CHAPTER IV
RESULTS AND DISCUSSION

As be described earlier in Chapter III, there were two parts of the silica synthesis experiment and the coreflood experiment. The experimental data were shown in Appendices.

4.1 Relative Particle Density of Reaction Mixtures

The relative particle density of the reaction mixture was determined in terms of absorbance at the wavelength of 500 nm. In this study, the initial concentration of TEOS in W/O microemulsion solutions was fixed at 0.1494 M.

4.1.1 The Effect of Ammonia Concentration

The aqueous ammonia acted as the catalyst as well as the reactant in this system. The concentration of NH_3 in this study was varied from 0.0156 to 0.1249 M and the H_2O:TEOS molar ratio was fixed at 7.67:1. Figure 4.1 illustrates that an increase in the concentration of ammonia results in increasing turbidity in the microemulsion solution due to the rapid formation of silica particle. Ammonia did not only enhance the rate of hydrolysis of TEOS, but also enhanced the rate of condensation of silanol group. Therefore, the rate of silica particles growth increased with increasing the ammonia concentration.

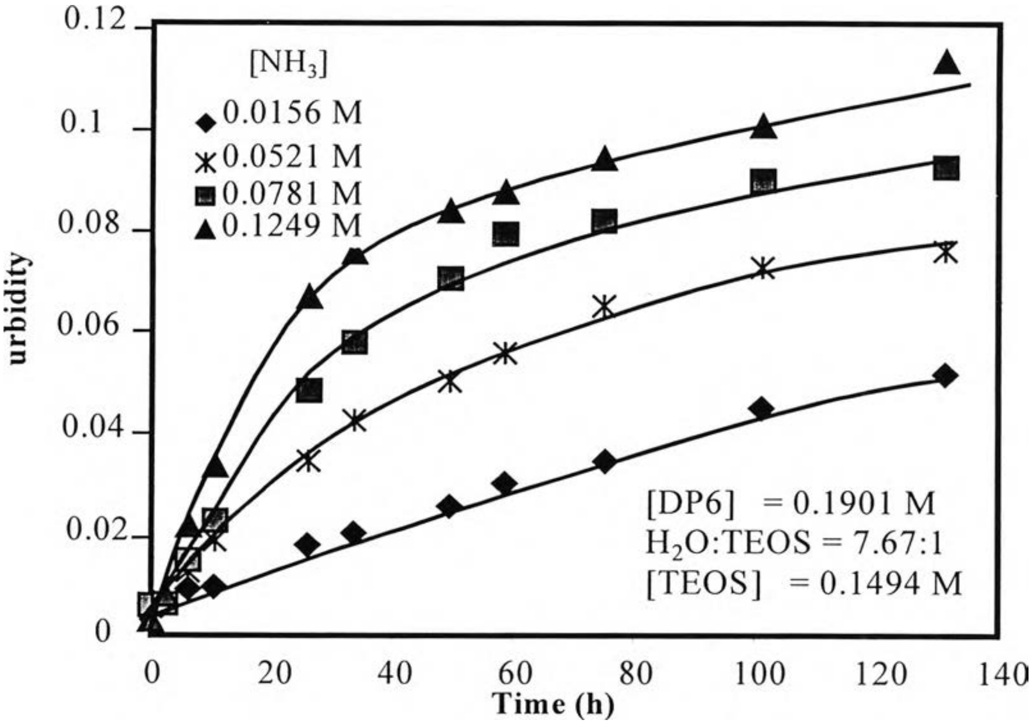


Figure 4.1 Turbidity of microemulsion solutions at different NH_3 concentrations.

4.1.2 The Effect of Surfactant Concentration

Figure 4.2 shows the effect of surfactant concentration on the relative silica particle density synthesized in W/O microemulsions containing 0.1494 M TEOS, 0.0156 M NH_3, H_2O:TEOS ratio of 7.67:1 and the concentration of DP6 surfactant was varied in the range of 0.1901 M to 0.3169 M. The relative turbidity decreased with increasing surfactant concentration. Hence, this result may indicate that the size of silica particles decreased when the surfactant concentration increased. This might be explained by a decreased in a number of TEOS reactants per micellar droplets. A number of micellar droplets increased with increasing surfactant concentration in the system at constant concentrations of TEOS and H_2O. Therefore, a number of TEOS precursors in each micellar droplet were decreased.

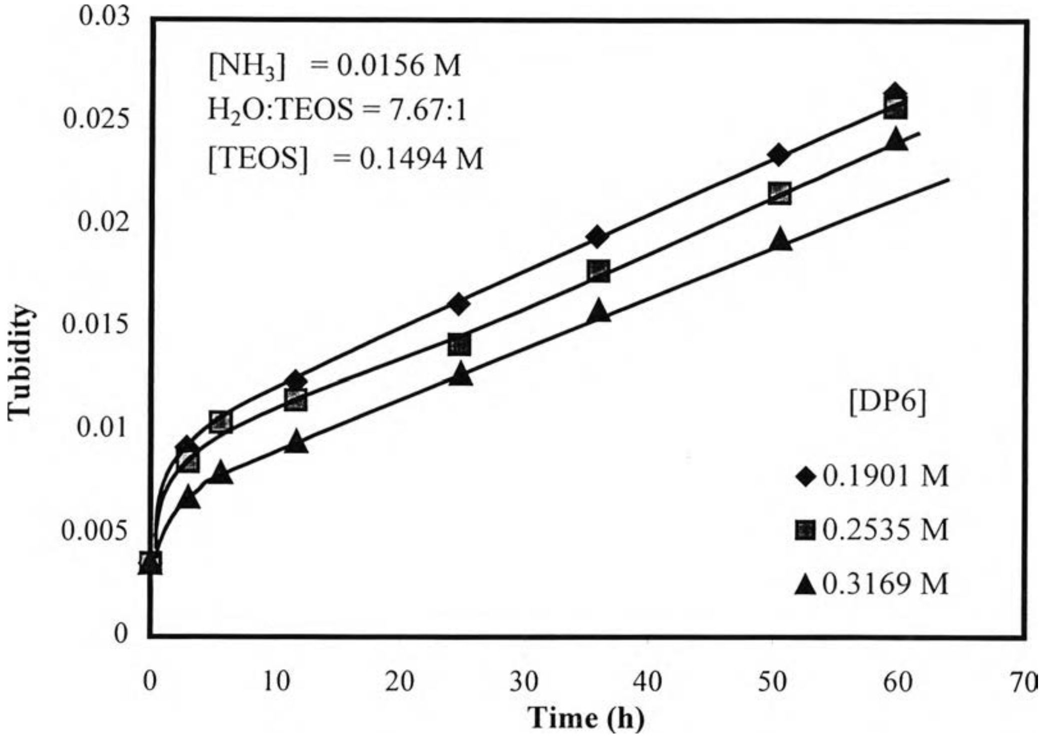


Figure 4.2 Turbidity of microemulsion solutions at different surfactant concentrations under studied conditions.

4.1.3 The Effect of H_2O to TEOS Molar Ratio

Figure 4.3 shows the effect of water to surfactant molar ratio on the relative particle density of microemulsions solution containing 0.1494 M TEOS, 0.1901 M DP6 and 0.0156 M NH_3. The concentration of water was varied in the range of 0.3976 M to 1.1462 M. At a H_2O:TEOS molar ratio equals 2.66:1, the phase separation occurred within 30 hours. Hence, as the H_2O:TEOS ratio increased, the relative particle density tended to decrease. From the results, water is necessary for the formation of stable silica suspension in microemulsions. It is very interesting to point out that all samples prepared with H_2O:TEOS molar ratio above the stoichiometric ratio (i.e., 2:1) were stable. The residue water needs to facilitate the adsorption of surfactant molecules onto the silica particles. Subsequently, the dynamic exchange between the microemulsion droplets was decreased.

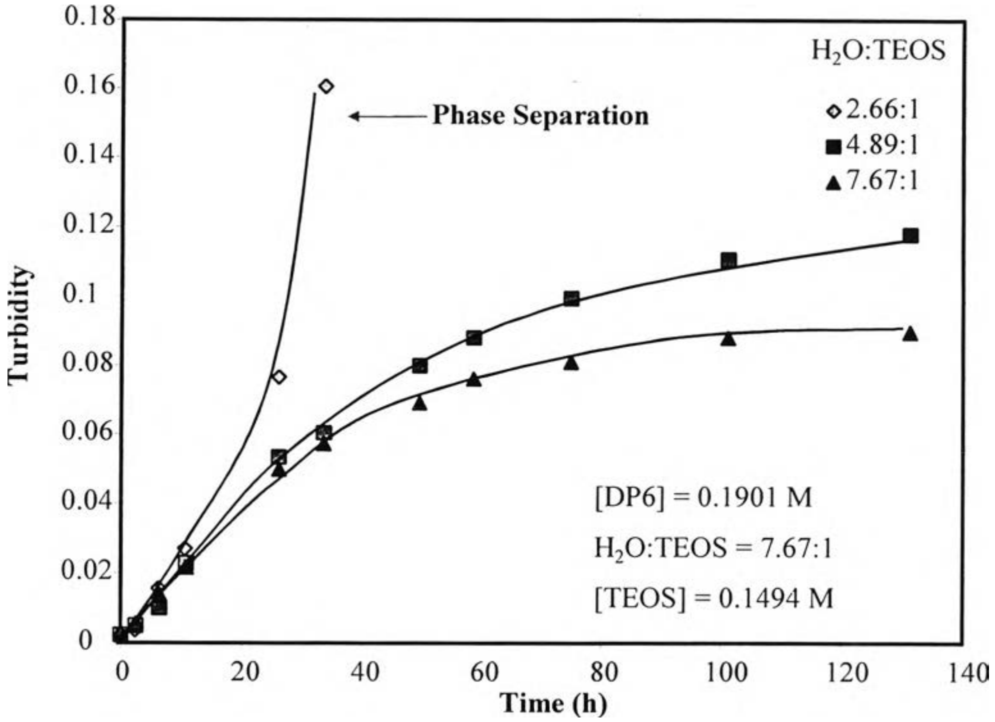


Figure 4.3 Turbidity of microemulsion solutions at different H_2O:TEOS molar ratios.

4.1.4 The Effect of Type and Concentration of Co-Surfactant

Figure 4.4 shows the effect of type and concentration of co-surfactants on the relative particle density in the system having [TEOS]= 0.1494 M, [DP6]= 0.1901 M, [NH_3]= 0.0156 M and H_2O:TEOS molar ratio = 7.66. The concentration of co-surfactant was varied from 0 M, 0.0637 M, 0.1594 M to 0.2550 M. Three types of alcohols 1-butanol, 1-octanol and 1-dodecanol were used as the co-surfactant. This result shows that 1-butanol was the most effective co-surfactant that affected the relative particle density of silica particles.

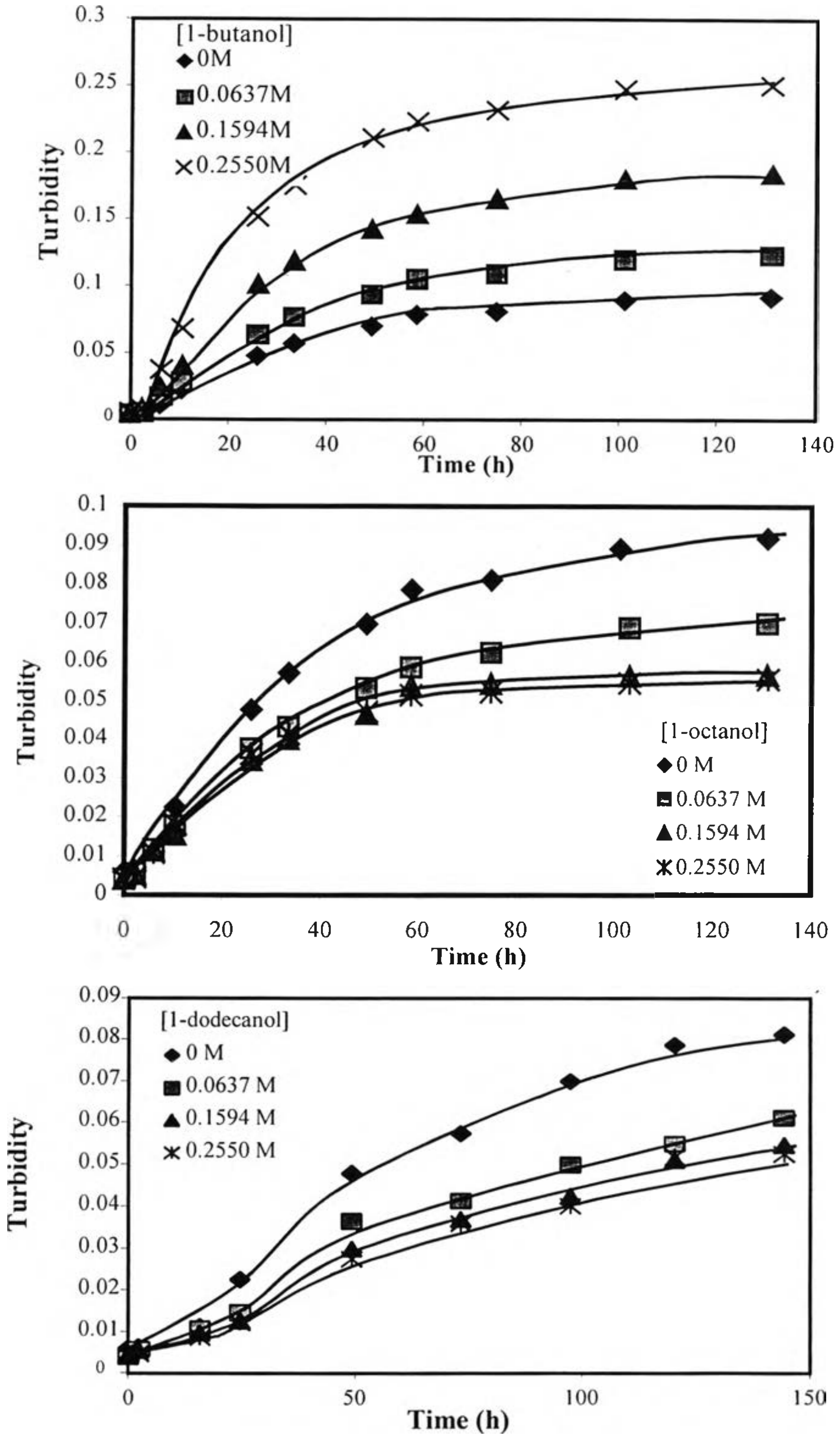


Figure 4.4 Turbidity of microemulsion solutions at different concentrations of three co-surfactants for the system containing 0.1494 M TEOS, 0.0156 M NH_3, 0.1901M DP6 and 7.67:1 molar ratio of H_2O:TEOS.

4.2 The Kinetics of TEOS Hydrolysis in Microemulsion Solutions

The concentration of TEOS was measured by using Fourier Transform Infrared Spectroscopy (FTIR). The concentration of TEOS during the reaction period was estimated from its peak height. The assumption of first order reaction kinetics was always found to be an excellent approximation. A typical evolution of FTIR spectra of microemulsions is shown in Figure 4.5.

A gradual decrease in Si-O-C streching bands of TEOS located at both 795 and 967 cm^{-1} indicated that TEOS was hydrolyzed during the reaction period. The formation of ethanol was evidenced by the increase in both 880 and 1050 cm^{-1} bands which were correspond to the C-C-O streching of ethanol.

The TEOS concentration measured from the absorbance of the Si-O-C streching at 967 cm^{-1} are shown as a function of time in Figure 4.6. The logarithm of TEOS concentration decreased linearly with time, indicating that the rate of TEOS hydrolysis was first order with respect to the concentration of TEOS as described by the following equation:

$$\frac{[TEOS]_t}{[TEOS]_0} = exp(-k_h t) \tag{4.1}$$

where $[TEOS]_t$ and $[TEOS]_0$ are the concentration of TEOS at reaction time t and at the start of the reaction, respectively. k_h is the apparent rate constant for TEOS hydrolysis which can be determined from the slope of linear fitting.

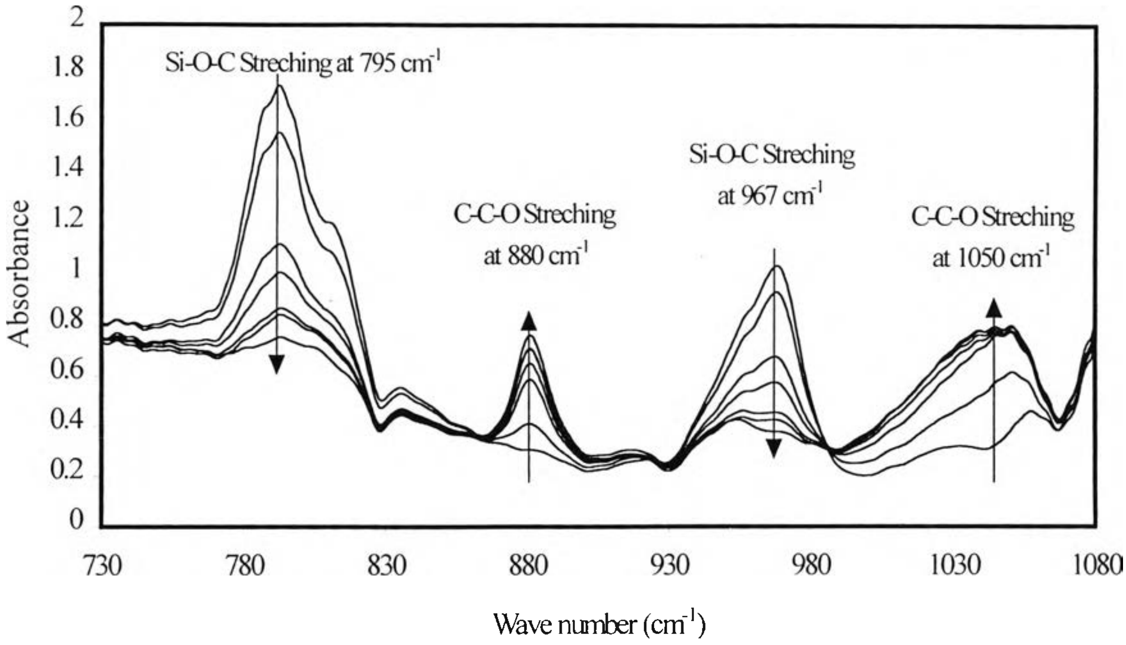


Figure 4.5 The evolution of FTIR spectrum of DP6/heptane microemulsions having composition H_2O:TEOS=7.67:1, 0.0781 M NH_3, 0.1901 M DP6 and 0.1494 M TEOS in heptane.

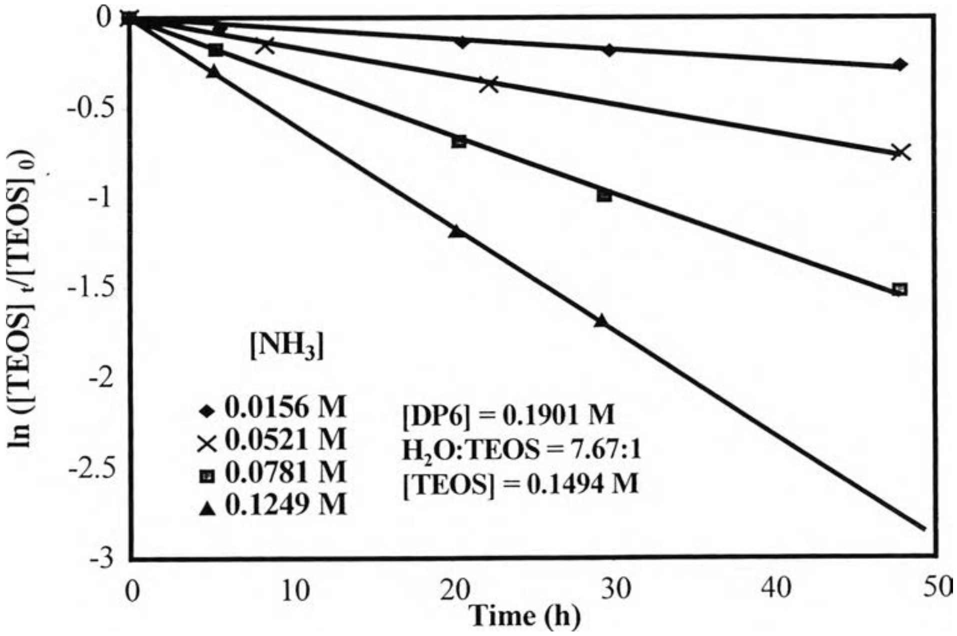


Figure 4.6 The time evolution of the concentration of TEOS hydrolyzed in W/O microemulsions at different ammonia concentrations.

4.2.1 The Effect of Ammonia Concentration

The studied microemulsion was prepared to have [DP6]= 0.1901 M, [TEOS]= 0.1494 M, [H_2O]= 1.1462 M and NH_3 concentration varied from 0.0156 M to 0.2550 M. Figure 4.7 shows that the apparent rate constant, k_h increases approximately linearly from 0.0057 h^{-1} at 0.0156 M NH_3 to 0.0578 h^{-1} at 0.2550 M NH_3, indicating that the rate of TEOS hydrolysis is approximately first order with respect to the aqueous ammonia concentration.

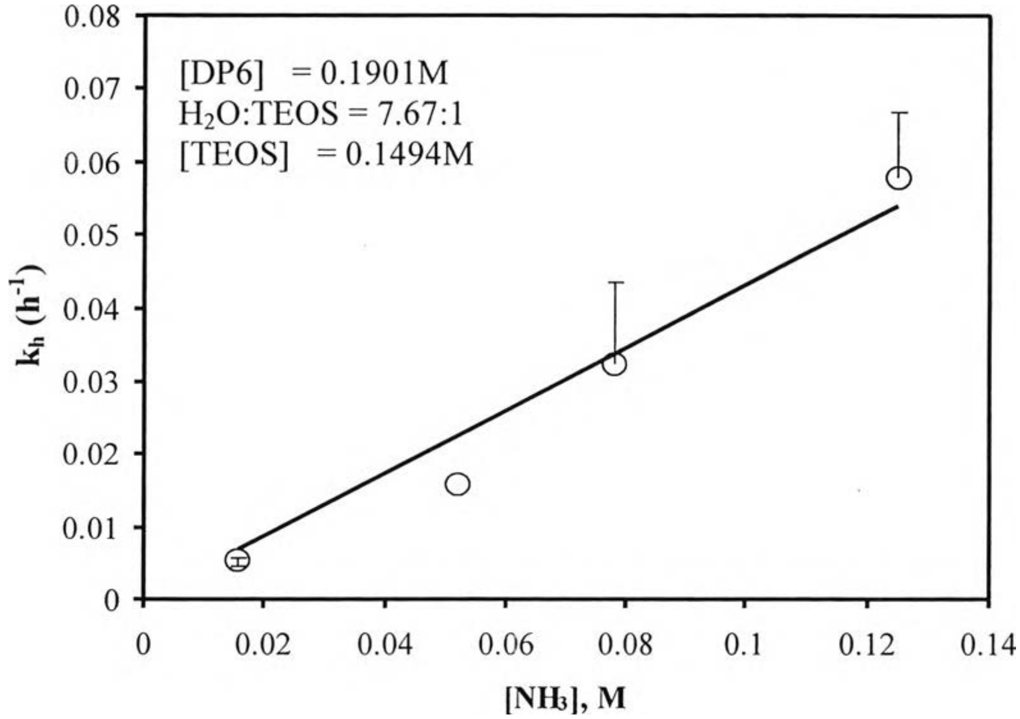


Figure 4.7 Specific hydrolysis rate constant, k_h versus the initial aqueous ammonia concentration.

Figure 4.8 shows the relationship between the concentration of ammonia and the delay time of the hydrolysis reaction which performs in terms of half-life time, $t_{1/2}$, when [TEOS]$_t$/[TEOS]$_0$ = 0.5. The delay time exponentially decreased from 120 h at 0.0156 M NH_3 to 12 h at 0.1249 M NH_3. It was clearly seen that the lower the ammonia concentration, the longer the delay time is preferred for coreflood experiment.

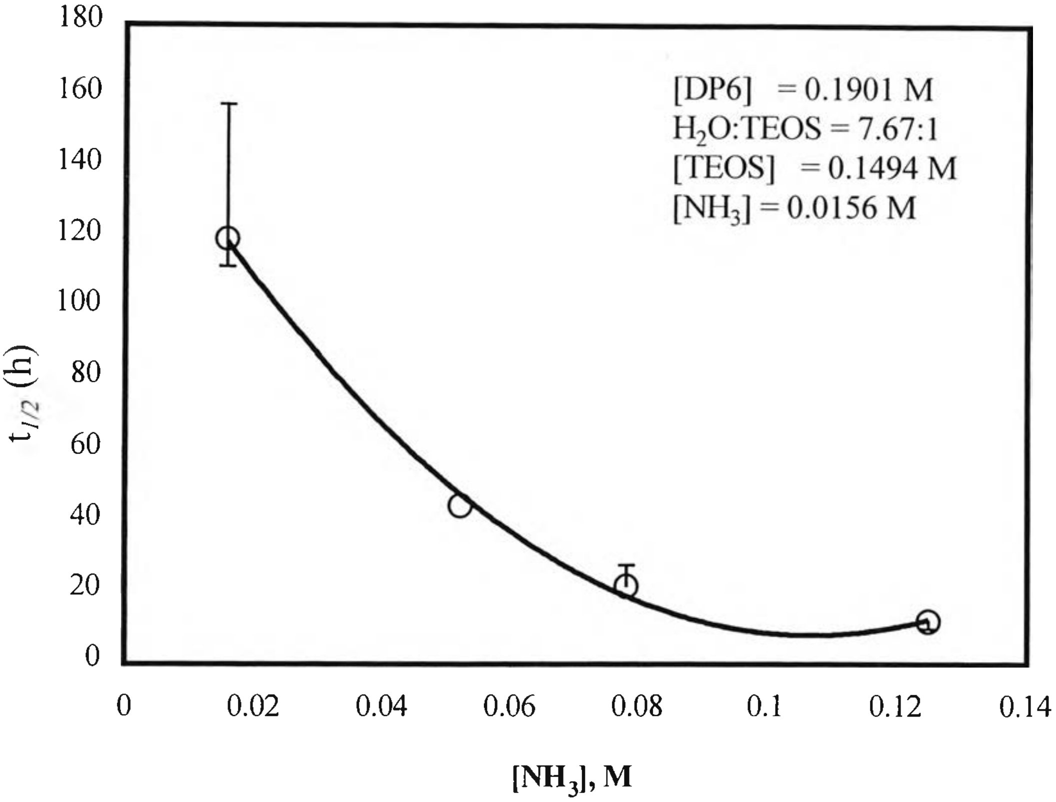


Figure 4.8 The delay time $t_{1/2}$ ($C/C_0 = 0.5$) versus initial aqueous ammonia concentration. .

4.2.2 The Effect of Surfactant Concentration

The microemulsion prepared contained [TEOS]= 0.1494 M, $[H_2O]$= 1.1462 M, $[NH_3]$= 0.0156 M and DP6 concentration varied in the range of 0.1014 M to 0.3169 M. Figure 4.9 shows that the apparent rate constant decreases from 0.0099 h^{-1} at 0.1014 M DP6 to 0.0074 h^{-1} at 0.1267 M DP6 and then the apparent rate constant decreases very slightly to 0.0043 h^{-1} at 0.3169 M.

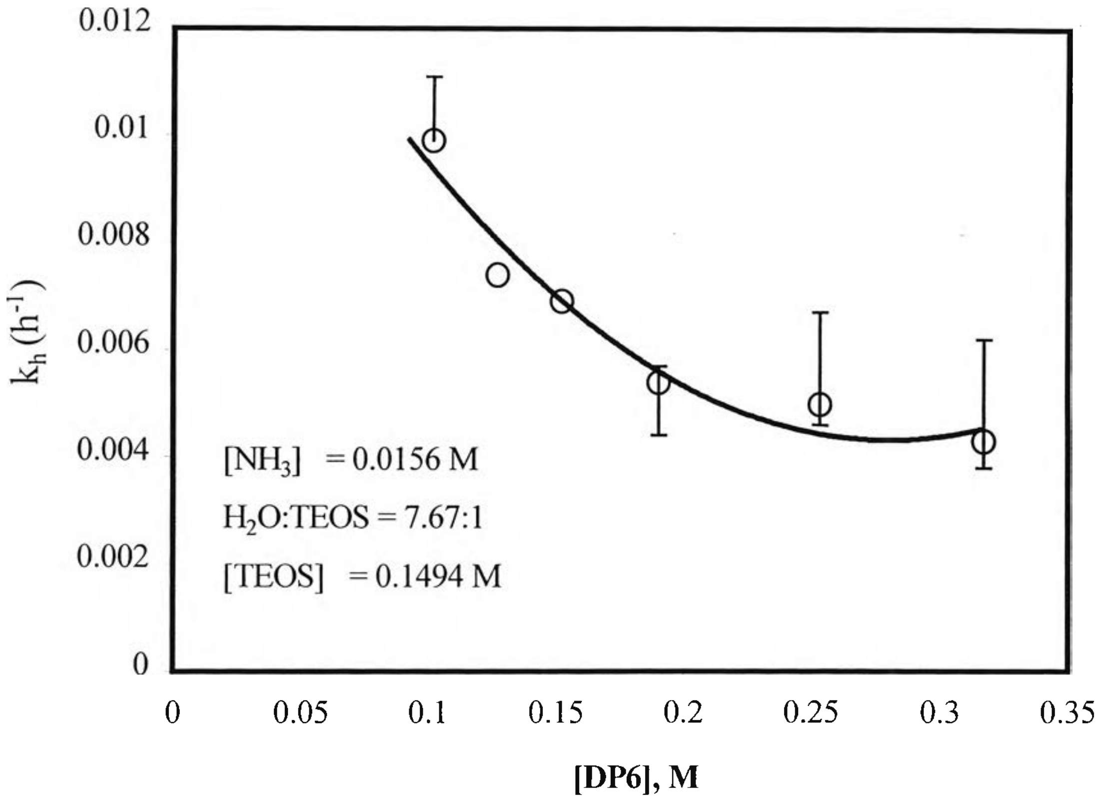


Figure 4.9 Specific hydrolysis rate constant k_h versus the initial DP6 surfactant concentration.

In the previous study, Chang and Fogler (1996) studied the effect of NP4 surfactant on the rate of TEOS hydrolysis. They found that surfactant concentration affected the rate of TEOS hydrolysis. The apparent reaction order with respect to [NP4] was estimated to be between 0.4 to 0.6.

The rate of TEOS hydrolysis in W/O microemulsion solutions depends upon the rate of transferring of TEOS molecules into the aqueous phase of microemulsion droplets, the higher the area of microemulsion droplets, the faster the rate of TEOS hydrolysis is observed. Conversely, when the concentration of surfactant increases until the rate of mass transfer does not depend upon the area of microemulsion droplets. The surfactants may act as the barrier to transferring of TEOS molecules into microemulsion droplets to contact with the hydroxyl ions (OH^-). Another probable reason is that a number of unbound water molecules decreases with an increase in surfactant concentration in order to facilitate the adsorption of surfactant onto the silica surface. As a result, the rate of TEOS hydrolysis is decreased.

4.2.3 The Effect of H_2O to TEOS Molar Ratio

The studied microemulsion was prepared to have [TEOS]= 0.1494 M, $[NH_3]$= 0.0156 M, [DP6]= 0.1901 M and water concentration varied from 0.3976 M to 1.1416 M. Figure 4.10 shows that the apparent rate constant, k_h, decreases very slightly from 0.0079 h^{-1} at H2O:TEOS molar ratio = 2.66:1 to 0.0057 h^{-1} at H_2O:TEOS molar ratio = 7.67:1. The result suggested that water did not significantly affect the rate of TEOS hydrolysis.

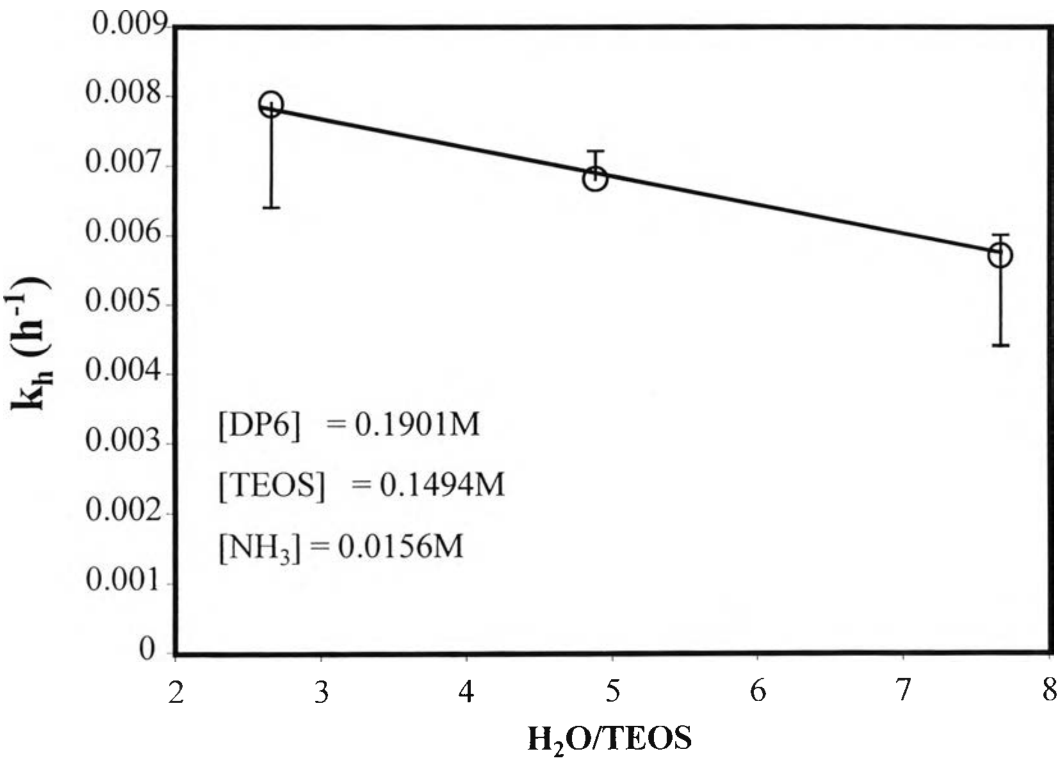


Figure 4.10 Specific hydrolysis rate constant k_h versus the initial H_2O:TEOS molar ratio.

4.2.4 The Effect of Type and Concentration of Co-Surfactant

Three types of alcohol (1-butanol, 1-octanol and 1-dodecanol) were used to act as co-surfactants. The concentration of alcohol used in this study was varied from 0 M, 0.0637 M, 0.1594 M and 0.2550 M. Figure 4.11 displays the influence of alcohol chain length and its concentration on the rate of TEOS hydrolysis for the system having [TEOS]= 0.1494 M, [DP6]= 0.1901 M, [NH_3]= 0.0156 M and H_2O:TEOS molar ratio = 7.66:1. As can be seen in Figure 4.11, for all co-surfactants, the rate of TEOS hydrolysis slightly increases with increasing the co-surfactant concentration. The closeness of the TEOS hydrolysis rate for 1-butanol, 1-octanol and 1-dodecanol indicated the chain-length of co-surfactant did not significantly affect the rate of TEOS hydrolysis.

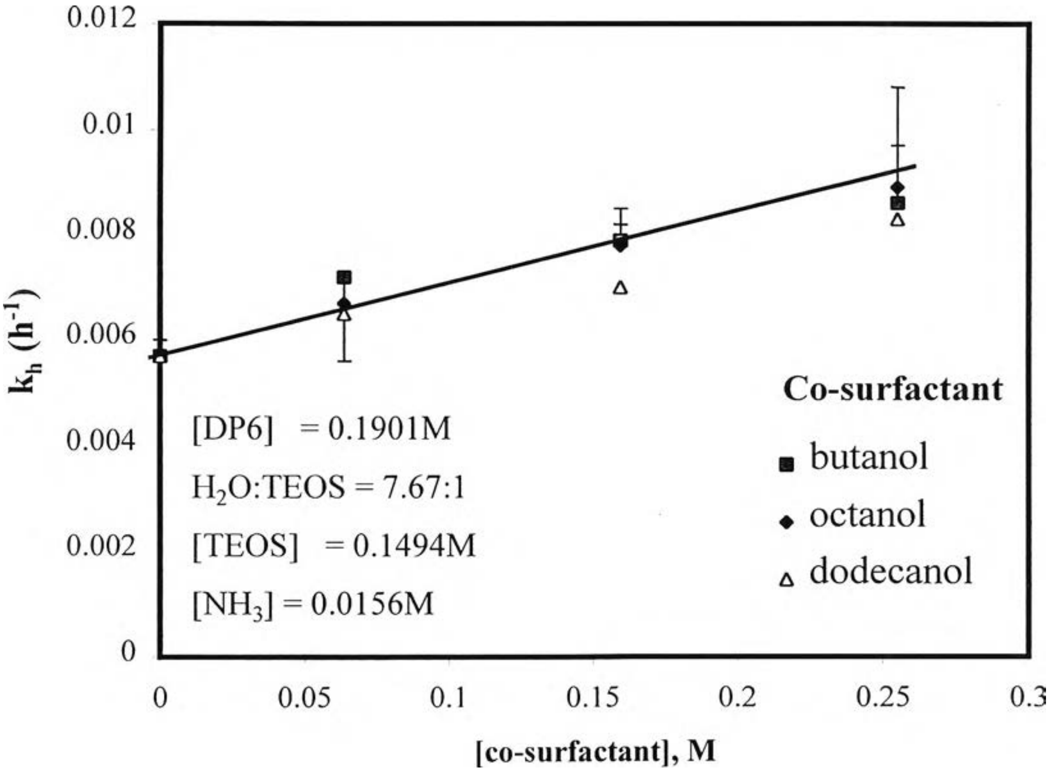


Figure 4.11 Specific hydrolysis rate constant k_h vs. the initial co-surfactant concentration.

Figure 4.12 shows the effect of concentration and type of co-surfactant on the delay time, $t_{1/2}$, of silica particles synthesized in the microemulsion solution. This result suggested that for all co-surfactants, the delay time decreased significantly with increasing the co-surfactant concentration. Again, the chain-length of alcohol did not significantly affect the rate of TEOS hydrolysis.

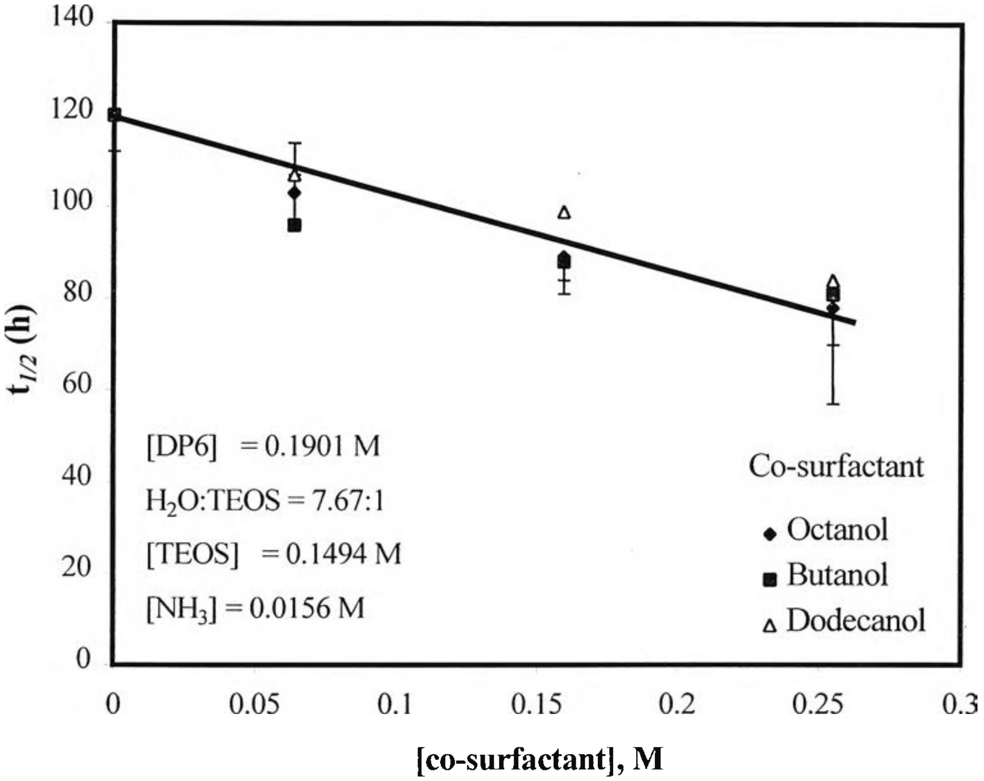


Figure 4.12 The delay time $t_{1/2}$ versus initial co-surfactant concentration.

4.3 Size and Morphology of Silica Particles

The size and morphology of the silica particles synthesized were determined by using Transmission Electron Microscope at 2 weeks after addition of TEOS into the W/O microemulsion solutions containing the different concentrations and type of co-surfactants. Three types of co-surfactants (1-butanol, 1-octanol and 1-didecanol) were used in this study. Figures 4.13 and 4.14 show the influence of the alcohol chain length and its concentration on the size of silica particles obtained from the system containing 0.1494 M TEOS, 0.0156 M NH_3 and water:TEOS molar ratio = 7.66:1.

The concentration of co-surfactant was only varied in the experiment. The size of synthesized silica particles varied with the type of co-surfactant by the order: 1-butanol> 1-octanol> 1-dodecanol. The average diameter, <D>, of the silica particles synthesized were 45.30 nm, 59.26 nm and 65.74 nm when 1-butanol concentration increased to 0.0637, 0.1594 and 0.255 M, respectively. Contrastly, for both 1-octanol and 1-dodecanol co-surfactants, the average diameter of the silica particles slightly decreased with an increase in the alcohol concentration. In addition, for the longer the alcohol chain-length, the smaller the size of silica particle was observed. This effect can be attributed to the fact that the interfaces with a long chain alcohol are more rigidity than those with the short chain alcohol. In general the chain length of the surfactant and co-surfactant used in the system should be the same to maximize the molecular interactions that stabilize surfactant-coated interfaces. If chain length mismatching is presented in the surfactant film, the excess hydrocarbon tails have more freedom to disrupt the molecular packing through conformational disorder. This disruption in the molecular packing leads to lower interaction energies and, hence, the lower film stability, which leads to the increase in the interdroplet dynamic exchanges of silica species within the microemulsion droplets.

Figures 4.15 and 4.16 show a significant effect of butanol on the diameter of the silica particles produced under the studied conditions.

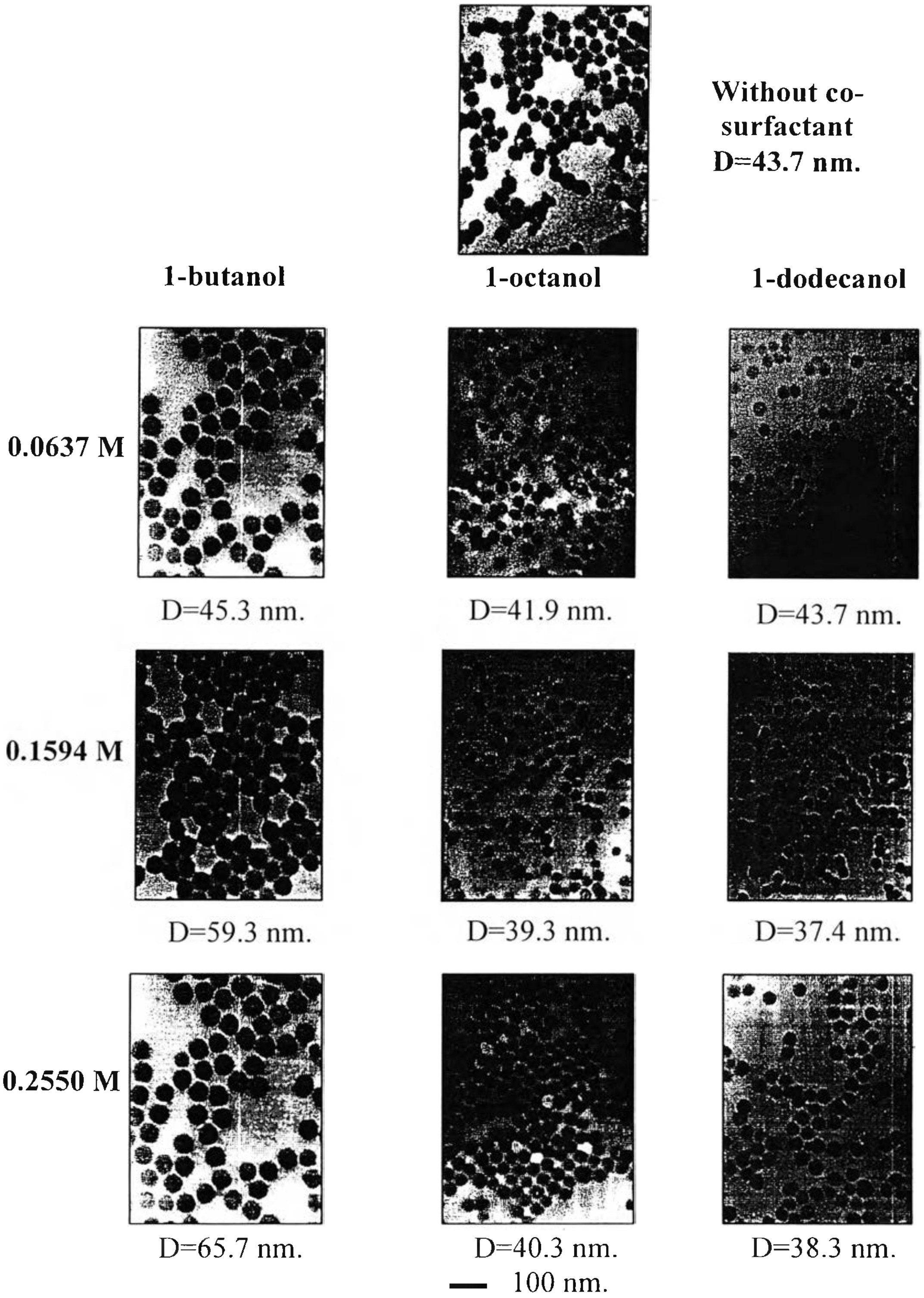


Figure 4.13 TEM micrographs of silica particles synthesized in W/O microemulsions with different types and concentrations of co-surfactants at 2 weeks. Composition of microemulsions: 0.0156 M NH_3, 0.1901 M DP6, 0.1494 M TEOS, and H_2O:TEOS= 7.67:1 in heptane.

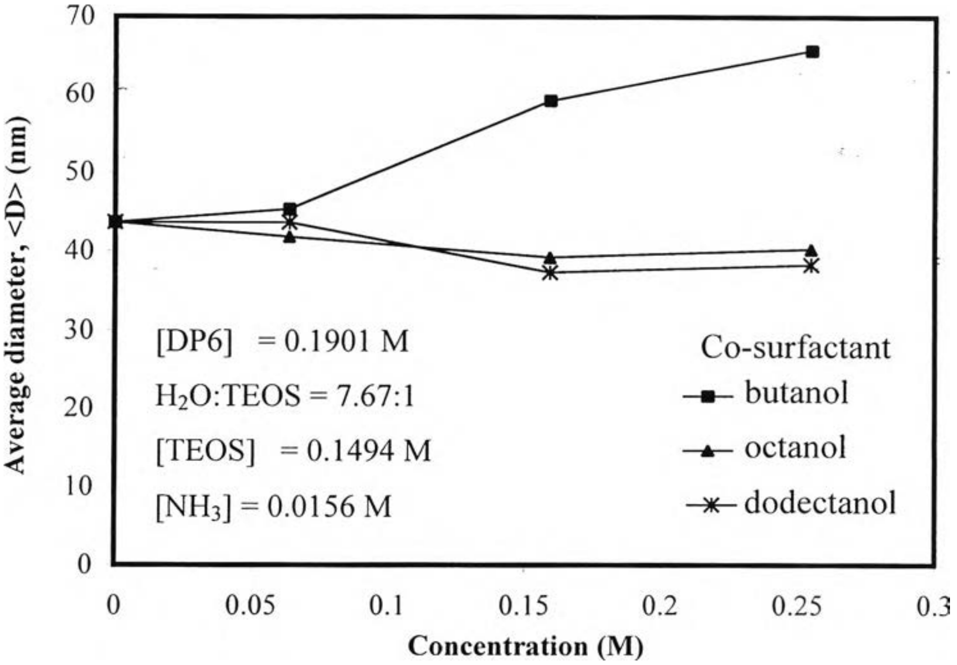


Figure 4.14 The effect of co-surfactant concentration on the size of silica particles synthesized in W/O microemulsions.

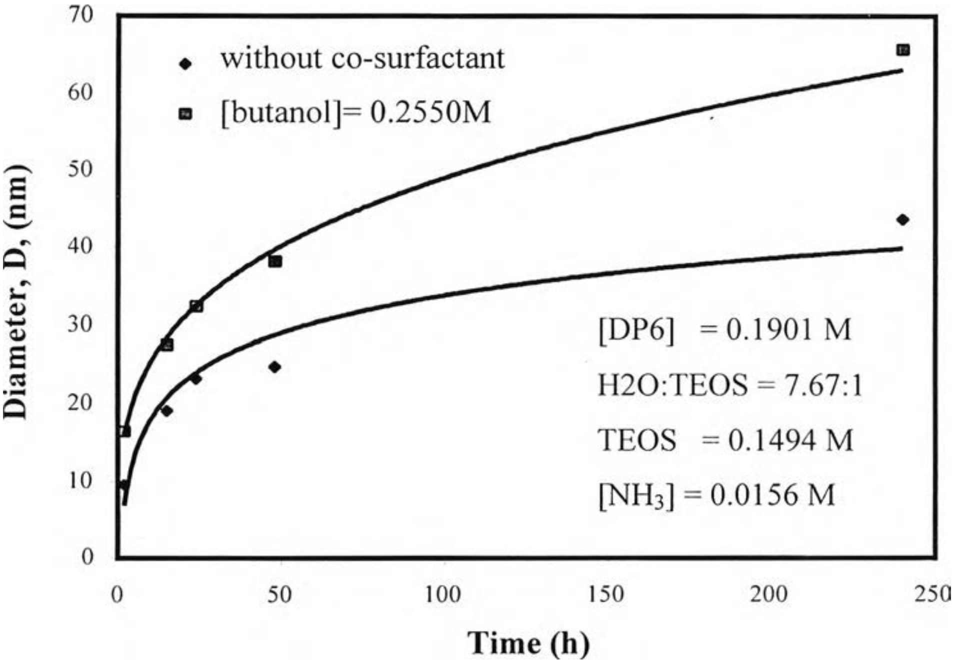
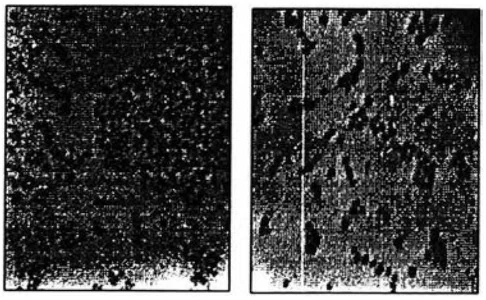


Figure 4.15 The size of silica particles synthesized in W/O microemulsions with and without 1-butanol as a function of time.

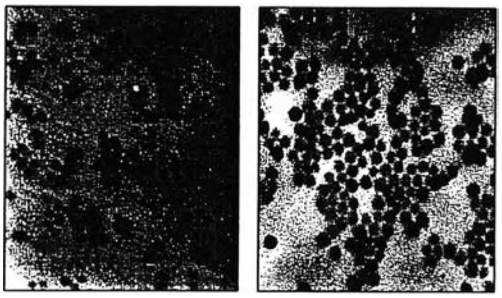
2 hours



without 1-butanol
9.6 nm.

0.2550 M 1-butanol
16.5 nm.

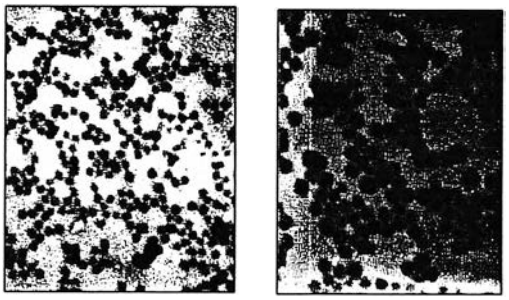
15 hours



without 1-butanol
19.1 nm.

0.2550 M 1-butanol
27.6 nm.

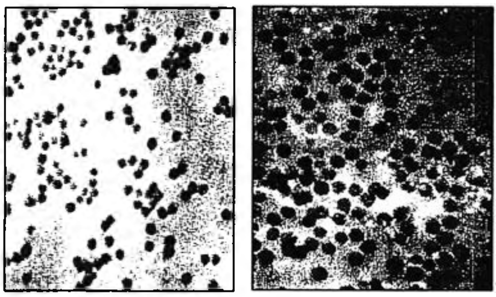
24 hours



without 1-butanol
23.3 nm.

0.2550 M 1-butanol
32.4 nm.

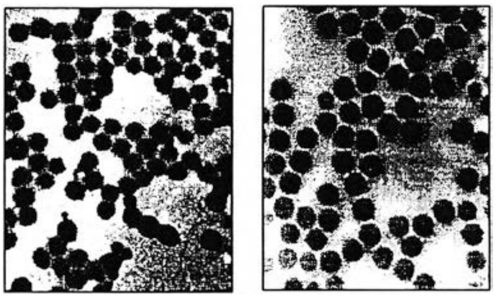
48 hours



without 1-butanol
24.7 nm.

0.2550 M 1-butanol
38.2 nm.

240 hours



without 1-butanol
43.7 nm.

0.2550 M 1-butanol
65.7 nm.

— 100 nm.

Figure 4.16 TEM Micrographs of silica particles synthesized in W/O microemulsions with and without 1-butanol at various times. Composition of microemulsions: 0.0156 M NH_3, 0.1901 M DP6, 0.1494 M TEOS, and H_2O:TEOS=7.67:1 in heptane.

Figure 4.17 illustrates the measured size distributions of silica particles synthesized with and without 1-butanol. The silica particles synthesized in nonionic W/O microemulsions without addition of co-surfactant and with addition of 0.2550 M 1-butanol had the same narrow size distribution with the approximate value between 10 and 25 nm.

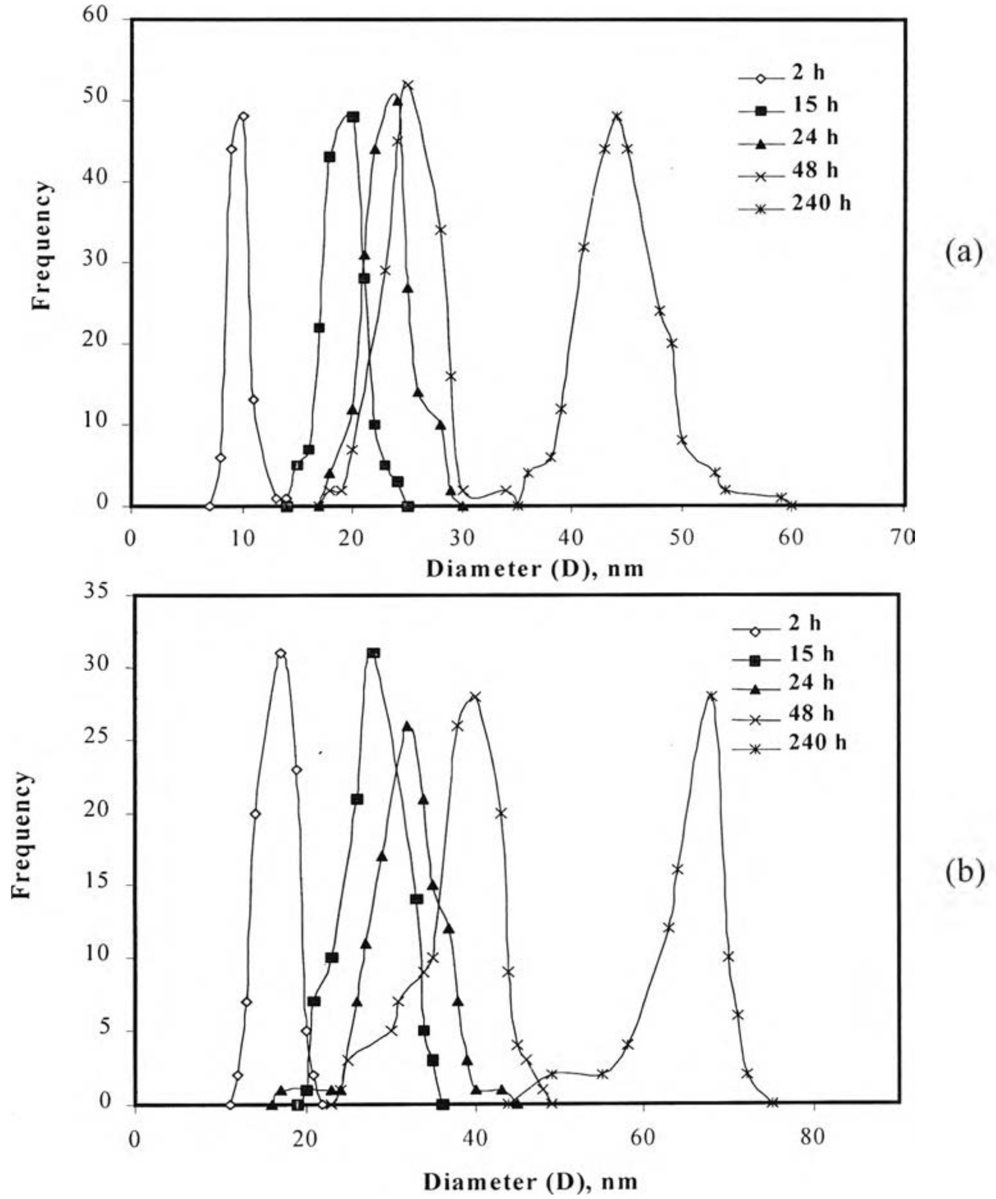


Figure 4.17 The size distributions of silica particles synthesized in W/O microemulsions with and without 1-butanol at various intervals. Composition of microemulsions: 0.0156 M NH_3, 0.1901 M DP6, 0.1494 M TEOS, and H_2O:TEOS=7.67:1 in heptane (a) without co-surfactant (b) 0.2550 M butanol.

4.4 Deposition of Silica Particles in Core Sample

From the results of the batch experiments, It can be concluded that in order to delay the kinetics of TEOS hydrolysis in W/O microemulsions, aqueous ammonia was a dominant parameter. A lower the ammonia concentration resulted in a longer the delay time, $t_{1/2}$, which is preferable for application in permeability reduction. The silica particle growth and the particle size were controlled by the addition of co-surfactant. It was found that 1-butanol was the most effective co-surfactant for synthesizing silica particles. The higher the concentration of 1-butanol, the larger the silica particle size which should be used to reduce the permeability of a core sample. Moreover, the addition of 1-butanol did not significantly affect the kinetics of TEOS hydrolysis as well as the delay time. Table 4.1 shows the composition of all reactants used to synthesize silica particles for the coreflood experiment.

Table 4.1 Composition of all reactants used to synthesize silica particles for coreflood experiment.

Composition	**Concentration (M)**
TEOS	0.1494
NH_3	0.0156
H_2O	1.1462
DP6	0.1901
1-Butanol	0.255
H_2O:TEOS	7.66
$t_{1/2}$ from batch experiment	81 h

The changes in permeability are calculated using Darcy's Law:

$$\frac{q}{A} = \frac{K}{\mu} \frac{\Delta P}{L} \tag{4.1}$$

Using Eq. (4.1), the ratio of the permeability at any time to the initial permeability, K/K_0, can be defined from measured values of pressure drop ratio, $\Delta P_0/\Delta P$, and viscosity ratio, μ/μ_0 :

$$\frac{K}{K_0} = \frac{\Delta P_0}{\Delta P} \frac{\mu}{\mu_0} \tag{4.2}$$

The pressure drop across the core sample was monitored every minute during microemulsion injection and converted to the permeability ratio accordingly. The ratio, K/K_0, is demonstrated as a function of time as shown in Figure 4.18

The first injection of microemulsion solutions gave the delay time of about 30 hours and the permeability ratio decreased to 0.7 at 80 hours and then tended to constant beyond 80 hours. The permeability ratio decreased due to the deposition of silica particles at the pore walls and the silica particle growth from the remaining of water and TEOS molecules in the inlet line and in the pore spaces. Once all the remaining reacting species were consumed, the permeability ratio reached the minimum value.

In order to increase the permeability reduction of the core sample, a second injection of the microemulsion solution having the same composition as the first one was carried out. The second injection had the delay time of about 80 hours. After that, the permeability ratio suddenly reduced to 0.47 and then tended to constant with the same phenomena as the first microemulsion injection.

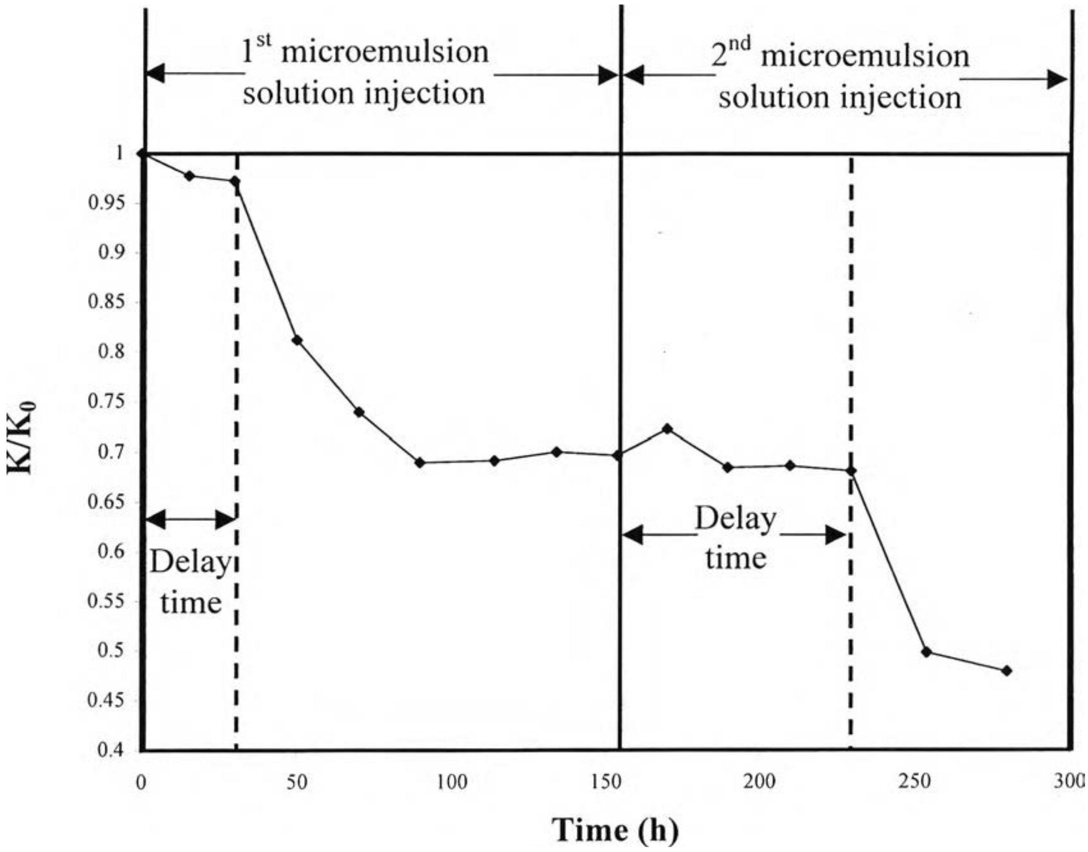


Figure 4.18 Permeability ratio, K/K_0, during microemulsion solutions with silica particles injection. Composition of microemulsions: heptane, 0.0156 M NH_3, 0.1901 M DP6, 0.1494 M TEOS, 1.1462 M H_2O, and 0.2550 M Butanol.