



CHAPTER IV

TEMPERATURE EFFECTS ON ADSOLUBLIZATION OF AROMATIC SOLUTES PARTITIONING TO DIFFERENT REGIONS IN CATIONIC ADMICELLES *

4.1 Abstract

This study examines the effect of temperature on the adsolubilization partition coefficient of sparingly soluble organic solutes. The adsolubilization of diphenylmethane, diphenylether, 4-bromotoluene and p-tolunitrile into cetylpyridinium chloride admicelles adsorbed on precipitated silica at pH of 8 were examined. The investigated adsolubilization temperatures were 20, 35, 50 and 65°C. Lowly polar solutes, i.e. diphenylmethane, diphenylether and 4-bromotoluene, are mainly adsolubilized into the admicelle core region. The partition coefficients of diphenylmethane and 4-bromotoluene are mainly controlled by the aqueous solubility of the solute. Specifically, the partitioning of diphenylether is perhaps additionally affected by the stronger negative charge in the vicinity of oxygen atom of diphenylether binding on the highly dissociated cationic CPC headgroups. Highly polar solute, p-tolunitrile is preferentially adsolubilized at the palisade and/or headgroup regions of the cationic admicelles. Its partitioning in the admicelle is possibly governed by the competitive factors between surfactant packing density in the admicelle and its aqueous solubility depending on the intra-admicelle mole fraction of p-tolunitrile.

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4.2 Introduction

The formation of aggregates by surfactant adsorbed at the solid/liquid interfaces has been well studied for decades [1]. The nature of these aggregates is much like that of micelles, thus these aggregates have thus been termed admicelles (adsorbed micelles) [1, 2]. As with micelles, admicelles can solubilize various kinds of sparingly soluble solutes in a phenomenon called adsolubilization. Numbers of its potential applications have been proposed and developed to date, including chemical separations [3, 4], semiconductor fabrication [5, 6], surface modification [7-11], drug delivery [12] and soil remediation [13].

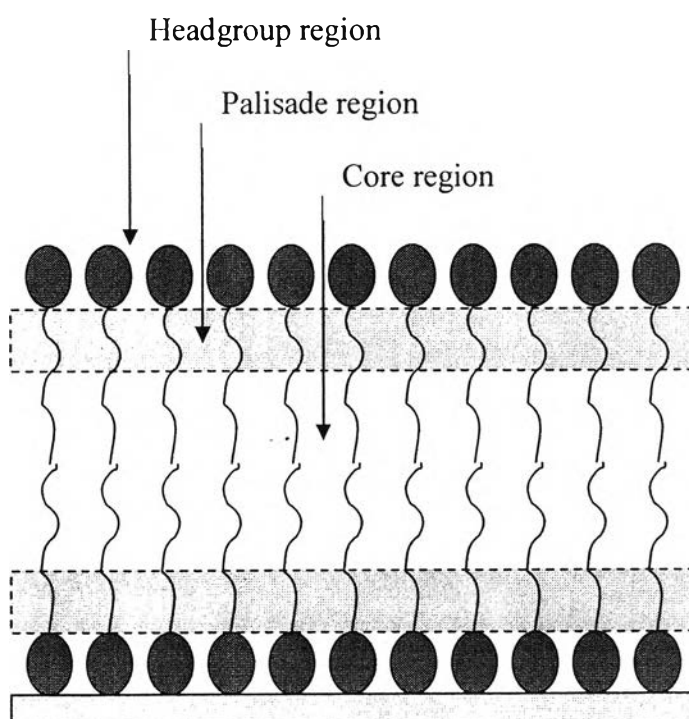


Figure 4.1 Schematic model of infinite bilayer admicelle. Polar solutes are expected to primarily partition within the palisade and headgroup regions, while less polar solutes would primarily partition in the core.

Figure 4.1 illustrates admicelle structure. Similar in nature to a micelle, the admicelle is characterized by three regions [14]. The outer region, consisting of the

surfactant headgroups, is the most polar and forms the admicelle/water and admicelle/solid interfaces. The inner region is referred to as the core region. This region consists of the hydrocarbon chains and is non-polar in nature. The region between the headgroups and the core is the palisade region. This region is intermediate in polarity, consists of the carbons near the headgroups, and is also characterized by water molecules that have penetrated the admicelle. Various studies have indicated that organic solutes partition into the regions of the admicelle that possess similar polarity. Thus, alkanes or other nonpolar solutes partition primarily to the core region, while polar components partition to the palisade region and the headgroup region. Partition coefficients have been used to elucidate the locus of adsolubilization in admicelle. The following trends have been proposed concerning the locus of adsolubilization and partition coefficients [14-17]: (1) if the solute partitions primarily to the core, the partition coefficients will increase as the intra-admicellar mole fraction of the solute increases; (2) if the solute partitions primarily to the palisade region, the partition coefficients will decrease as the intra-admicellar mole fraction of the solute increases; and (3) if the solute partitions to both the core and the palisade, the partition coefficient will remain constant as the intra-admicellar mole fraction of the solute increases.

A majority of the work done to date has examined the effects of various system parameters on the maximum amount of adsolubilized solutes. These have included studies of the effects of solute polarity, surfactant type, solution pH, solution ionic strength and solid substrate on adsolubilization [1, 18]. The results have indicated that the maximum amount of a solute adsolubilized can be altered by controlling the amount of surfactant present at the solid/liquid interface as well as the structure of the adsorbed layers and the chemical conditions of the solution. To-date, most of these studies has been conducted at ambient temperature. However, to undergoes corresponding reactions, some of the applications such as admicellar polymerization have to be performed at higher temperatures [2, 7-11, 16, 19] which will change equilibrium of both surfactant adsorption and adsolubilization. Because it is still lack of information about temperature effect on adsolubilization, this study therefore aims to investigate the impact of temperature on the ability of the admicelle to adsolubilize various sparingly soluble solutes possessing different polarities. The

studied solutes were neutral and organic. This study will provide insight into changes in adsolubilization as a function of changing system temperature.

4.3 Materials and Methods

4.3.1 Materials

Precipitated silica, Hi-Sil[®] 233, with a specific surface area of 150 m²/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), 4-bromotoluene (99+ wt%) from Fluka (St. Louis, MO) and p-tolunitrile (98+ wt%) from Fluka (St. Louis, MO) as shown in Table 4.1 with their useful physicochemical properties [20]. 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.

Table 4.1 Physicochemical properties of the studied solutes at 25 °C [20].

| Solutes | Chemical Formula | Aqueous Solubility at 25 °C (mol/L) | Melting Point (°C) | Boiling Point (°C) | Dipole Moment (Debye) |
|-----------------|-----------------------------------|-------------------------------------|--------------------|--------------------|-----------------------|
| Diphenylmethane | C ₁₃ H ₁₂ | 8.381 x 10 ⁻⁵ | 25.2 | 264 | 0.26 |
| Diphenylether | C ₁₂ H ₁₀ O | 1.06 x 10 ⁻⁴ | 26.8 | 259 | 1.16 |
| 4-Bromotoluene | C ₇ H ₇ Br | 6.43 x 10 ⁻⁴ | 28.5 | 184 | 1.90 |
| p-Tolunitrile | C ₈ H ₇ N | 7.86 x 10 ⁻³ | 29.5 | 217 | - |

4.3.2 Experimental Procedures

4.3.2.1 *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, 35, 50 or 65 °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 $\lambda = 258$ nm [21] 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.

4.3.2.2 *Adsolubilization*

The adsolubilization isotherms have also been examined at 20, 35, 50 and 65 °C. The appropriate initial surfactant concentrations for the adsolubilization studies were determined from the adsorption isotherms. An “appropriate concentration” is one that equilibrates just below (~90% of) the critical micelle concentration (CMC), 0.91 mM [22], ensuring that (1) no micelles is present in the bulk solution and (2) near maximum surface coverage is achieved. The initial surfactant concentration was chosen for each temperature. 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 [14]. The

wavelengths used for analyzing diphenylmethane, diphenylether, 4-bromotoluene and p-tolunitrile were 262, 269, 248 and 272 nm, respectively [23]. 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 [14-17] 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

$$K_p = \frac{X_{ia}}{X_w} \quad (4.1)$$

between the intra-admicellar mole fraction of the solute to the solute concentration in the supernatant; aqueous bulk phase X_w .

4.3.2.3 Determination of Aqueous Solubility of Solutes

Excess amount of solute was added to 20 mL de-ionized water in a glass vial and then sealed and vigorously stirred at room temperature for 3 days. This aqueous solution was then brought into water bath with temperature controlling accuracy of $\pm 0.1^\circ\text{C}$. The solution has been kept in the water bath at desired temperature for 10 days prior to determining the amount of dissolved solute in the aqueous phase by UV spectrophotometry at wavelengths of 262, 269, 248 and 272 nm for diphenylmethane, diphenylether, 4-bromotoluene and p-tolunitrile, respectively.

4.4 Results and Discussion

4.4.1 Surfactant CPC Adsorption on Silica Powder

The adsorption isotherms for CPC at the investigated temperatures are shown in Figure 4.2. At the same equilibrium bulk concentration of CPC, the amount of adsorbed CPC decreased as the temperature increased from 20 to 65 °C. The

maximum (plateau) adsorbed amounts of CPC on silica were roughly 275, 255, 235 and 220 at 20, 35, 50 and 65°C, respectively. These results indicate the maximum adsorbed amount of CPC decreased with increasing temperature implying that the interaction between adsorbed CPC head group and silica surface and the attractive hydrophobic interactions between CPC tails were simultaneously reduced by the increase in temperature.

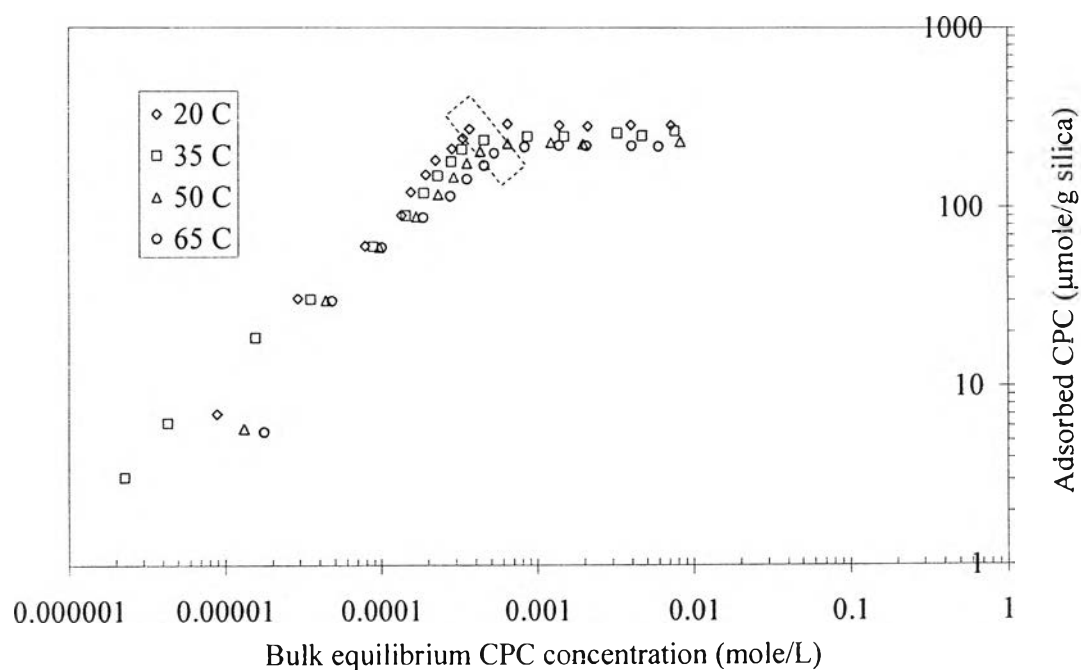


Figure 4.2 Adsorption isotherms of CPC surfactant on silica Hi-Sil[®] 233 at 20, 35, 50 and 65°C. The “boxed” area shows the CPC concentrations used for adsolubilization studies.

This is consistent with an increase in the CMC of CPC upon increasing temperature observed elsewhere [24]. The CPC concentrations selected for adsolubilization were in the region just before the plateau region (see Table 3.2). These CPC concentrations provide nearly complete coverage while insuring the absence of micelles.

Table 4.2 Amount of adsorbed CPC on silica in CPC adsorption region 3 (just before plateau adsorption) for adsolubilization studies at 20, 35, 50 and 65 °C.

| Temperature (°C) | Adsorbed amount of CPC ($\mu\text{mol/g silica}$) |
|------------------|--|
| 20 | 275 \pm 3 |
| 35 | 252 \pm 4 |
| 50 | 235 \pm 3 |
| 65 | 221 \pm 5 |

4.4.2 Adsolubilization

4.4.2.1 *Diphenylmethane*

Adsolubilization of diphenylmethane was investigated at only 3 temperatures, (20, 35 and 50 °C) to avoid fast vaporization during sampling at too high temperature (i.e. 65°C) (see Figure 4.3). Results show that as the intramicellar mole fraction of diphenylmethane monotonically increased, the partition coefficients increased linearly for all 3 temperatures. This is possibly due to expansion of the micelle, providing an environment that is increasingly favorable for the inclusion of more diphenylmethane molecules primarily in the core [17]. However, it has been observed that naphthalene which has similar molecular properties with diphenylmethane partitions primarily near the cationic surfactant headgroups (palisade) region in surfactant aggregates [14, 25-28] due to the cation- π interaction between naphthalene and cationic surfactant headgroups. As dipole moment of diphenylmethane is higher than that of naphthalene, we believed that diphenylmethane is dominantly solubilized into the core close to the palisade region of the micelles (solubilized diphenylmethane possibly still contact with penetrating water molecules) due to the relatively strong cation- π binding of this aromatic solute in the vicinity of the cationic CPC headgroups and additional dipole-dipole attractions. Figure 4.3 also indicates the impact of temperature on the partition coefficient. As the temperature increased from 20 to 35 °C, the partition coefficient did not change significantly. When the temperature increased from 35 to 50 °C, the

partition coefficient substantially decreased. This behavior is consistent with the temperature-dependency of benzene solubilization in CPC and SDS micelles [29].

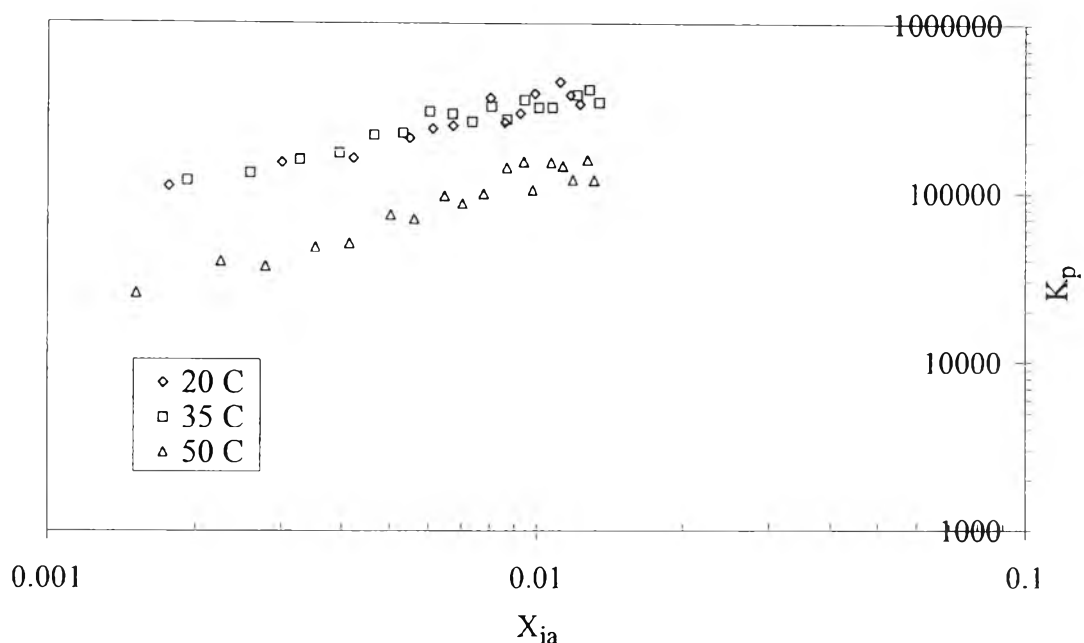


Figure 4.3 K_p - X_{ia} graph for the adsolubilization of diphenylmethane in CPC-Hi-Sil[®] 233 aqueous solution at 20, 35 and 50 °C.

To explain these temperature-dependences, one has to consider 2 possible factors affecting the partition coefficient: (1) an increase in the packing density of the admicelle will decrease the partition coefficient, as the tighter packing inhibits adsolubilization [14]. Increases in temperature decrease the surfactant aggregation number in the admicelle just as it does in micelles, implying a lower packing density [30]. This lower packing density can cause two opposing effects, an increased capacity due to looser packing, and a lower capacity for nonpolar solutes as the looser structure allows deeper penetration of water molecules. We would therefore expect increasing temperature to increase the partition coefficient of solutes that partition primarily into/near the palisade and headgroup regions and decrease the partition coefficient of those that partition only to the core. (2) On the other hand, solute hydrophilicity (aqueous solubility) changes with temperature. As the solubility of solutes increases, the chemical potential difference

between the solute molecules in the aqueous phase and that in the admicellar phase decreases, leading to decreases in the partition coefficient.

Considering those factors, we believed that the reason why the partition coefficients from 20 to 35°C did not change significantly is compensation between (1) the positive effect from reduction of the surfactant packing density providing more sites for diphenylmethane solubilization in/near palisade region, which is also promoted by increasing the degree of dissociation of surfactant headgroups and (2) the negative effect from an increase in solute aqueous solubility (see Figure 4.4) with the temperature increase.

For the change from 35 to 50°C, the change in the amount of adsorbed CPC per g silica (17 $\mu\text{mole/g}$ silica) is less than for the change from 20 to 35°C (23 $\mu\text{mole/g}$ silica). This smaller decrease in surfactant adsorption density while diphenylmethane aqueous solubility abruptly increased may suggest that the effect of packing density change is still insignificant. We therefore suggest that the abrupt decrease in the partition coefficient from 35 to 50°C is probably due to the increase in diphenylmethane aqueous solubility over this temperature range.

4.4.2.2 *4-Bromotoluene*

4-Bromotoluene behaved similarly to diphenylmethane as shown in Figure 4.5. The partition coefficient always increased with increasing intra-admicellar mole fraction of 4-bromotoluene indicating to preferential adsolubilization into the admicelle core. At the same intra-admicellar mole fraction, the change in partition coefficient is not sensitive to temperature changing from 20 to 35°C. However, as the temperature increased to 50°C, the partition coefficient reduced significantly, most likely as a result of the change in aqueous solubility (Figure 4.4).

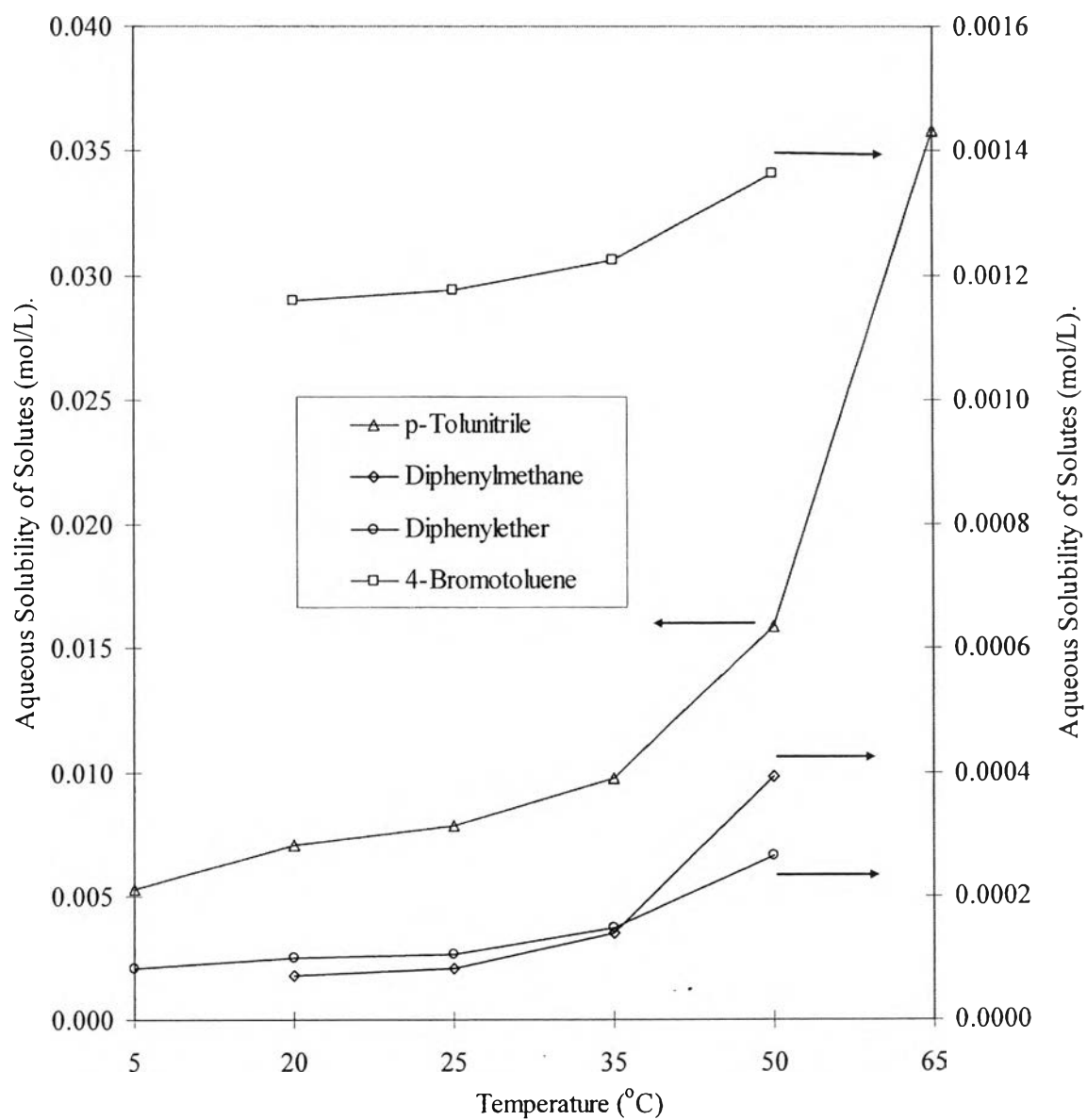


Figure 4.4 Aqueous solubility of the studied solutes at various temperatures.

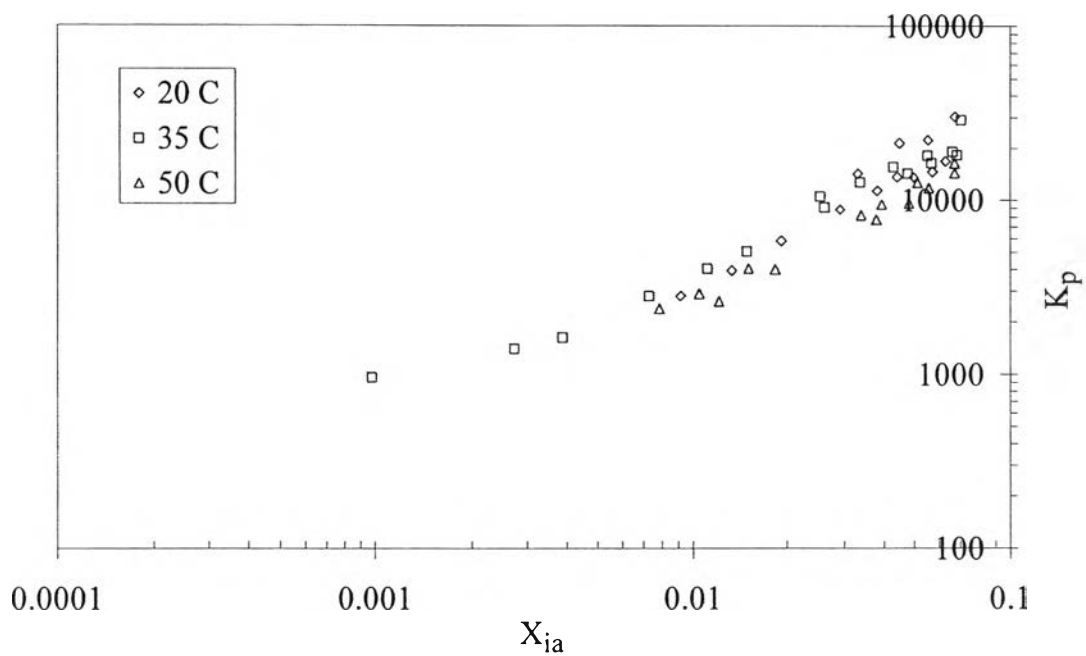


Figure 4.5 K_p - X_{ia} graph for the adsolubilization of 4-bromotoluene in CPC-Hi-Sil[®] 233 aqueous solution at 20, 35 and 50 °C.

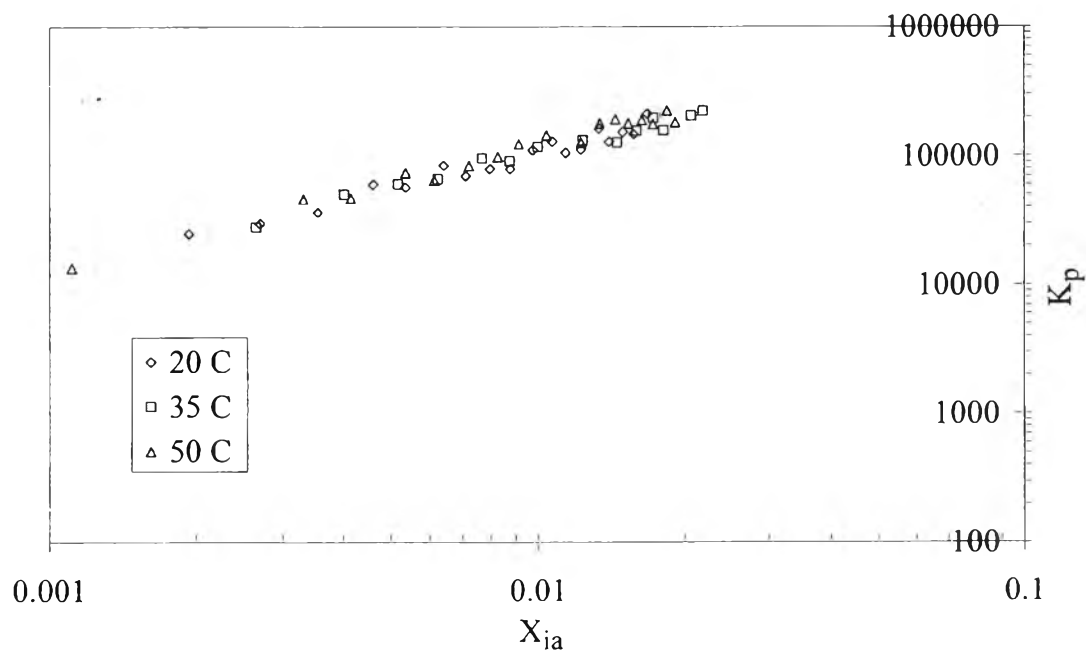


Figure 4.6 K_p - X_{ia} graph for the adsolubilization of diphenylether in CPC-Hi-Sil[®] 233 aqueous solution at 20, 35 and 50 °C.

4.4.2.3 Diphenylether

The partition coefficient of diphenylether versus its intramicellar mole fraction at various temperatures is shown in Figure 4.6. Similar to diphenylmethane, the partition coefficient increased with increasing intramicellar mole fraction, suggesting that diphenylether is preferentially adsorbed into the core region of CPC micelles and possibly near the palisade region due to higher dipole moment than diphenylmethane for all studied temperatures. However, the results anomalously show the temperature dependence of the partition coefficient is not clear. No significant change in the partition coefficient occurred as the temperature was varied from 20 to 35 to 50 °C while the aqueous solubility of diphenylether changed abruptly in the range of 35 to 50 °C (Figure 4.4). This insignificant change upon temperature increasing suggests some additional factors which are strong enough to compensate the negative effect caused by the increase of solute aqueous solubility, have to be considered (other than the hydrophobic interaction between diphenylether and surfactant tails and the cation- π binding as observed with diphenylmethane). We believe that additional solute/micelle attractions might come from dipole-dipole attraction between the cationic surfactant headgroup and highly electronegative oxygen atom segment of diphenylether which is not present in diphenylmethane. This also suggests that diphenylether is adsorbed more in the palisade region than diphenylmethane.

Accordingly, as temperature increased, the micelle would be loosening and the CPC headgroups would be more dissociated which would increase both attractive forces, the cation- π and dipole-dipole attractions, with diphenylether. The increase in both attractive forces simultaneously would promote the partitioning of diphenylether into the micelles and compensate for the negative effect on the partition coefficient from the increase of solute aqueous solubility. This additional effect of dipole-dipole interaction was also observed by AFM studying on CPC micelles on mica surface [31].

Compared with the adsorption of 4-bromotoluene which possibly resides in the same location in the micelles; although Br possesses rather high electronegativity, 2.96, its Br-C dipole bond has an electronegativity difference

of 0.41, which is half that of the O-C (0.89) in diphenylether [32]. Consequently, the effect of additional dipole-dipole attraction at the CPC headgroup is much weaker than that cause by diphenylether, and therefore could not compensate for increases in solute solubility for its case.

4.4.2.4 *p*-Tolunitrile

The adsolubilization of *p*-tolunitrile at 20, 35, 50 and 65 °C is illustrated in Figure 4.7. It indicates that the partition coefficient initially decreased with increasing intra-admicellar mole fraction of *p*-tolunitrile until it becomes nearly constant or slightly increasing at high intra-admicellar mole fractions. The decreasing in the partition coefficients at low intra-admicellar mole fraction points out that *p*-tolunitrile is mainly adsolubilized into palisade region and/or CPC headgroup region of the admicelles and is able to adsolubilize deeper into the admicelle when those hydrated regions are saturated, giving a slight increase in the partition coefficient at high intra-admicellar mole fraction.

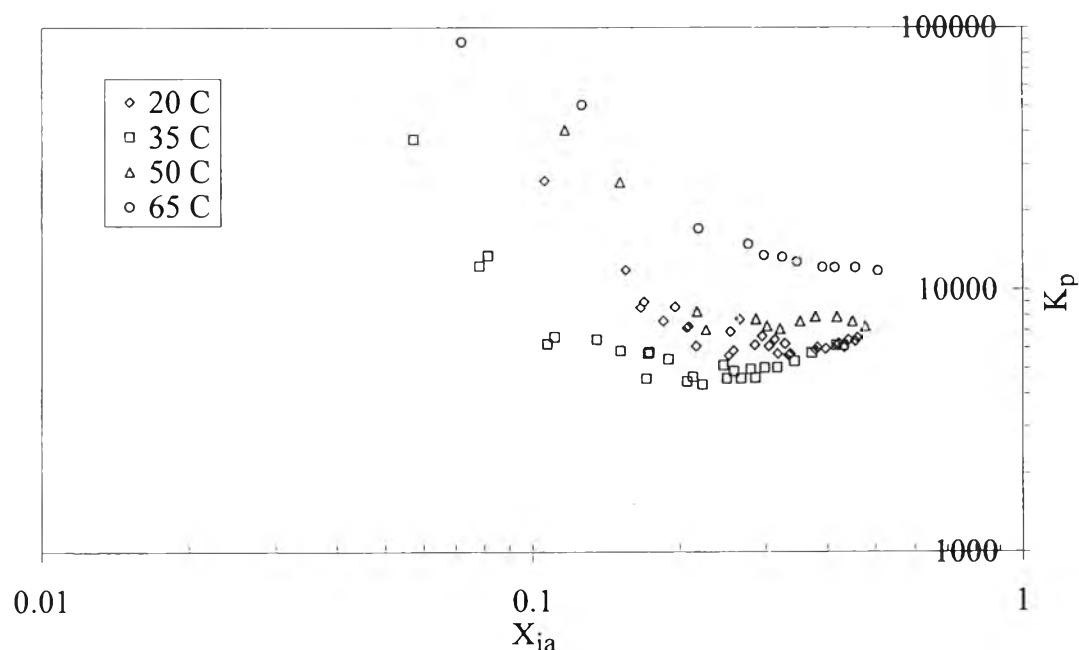


Figure 4.7 K_p - X_{ia} graph for the adsolubilization of *p*-tolunitrile in CPC-Hi-Sil[®] 233 aqueous solution at 20, 35, 50 and 65 °C.

The results clearly reveal the temperature dependence of the partition coefficients. Figure 4.7 demonstrates that the partition coefficients at $35 < 20 < 50 < 65$ °C for all studied ranges of the intra-admicellar mole fraction. The locus of adsolubilization for p-tolunitrile is near the CPC headgroup which should increase in effective area with increasing temperature. We suggest that two key factors affect the partition coefficient: (1) increasing aqueous solubility of p-tolunitrile with increasing temperature (Figure 4.4) reduces the partition coefficient while (2) a more loosely packed admicelles provides more volume or sites for p-tolunitrile adsolubilization and thus increase the partition coefficient. Therefore, the decreasing partition coefficient when the temperature goes from 20 to 35 °C is dominant due to the increase in the solubility, while the increase in the partition coefficients in the 35 to 50 to 65 °C range is probably governed by decrease in the packing density of surfactant molecules in the admicelle.

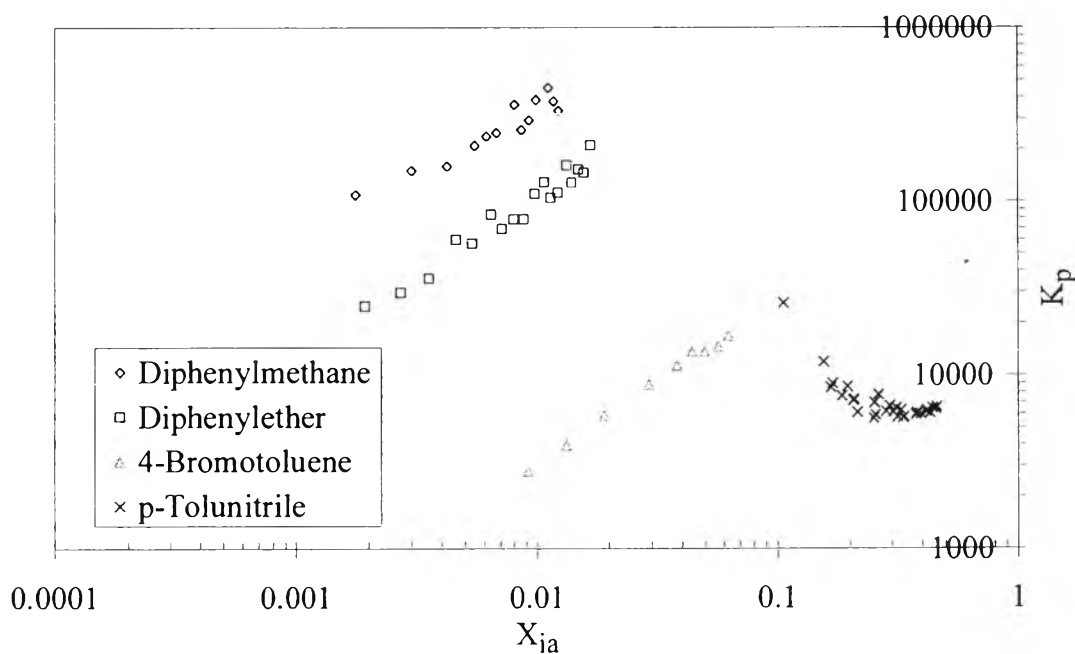


Figure 4.8 K_p - X_{ia} graph for the adsolubilization of diphenylmethane, diphenylether, 4-bromotoluene and p-tolunitrile in CPC-Hi-Sil[®] 233 aqueous solution at 20 °C.

Figure 4.8 compares the partition coefficients for all studied solutes. For the solutes mainly adsolubilizing at the core region, the magnitude of the partition coefficient of diphenylmethane > diphenylether > 4-bromotoluene. This order is consistent with the reversed order of the aqueous solubility of these solutes, revealing that solutes with lower polarity have higher “compatibility” with the admicellar interior. The partition coefficient of the solute mainly adsolubilized at the core region is not always higher than the solute mainly adsolubilized at palisade/headgroup region as can be seen with 4-bromotoluene and p-tolunitrile. That means the comparison of partition coefficient magnitude could not be considered from the solute aqueous solubility even though the solute locales in the admicelles are clearly different.

4.5 Conclusions

The adsolubilization of diphenylmethane, diphenylether, 4-bromotoluene and p-tolunitrile into cetylpyridinium chloride admicelles adsorbed on precipitated silica at pH 8 was studied. The adsolubilization temperatures were 20, 35, 50 and 65°C. Lowly polar solutes, i.e. diphenylmethane, diphenylether and 4-bromotoluene, are mainly adsolubilized into the admicelle core, possibly still close to the palisade region. The partition coefficients of diphenylmethane and 4-bromotoluene are mainly controlled by the aqueous solubility of the solute. Specifically, the partitioning of diphenylether is probably additionally affected by the stronger negative charge in the vicinity of oxygen atom of diphenylether binding on the highly dissociated cationic CPC headgroups. Highly polar solute, p-tolunitrile is preferentially adsolubilized at the palisade and/or headgroup regions of the cationic admicelles. Its partitioning in the admicelle is possibly governed by the competitive factors between surfactant packing density in the admicelle and its aqueous solubility depending on the intra-admicelle mole fraction of p-tolunitrile

4.6 Acknowledgement

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