

CHAPTER IV

RESULTS AND DISCUSSION

4.1 CTAB Adsorption on Hi-Sil 255

4.1.1 Effect of Electrolyte Types on CTAB Adsorption

The CTAB adsorption isotherms in the presence and absence of 1 mM electrolytes are shown in Figure 4.1. The addition of electrolytes to the system results in a shift of the CTAB adsorption isotherm to lower equilibrium CTAB concentrations if the CTAB equilibrium concentration is lower than its CMC. Therefore the presence of electrolytes has higher CTAB adsorption than the absence of electrolytes at the same equilibrium CTAB concentrations. It is presumably because anions of electrolyte bind head groups of cationic surfactants, resulting in a decrease in repulsion between head groups of cationic surfactants. The effect leads to a closer packing of surfactant monomers into surfactant aggregates; therefore, CTAB adsorption is enhanced. Additionally, the addition of electrolyte significantly affects CMC.

At low equilibrium CTAB concentrations well below the CMC, the increase of CTAB adsorption in the presence of electrolytes can be ranked in the following order: $\text{MgSO}_4 > \text{NaCl} > \text{Na}_2\text{CO}_3 > \text{MgCl}_2$ possibly because the divalent anions have more degree of binding than monovalent anions, resulting in a decrease in electrostatic repulsion between head groups of cationic surfactants. However, the CTAB adsorption in the present of Na_2CO_3 is lower than that of NaCl possibly due to twice dissociation of monovalent cation (Na^+ ion) for Na_2CO_3 , resulting in an increase in the competitive adsorption between the cation of surfactant and the Na^+ ion of Na_2CO_3 onto the negatively charged sites of the silica. The CTAB adsorption in the present of MgCl_2 is lower than that of NaCl possibly due to twice dissociation of monovalent anion (Cl^- ion) for MgCl_2 , resulting in a rise in binding of Cl^- ions to head groups of cationic surfactants. An increase in binding of Cl^- ions can obstruct the packing of surfactant monomers into surfactant aggregates. Therefore, the packing of surfactant monomers into surfactant aggregates can be more difficult.

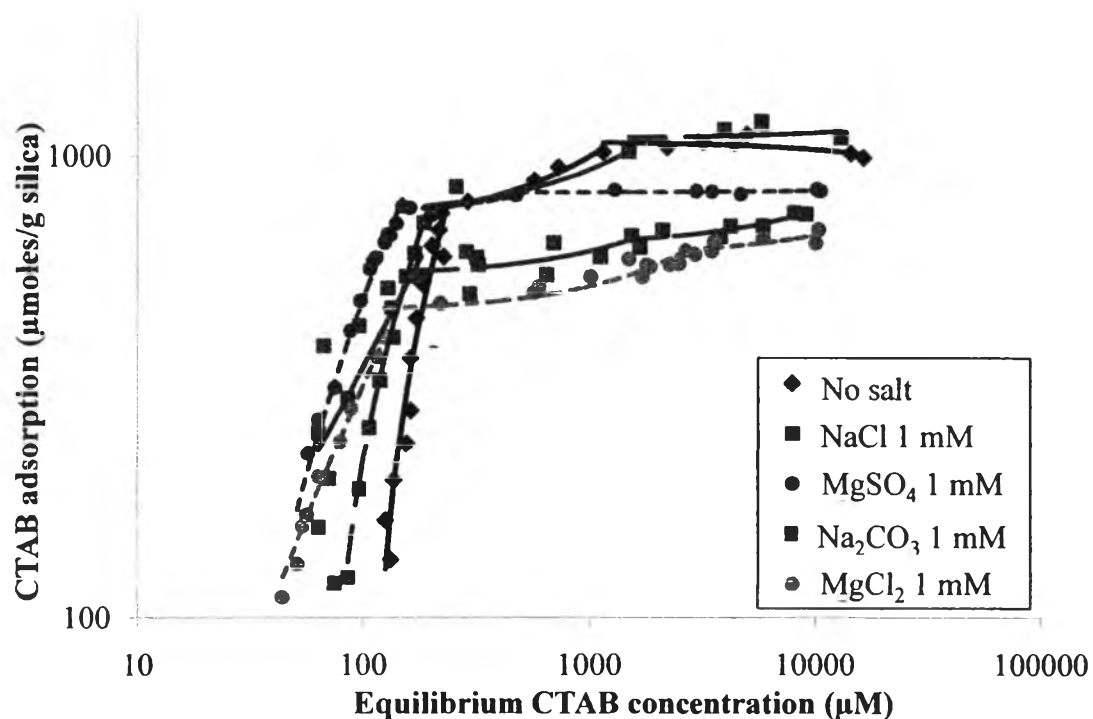


Figure 4.1 Adsorption isotherms for CTAB in the absence and presence of 1 mM electrolytes: NaCl, Na₂CO₃, MgCl₂, and MgSO₄.

Moreover, above the CMC, the maximum of CTAB adsorption per gram of silica as concluded in Table 4.1. The presence of electrolytes, especially MgSO₄ and MgCl₂ (divalent cations), causes the reduction of maximum CTAB adsorption. It is possibly due to the competitive adsorption between the cation of surfactant and the cation of electrolyte onto the negatively charged sites of the silica.

In addition, the results reveal that the maximum adsorption of CTAB onto the precipitated silica was found to be decreased as summarized in Table 4.1. According to the tendency to reduce the maximum CTAB adsorption, the electrolytes can be ranked as follows: NaCl > MgSO₄ > Na₂CO₃ > MgCl₂. The possible explanation is that Na⁺ ion, which is the small and hard ion, has a high affinity for water leading to be weak interaction with the silica surface, in the other hand, Mg²⁺ ion, which is large and soft ion, has a strong interaction on the silica surface (Howard *et al.*, 2009). That is, the soft Mg²⁺ ions could adsorb at the surface of silica more than the hard Na⁺ ions. Therefore, it is reasonable reason that why

divalent cation makes the maximum adsorption of CTAB had lower than that in monovalent cation. However, the maximum adsorption of CTAB in the presence of Na_2CO_3 is lower than that of MgSO_4 possibly due to twice dissociation of monovalent cation (Na^+ ion) for Na_2CO_3 , causing an increase in the adsorption of the Na^+ ion onto the negatively charged sites of the silica. The maximum CTAB adsorption in the presence of MgCl_2 is lower than that of MgSO_4 possibly due to twice dissociation of monovalent anion (Cl^- ion) for MgCl_2 . An increase in the Cl^- ions can obstruct the adsorption of cations of surfactant monomers onto the silica surface. Therefore, the adsorption of cationic surfactants onto the silica surface can be more difficult.

Table 4.1 The maximum CTAB adsorption in the absence and presence of 1 mM electrolytes: NaCl , Na_2CO_3 , MgCl_2 , and MgSO_4

System	Maximum CTAB adsorption ($\mu\text{mol/g}$ silica)
No salt	1046.88
NaCl 1 mM	1114.79
MgSO_4 1 mM	839.28
Na_2CO_3 1 mM	699.46
MgCl_2 1 mM	647.73

The CTAB adsorption isotherms in the presence of 10 mM electrolytes are shown in Figure 4.2. The results in the presence of electrolytes at concentration 10 mM are very similar to those obtained at concentration 1 mM, although the CTAB adsorption isotherm in the presence of 10 mM Na_2CO_3 has a very sharp increase in the isotherm slope. At low equilibrium CTAB concentrations well below the CMC, the increase of CTAB adsorption in the presence of electrolytes can be ranked in the following order: $\text{MgSO}_4 > \text{NaCl} > \text{Na}_2\text{CO}_3 > \text{MgCl}_2$ possibly because the divalent anions have more degree of binding than monovalent anions, resulting in a decrease in electrostatic repulsion between head groups of cationic surfactants.

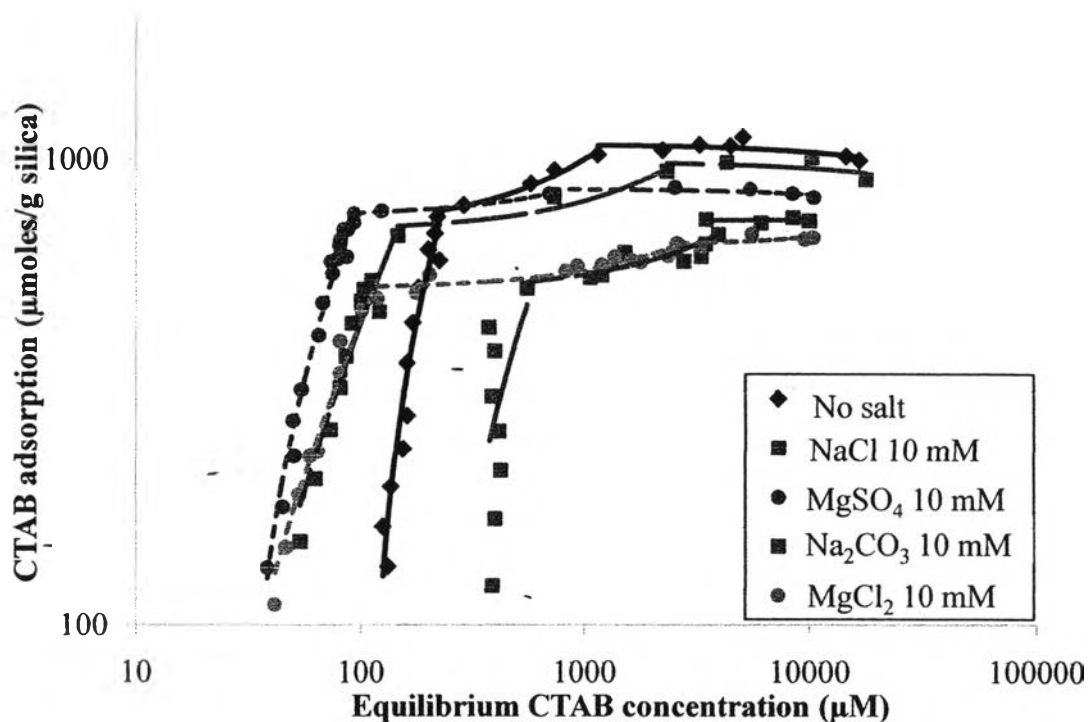


Figure 4.2 Adsorption isotherms for CTAB in the absence and presence of 10 mM electrolytes: NaCl, Na₂CO₃, MgCl₂, and MgSO₄.

Moreover, the maximum adsorption of CTAB onto the precipitated silica was found to be decreased. According to the tendency to reduce the maximum CTAB adsorption, the electrolytes can be ranked as follows: NaCl > MgSO₄ > Na₂CO₃ > MgCl₂, as shown in Table 4.2. The possible explanation is that Na⁺ ion, which is the small and hard ion, has a high affinity for water leading to be weak interaction with the silica surface, in the other hand, Mg²⁺ ion, which is large and soft ion, has a strong interaction on the silica surface (Howard *et al.*, 2009). That is, the soft Mg²⁺ ions could adsorb at the surface of silica more than the hard Na⁺ ions. Therefore, the divalent cation makes the maximum adsorption of CTAB had lower than that in the monovalent cation.

Table 4.2 The maximum CTAB adsorption in the absence and presence of 10 mM electrolytes: NaCl, Na₂CO₃, MgCl₂, and MgSO₄

System	Maximum CTAB adsorption ($\mu\text{mol/g silica}$)
No salt	1046.88
NaCl 10 mM	960.77
MgSO ₄ 10 mM	850.75
Na ₂ CO ₃ 10 mM	741.26
MgCl ₂ 10 mM	668.57

Figure 4.3 shows the CTAB adsorption isotherms in the presence of 0.1 mM electrolytes. The results in the presence of electrolytes at concentration 0.1 mM are very similar to those obtained at concentration 1 mM. At low equilibrium CTAB concentrations well below the CMC, the increase of CTAB adsorption in the presence of electrolytes can be ranked in the following order: MgSO₄ > NaCl > Na₂CO₃ > MgCl₂ possibly because the divalent anions have more degree of binding than monovalent anions, resulting in a decrease in electrostatic repulsion between head groups of cationic surfactants.

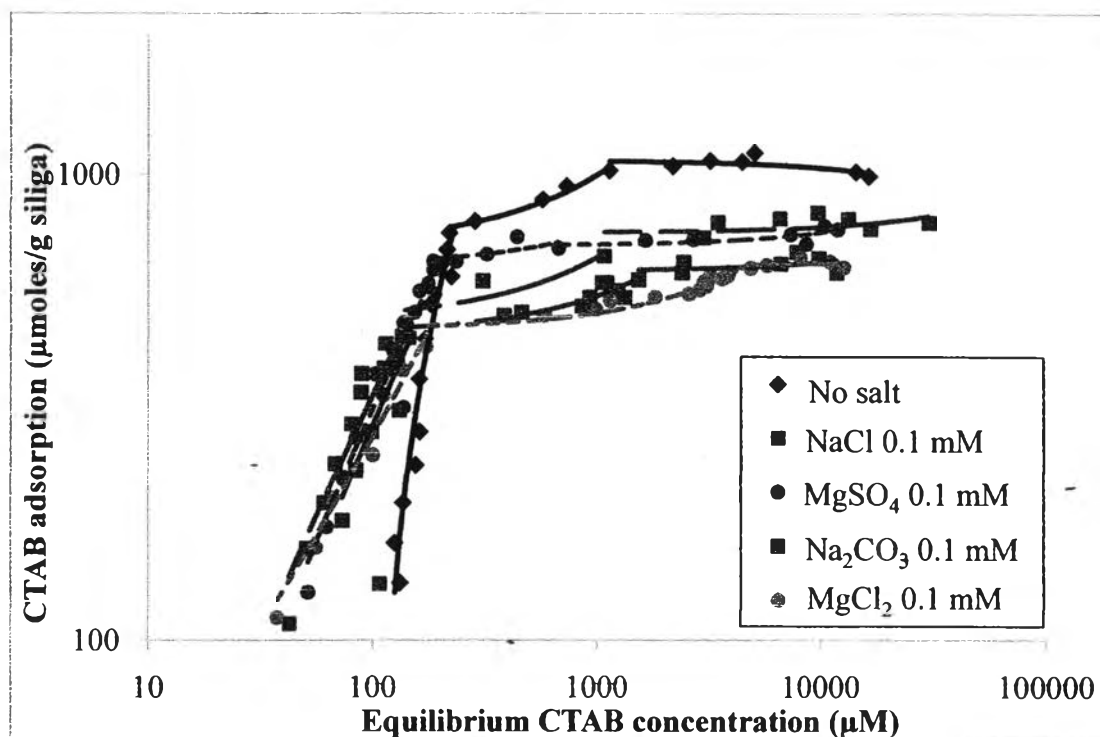


Figure 4.3 Adsorption isotherms for CTAB in the absence and presence of 0.1 mM electrolytes: NaCl, Na₂CO₃, MgCl₂, and MgSO₄.

Moreover, the maximum adsorption of CTAB onto the precipitated silica was found to be decreased. According to the tendency to reduce the maximum CTAB adsorption, the electrolytes can be ranked as follows: NaCl > MgSO₄ > Na₂CO₃ ≈ MgCl₂, as shown in Table 4.3. The possible explanation is that Na⁺ ion, which is the small and hard ion, has a high affinity for water leading to be weak interaction with the silica surface. On the other hand, Mg²⁺ ion, which is large and soft ion, has a strong interaction on the silica surface (Howard *et al.*, 2009). That is, the soft Mg²⁺ ions could adsorb at the surface of silica more than the hard Na⁺ ions. Therefore, the divalent cation makes the maximum adsorption of CTAB had lower than that in the monovalent cation.

Table 4.3 The maximum CTAB adsorption in the absence and presence of 0.1 mM electrolytes: NaCl, Na₂CO₃, MgCl₂, and MgSO₄

System	Maximum CTAB adsorption ($\mu\text{mol/g silica}$)
No salt	1046.88
NaCl 0.1 mM	775.60
MgSO ₄ 0.1 mM	736.61
Na ₂ CO ₃ 0.1 mM	640.51
MgCl ₂ 0.1 mM	646.29

4.1.2 Effect of Electrolyte Concentration on CTAB Adsorption

To investigate the effect of ionic strength on CTAB adsorption, MgSO₄ concentration was varied from 0.1 to 1 and 10 mM. The CTAB adsorption isotherms, plotted on a log-log scale, are presented in Figure 4.4. The result indicated that the CTAB adsorption increased with increasing MgSO₄ concentration. However, the maximum CTAB adsorption considerably increased when the MgSO₄ concentration was increased from 0.1 to 1 mM and slightly increased when the MgSO₄ concentration was increased from 1 to 10 mM, as shown in Table 4.4. An increase in MgSO₄ concentration could reduce the electrostatic repulsion between positively charged head groups of adsorbed CTAB on the surface of silica (Rosen, 1988). It is presumably due to the binding head groups of cationic surfactants increased with increasing anions of MgSO₄ in the system; therefore, CTAB adsorption is enhanced.

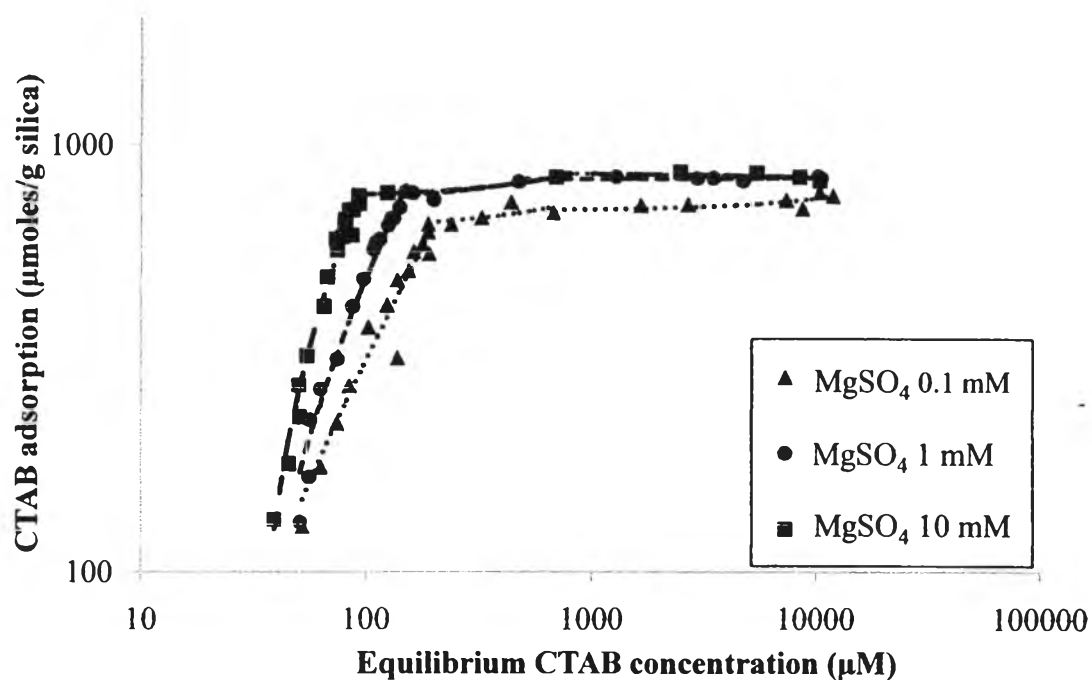


Figure 4.4 Adsorption isotherms of CTAB in the presence of 0.1, 1, and 10 mM MgSO_4 .

Table 4.4 The maximum CTAB adsorption in the presence of MgSO_4 at various concentrations

System	Maximum CTAB adsorption ($\mu\text{mol/g silica}$)
MgSO_4 0.1 mM	736.61
MgSO_4 1 mM	839.28
MgSO_4 10 mM	850.75

Figure 4.5 shows the CTAB adsorption isotherms in the presence of MgCl_2 at various concentrations, plotted on a log-log scale. It could be seen obviously that the CTAB adsorption increased with increasing MgCl_2 concentration, similar to the results of MgSO_4 obtained. As shown in Table 4.5, the maximum CTAB adsorption slightly increased when the MgCl_2 concentration was increased

from 1 to 10 mM. An increase in MgCl_2 concentration could reduce the electrostatic repulsion between positively charged head groups of adsorbed CTAB on the surface of silica (Rosen, 1988). It is presumably due to the binding head groups of cationic surfactants increased with increasing anions of MgCl_2 in the system; therefore, CTAB adsorption is enhanced.

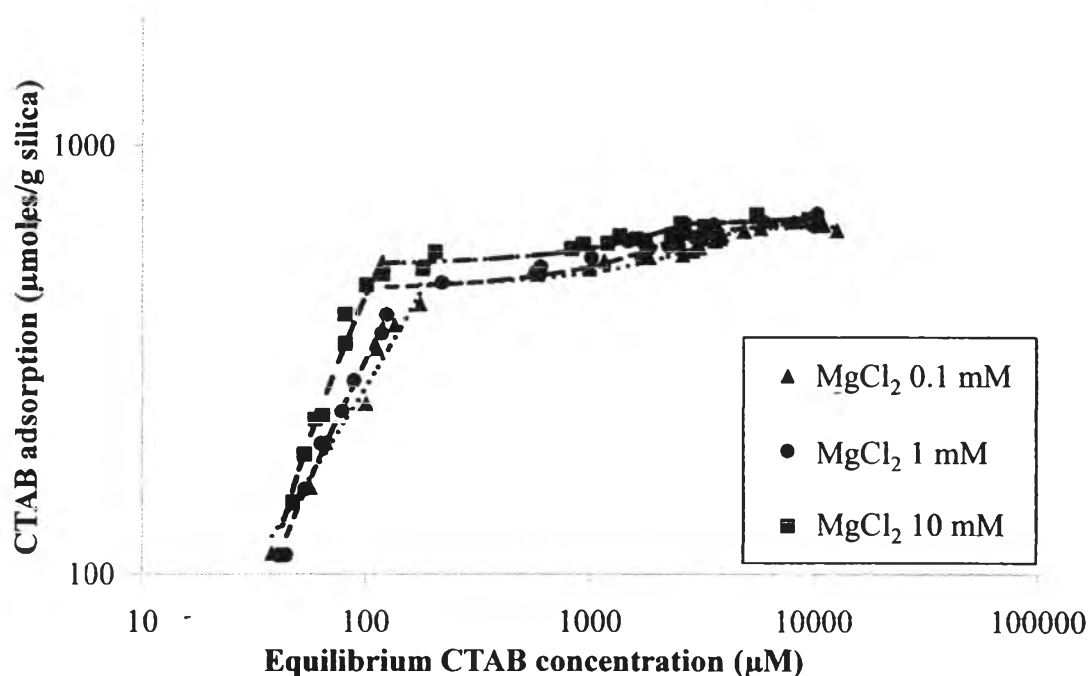


Figure 4.5 Adsorption isotherms of CTAB in the presence of 0.1, 1, and 10 mM MgCl_2 .

Table 4.5 The maximum CTAB adsorption in the presence of MgCl_2 at various concentrations

System	Maximum CTAB adsorption ($\mu\text{mol/g silica}$)
MgCl_2 0.1 mM	646.29
MgCl_2 1 mM	647.73
MgCl_2 10 mM	668.57

Figure 4.6 shows the CTAB adsorption isotherms in the presence of Na_2CO_3 at various concentrations, plotted on a log-log scale. The results indicated that the CTAB adsorption increased with increasing Na_2CO_3 concentration, similar to the results of MgSO_4 and MgCl_2 obtained. However, the CTAB adsorption isotherm in the presence of 10 mM Na_2CO_3 had a very sharp increase in the isotherm slope at the low CTAB equilibrium concentration possibly due to some reactions that occurred from adjusting pH by using HCl, leading to the change in ionic strength. As shown in Table 4.6, the maximum CTAB adsorption considerably increased when the Na_2CO_3 concentration was increased from 0.1 to 1 mM and slightly increased when the MgSO_4 concentration was increased from 1 to 10 mM. An increase in Na_2CO_3 concentration could reduce the electrostatic repulsion between positively charged head groups of adsorbed CTAB on the surface of silica (Rosen, 1988). It is presumably due to the binding head groups of cationic surfactants increased with increasing anions of Na_2CO_3 in the system; therefore, CTAB adsorption is enhanced.

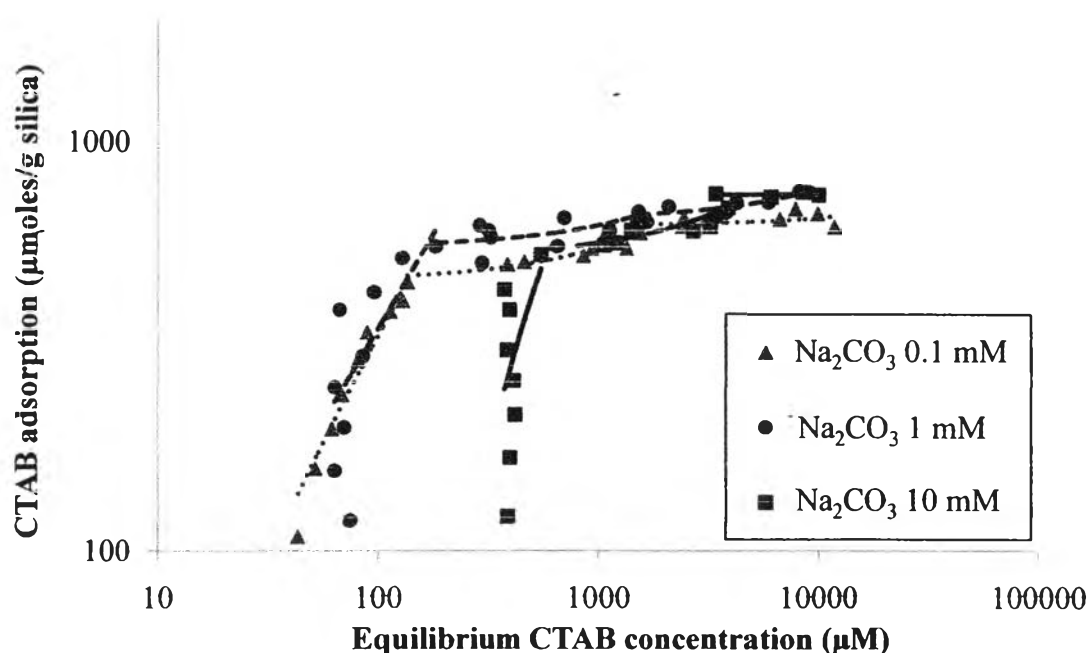


Figure 4.6 Adsorption isotherms of CTAB in the presence of 0.1, 1, and 10 mM Na_2CO_3 .

Table 4.6 The maximum CTAB adsorption in the present of Na₂CO₃ at various concentrations

System	Maximum CTAB adsorption ($\mu\text{mol/g silica}$)
Na ₂ CO ₃ 0.1 mM	640.51
Na ₂ CO ₃ 1 mM	699.46
Na ₂ CO ₃ 10 mM	741.26

Figure 4.7 shows the CTAB adsorption isotherms in the present of NaCl at various concentrations, plotted on a log-log scale. The result indicated that the CTAB adsorption increased with increasing NaCl concentration at the low CTAB equilibrium concentration. It is possibly because the binding head groups of cationic surfactants increased with increasing anions of NaCl in the system, resulting in a decrease of repulsion between head groups of cationic surfactants.

Interestingly, in the case of NaCl at the high CTAB equilibrium concentration, the CTAB adsorption greatly increased when the NaCl concentration was increased from 0.1 to 1 mM and then slightly decreased when the NaCl concentration was increased from 1 to 10 mM. As shown in Table 4.7, the maximum CTAB adsorption increased with increasing NaCl concentration and reached the maxima at a NaCl concentration of 1 mM. With further increasing NaCl concentration from 1 to 10 mM, the maximum CTAB adsorption decreased slightly. It is possibly because, at lower NaCl concentration, chloride ion (Cl⁻) could cause the reduction of repulsive force between head groups of cationic surfactants. However, at higher NaCl concentration, sodium ion (Na⁺) may be adsorbed more on the negatively charged surface causing less amount of CTAB adsorbed on precipitated silica. It is presumably because the chloride ion (Cl⁻) binds poorly in comparison to the bromide ion (Br⁻), resulting in a greater electrostatic repulsion between head groups of cationic surfactants and a greater surface charge (Atkin *et al.*, 2003).

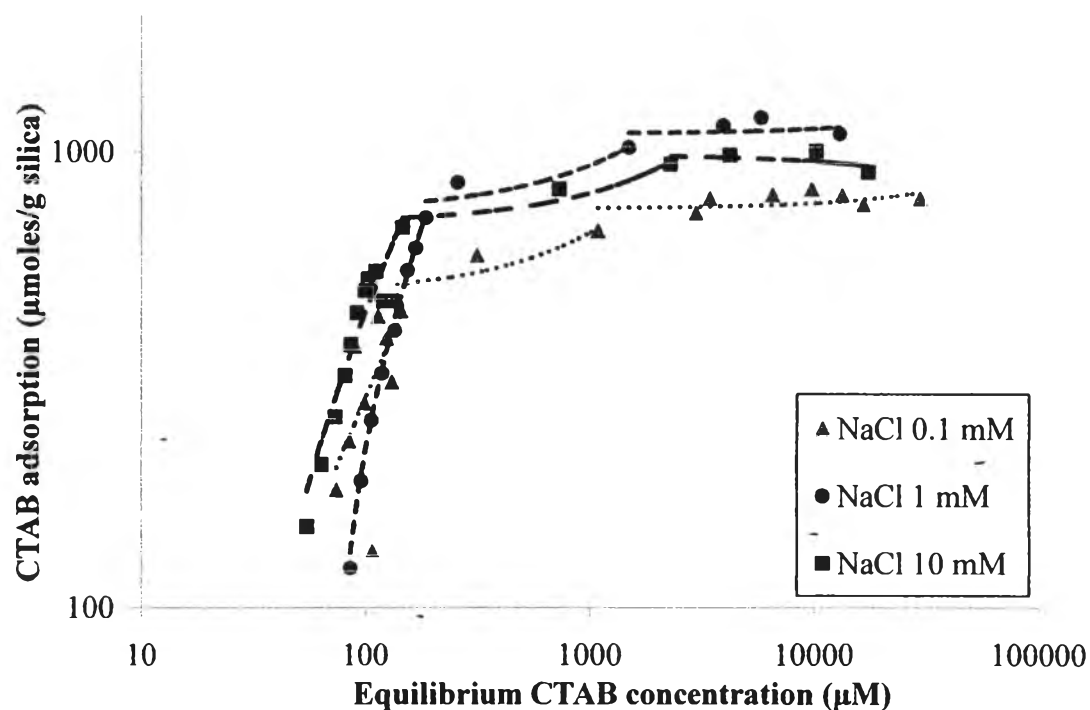


Figure 4.7 Adsorption isotherms of CTAB in the presence of 0.1, 1, and 10 mM NaCl.

Table 4.7 The maximum CTAB adsorption in the presence of NaCl at various concentrations

System	Maximum CTAB adsorption ($\mu\text{mol/g silica}$)
NaCl 0.1 mM	775.60
NaCl 1 mM	1114.79
NaCl 10 mM	960.77

Summarily, to investigate the effect of electrolyte concentration, the CTAB adsorption increased with increasing electrolyte concentration corresponding to the results of MgSO_4 , MgCl_2 , Na_2CO_3 , and NaCl obtained. An increase in electrolyte concentration could reduce the repulsion between positively charged head groups of adsorbed CTAB on the surface of silica (Rosen, 1988). It is

presumably due to the binding head groups of cationic surfactants increased with increasing anions of electrolyte in the system.

4.2 Adsolubilization

4.2.1 Effect of Electrolyte Types on Adsolubilization

The adsolubilizations for CTAB in the absence and presence of 1 mM electrolytes are presented in Figure 4.8. The addition of electrolytes to the system causes an increase of adsolubilization of acetophenone. Possibly, it is because anions of electrolyte bind head groups of cationic surfactants, resulting in a decrease in the repulsive interaction between head groups of cationic surfactants. The effect leads to the higher amounts of adsorbed CTAB.

Moreover, the adsolubilizations in the presence of 1 mM electrolytes are shown in Figure 4.8. According to the tendency to increase the adsolubilization of acetophenone, the electrolytes can be ranked as follows: $\text{NaCl} > \text{MgSO}_4 \approx \text{Na}_2\text{CO}_3 > \text{MgCl}_2$. The possible explanation is that CO_3^{2-} ion and SO_4^{2-} ion, which is the small and hard anion, has a high affinity for water leading to be weak degree of binding head groups of cationic surfactants. The effect of CO_3^{2-} ion was the same as that for SO_4^{2-} ion. On the other hand, Cl^- ion, which is large and soft anion, has a strong degree of binding head groups of cationic surfactants (Subramanian *et al.*, 2000). That is, the soft Cl^- ions could bind head groups of cationic surfactants more than the hard CO_3^{2-} ions and SO_4^{2-} ions. Therefore, it is reasonable reason that why soft anion makes the adsolubilization of acetophenone had higher than that in hard anion. However, MgCl_2 has the lowest adsolubilization of acetophenone possibly due to twice dissociation of soft anion (Cl^- ion) for MgCl_2 . An increase in the Cl^- ions can obstruct packing of surfactant monomers into surfactant aggregates. Therefore, the packing of surfactant monomers into surfactant aggregates can be more difficult, leading to the lower amounts of adsorbed CTAB.

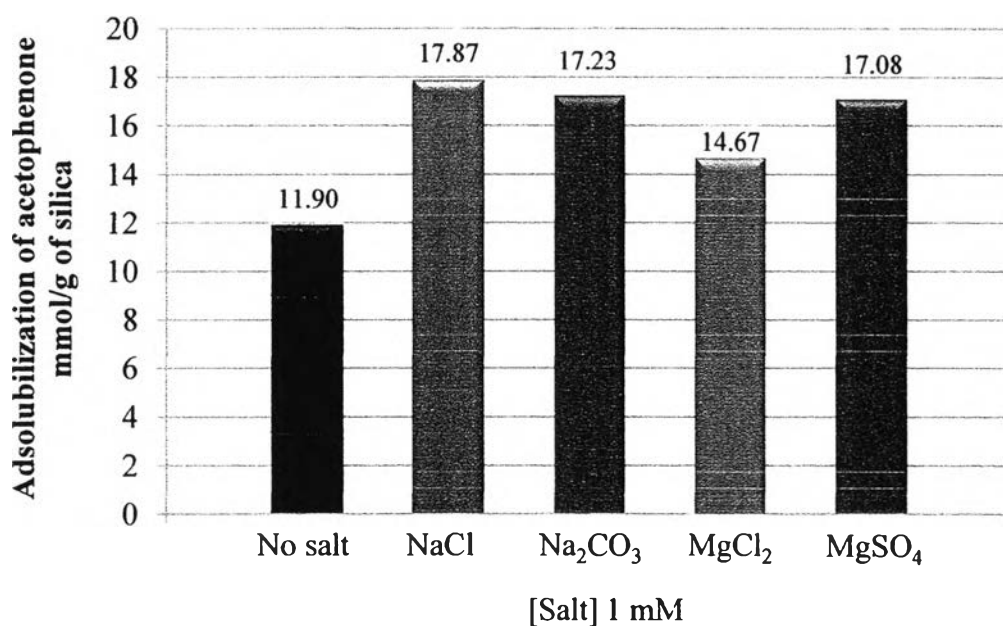


Figure 4.8 Adsolubilizations for CTAB in the absence and presence of 1 mM electrolytes: NaCl, Na₂CO₃, MgCl₂, and MgSO₄.

4.2.2 Effect of Electrolyte Concentration on Adsolubilization

To investigate the effect of ionic strength on adsolubilization, NaCl concentration was varied from 0.1 to 10 mM. The adsolubilization of acetophenone are shown in Figure 4.9. The result indicated that the adsolubilization of acetophenone fluctuated slightly when NaCl concentration changed. It might be because the adsolubilization of acetophenone seemed to depend mainly on the amount of adsorbed CTAB on silica (Asvapathanagul *et al.*, 2005). Another way of saying this was that the presence of NaCl to the system, impact of the change in NaCl concentration on adsolubilization of acetophenone decreased. Therefore the change in NaCl concentration had insignificant effect on the adsolubilization of acetophenone

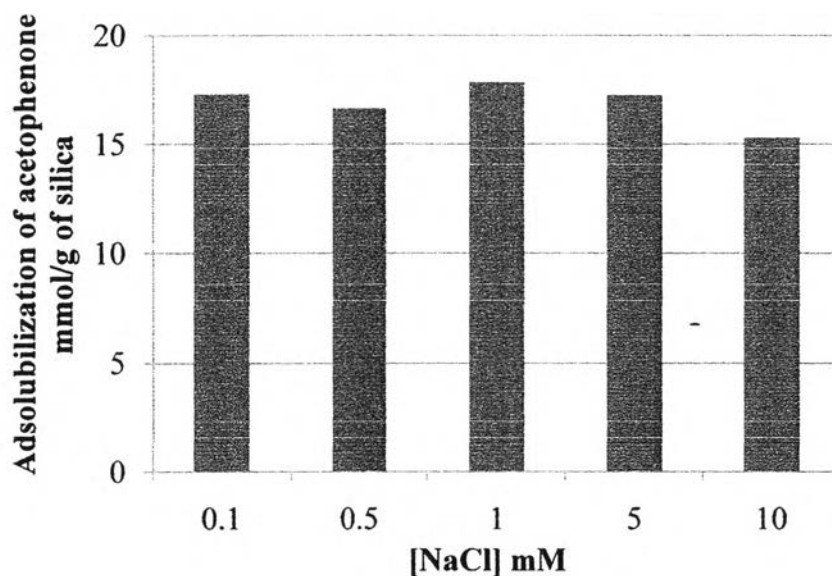


Figure 4.9 Adsolubilizations for CTAB in the presence of NaCl at various concentrations.

Figure 4.10 shows the adsolubilizations for CTAB in the presence of Na_2CO_3 at various concentrations. Na_2CO_3 concentration was varied from 0.1 to 10 mM. It could be seen obviously that the adsolubilization of acetophenone fluctuated slightly when Na_2CO_3 concentration changed. It might be because the adsolubilization of acetophenone seemed to depend mainly on the amount of adsorbed CTAB on silica (Asvathanagul *et al.*, 2005). Therefore, Na_2CO_3 concentration had insignificant effect on the adsolubilization of acetophenone.

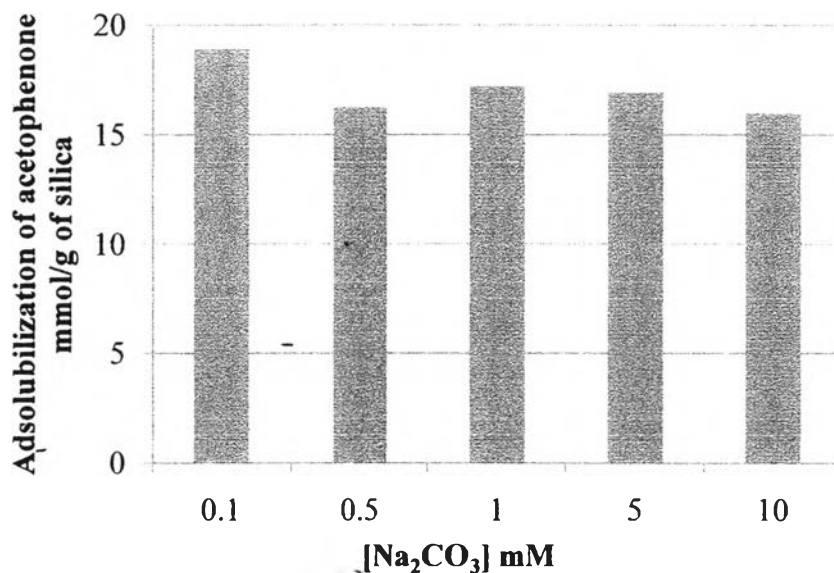


Figure 4.10 Adsolubilizations for CTAB in the presence of Na₂CO₃ at various concentrations.

Figure 4.11 shows the adsolubilizations for CTAB in the presence of MgSO₄ at various concentrations. MgSO₄ concentration was varied from 0.1 to 10 mM. The result indicated that the adsolubilization of acetophenone fluctuated when MgSO₄ concentration changed. It might be because the adsolubilization of acetophenone seemed to depend mainly on the CTAB adsorption onto silica surface (Asvapathanagul *et al.*, 2005). Therefore MgSO₄ concentration had insignificant effect on the adsolubilization of acetophenone.

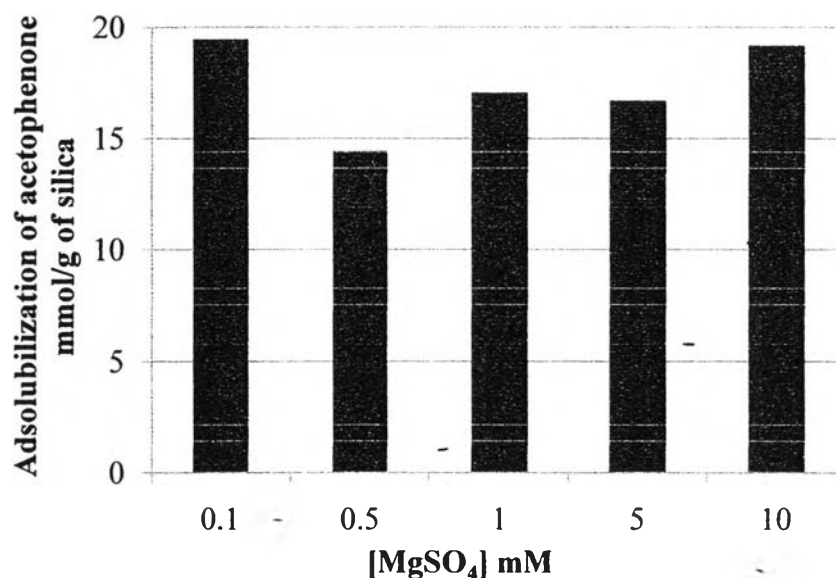


Figure 4.11 Adsolubilizations for CTAB in the presence of MgSO₄ at various concentrations.

Figure 4.12 shows the adsolubilizations for CTAB in the presence of MgCl₂ at various concentrations. MgSO₄ concentration was varied from 0.1 to 10 mM. It could be seen obviously that the adsolubilization of acetophenone fluctuated when MgCl₂ concentration changed. It might be because the adsolubilization of acetophenone seemed to depend mainly on the CTAB adsorption onto silica surface (Asvapathanagul *et al.*, 2005). Therefore, the change in MgCl₂ concentration had insignificant effect on the adsolubilization of acetophenone.

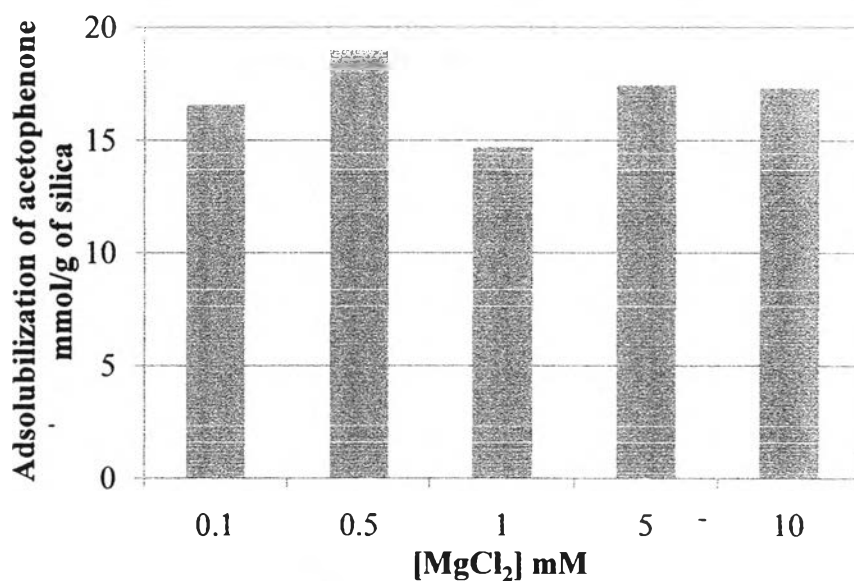


Figure 4.12 Adsolubilizations for CTAB in the presence of MgCl₂ at various concentrations.

Briefly, to investigate the effect of electrolyte concentration on adsolubilization, the adsolubilization of acetophenone fluctuated when electrolyte concentration changed corresponding to the results of NaCl, Na₂CO₃, MgSO₄, and MgCl₂ obtained. It might be because the adsolubilization of acetophenone seemed to depend mainly on the amount of adsorbed CTAB on silica surface (Asvapathanagul *et al.*, 2005). Therefore, electrolyte concentration had insignificant effect on the adsolubilization of acetophenone.