CHAPTER V

DIFFERENCE BETWEEN ADSOLUBILIZATION OF AROMATIC SOLUTES IN CATIONIC ADMICELLES IN HIGH REGION II AND III OF SURFACTANT ADSORPTION ISOTHERM[*]

5.1 Abstract

The different adsolubilization properties of cetylpyridinium chloride admicelles in the surfactant adsorption region II and region III have been elucidated through the adsolubilization of aromatic solutes, i.e. diphenylmethane, diphenylether and p-tolunitrile. The results show that, while highly hydrophobic solutes, i.e. diphenylmethane and diphenylether, partition into both the palisade and core regions of the admicelles, they primarily partition into the core region. They also exhibit a higher partition coefficient when surfactant adsorption is in region II than when adsorption is in region III, at both 20 °C and 50 °C. A preference of surfactant adsorption region (high region II and region III) for adsolubilization of hydrophilic p-tolunitrile would be governed by cation-π and dipole-dipole attractive forces or surfactant packing density in admicelle. Additionally, ability of a surfactant molecule to adsolubilize solute would be primarily controlled by attractive interaction between solute and surfactant molecules or surfactant packing density in admicelle.

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[*] Manuscript in preparation

5.2 Introduction

This work extends our previous study of the effect of temperature on adsolubilization in admicelles in adsorption region III [1]. Figure 5.1 shows the typical S-shape of surfactant adsorption isotherm for ionic surfactant adsorbed onto a polar substrate. The shape of the isotherm is believed to reflect distinct modes of adsorption [2]. In region I the surfactant adsorbs mainly by ion exchange, possible with the hydrophobic group more or less prone on the substrate. In region II, there is a marked increase in adsorption resulting from interaction of the hydrophobic chains of oncoming surfactant ions with those previously adsorbed surfactant creating two-dimensional surface aggregates called admicelles [3 , 4]. In this adsorption region the original charge of solid is neutralized by the adsorption of oppositely charged surfactant ions and eventually reversed, so that at the end of region II, the solid surface has acquire a charge of the same sign as the surfactant ion. In region III the slope of the isotherm is reduced because adsorption now must overcome electrostatic repulsion between the oncoming ions or charged molecule and the similar charged solid (adsorption in this fashion is usually complete (region IV) in the neighbourhood of the critical micelle concentration [2]). This difference in the slopes also implies that the microenvironment and molecular interactions in the admicelles in the surfactant adsorption region II is distinctly different from those in region III. This will affect the key interactions between solute and surfactant, i.e. hydrophobic, cation-π and dipole-dipole interactions in case that solute is *neutral* aromatic, which play a role in alteration of a solute partition coefficient in adsolubilization system [6]. Repetitive results already discussed in the previous corresponding work [1] may be neglected in the discussion part.

This work studied the effect of the different degrees of surfactant adsorption (between region II and III) on adsolubilization of benzene derivatives at 20 °C and 50 °C.
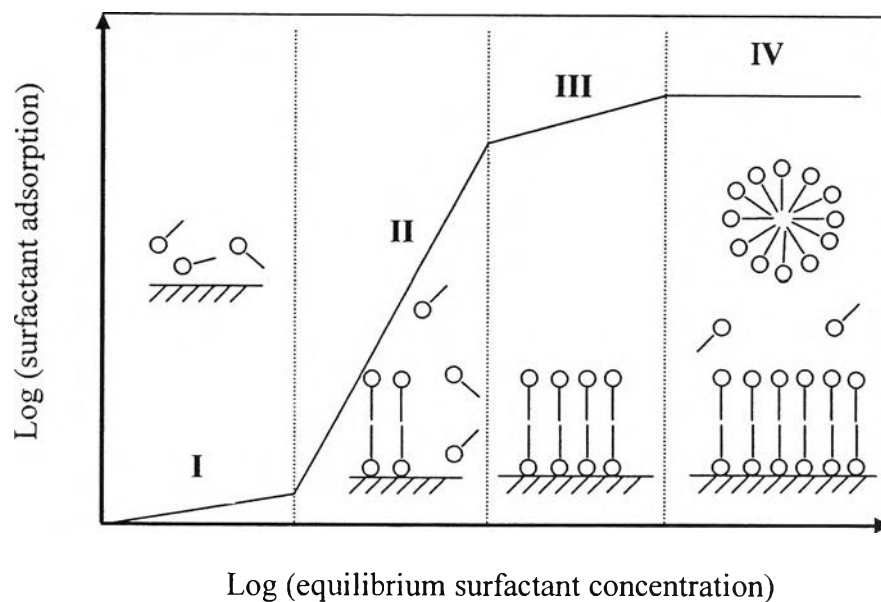
Figure 5.1 S-Shape adsorption isotherm for an ionic surfactant on an oppositely charged substrate.

Table 5.1 Physicochemical properties of the studied solutes [7].

Solutes	Chemical Formula	Aqueous Solubility at 25 °C (mol/L)	Melting Point (°C)	Boiling Point (°C)
Diphenylmethane	$C_{13}H_{12}$	8.381×10^{-5}	25.2	264
Diphenylether	$C_{12}H_{10}O$	1.06×10^{-4}	26.8	259
p-Tolunitrile	C_8H_7N	7.86×10^{-3}	29.5	217

5.3 Materials and Methods

5.3.1 Materials

Precipitated silica, Hi-Sil® 233, with a specific surface area of 150 m^2/g was supplied by PPG Industries Inc. (Pittsburgh, PA) and used as the solid substrate. The cationic surfactant cetylpyridinium chloride (CPC) was obtained from Sigma (St. Louis, MO). The studied solutes include diphenylmethane (99+ wt%) from Aldrich (St. Louis, MO), diphenylether (99+ wt%) from Aldrich (St. Louis, MO) and p-tolunitrile (98+ wt%) from Fluka (St. Louis, MO) as shown in Table 5.1 with their useful physicochemical properties [7]. The solvent was de-ionized water with a resistivity of 18.2 MΩ-cm purified by a Barnstead E-pure water system. All chemicals were used as received.

5.3.2 Experimental Procedures

5.3.2.1 Surfactant Adsorption / Admicelle Formation

Surfactant stock solutions were made and adjusted to pH 8 with a dilute sodium hydroxide solution. These solutions were diluted with pH 8 de-ionized water to form a series of 20 mL solutions with varying surfactant concentrations. These were added to vials containing 0.4 g of silica and then sealed. The mixtures were shaken daily and allowed to equilibrate for two days at temperatures of 20 or 50 °C. They were then allowed to settle at those constant temperatures for one day. After that the supernatants were removed and centrifuged by a Fisher Scientific model MARATHON 300 at 3000 rpm for 15 minutes. The supernatants were removed and analyzed for the bulk surfactant concentrations through UV spectroscopy at λ = 258 nm [8] by using a SHIMADZU UV spectrophotometer model UV-1201S. Through a simple mass-balance, the amount of surfactant adsorbed per gram of silica was calculated and plotted as a function of the surfactant equilibrium bulk concentration.

5.3.2.2 Adsolubilization

The adsolubilization isotherms have also been examined at 20 and 50 °C. The studied surfactant concentrations in adsorption region II and III for the adsolubilization studies were determined from the adsorption isotherms. There

are only two studied surfactant concentrations; one in region II and another in region III. Both concentration are in the high zone of the adsorption isotherm aiming to maintain the admicelles covering on the whole solid surface (minimize the presence of adsorbed surfactant monolayer area) because our work focused only on studying the effect of different packing density of surfactant molecules in the admicelles on adsolubilization. There are no micelles present in the systems. The initial surfactant concentration was chosen for each temperature and region from the adsorption isotherms. Solute was then added into a pH 8 surfactant solution to make a stock solution with a concentration equal to the aqueous solubility of the solute. The solute stock solutions were then diluted to varying solute concentrations by adding pH 8 surfactant solution of the same surfactant concentration. Twenty millilitres was added to a vial with 0.4 g of silica and then sealed. The vials were shaken daily and allowed to equilibrate for 3 days at constant temperature. The samples were allowed to settle for 1 day before the supernatant was removed from the vials and then quickly centrifuged at room temperature. The supernatant was removed for analysis of the equilibrium solute bulk concentration using a dual-wavelength UV spectroscopic technique [9]. The wavelengths used for analyzing diphenylmethane, diphenylether and p-tolunitrile were 262, 269 and 272 nm, respectively [10]. Calibration curves were developed, and the measured absorbance used to calculate the solute concentrations in the supernatant. Through a simple mass-balance, the amount of adsolubilized solute in the admicelles per gram of silica was calculated. This data was converted to the intra-admicellar mole fractions of solutes X_{ia} and plotted against their partition coefficients K_p [9 , 11-13] for indirectly determining the locus of solutes in the admicelle and the relative ability of the admicelle to adsolubilize the studied solutes. The partition coefficients were defined as the ratio

$$K_p = \frac{X_{ia}}{X_w} \qquad (5.1)$$

between the intra-admicellar mole fraction of the solute to the solute concentration in the supernatant; aqueous bulk phase X_w. The amount of adsolubilized solute per g silica was plotted against X_{ia}.
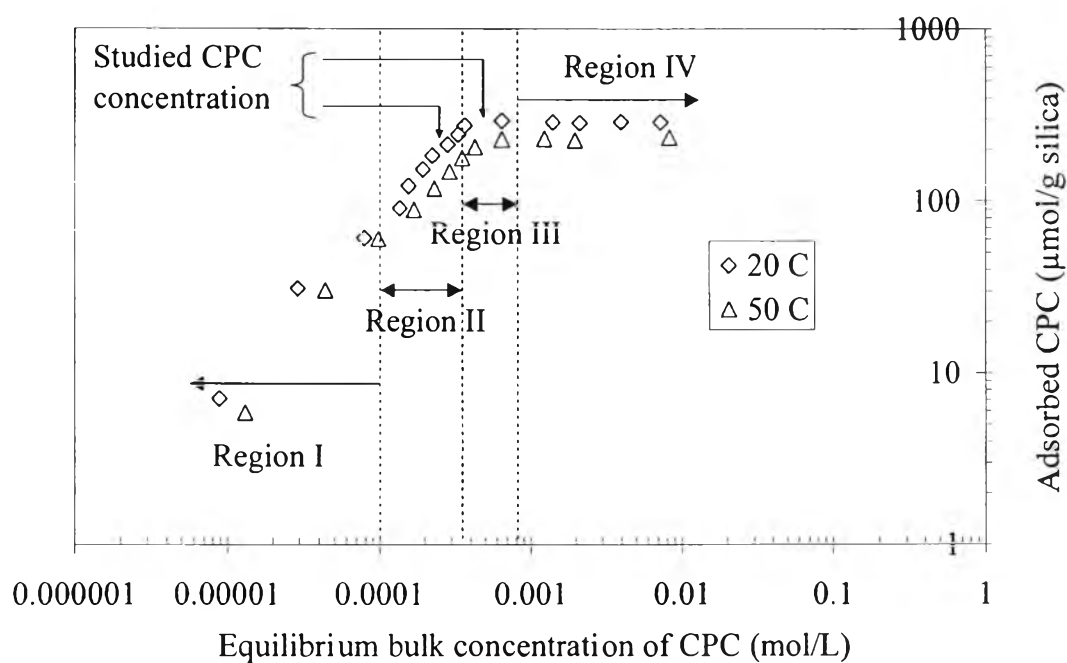

Figure 5.2 Adsorption isotherms of CPC on silica powder, Hi-Sil® 255 at 20 °C and 50 °C.

5.4 Results and Discussion

5.4.1 CPC Adsorption on Silica Powder

The adsorption isotherms for CPC at the investigated temperatures are shown in Figure 5.2. The adsorption isotherms for both 20 °C and 50 °C are sigmoidal starting from very low surfactant concentration exhibiting monolayer adsorption of the surfactant in region I until an equilibrium surfactant concentration of ~ 0.1 mM where the isotherm moves to region II Admicelle formation in region II develops as surfactant concentration increased until the equilibrium surfactant concentration reached ~ 0.35 mM. After that, the slope of the isotherm reduced as adsorbing molecules must overcome electrostatic repulsion between the oncoming

ions and similar charged silica surface [2]. The plateau adsorption, region IV, was reached at surfactant concentration ~ 0.8 mM as considered as the CMC of CPC – close to CMC of 0.91 mM reported elsewhere [14].

Table 5.2 Amount of adsorbed CPC on silica in CPC adsorption region II and III (just before plateau adsorption) for adsolubilization studies at 20 and 50 °C.

Temperature (°C)	Adsorbed amount of CPC (μmol/g silica)	
	Region II	Region III
20	216±2	275±3
50	213±2	235±3

5.4.2 Adsolubilization of Diphenylmethane

Figure 5.3 shows the graph of K_p-X_{ia} for the adsolubilization of diphenylmethane in CPC admicelles for region II and region III surfactant adsorption at 20 °C and 50 °C. All studied partition coefficients K_p gradually increased and become approximately constant with increasing X_{ia}. This implies that at low X_{ia}, diphenylmethane was preferentially adsolubilized into the core region. Hydrophobic compatibility plays a vital role in this step. After that, when X_{ia} increased, the core region tends to be saturated and solute partition at palisade region possibly becomes more distinct due to cation-π interaction between diphenylmethane and cationic headgroup of surfactant.

The partition coefficients for region III are lower than those for high region II at both temperatures. If we consider the surfactant/solute compatibility, diphenylmethane which possesses very low aqueous solubility indicating its high hydrophobicity would prefer, in theory, partitioning into hydrophobic core of the admicelles for region III, which is consistent with the trend of K_p-X_{ia} curves. However, as observed, K_p for region III is lower than that for high region II, thus the effect of surfactant packing density in the admicelles must be accounted for. Lowering the packing density of surfactant molecules in admicelles increases K_p [9, 15]. This is consistent with results of the looser packed surfactant molecules in the

admicelles at the high region II. However, in reality, this looser packing also allows more water molecules to penetrate into the admicelle interior [16], that is, palisade region expands toward the admicelle core as the transition from region III to high region II occurs. This should inhibit the adsolubilization of nonpolar diphenylmethane. It is thus suggested that even though the core region is looser in region II than in region III, the hydrophobicity of the core is still maintained; apparently allowing insignificant amounts of water molecules to penetrate into the core, while the distance between surfactant molecules incorporating in the admicelles increased.
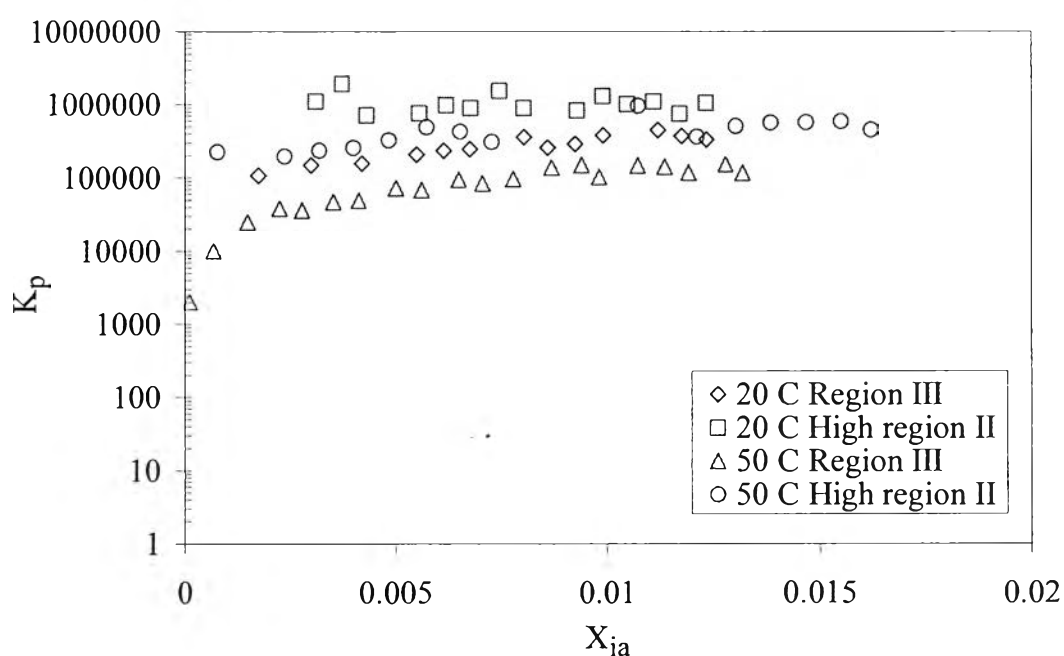

Figure 5.3 K_p-X_{ia} Correlation of adsolubilization of diphenylmethane in CPC admicelles for surfactant adsorption (high) region II and region III at 20 °C and 50 °C.
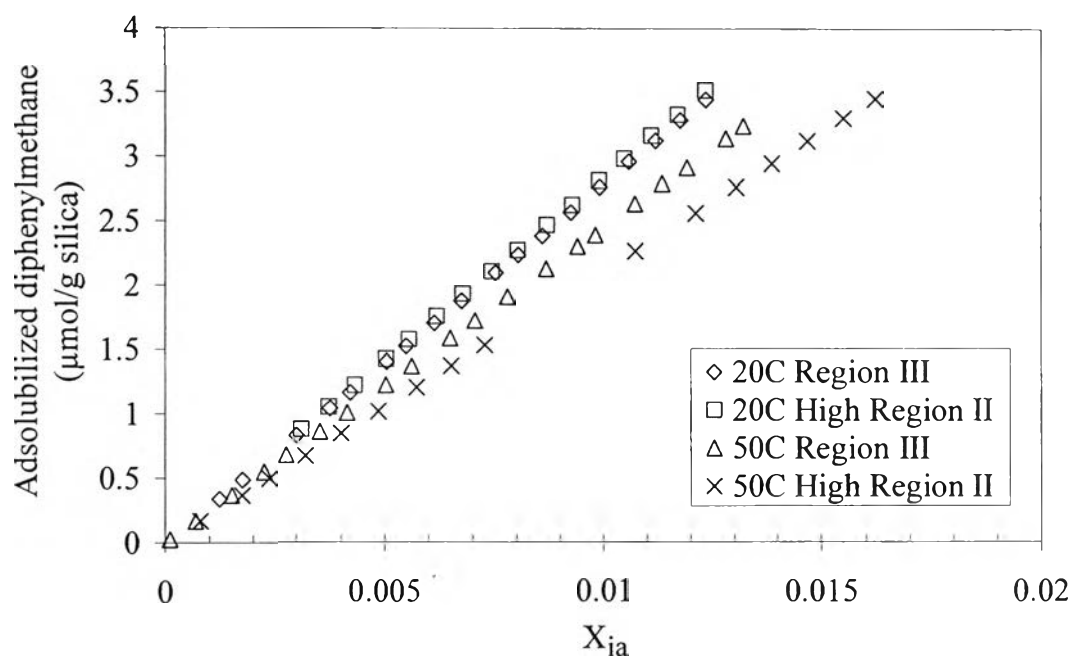
Figure 5.4 Correlation between the adsolubilized amount of diphenylmethane in CPC admicelles and X_{ia} for surfactant adsorption (high) region II and region III at 20 °C and 50 °C.

Figure 5.4 represents the plot of the amount of adsolubilized diphenylmethane in CPC admicelles against X_{ia}. At 50 °C, it was found that the curve of the adsolubilized amount of diphenylmethane in CPC admicelles vs X_{ia} for the high region II and region III shows the adsolubilized amount of diphenylmethane / g silica for high region II is lower than that for the region III at the same X_{ia}. This is normal case for which smaller amount of admicelles adsolubilizes smaller amount of solute. However, at 20 °C the curve of the adsolubilized amount of diphenylmethane in CPC admicelles vs X_{ia} for the high region II and region III is almost the same, increasing surfactant adsorption did not help adsolubilizing larger amount of adsolubilized solute at these regions of high surfactant packing density (high region II and region III). It implies that the adsolubilizing ability of a surfactant molecule decreased as degree of surfactant adsorption increased. The reason behind this phenomenon should be denser packing density of surfactant molecules incorporating in admicelle inhibiting subsequent adsolubilization.

5.4.3 Adsolubilization of Diphenylether

The K_p-X_{ia} correlation of adsolubilization of diphenylether in CPC admicelles for surfactant adsorption (high) region II and region III at 20 °C and 50 °C is shown in Figure 5.5. All trends of these curves are similar to those of diphenylmethane adsolubilizaiton, that is, diphenylether is adsolubilized into both palisade and core regions of the admicelles; however, it prefers being adsolubilized into the core region of the admicelles. Moreover, the transition from the region III to high region II also produced the similar trend of K_p at the same X_{ia} as observed for the diphenylmethane adsolubilization, at both 20 °C and 50 °C. This implies that the surfactant packing density in the admicelles plays a dominant role in controlling driving force to transfer a diphenylether molecule from aqueous phase to the admicellar phase.
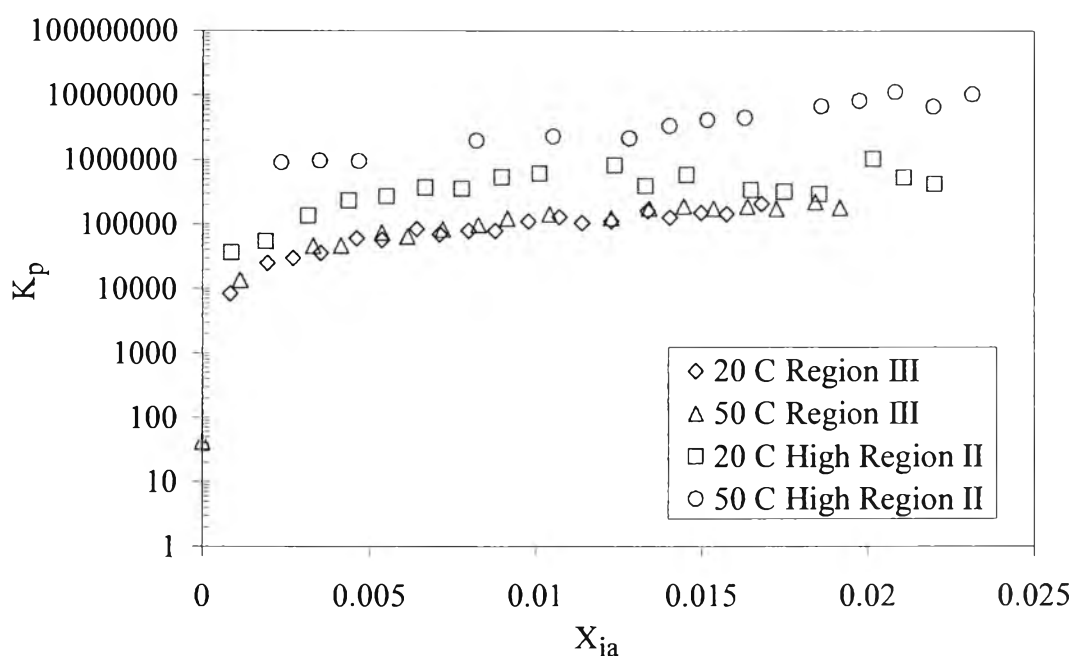

Figure 5.5 K_p-X_{ia} Correlation of adsolubilization of diphenylether in CPC admicelles for surfactant adsorption (high) region II and region III at 20 °C and 50 °C.

Figure 5.6 shows the correlation between the adsolubilized amount of diphenylether in CPC admicelles and X_{ia} for surfactant adsorption (high) region II and region III at 20 °C and 50 °C. The adsolubilized amount of diphenylether at both 20 °C and 50 °C, K_p for high region II is lower than K_p for region III. This result is similar to that of diphenylmethane adsolubilization at 50 °C, that is, as normal case, increasing in adsorbed surfactant from high region II to region III enhances the amount of adsolubilized solute.
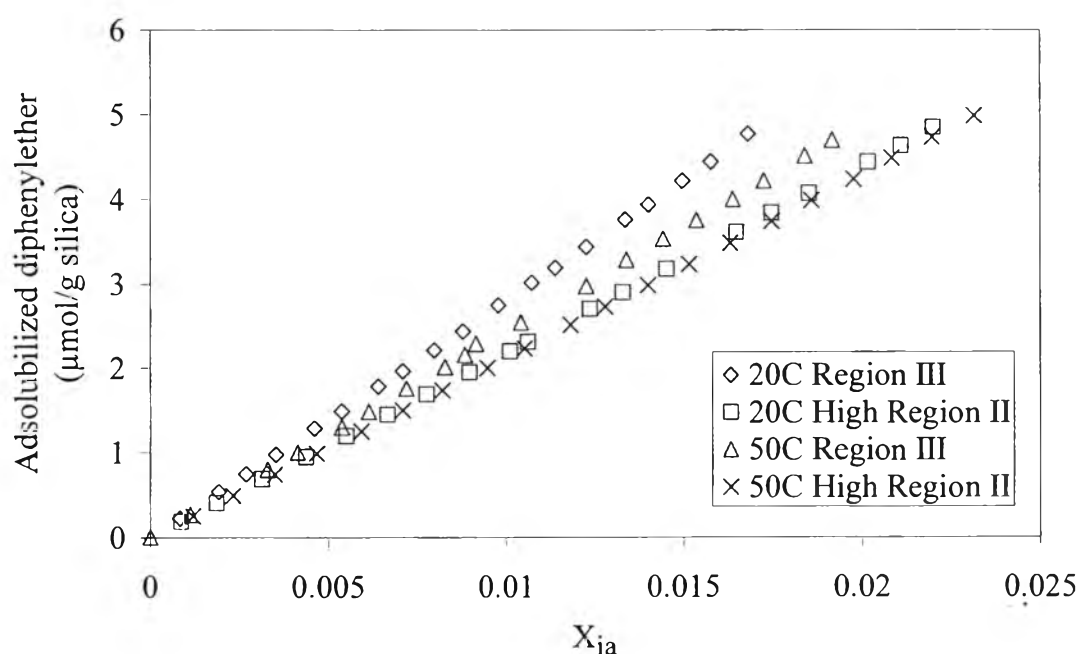

Figure 5.6 Correlation between the adsolubilized amount of diphenylether in CPC admicelles and X_{ia} for surfactant adsorption (high) region II and region III at 20 °C and 50 °C.

In addition, increasing surfactant adsorption at 20 °C has noticeably stronger affect on the amount of adsolubilized diphenylether than that of diphenylmethane. It could be due to additional effect from an additional dipole-dipole attraction between the surfactant headgroup and the highly electronegative segment (oxygen atom between two benzene rings in diphenylether molecular structure) combined with cation-π and hydrophobic interactions between aromatic

rings of solute and cationic surfactant headgroups – diphenylmethane possesses only the last two interactions [5]. This additional force is possibly strongly promoted by an increase in the positive charge density in the vicinity of surfactant headgroup/palisade region as surfactant packing density in admicelle is increased when surfactant adsorption goes from high region II to region III. As a result, it implies that the effect from this strong attraction overcomes the opposite impact of an increase in surfactant packing density as surfactant adsorption goes from high region II to region III retarding subsequent adsolubilization (as also seen in the case of diphenylmethane at 20 °C).
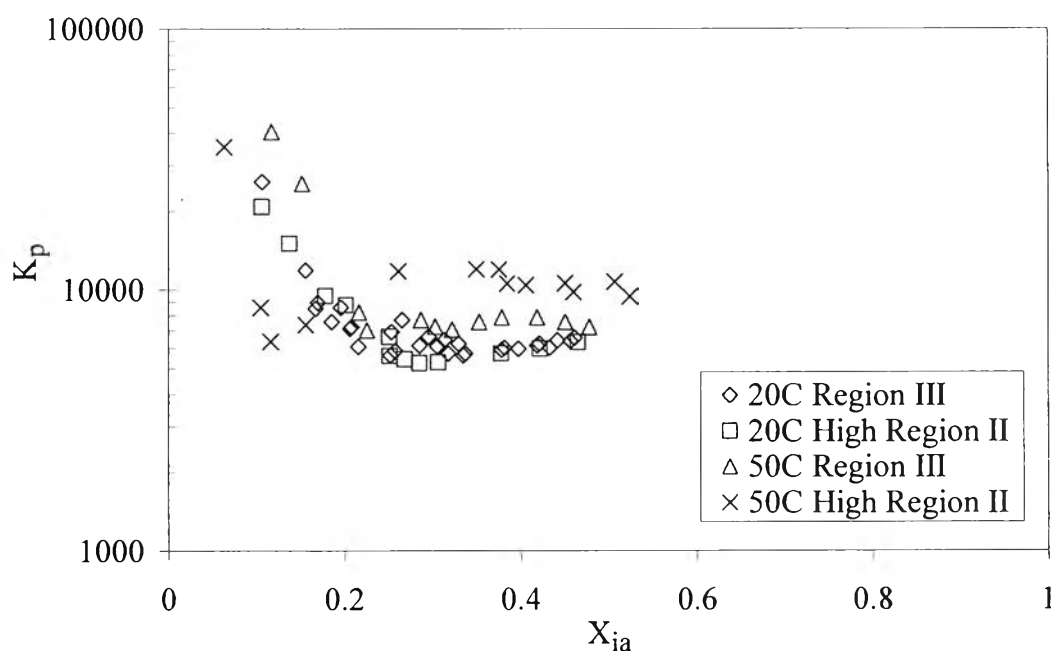

Figure 5.7 K_p-X_{ia} Correlation of adsolubilization of p-tolunitrile in CPC admicelles for surfactant adsorption (high) region II and region III at 20 °C and 50 °C.

5.4.4 Adsolubilization of p-Tolunitrile

The K_p-X_{ia} correlation of adsolubilization of p-tolunitrile in CPC admicelles for surfactant adsorption (high) region II and region III at 20 °C and 50 °C is shown in Figure 5.7. For all curves, initially K_p decreased as X_{ia} increased, then K_p tends to nearly unchanged or gradually increase as the X_{ia} increased latterly. This

means p-tolunitrile is primarily adsolubilized into the palisade region initially, then the palisade region may reach solute saturation and the subsequently adsolubilized p-tolunitrile tends to partition at the core region as X_{ia} increased. At 20 °C, K_p of the high region II and region III is close to each other at the same X_{ia} meaning that the transition of surfactant adsorption from high region II to region III does not affect the driving force for transferring a p-tolunitrile molecule from aqueous phase to admicellar phase. The phenomenon at 50 °C is more complicated. K_p for high region II is lower than that for region III at low X_{ia} until $X_{ia} \sim 0.2$. After that as X_{ia} increased, K_p for high region II becomes higher than that for region III. This indicates that the admicelles for high region II and region III existing at $X_{ia} \sim 0.2$ have the same microenvironment in the admicellar phase conductive to p-tolunitrile at 50 °C. The lower of K_p for high region II than that for region III is possibly due to the weaker positive charge density in vicinity of the admicelle/water interface and the palisade region – lower packing density of surfactant cationic headgroups at the admicelle/water interface which can attract to the π-electrons of the p-tolunitrile. This effect tends to disappear as X_{ia} increases because those positive charges are neutralized (at $X_{ia} \sim 0.2$). After this point, the surfactant packing argument is favorably taken into account, that is, K_p for high region II is higher than that for the region III because the surfactant molecules for high region II are packed in the admicelles looser than those for the region III.

Figure 5.8 shows the correlation between the adsolubilized amount of p-tolunitrile in CPC admicelles and X_{ia} for surfactant adsorption (high) region II and region III at 20 °C and 50 °C. At 50 °C, the curves for the adsorption (high) region II and region III are similar exhibiting that increasing amount of adsorbed surfactant did not increase amount of adsolubilized solute. It also implies that the ability of a surfactant molecule to adsolubilized diphenylmethane for high region II may be higher than that for region III at 50 °C. Nevertheless, subsequent adsolubilization was inhibited by an increase in surfactant packing density in admicelle as surfactant adsorption increased.

At 20 °C, it was found that the curve of the adsolubilized amount of p-tolunitrile in CPC admicelles vs X_{ia} for the high region II and region III shows the adsolubilized amount of p-tolunitrile / g silica for the high region II is lower than that

for the region III at the same X_{ia}. This phenomenon indicates that increasing in adsorbed surfactant from high region II to region III enhances the amount of adsolubilized p-tolunitrile. Additionally, it would be weakly controlled by the surfactant packing density.
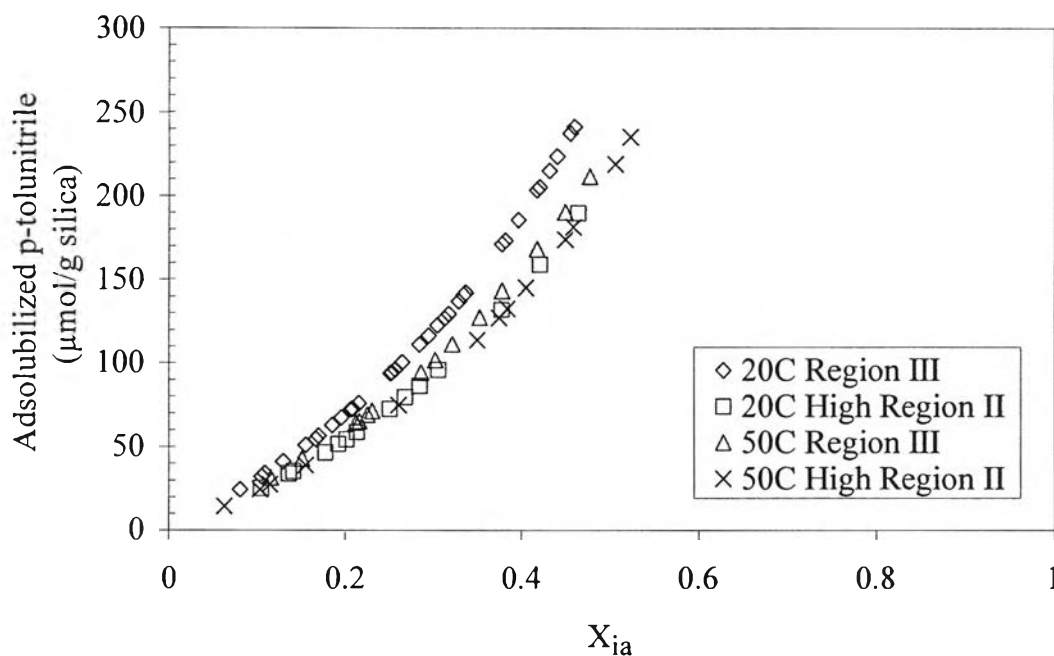

Figure 5.8 Correlation between the adsolubilized amount of p-tolunitrile in CPC admicelles and X_{ia} for surfactant adsorption (high) region II and region III at 20 °C and 50 °C.

5.5 Conclusions

The different adsolubilization properties of CPC admicelles in the surfactant adsorption (high) region II and region III have been investigated through the adsolubilization of aromatic solutes, i.e. diphenylmethane, diphenylether and p-tolunitrile. It was concluded that (1) highly hydrophobic solutes, i.e. diphenylmethane and diphenylether, prefer partitioning into the admicelles in high region II (than that in the region III) at both 20 °C and 50 °C, (2) a preference of surfactant adsorption region (high region II and region III) for adsolubilization of hydrophilic p-tolunitrile would be governed by cation-π and dipole-dipole attractive

forces or surfactant packing density in admicelle, (3) ability of a surfactant molecule to adsolubilize solute would be primarily controlled by attractive interaction between solute and surfactant molecules or surfactant packing density in admicelle and (4) even the core region is loosen when surfactant adsorption transits from region III to high region II, the hydrophobicity of the core should be still maintained; apparently allowing insignificant amount of water molecules to penetrate into the core, while the distance between surfactant molecules incorporating in the admicelles increased.

5.6 Acknowledgements

5.7 References

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