CHAPTER VI
EFFECT OF ADSOLUBILIZED SOLUTES ON 2-D STRUCTURE OF CATIONIC ADMICELLES*

6.1 Abstract

The effect of adsolubilized solutes possessing different polarities and loci of adsolubilization on the two-dimensional structural transformation of cationic admicelles was studied. Cetylpyridinium chloride (CPC) was used to form admicelles on mica surfaces below its critical micelle concentration (~80% of CMC). The studied solutes include n-hexane, naphthalene, diphenylmethane, diphenylether, diphenylamine and 4,4′-bipyridine. In the presence of adsolubilization, it was concluded that both hydrophobic interactions and cation-π binding tend to induce cationic admicelle structural transformation from full-cylinders to bilayer. There is evidence that the effect of the hydrophobic interactions is possibly stronger than the cation-π binding. In addition, the influence of adsolubilized solutes (in the same molecular series) on the admicelle structure should be examined by comparing solute dipole moment instead of solute aqueous solubility.

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6.2 Introduction

I n 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 and they 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. Various areas involving adsolubilization have been examined to date, including chemical separation [3, 4], semiconductor [5, 6], surface modification [7-11], drug delivery [12] and soil remediation [13].

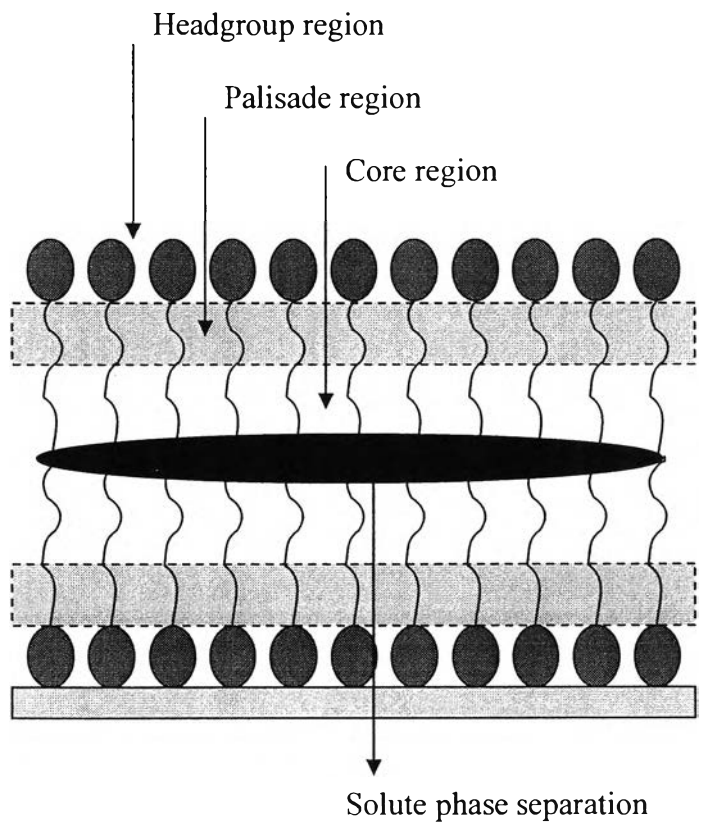

Figure 6.1 T ypical model of an extensive admicelle bilayer with solute phase separation. Polar solutes are expected to primarily partition within the palisade and headgroup regions, while less polar solutes would primarily partition in the core. The solute phase separation may exist for some highly hydrophobic solutes at high solute concentration.

The admicelle provides three main regions for adsolubilization [14]; i.e. surfactant headgroup, palisade and core regions, and where a solute partitions is dependent upon the physicochemical compatibility between each region and the adsolubilized solute as shown in Figure 6.1. The headgroup, palisade and core regions typically accommodate the partition of solutes possessing high, medium and low polarity, respectively. At very high solute concentration, some hydrophobic solutes may demonstrate phase separation in admicelles [15] as also seen in micelles [16, 17].

The solution-side structure of admicelle at solid/liquid interface can be directly imaged by atomic force microscopy (AFM), which has revealed various shapes of admicelles [18-24]. On hydrophobic surfaces, e.g. graphite, surfactant adsorbs as half-spherical, half-cylindrical or monolayer admicelle, while on hydrophilic surfaces (silica and mica) surfactant adsorbs as full-spherical, full-cylindrical and bilayer admicelles depending upon surfactant type, surfactant structure, surfactant concentration, additives and solution properties. As with micelles, admicelle shape is mainly controlled by intermolecular forces among surfactant molecules in the admicelle, with additional influence from surfactant-solid surface interactions, which provide different admicelle shapes [23, 24].

Admicelle shapes have been observed playing key roles in adsolubilization potential because the shape determines the packing density of surfactant molecules in admicelles which results in different potential to solubilize sparingly organic solutes [14, 25]. The influences of ionic additives, i.e. counterions and co-ions, interacting with surfactant ionic headgroups, have been studied. The results provide well-understood concepts of admicelle structural transition [20]. For aromatic solutes, the adsolubilization of naphthalene and naphthols in cationic admicelles cause the admicelle to transform to a form with a lower admicelle/water interfacial curvature, e.g. full-cylinders $\rightarrow$ featureless bilayer [25]. It was shown that admicelles with lower interfacial curvature have lower adsolubilization capacities, believed to be caused by denser packing of surfactant molecules in the admicelles [14]. Styrene adsolubilization affecting the admicelle structure was also recently studied by our group [15]. The incorporation of styrene induced the structure of $C_{16}TAB$ admicelles in the same manner as naphthalene and naphthol did. The admicelle structural

transition due to the incorporation of these aromatic molecules is thought to be governed by the cation-π binding in vicinity of the cationic surfactant headgroups. n-Alcohols partitioning into cationic admicelle immediately transform the admicelle structure from lower to higher admicelle/water interfacial curvature in contrast to aromatic adsolubilization [26].

This study aims to elucidate the effect of polarity and localization of organic solutes partitioning into the cationic admicelles on the admicelle structural transformation interpreted via AFM. The surfactant concentration for admicelle formation without pH-adjustment was kept below the CMC to avoid a competitive effect from micellar solubilization. The results will also provide the insight in the nature of electrostatic and hydrophobic interactions between solute and surfactant molecules in the admicelles.

6.3 Materials and Methods

6.3.1 Materials

Mica discs was purchased from Ted Pella, Inc. (Redding, CA) and used as the solid substrate. The mica disc was freshly cleaved just before use. The cationic surfactant cetylpyridinium chloride (CPC) monohydrate 99+% was obtained from Sigma (St. Louis, MO). The studied solutes are n-hexane 99% (Fluka, St. Louis, MO), naphthalene 99+wt% (Sigma, St. Louis, MO), diphenylmethane 99+wt% (Aldrich, St. Louis, MO), diphenylether 99+wt% (Aldrich, St. Louis, MO), diphenylamine 98+wt% (Fluka, St. Louis, MO) and 4,4′-bipyridine 99% (Riedel-deHaën, Seelze). De-ionized water with a resistivity of 18.2 MΩ-cm was obtained from a Barnstead E-pure water system. All chemicals were used as received.

6.3.2 Experimental Procedures

6.3.2.1 Sample Preparation

An aqueous CPC solution of 0.72 mM (80% of its CMC, 0.91 mM [27]) was prepared with no pH adjustment. The surfactant solution was then mixed with solute. The studied solute concentrations in the surfactant solution are shown in Table 5.1 [28, 29]. Most of them are at their aqueous solubilities.

Table 6.1 Physicochemical properties of studied solutes at 25°C

Solute	Aqueous solubility [28] (mol/L)	Dipole moment [29] (D)	Liquid volume [29] (cm^3/mol)
n-Hexane	1.10×10^{-4}	0	131.3
Naphthalene	2.34×10^{-4}	0	130.8
4,4'-Bipyridine	2.90×10^{-2}	-	141.0
Diphenylmethane	8.38×10^{-5}	0.26	167.8
Diphenylether	1.06×10^{-4}	1.16	160.8
Diphenylamine	3.13×10^{-4}	1.08	159.7

6.3.2.2 Atomic Force Microscopy

Atomic force microscopy was performed using a multimode scanning probe microscope with E-scanner controlled by Nanoscope IIIa (Veeco Instruments, NY). The experiment was conducted in contact mode directly imaging in the aqueous solution. The imaging method was to use the double layer (or steric) repulsion between the AFM tip and adsorbed surface layer by "flying" the tip over the adsorbed layer on the mica surface [18-21]. Silicon nitride model NP cantilever (Veeco Instruments, NY) with a nominal spring constant of 0.06 N/m was used. It was cleaned with methanol and de-ionized water and then dried prior to use.

For observation of initial admicelle structure, the mica disc was freshly cleaved and mounted on a metal disc. The metal disc was then mounted on top of the scanner and the fluid cell placed on top. A prepared aqueous solution was then placed on the mica disc by injection through the fluid cell port. The system was allowed to equilibrate thermally for 10 minutes before imaging.

To investigate the equilibrium admicelle structure, the admicelle formation on mica surface was equilibrated in the surfactant-solute aqueous solution for 10 days in separate glass vials. The wet mica disc was then removed from the solution and mounted in the fluid cell along with the equilibrium aqueous solution in the vial.

Imaging processing used scan rates, integral gains, proportional gains and *z*-deflection ranges of 12-15 Hz, 0.15-0.3, 3 and 1-1.5 nm, respectively. All experiments were performed at room temperature (23°C). All images are raw deflection images that have been flattened along the scan lines to remove any tilt from the sample. No other image processing was used. Only key images were presented in this paper.

6.4 Results and Discussion

6.4.1 Surfactant Adsorption on Mica Surface

At a bulk surfactant concentration of 80% of CMC, the initial structure of the CPC admicelles on mica surface is ordered full-cylindrical aggregates (see Figure 6.2), similar to C_{16}TAB admicelles under similar conditions [15]. Even below the CMC, the admicelles covered the entire mica surface with no observed discontinuities. The center-to-center distance between the next nearest neighbor cylindrical aggregates was ~7 nm. This distance is close to a theoretical diameter of an admicelle, 6.84 nm, as equal to twice the fully extended CPC chain length. This chain length was calculated as a summation of (1) fully extended length of n-C_{16}, 2.174 nm [30] (2) twice molecular radius of gyration of pyridine for approximate surfactant headgroup length, 0.588 nm [29] and (3) the diameter of a hydrated Cl^- ion, 0.664 nm [31]. A close proximity between the theoretical admicelle diameter and the experimental center-to-center distance indicates that the admicelles are fairly tightly packed on mica surface and is consistent with the alignment of cylindrical admicelle structure obtained from molecular dynamic simulation [32].

After 10 days of equilibration, AFM images still showed the same surface pattern (full-cylindrical aggregates) and center-to-center distance. This equilibrium structure is different from the cationic C_{16}TAB admicelles (with the same alkyl tail as CPC but different headgroup) which is transformed from ordered full-cylindrical to featureless bilayer aggregates at equilibrium [15]. The unchanged structure of CPC admicelles is possibly stabilized by stronger electrostatic repulsive forces between CPC charged headgroups which is represented by lower degree of cation binding, 0.63 at 25°C, than 0.83 at 25°C of C_{16}TAB [33].

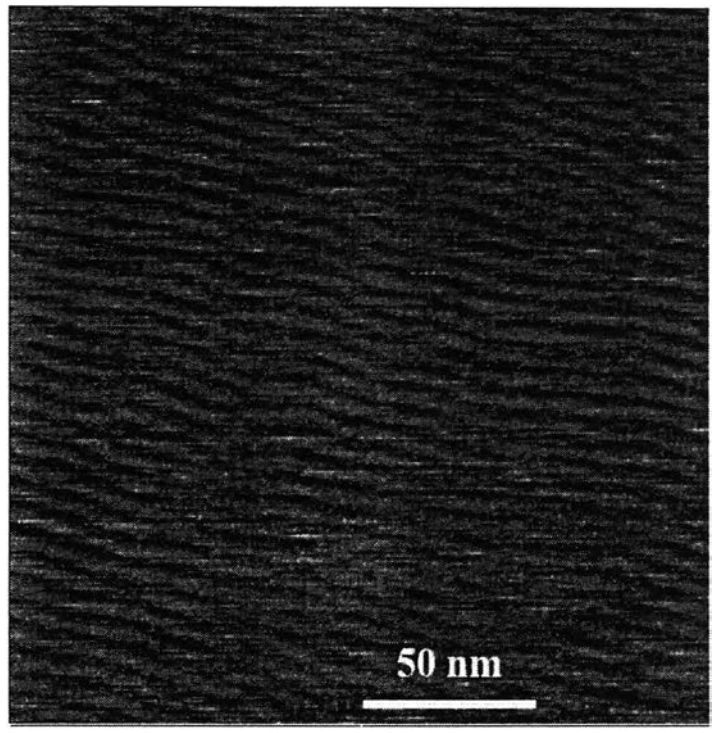

Figure 6.2 AFM micrograph of CPC admicelles on mica surface at an equilibrium concentration of 720 μM (a) and initial adsorption (< 1 hour).

6.4.2 Adsolubilization

6.4.2.1 Adsolubilization of n-Hexane

The adsolubilization of n-hexane was conducted at its aqueous solubility as shown in Table 6.1. The initial and equilibrium AFM topographic images of CPC admicelles in the presence of n-hexane are shown in Figure 6.3a-6.3c. The initial admicelle structure was observed as continuous, ordered full-cylindrical aggregates (Figure 6.3a). The admicelle structure was transformed to a featureless bilayer aggregates at equilibrium (Figure 6.3b). Because solubilized n-hexane normally resides in the core region of micelles [34], just hydrophobic interactions dominantly due to n-hexane/alkyl tail mixing is corresponded. It is thus suggested that the hydrophobic interaction induce the admicelle/water interfacial curvature from high to low value. At equilibrium, while most of the mica surface was covered by admicelles, discontinuous surface coverage was still observed (Figure 6.3c). Lower surface coverage observed in some areas is possibly due to a lowering

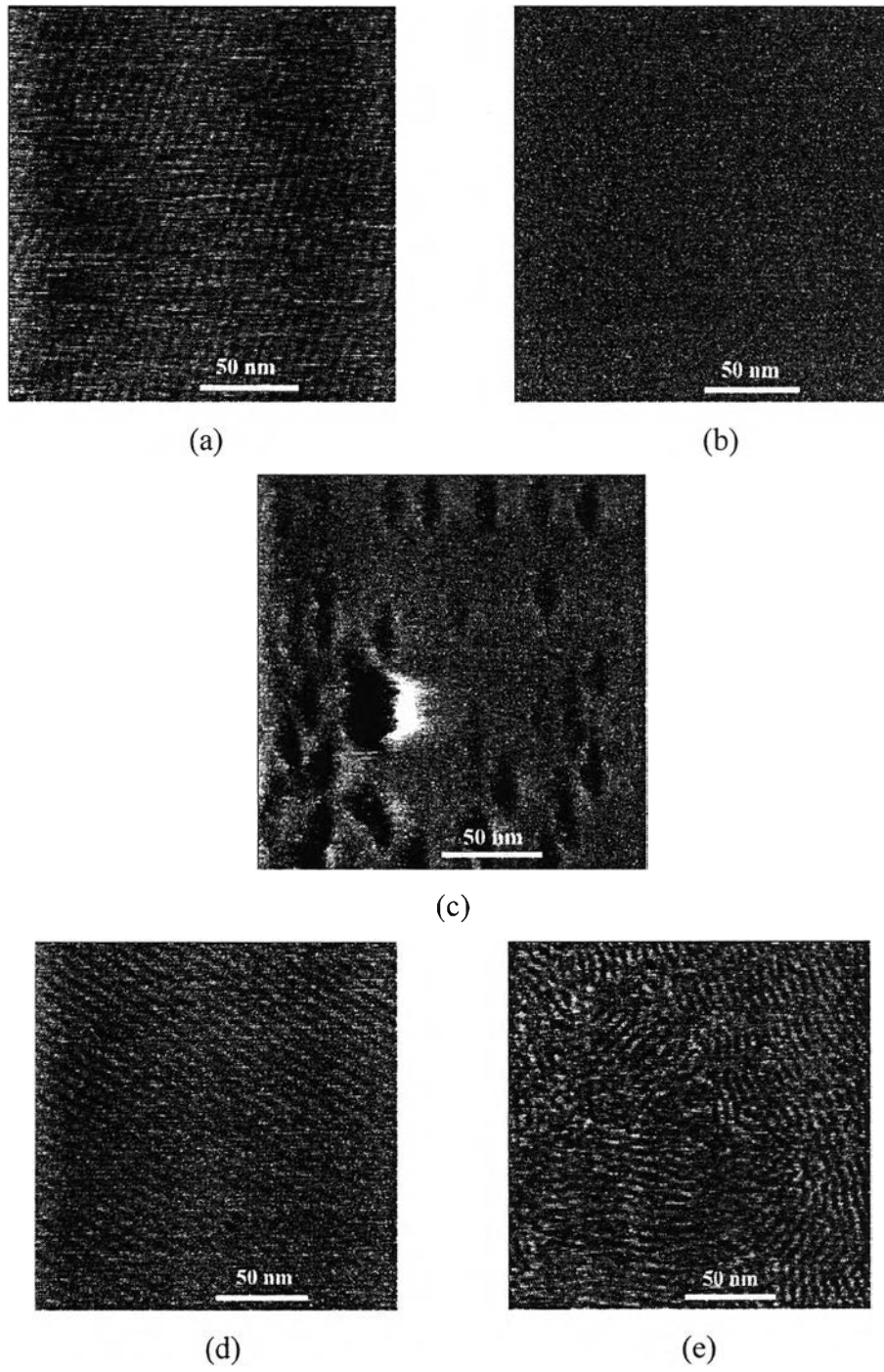

Figure 6.3 AFM micrograph of CPC admicelles solubilizing solutes, n-hexane or diphenylmethane, on mica in the corresponding solute/CPC aqueous solution. The total concentrations of CPC, n-hexane and diphenylmethane are 720 μM (below CMC), 110 μM and 83.8 μM, respectively. For n-hexane: (a) < 1 hour, (b) and (c) 10 days. The featureless surface shown in (b) dominated, with occasional patches like that shown in (c). For diphenylmethane: (d) < 1 hour and (e) 10 days.

of the aqueous bulk polarity at equilibrium leading to more favourable surfactant partitioning into aqueous bulk solution.

6.4.2.2 Adsolubilization of Naphthalene

Adsolubilization of naphthalene was performed at its aqueous solubility, about twice that of n-hexane. The liquid molar volume of naphthalene is nearly the same as that of n-hexane indicating similar molecular volumes (see Table 6.1). We will use this assumption in comparing the effect of the two on admicelle structure. The results show that the initial and equilibrium structures of admicelles solubilizing naphthalene are the same as the structure of the admicelles without any solute.

It has been observed that naphthalene partitions primarily near the cationic surfactant headgroups (palisade) region in micelles [35-38] and admicelles [14]. Basically, the negatively charge π-electrons of naphthalene will form the strong complex with the positively charged surfactant headgroups called cation-π binding [16] resulting in a reduction in surfactant headgroup-headgroup interaction leading to lower admicelle/water interfacial curvature. However, this effect was not observed for this case. That means that the CPC headgroup-headgoup electrostatic repulsive interaction is very strong enough to overcome the opposite effect of the cation-π binding. In comparison, this suggests that the effect of hydrophobic force on the admicelle structural transformation as observed with n-hexane is possibly stronger than the cation-π binding although total naphthalene concentration was higher than that of n-hexane.

6.4.2.3 Adsolubilization of 4,4′-Bipyridine

4,4′-Bipyridine, having molecular dimensions similar to naphthalene, was studied at two concentrations, (1) equal to the studied concentration of naphthalene (naphthalene aqueous solubility) and (2) at its aqueous solubility (~100 times of naphthalene aqueous solubility). Its polarity as shown from aqueous solubility is much higher than naphthalene. It was observed that at 4,4′-bipyridine concentration equal to the naphthalene solubility the structure of admicelles is unchanged after initial adsolubilization; ordered full-cylindrical aggregates which convert to a featureless bilayer at equilibrium. This suggests that a highly polar

solute may has higher potential to transform the admicelle structure at equilibrium. However, it is still not strong enough to make an immediate change in the admicelle structure. Compared with naphthalene, the reason behind this higher potential transformation should be the additional effect from highly concentrated negatively charge at the negative poles of 4,4′-bipyridine; that are, nitrogen atoms, binding with the cationic surfactant headgroups at the admicelle/water interface.

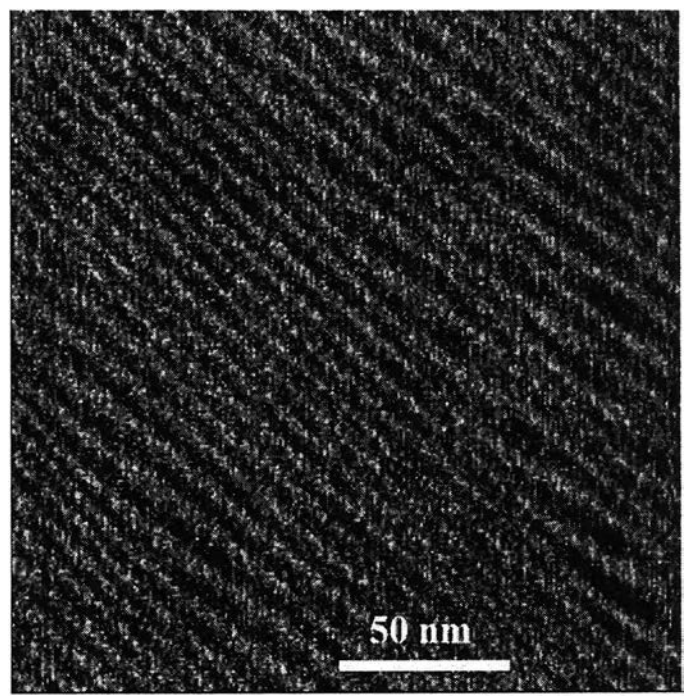

Figure 6.4 AFM micrograph of CPC admicelles solubilizing 4,4′-bipyridine in a 4,4′-bipyridine/CPC aqueous solution for adsolubilization time of 10-20 minutes. The total concentrations of CPC and 4,4′-bipyridine are 720 μM (below CMC) and 29000 μM (aqueous solubility of 4,4′-bipyridine).

At 4,4′-bipyridine concentration equal to its aqueous solubility, the structural transformation behavior of the admicelles was different. Initially after adsolubilization, the full-cylindrical admicelles were locally swollen (Figure 6.4), suggesting an uneven distribution of solute in the admicelles. Some parts of the admicelle have larger diameter than the diameter of normal full-cylindrical admicelles without the presence of solute, indicating pure solute phase is

formed in the admicelle at this initial stage. This phenomenon was observed at 10-20 minutes after adsolubilization. After that the admicelles were transformed to normal ordered full-cylindrical aggregates (with rather constant diameter) similar to the admicelles without the adsolubilized solute. The diameter of this admicelle seems rather equal to the diameter of the admicelle without solute. This means that pure solute phase separation in the admicelles disappears. The equilibrium admicelle structure was a featureless bilayer in the same manner of previous case.

6.4.2.4 Adsolubilization of Diphenyl Derivatives

The effect of solute polarity on admicelle structure was additionally studied by varying a series of diphenyl derivative solutes possessing different aqueous solubility and dipole moments, i.e. diphenylmethane, diphenylether and diphenylamine. Normally, molecular polarity is considered from the aqueous solubility or dipole moment of such molecule. Both properties generally change in the same direction for the same molecular series. However, in our studies, the aqueous solubilities of the solutes run diphenylmethane < diphenylether < diphenylamine, while the dipole moment are diphenylmethane < diphenylamine < diphenylether (see Table 6.1). The molecular volumes of these solutes are similar due to their similar molecular dimensions; therefore; the effect of occupied volume per molecule in admicelle will be neglected. The studied solute concentrations are their aqueous solubility. As with naphthalene, these molecules are expected to reside in the palisade region of the admicelle near the surfactant headgroups due to the cation-π binding.

For diphenylmethane, its aqueous solubility is lower than that of naphthalene implying higher hydrophobicity. It was found that immediately after adsorption/adsolubilization the admicelle structure was still ordered full-cylinders (Figure 6.3d). The alignment of these admicelles became more disordered when the adsolubilization reached equilibrium (Figure 6.3e). This equilibrium structure is an intermediate structure between full-cylinders and featureless bilayer as similarly observed in the structural transformation of C_{16}TAB admicelles due to styrene adsolubilization [15]. Compared with the case of naphthalene, diphenylmethane adsolubilization has a stronger effect on admicelle structural transformation. The

additional effect, other than the cation-π binding, is possibly created by a presence of $-CH_2-$ group between two phenyl groups in diphenylmethane molecular structure. This increases the molecular volume and the dipole moment of the solute (diphenylmethane > naphthalene). The increase in the dipole moment suggests that more concentrated negative charges at the negative pole of diphenylmethane play an additional role to neutralize the surfactant headgroups.

It was observed that the initial structure of the diphenylamine/CPC admicelles was full-cylinders meaning that the influence of the incorporation of diphenylamine, as same as diphenylmethane, is still not strong enough to transform admicelle structure instantly. However, the equilibrium structure was a featureless bilayer. This equilibrium structure indicates that increasing polarity of solute molecule additionally promotes the potential to neutralize CPC surfactant headgroups by more concentrated negative charge distributing at one pole of the solute molecule, possibly -NH- group between two phenyl groups. This dominantly reduces CPC headgroup-headgroup repulsion and consequently induces the admicelle structural transformation from full-cylinders to featureless bilayer.

Diphenylether was also studied at its aqueous solubility which is lower than diphenylamine; however, its dipole moment is higher. Results demonstrate that the initial structure of admicelles solubilizing diphenylether (at it aqueous saturation) is transformed to featureless bilayer immediately after adsolubilization, showing that the anion binding effect at the CPC headgroups is very strong. The equilibrium admicelle structure was also observed as a featureless bilayer.

Although the aqueous solubility of diphenylether is lower than diphenylamine, the effect of adsolubilized diphenylether on the admicelle transformation is much stronger. This indicates that the negative charge in the proximity of the oxygen atom in diphenylether is stronger / more concentrated than that in the proximity of the nitrogen atom in diphenylamine, resulting in a higher dipole moment than diphenylamine although its aqueous solubility is lower. The higher dipole moment of diphenylether is also confirmed by the bond electronegativity difference (BED), that is, C-O bond in diphenylether possesses higher BED (0.89) than that of N-H (0.84) and N-C (0.49) in diphenylamine [39].

Thus, the potential to significantly lessen the surfactant headgroup-headgroup repulsion in CPC admicelles is in order of diphenylmethane < diphenylamine < diphenylether. This order is the same as the trend of their dipole moments but not of their aqueous solubility. Therefore, we suggest that the dipole moment should be preferentially used to compare the solute effect on admicelle structural transformation and also the relative locations of solutes in the admicelles.

However, high solute dipole moment has not always caused a strong instant effect on CPC headgroups, as observed for 4,4′-bipyridine adsolubilization earlier. 4,4′-Bipyridine possesses very high aqueous solubility as shown in Table 6.1. The experimental value of the dipole moment is unknown; however, because its aqueous molar solubility is ~300 times of diphenylether, this would suggest that it has a much higher dipole moment than that of diphenylether. Even at the high aqueous solubility of 4,4′-bipyridine, the initial admicelle structure did not immediately change upon adsolubilization while just a small amount of diphenylether (~300 times smaller than 4,4′-bipyridine concentration) could transform the admicelle structure to featureless bilayer immediately after adsolubilization. This suggests that comparing the potential for admicelle structural transformation using the dipole moment is valid only for solutes in the same molecular series. This weaker effect of 4,4′-bipyridine may be due to its small occupied volume/molecule in the admicelles. The dominant effect of solubilized dipole molecules should be better characterized by the presence of functional group possessing different electron affinity than the solute concentration. In this case N-C bond in 4,4′-bipyridine also has BED lower than that of C-O in diphenylether [39].

6.5 Conclusions

Two-dimensional structural transformation of admicelles was studied to investigate the effect of adsolubilized solutes on cationic admicelle structure by varying solute polarity and localization. It was concluded that (1) both hydrophobic interaction and cation-π binding tend to induce cationic admicelle transformation from full-cylinders to bilayer; (2) the hydrophobic interaction is stronger than the

cation-π binding; and (3) the influence of adsolubilized solutes (in the same molecular series) on CPC admicelle structure should be compared by solute dipole moment, which represents an additional degree of anion binding on the cationic surfactant headgroups in the admicelles, instead of comparing by solute aqueous solubility.

6.6 Acknowledgement

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