involves in the initial hydration shell. Thus, it appeared that water might preferentially hydrate some of the oxyethylene groups along the polar chain, and that further water addition resulted in gradual formation of free water domains rather than in the complete hydration of all the oxyethylene groups.

The overall mechanism of particle nucleation and growth involves both intra- and inter- micellar processes. The monodispersity of the particles indicates that the nucleation probably occurs over a limited period. Besides monomer diffusion to existing particles, the particle growth also involves aggregation of nuclei during micelle-micelle collisions. Faster hydrolysis can be expected at a larger water to surfactant molar ratio (r), which would favor the formation of smaller particles (Burgna, 1994).

Chang and Fogler (1996) studied the effect of molecular structure of surfactant on the formation of silica particles in nonionic w/o microemulsions. They found that for the longer the head and tail groups of surfactant, it seemed to provide the stronger steric film barriers to the interdroplet exchange of silica reacting species than those of the shorter one. As a result, the smaller particles were formed.

The effects of alcohol as a co-surfactant on the interfacial properties of the microemulsions droplets have also been studied. Arriagada and Osseo-Assare (1990) studied the effect of the addition of benzyl alcohol in the AOT w/o microemulsion. They found that the silica particle growth and the particle size were increased by the addition of benzyl alcohol. Esquena *et al.* (1997) studied the effect of alcohol concentration and chain length on the silica particle size in microemulsion media using block copolymers and nonionic surfactant. The results showed that the higher the cosurfactant concentration and the shorter the chain length resulted in the larger the particles.