



## CHAPTER IV

### RESULTS AND DISCUSSION

The adsorption isotherm of the various surfactant-solid combinations was studied. Cetylpyridinium chloride (CPC), 4-octylphenol polyethoxylate (OP(EO)<sub>10</sub>), and sodium dodecyl benzene sulfonate (SDBS) were respectively representatives for cationic, non-ionic and anionic surfactant. Activated carbons and multi-walled carbon nanotubes (MWCNTs) were used as carbonaceous adsorbents.

#### 4.1 Specific Surface Area, Average Pore Diameter and Pore Volume of Carbonaceous Adsorbents

The specific surface area, average pore diameter and pore volume of carbonaceous adsorbents used in this work are shown in Table 4.1.

**Table 4.1** The specific surface area, average pore diameter and pore volume of activated carbons and multi-walled carbon nanotubes

<b>Carbonaceous adsorbents</b>	<b>Specific surface area (m<sup>2</sup>/g)</b>	<b>Average pore diameter (nm)</b>	<b>Pore volume (cc/g)</b>
Activated carbon	713.5	2.349	0.419
Multi-walled carbon nanotubes	273.4	59.34	4.056

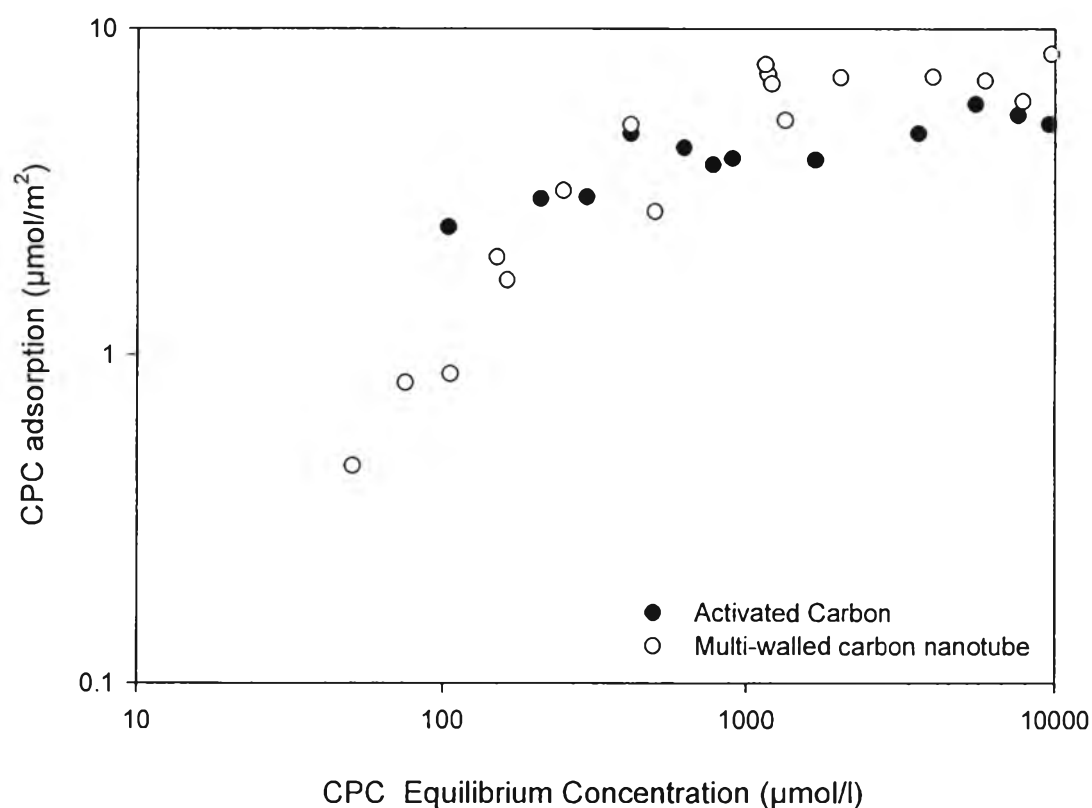
#### 4.2 Adsorption Isotherm of Surfactants on Activated Carbon and Multi-walled Carbon Nanotubes

The adsorption isotherms for the solutions of CPC, SDBS and OP(EO)<sub>10</sub> on activated carbon and multi-walled carbon nanotube at 25°C are shown in Figure 4.1-4.3. The surfactant adsorption isotherm is the relationship between the amounts of adsorbed surfactant per specific surface area of carbonaceous adsorbent and the equilibrium concentration of surfactant. Surfactant adsorption on carbonaceous

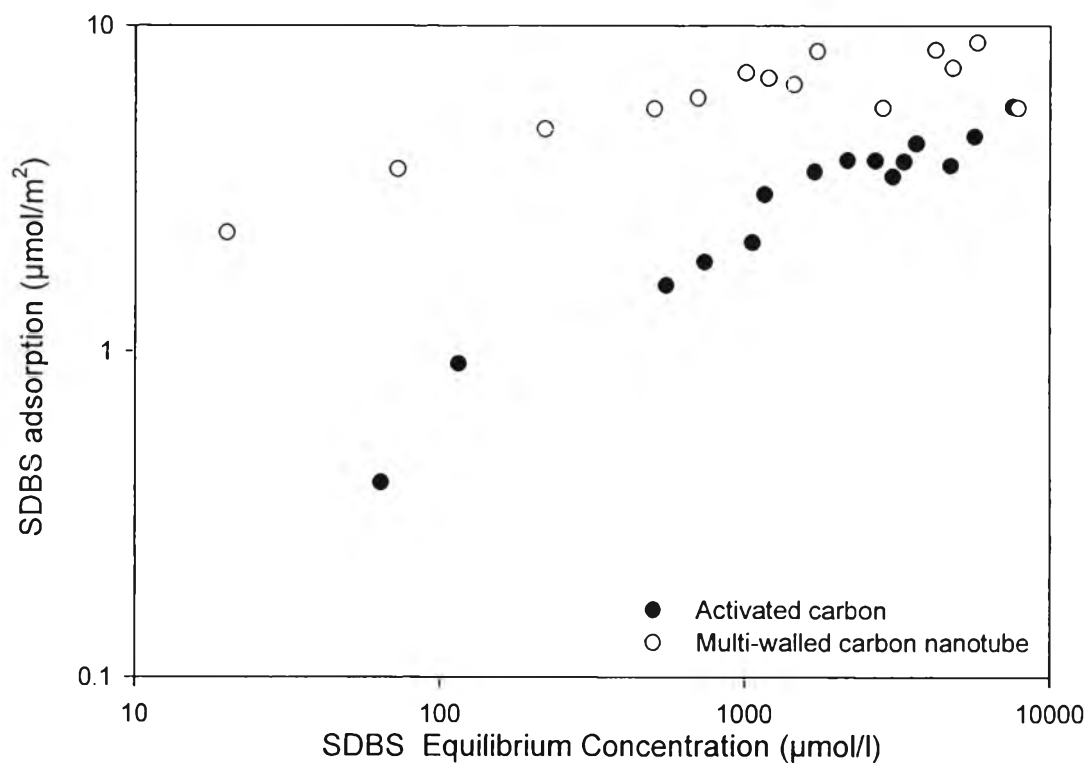
adsorbents is calculated from the difference between the initial,  $C_0$  ( $\mu\text{mol/L}$ ) and equilibrium,  $C_e$  ( $\mu\text{mol/L}$ ) concentration by following formula:

$$\Gamma = \frac{(C_0 - C_e) * V}{W * A_s} \quad (4.1)$$

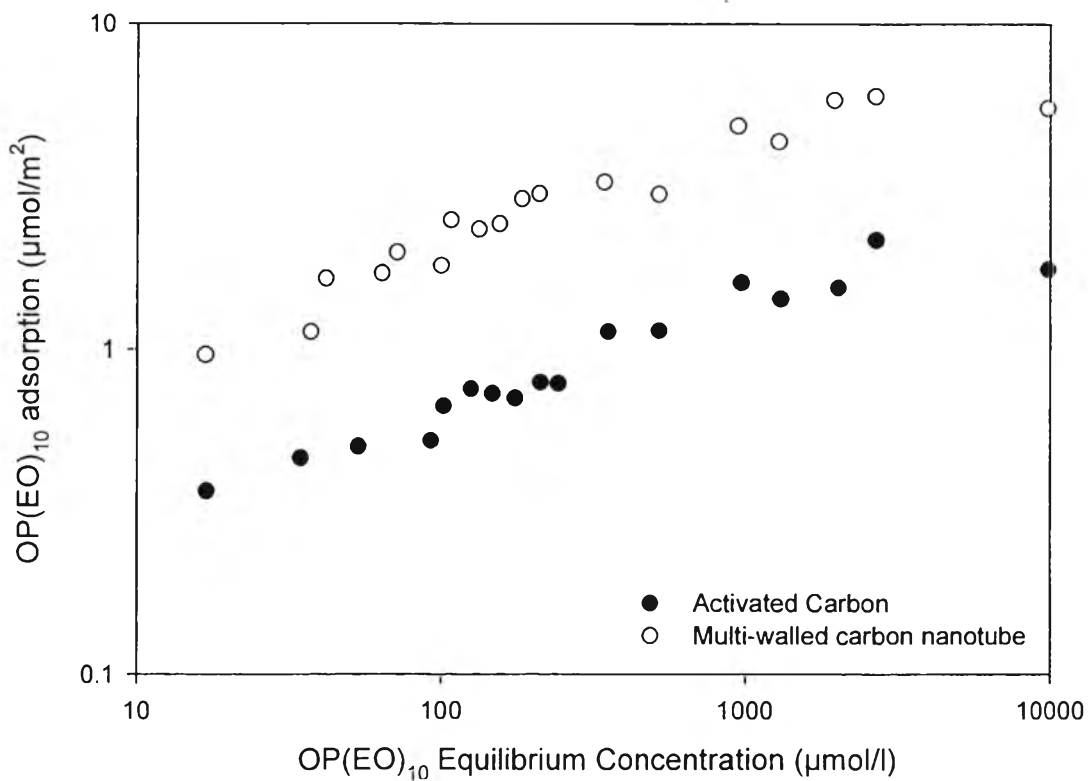
where  $\Gamma$  is the amount of adsorbed surfactant per specific area of adsorbent ( $\mu\text{mol/m}^2$ ).  $V$  is the volume of a surfactant solution (mL),  $W$  is the weight of carbonaceous adsorbents (mg), and  $A_s$  is the specific surface area of carbonaceous adsorbents ( $\text{m}^2/\text{g}$ ).



**Figure 4.1** Adsorption isotherm of CPC on activated carbons (●) and multi-walled carbon nanotubes (○) 25 °C.



**Figure 4.2** Adsorption isotherm of SDBS on activated carbons (●) and multi-walled carbon nanotubes (○) 25 °C.



**Figure 4.3** Adsorption isotherm of  $\text{OP}(\text{EO})_{10}$  on activated carbons (●) and multi-walled carbon nanotubes (○) 25 °C.

In this experiment, all surfactants had the benzene rings in the alkyl chain part of surfactant molecules to enhance the binding and surface coverage of surfactant molecules to graphite (Islam *et al.*, 2002). For all carbonaceous adsorbents, the surfactant adsorptions gradually increase with increasing surfactant concentration until before the critical micelle concentration (CMC) and reach the plateau at about the CMC which the maximum surfactant adsorption can be noticed. The CMC are known for OP(EO)<sub>10</sub>, CPC and SDBS as shown in Table 4.2.

**Table 4.2** Critical micelle concentration (CMC) and molecular weight for OP(EO)<sub>10</sub>, CPC and SDBS surfactants at 25°C

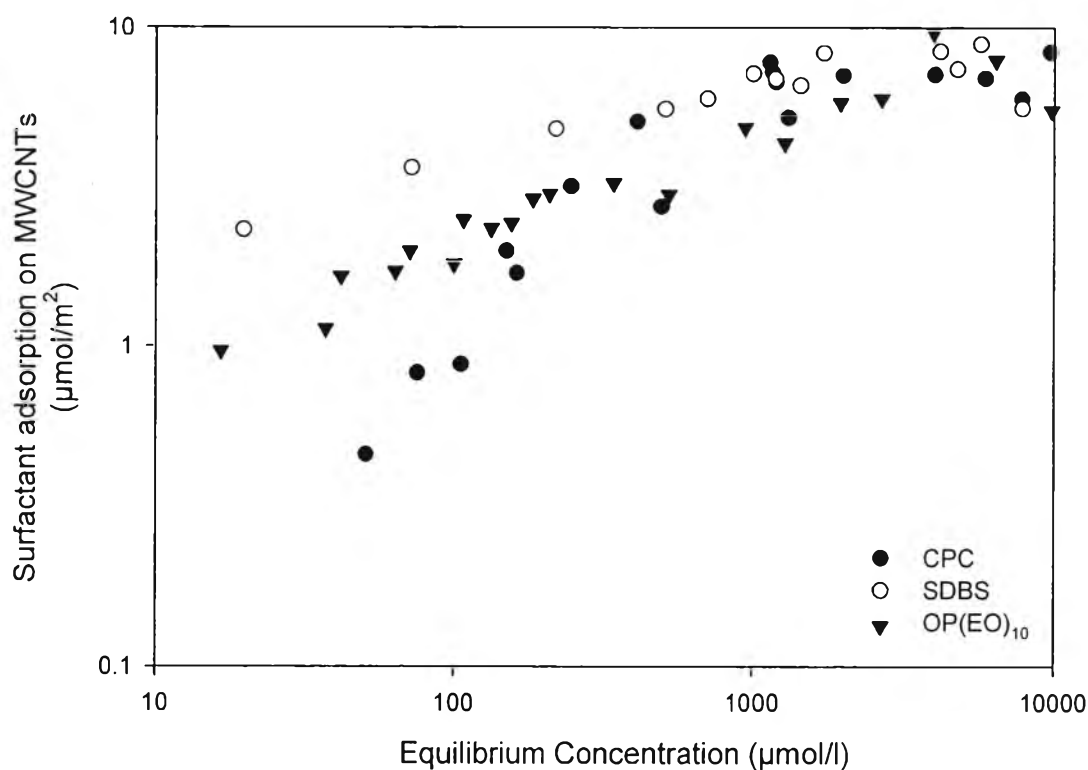
Surfactant	OP(EO) <sub>10</sub>	CPC	SDBS
CMC (mM)	0.24 (Thongpae, 2008)	0.95 (Supalassate, 2004)	3.0 (Hait <i>et al.</i> , 2003)
Molecular weight	625	339.99	348.48

As shown in Figure 4.1-4.3, it can be noted that the maximum surfactant adsorption of any given surfactant on MWCNTs was higher than on activated carbon as a result from the pore volume and the average pore diameter. The higher the average pore diameter or pore volume, the greater the space of adsorbent for adsorption as shown in Table 4.1.

#### 4.2.1 Adsorption Isotherm of CPC, SDBS and OP(EO)<sub>10</sub> on Multi-walled Carbon Nanotubes

The  $pH_{pzc}$  values defined for MWCNTs adsorbents was 7.3 (Carabinero *et al.*, 2011). For pH values lower than  $pH_{pzc}$ , the adsorbent presents a positive surface charge. On the other hand, the adsorbent acts as a negative surface when the pH value is higher than  $pH_{pzc}$ . The dissolved SDBS is negatively charged in water solution, because it possesses  $SO_3^-$ . The adsorption of SDBS on MWCNTs performs when the adsorbent presents a positive surface charge. For MWCNTs, the positively charge occurs for  $pH < 7.3$ . Thus, this behaviour explains the high adsorption capacity of SDBS solution on MWCNTs. Whereas, the OP(EO)<sub>10</sub> and CPC solutions are neutrally and positively charged, respectively. The adsorption still

occurs on a positive surface charge, since the pH values of CPC and OP(EO)<sub>10</sub> solution are 5.4 and 6.1, respectively. Therefore, the adsorption of CPC and OP(EO)<sub>10</sub> are lower compared to SDBS. Among the remaining two, the pH value of CPC is lower than of OP(EO)<sub>10</sub>. The lower the pH values from the  $pH_{pzc}$ , the more positive the surface of the adsorbent. For the higher positive surface charge of MWCNTs in CPC solution, the repulsive interaction between CPC surfactant and the surface of MWCNTs affects the adsorption decreased. Thus, the order of surfactant adsorption on MWCNTs is SDBS > OP(EO)<sub>10</sub> > CPC as shown in Figure 4.4.

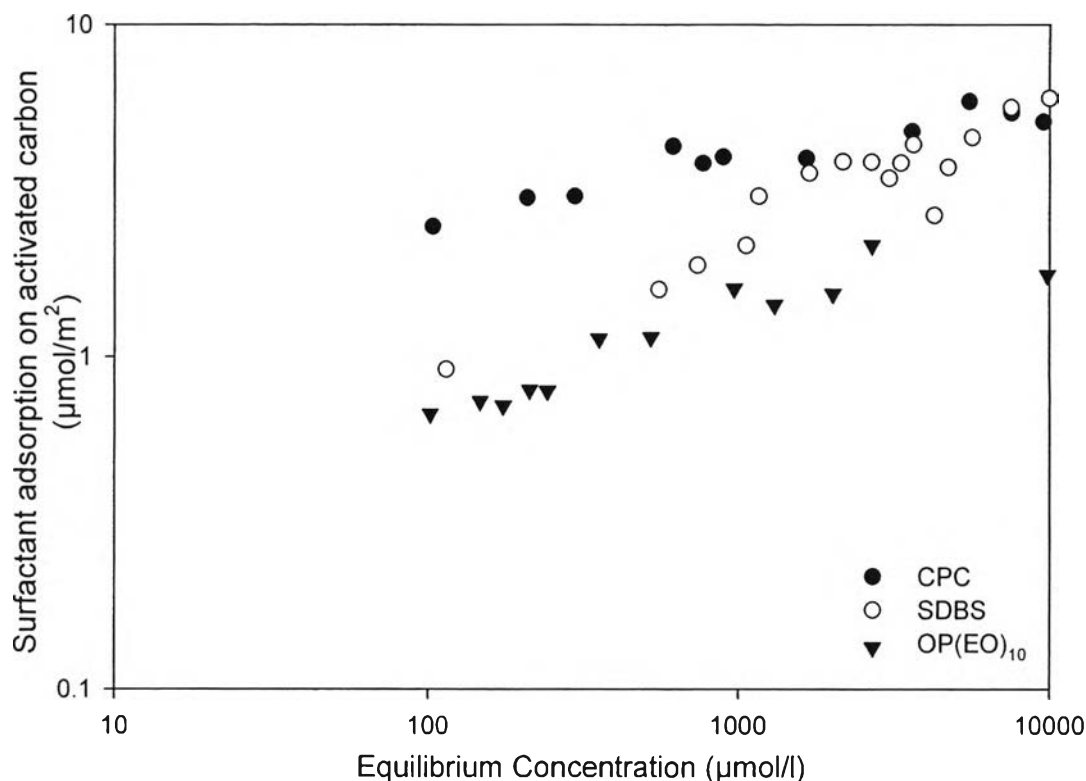


**Figure 4.4** Adsorption isotherm of CPC (●), SDBS (○) and OP(EO)<sub>10</sub> (▼) on multi-walled carbon nanotubes 25 °C.

#### 4.2.2 Adsorption Isotherm of CPC, SDBS and OP(EO)<sub>10</sub> on Activated Carbon

For activated carbons, the  $pH_{pzc}$  value was 6.0 (Machado *et al.*, 2011) while the pH value of CPC, OP(EO)<sub>10</sub> and SDBS are 5.6, 6.3 and 6.6, respectively. As mentioned before, the surface charge of activated carbons in CPC and OP(EO)<sub>10</sub>-solution are positive because the pH values are lower than  $pH_{pzc}$ . As the activated carbons presents the negative surface charge in SDBS solution due to the higher pH value than  $pH_{pzc}$ . The interaction between the activated carbons surface and all surfactants are repulsion when the pH values are used as the explanation. Thus, the pH values explanation is replaced by the chain length of surfactant to describe the adsorption of surfactant solution on activated carbon.

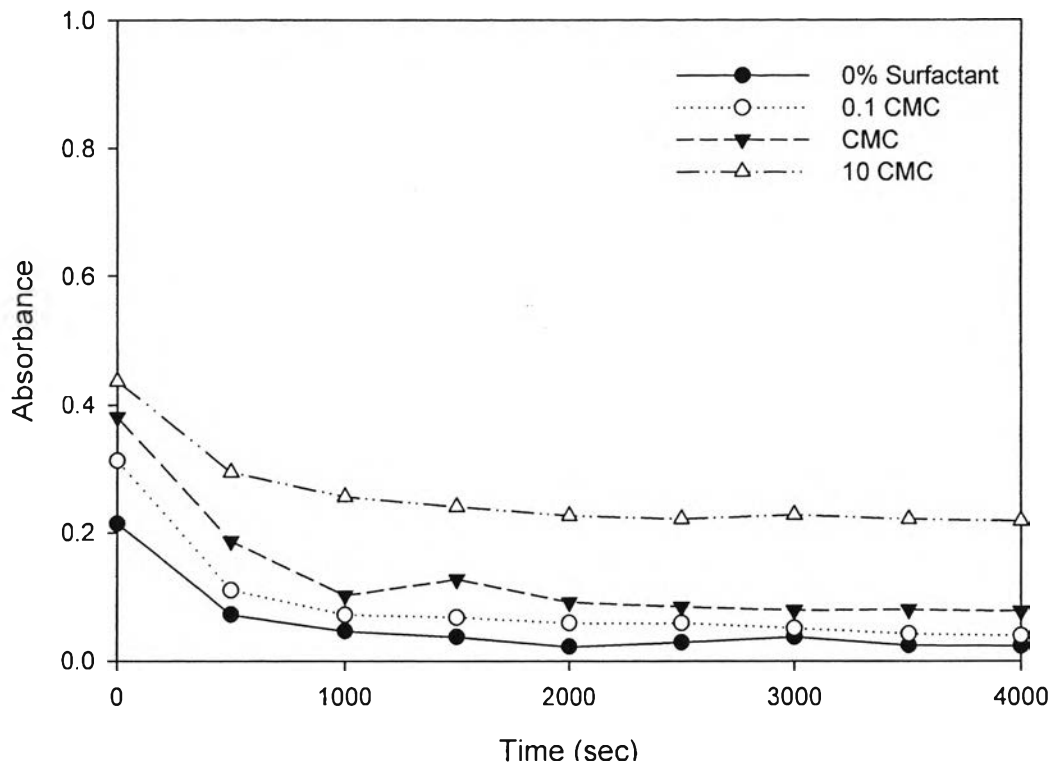
In terms of chain length, the hydrophobic chain groups generally tend to lay flat on the graphitic surface since the graphitic unit cells match well the methylene units of hydrocarbon chains. Therefore, the chain length of the surfactants significantly affects the efficiency of adsorption. The adsorption capacities of surfactants on the activated carbons increase with the increasing chain length or hydrophobic group with an order of CPC > SDBS > OP(EO)<sub>10</sub> as shown in Figure 4.5. As observed, CPC had the longest flexible aliphatic tail (have a 16 carbon alkyl chain) on the aromatic pyridine ring (Yang *et al.*, 2010) followed by SDBS having an lower carbon atoms (12-carbon alkyl chain) which also had the higher ability in order to improve surfactant energetics compared to OP(EO)<sub>10</sub> (have a 8 carbon alkyl chain).



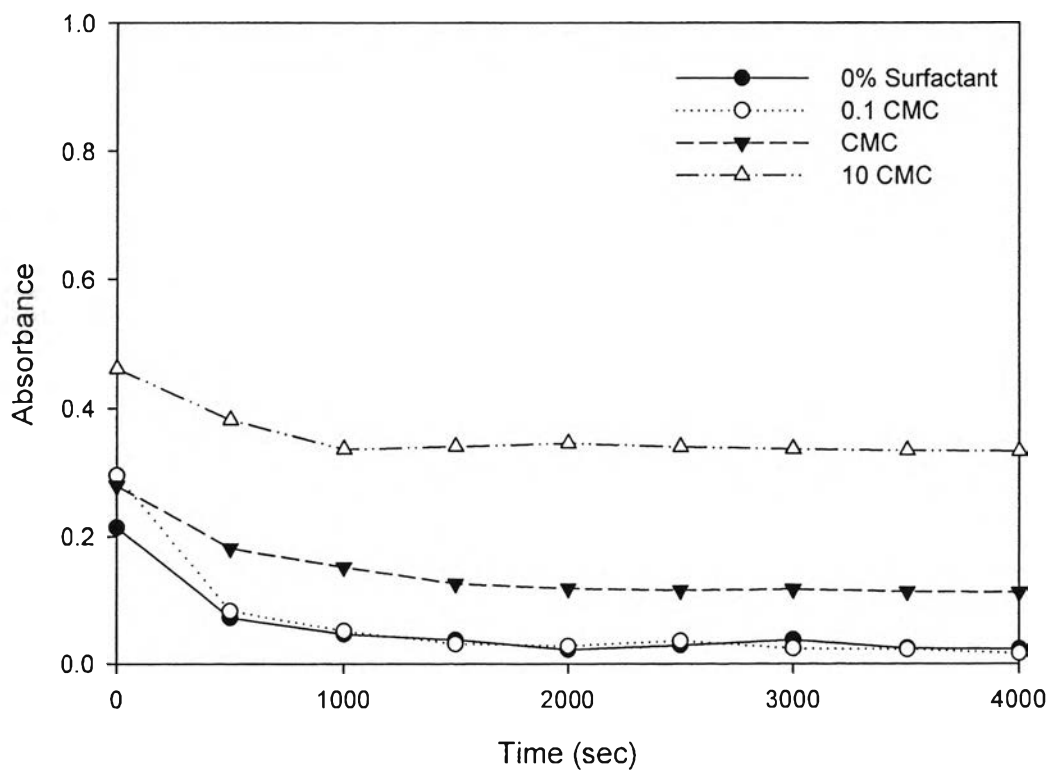
**Figure 4.5** Adsorption isotherm of CPC (●), SDBS (○) and OP(EO)<sub>10</sub> (▼) on activated carbon.

### 4.3 Dispersability of MWCNTs in Aqueous Surfactant Solutions

The dispersing ability of MWCNTs in CPC, SDBS and OP(EO)<sub>10</sub> solution with different concentration were demonstrated by UV-Vis measurement of the dispersions for various times as shown in Figure 4.6, 4.7 and 4.8, respectively. When dispersed in a liquid, surfactants are known to exhibit vastly differently behaviour based on their concentration. At very low concentration (0.1 CMC), surfactants are adsorbed on the hydrophobic surface of MWCNTs similar to monomers which cannot stabilize the suspensions of MWCNTs as well as without surfactant solution. At CMC, the MWCNTs surfaces are almost saturated by the surfactants. Therefore, the surface of MWCNTs becomes hydrophilic due to the hydrophilic heads group of the surfactants oriented toward the bulk solution. Above the CMC, the surfactant may start to form aggregates or micelles on MWCNTs surface, which can further increase the dispersion on MWCNTs.

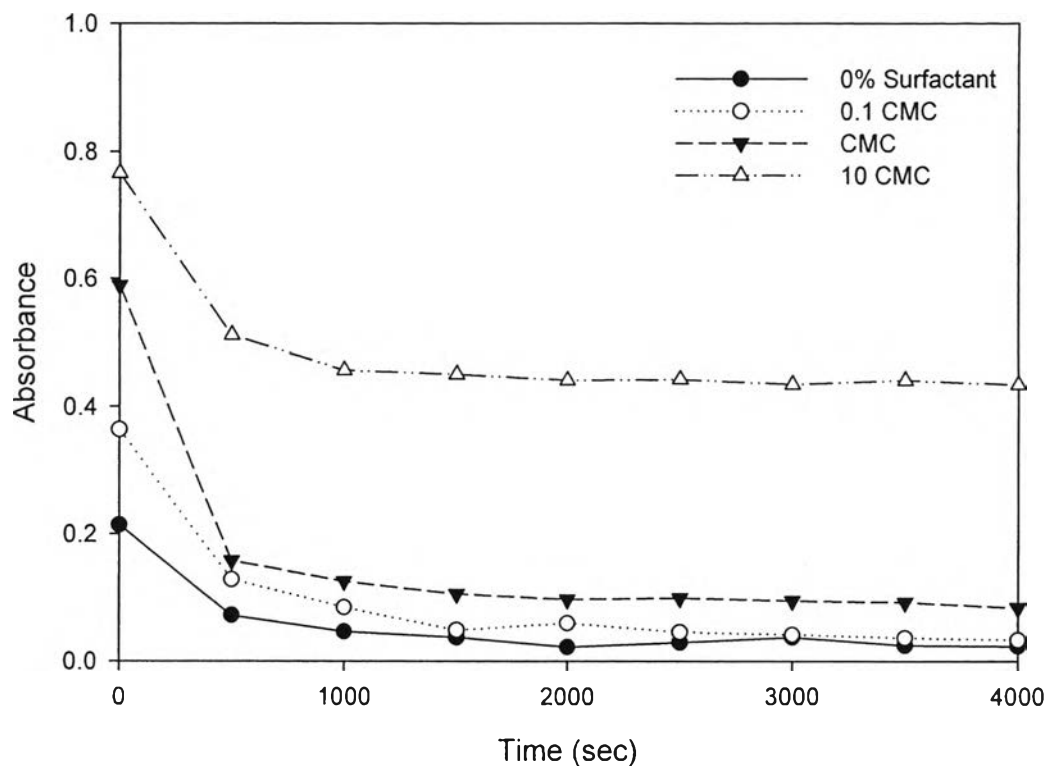


**Figure 4.6** Colloidal stability of the dispersed MWCNTs with different concentrations of CPC and without surfactant at 25°C.



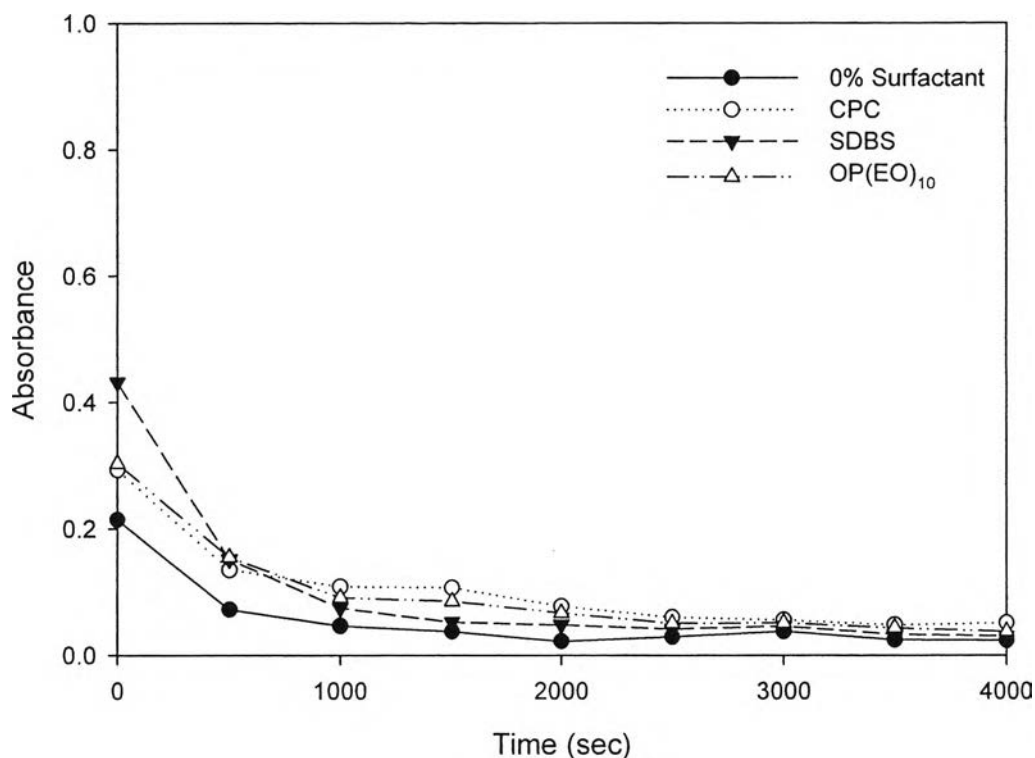
**Figure 4.7** Colloidal stability of the dispersed MWCNTs with different concentrations of SDBS and without surfactant at 25°C.





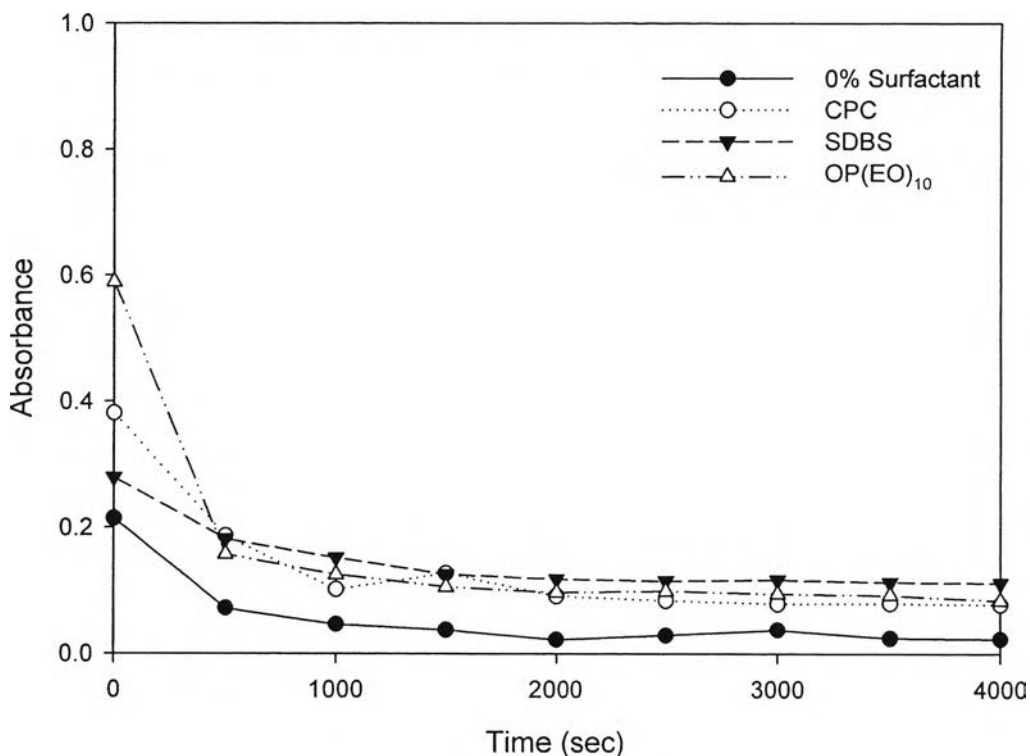
**Figure 4.8** Colloidal stability of the dispersed MWCNTs with different concentrations of OP(EO)<sub>10</sub> and without surfactant at 25°C.

Figure 4.9, 4.10 and 4.11 exhibit the dispersion stability of MWCNTs in the presence of the different surfactant concentrations; 0.1 CMC, CMC and 10 CMC, respectively, are illustrated by the UV-Vis measurement of the suspension as a function of time. The results showed that the dispersability of MWCNTs without surfactant solution is not different from the system with the 0.1 CMC of surfactant. It should be considered that all surfactants are not able to stabilize the MWCNTs dispersion at 0.1 CMC as shown in Figure 4.9. This is ascribed to the insufficient surfactant molecules to adsorb and disperse the agglomerate MWCNTs. Therefore, the higher surfactant equilibrium concentrations are required to reach the maximum dispersion of MWCNTs. The UV-Vis absorbances of the dispersions obviously enlarge at CMC as a result of the increased micelle formation or surfactant aggregations to disperse the MWCNTs.



**Figure 4.9** Colloidal stability of the dispersed MWCNTs with surfactant at 0.1 CMC and without surfactant at 25 °C.

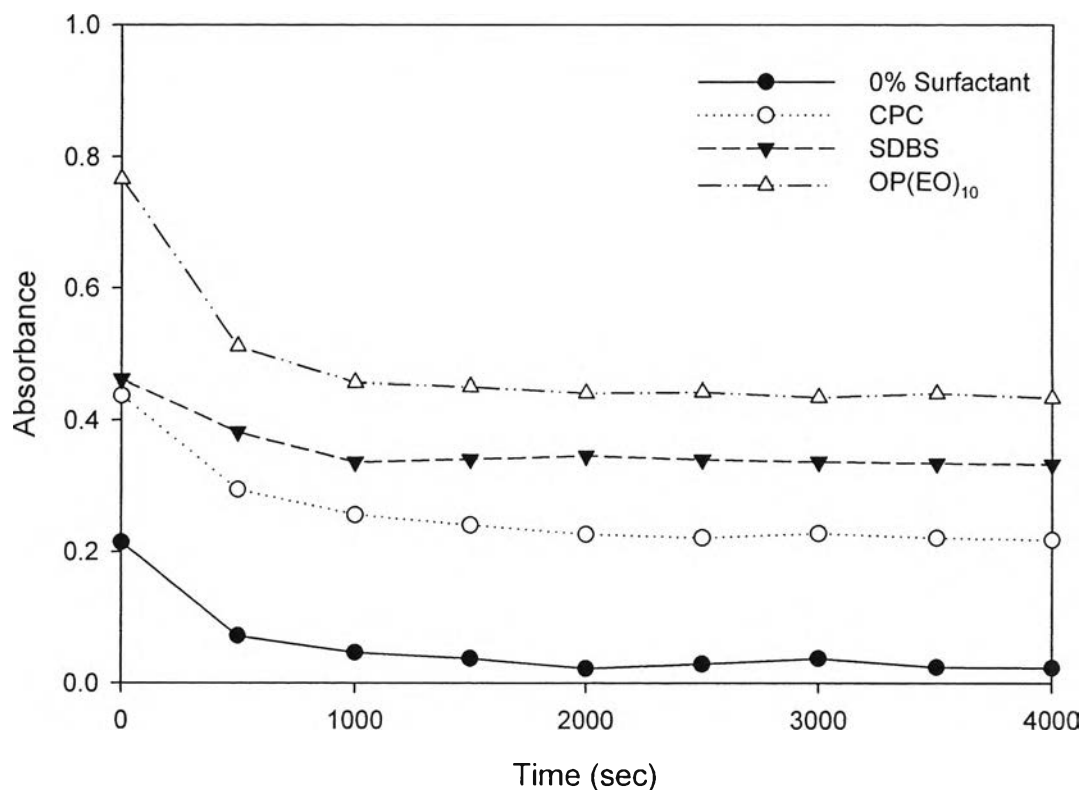
At CMC, the anionic surfactant SDBS is favorably adsorbed by the MWCNTs because of the electrostatic attraction. In addition, the head group of SDBS is smaller than that of OP(EO)<sub>10</sub>; its small size may increase its packing density compared to that of OP(EO)<sub>10</sub> causing the SDBS disperses better than OP(EO)<sub>10</sub>. Besides, the charge stabilization of MWCNTs, which are formed from the electrostatic repulsion of SO<sub>3</sub><sup>-</sup> via Coulomb interactions, may be more important than the steric repulsion of OP(EO)<sub>10</sub> headgroup. Thereby, the greater dispersion ability of SDBS compared to OP(EO)<sub>10</sub> and CPC, respectively, can be explained in terms of charge, headgroup size and graphite-surfactant interactions.



**Figure 4.10** Colloidal stability of the dispersed MWCNTs with surfactant at CMC and without surfactant at 25 °C.

At very high surfactant concentration (10 CMC), the MWCNTs surface is presumable fully-covered by micelles. The amount of micellation affects the MWCNTs dispersion stability as demonstrated in Figure 4.11. The results showed that the order of dispersing ability of MWCNTs was  $OP(EO)_{10} > SDBS > CPC$ . It was ascribed to the steric hindrance of the headgroup of  $OP(EO)_{10}$  which can assist the MWCNTs suspension.

However, the surface of MWCNTs are positively charged in three surfactants. For cationic surfactant, the electrostatic repulsion between the same charge of CPC surfactant and MWCNTs surface affects the low adsorption. Consequently, the CPC surfactant adsorption is insufficient to disperse the agglomerates of MWCNTs. This causes the lower MWCNTs suspension for all CPC surfactant concentrations.



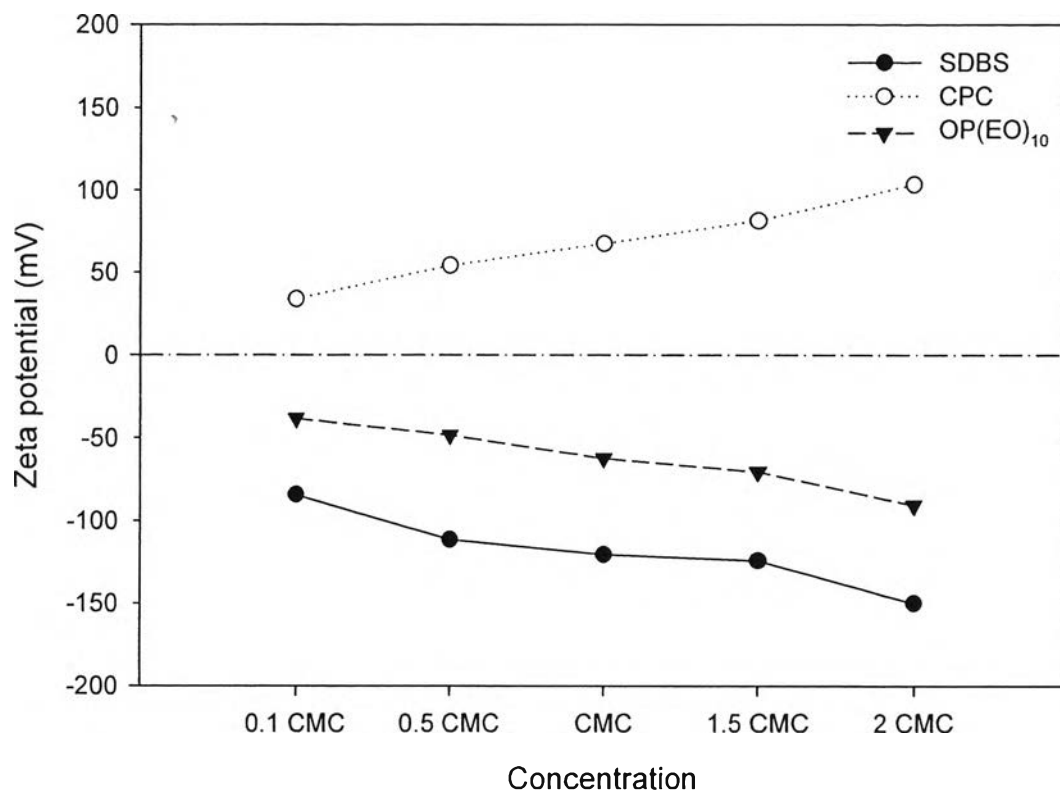
**Figure 4.11** Colloidal stability of the dispersed MWCNTs with surfactant at 10 CMC and without surfactant at 25 °C.

#### 4.4 Zeta Potential of MWCNTs in Surfactant Solution

Zeta potential is the electrical voltage difference between the surface of each colloid and its suspending liquid. The zeta potential is an important parameter to understand the suspension of colloid particles in aqueous solutions. If their surface charge is relatively high, then adjacent colloids will repel each other and tend to maintain their individuality. The force of gravity is insignificant on such small colloids. On the other hand, a colloid with little or no charge has little resistance to the natural tendency for fine particles into aggregates. In this work, the effect of various surfactant concentration to the zeta potential of MWCNTs was investigated as shown in Figure 4.12.

The results showed that the zeta potential values of MWCNTs increase with the increasing surfactant concentration for all surfactant solution since the more surfactant molecules can adsorb on the MWCNTs surface. Moreover, the maximum value of zeta potential takes place at the fully-covered of surfactant on the surface of MWCNTs. The hydrophobic group of surfactant occurs in the tail-down configuration and the hydrophilic head group of surfactants orientated toward the bulk solution. Thus, the zeta potential of MWCNTs in SDBS solution shows more negative value with the increasing surfactant concentration. Similarly, the zeta potential of MWCNTs in CPC solution becomes more positive with the increasing surfactant concentration as a result from the hydrophilic head group of surfactant. For OP(EO)<sub>10</sub>, the zeta potential value of MWCNTs was also negatively charged which is ascribe to the bound water-more bound water with ethoxylate group.

The maximum absolute value of zeta potential of MWCNTs is found in SDBS solution according to OP(EO)<sub>10</sub> and CPC, respectively. This relationship relates to the dispersion ability of MWCNTs in surfactant solution at CMC. However, the hydrophilic head group of non-ionic surfactant, the polyethylene oxide, provides the higher dispersion ability from steric hindrance than Coulombic force of anionic surfactant at high surfactant concentration, the zeta potential value of MWCNTs in this surfactant concentration is insignificant. In addition, at very high surfactant concentration (10 CMC), the MWCNTs particles form individually dispersions which fail to see the small moving-particle by naked eye.



**Figure 4.12** Zeta potential of MWCNTs at natural pH of surfactant solution.