Influence of Strongly Bound Counterions on the Phase Behaviour of Ionic Amphiphiles

by

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Thesis submitted to the
Jawaharlal Nehru University
for the award of the degree of
Doctor of Philosophy

July 2007

Raman Research Institute
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Declaration

I hereby declare that the work reported in this thesis is entirely original. This thesis is composed independently by me at Raman Research Institute under the supervision of Dr. V. A. Raghunathan. I further declare that the subject matter presented in this thesis has not previously formed the basis for the award of any degree, diploma, membership, associateship, fellowship or any other similar title of any university or institution.

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Certificate

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Acknowledgement

I am deeply indebted to my thesis supervisor Dr. V. A. Raghunathan for everything I have learnt from him. Without his inspiring guidance this thesis would not have been possible. I would like to thank him for all his advice, encouragement and academic support during the entire course of this work. He has not only been a great supervisor but also a very good friend. It is always a pleasant experience to talk with him about all sorts of academic and non-academic issues.

A part of this thesis work has been done in collaboration with Prof. A. K. Sood at the Indian Institute of Science, Bangalore. I would like to thank him and his group members for very useful time I have spent with them. I express my gratitude to Prof. Ravi Subrahmanyan for all the academic interactions and also for his sensitive views on students' issues. I am extremely thankful to Dr. Yashodhan Hatwalne for his constant interest in my work and also for many helpful discussions. I thank Dr. Madan Rao, Dr. Ranjini Bandyopadhyay, Dr. Arun Roy, Dr. Abhishek Dhar and Dr. R. Pratibha for many pleasant discussions with them. I express my gratitude to Prof. N. V. Madhusudana and Prof. B. K. Sadashiva for their valuable comments and suggestions about my work. I am also thankful to all other faculty members of the soft condensed matter group for their encouragement and help.

A special thanks to Mr. Mani from whom I have had various technical support for my experimental work. I thank Mr. Dhason, Mr. Ram and Mr. Ishaq for their help. Also the technical support from Ms. K. N. Vasudha is sincerely acknowledged. I am thankful to Amarnath, Shreenivasa, Uma and Santanu for their help in preparing some of the chemicals in the chemistry laboratory.

I would like to express my deep gratitude to the highly efficient and extremely helpful library staff, especially to Mr. Patil, Mr. Nagaraj, Mr. Kiran, Ms. Girija, Mr. Manjunath, Mr. Ratnakar, Ms. Vrinda, Ms. Geetha, Mr. Hanumanthappa and Mr. Chowdappa.

I thank all the staff in the administrative department. Special thanks to Mr. Krishnamaraju, Mr. Radhakrishna, Ms. Marisa and Ms. Radha for their help in making official matters very easy. I am

thankful to all the hostel staff, canteen staff and everyone at RRI for making my stay enjoyable. I also enjoyed my stay at RRI because of its beautiful natural surroundings.

I acknowledge everyone at the computer section with special thanks to Mr. Vivek, Mr. Sunil, Mr. Jacob, Mr. Nandu and Mr. Sridhar.

I was fortunate to get Rema and Sanat as my lab seniors from whom I learnt a lot. I am thankful to them not only for valuable scientific discussions but also for their friendship in all other respects. I am also thankful to all of my other lab-mates; Bibhu, RK, Arif, Tripta, Debashis, Balakrishnaprabhu and Lakshmanan. My heartfelt thanks to Dipanjan and Brindaban for their friendship since my university days. I would also like to thank Sutirtha, Chandreyee, Abhijit, Debs, Archana, Saleh, Amit, Alpana and Antara for the wonderful time I spent with them. Although Javed is no more with us, he will be remembered always as a real friend. I thank Subhankar, Subhashis, Raktim, Priyabrata, Somenath and Falgun for their trusted friendship. I also thank Surajit, Rajkumar, Ganesh and Manjula for their help at various occasions. I sincerely thank to all my other friends with whom I enjoyed many evenings on the RRI football ground and badminton court.

I thank Usha, Divya and Maya for the time I enjoyed with them.

My sincere regards to my parents and grandmother for everything they have done for me. Their constant support and sacrifices have made my way very smooth. I profusely thank my brother Kamal for his encouragement and support throughout my academic career. It is impossible to express my deep sense of thanks to Sona who has constantly given me all kind of support during my good and tough times. Her keen desire inspires me to go ahead and to do better. It is also my pleasure to thank every member of my family for their help in various ways.

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Preface

This thesis deals with the influence of strongly bound counterions on the self-assembled structures formed by some ionic amphiphiles. The physical properties of aqueous solutions of these ionic amphiphiles are very sensitive to the nature of the counterions. In particular, counterions that have a tendency to adsorb on the surfactant micelle are known to dramatically modify the viscoelastic properties of their dilute aqueous solutions through the formation of long worm-like micelles. Our motivation was to get some insight into the effect of such counterions, introduced by added salts, in the concentrated regime. It is found that the nature of such counterions significantly affect the structure of liquid crystalline phases found in such systems.

The cationic surfactants used in these studies form cylindrical micelles over a wide range of water content, and the addition of certain counterions is found to transform these micelles into mesh-like aggregates. At high water content these aggregates form a random mesh phase, which is a lamellar phase with no long-range trans-membrane correlations of the in-plane structure. At low water content they, however, lock into a three dimensional structure. The structure and stability of these mesh phases are found to depend crucially on factors such as the length of the hydrocarbon chain of the surfactant, its hydrophilic part, and the nature of the surfactant counterion. The phase diagrams of these systems have been determined using polarizing optical microscopy and x-ray diffraction. The mesh phases are always found to intervene between the hexagonal and lamellar phases. Interestingly, in the case of an anionic surfactant the mesh phases are not formed in the presence of strongly bound counterions, but a new transition sequence is found between the hexagonal and lamellar phases, which seems to involve a gradual change in the micellar morphology from cylindrical to planar.

We have studied the influence of salts on the coexistence of two lamellar phases in a cationic surfactant-water system. All the salts studied are found to behave in a quantitatively similar fashion irrespective of the nature of the counterion, in striking disagreement with some recent theoretical predictions.

The influence of a strongly bound counterion on the structure of cationic surfactant-DNA complexes was investigated using x-ray diffraction. The competition between the counterion and DNA to bind to the micelle is found to lead to the formation of some novel structures of these complexes. A partial phase diagram of these structures has been determined from x-ray data.

In **chapter 1**, we introduce amphiphilic molecules and their self-assembled structures. The general phase behaviour of amphiphile-water system and the influence of additives on it have been discussed. A short description of x-ray diffraction and polarizing optical microscopy techniques used to identify the ordered phases of these systems has been given.

Amphiphilic molecules have one or more hydrophobic chains attached to a hydrophilic head group. They self-assemble in aqueous solutions to form aggregates above a critical micellar concentration (CMC). Various types of aggregates are formed depending upon the geometrical shape of the molecules (Fig. 1). At higher concentrations, they form liquid crystalline phases with long range orientational order and some degree of positional order. Most commonly observed structures are the hexagonal phase consists of long cylindrical micelles arranged on a two-dimensional hexagonal lattice, and the lamellar phase made up of a one-dimensional stack of bilayers. Frequently a bicontinuous cubic phase, which is optically isotropic, has been observed in between these two classical phases. In some systems a number of birefringent phases are seen instead at these intermediate compositions, which are known as 'intermediate phases'. Simple inorganic to very complex organic salts and co-surfactants are reported to have strong influence on the interactions between the amphiphilic molecules on their self-assembled structures. This chapter also contains a brief description of x-ray diffraction and optical polarizing microscopy techniques employed to determine the liquid crystalline structures.

In **chapter 2**, we present the effects of the organic salt 3-sodium-2-hydroxy naphthoate (SHN) on the phase behaviour of three cationic surfactants, namely, cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC) and dodecyltrimethylammonium bromide (DTAB). At low amounts of SHN, the phase behavior of CTAB-SHN-water system is similar to that of the CTAB-water binary system, which exhibits a hexagonal (H_I) phase over a wide range of water content. With increasing SHN concentration a lamellar phase with curvature defects is

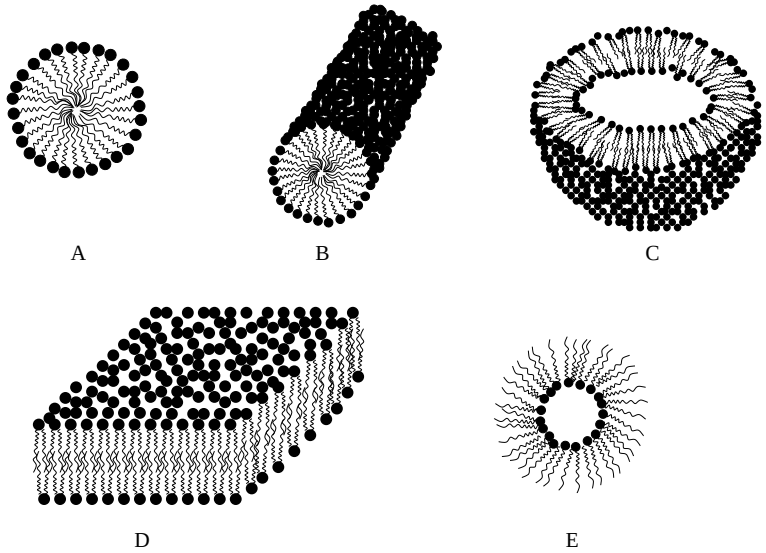

Figure 1: Various self assembled structures of amphiphilic molecules : (A) spherical micelle, (B) cylindrical micelle, (C) vesicle, (d) bilayer and (E) inverted micelle. In all these structures, the molecules expose their hydrophilic head group to water and shield their hydrophobic tail from water.

found instead of the H_I phase. These defects are revealed by the presence of a diffuse peak in the small angle region in the perpendicular direction to the peaks corresponding to the lamellar stacking. At lower temperatures (<~60 °C) this phase transforms into a regular lamellar phase via an intermediate phase on decreasing the water content. The intermediate phase shows a number of x-ray diffraction peaks indicating an ordered 3-D phase. Although the optical textures were identical, the regular lamellar phase was distinguished from the one with curvature defects by the absence of any diffuse peak in the small angle region. The formation of these curvature defects in a mixed surfactant system has been explained in terms of the tendency of one of the surfactant species to aggregate into spherical or cylindrical micelles, both of which have high positive values of mean curvature. The micro environment in the edge of these defects is very similar to that in the micelles, and hence their formation helps to reduce the overall energy of the system. At still higher SHN concentration a nematic phase is found. The high viscosity and flow alignment indicate this phase to be made up of long worm like micelles. A partial ternary phase diagram has been constructed, which exhibits a high degree of symmetry about the equimolar CTAB/SHN composition, reminiscent of the phase behavior of mixtures of anionic and cationic surfactants (Fig. 2).

On replacing the bromide (Br^-) counterion of the surfactant by chloride (Cl^-), the CTAC-

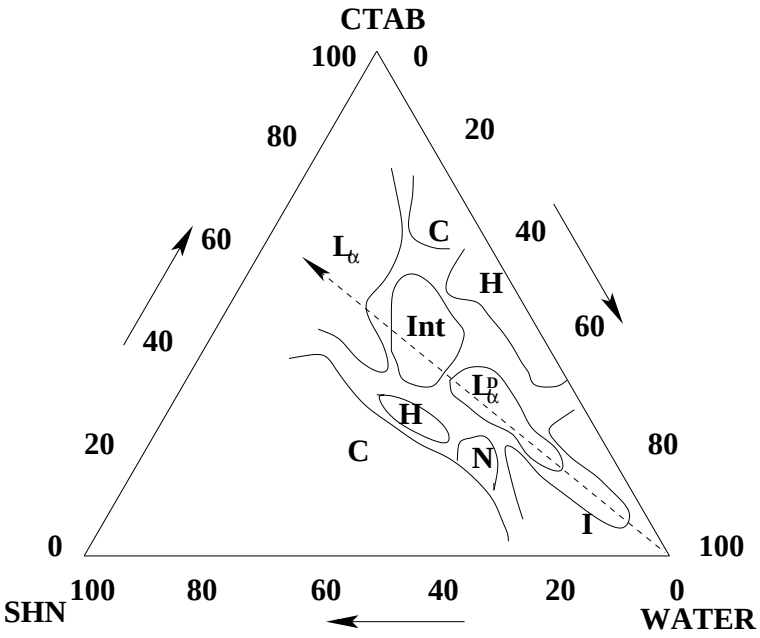

Figure 2: Phase diagram of CTAB-SHN-water system at T = 30 °C. The concentrations are in wt%. $I, L_\alpha^D, L_\alpha, H, Int, N$ and C denote the isotropic, lamellar with curvature defects, regular lamellar phase, hexagonal phase, intermediate phase, nematic phase and crystalline phase respectively. The dashed line indicates samples with equimolar CTAB/SHN composition.

SHN-water system shows only a regular lamellar phase around the equimolar composition. In this case, most of the chloride ions are supposed to be released into water giving rise to an uniform microenvironment of the bilayer. On decreasing the chain length, it is found that although the DTAB-SHN system forms curvature defects, the average defect separation decreases with surfactant concentration, which is opposite to the trend seen in the CTAB-SHN system. The absence of a 3-D intermediate phase in DTAB-SHN -water system might be related to this difference.

Chapter 3 describes the modelling of the structure of the intermediate phase observed in CTAB-SHN system. In the CTAB-SHN system, consisting of oppositely charged molecules, an increase in the surfactant concentration is accompanied by a corresponding increase in the ionic strength due to the released Br^- and Na^+ counterions. Hence the effects of salt and surfactant concentration on the phase behavior cannot be separated. Therefore, we have studied the phase behavior of the surfactant CTAHN, which is formed by the complexation of CTAB and SHN, as a function of NaBr concentration. In order to understand the influence of the chain length of the surfactant molecule on inducing the mesh phase, we also discuss the DTAB-SHN-water system.

X-ray diffraction data from oriented samples of CTAB-SHN system in the intermediate phase show the existence of a 3D lattice with rhombohedral symmetry. The intermediate phase which is modelled as an 'ordered mesh phase' is also recovered in the CTAHN-water system at high NaBr concentrations whereas it shows only a regular lamellar phase without any added salt. The ordered mesh phase is absent in the DTAB-SHN system and only the lamellar phase with curvature defects is observed over a wide range of surfactant concentration (ϕ_s). The lamellar phase with curvature defects is modelled as 'random mesh phase' and is found to consist of a stack of 2-D network of rod-like aggregates, with no long-range positional correlations of the in-plane structure along their normal. In the model, three rods meet at each node to give rise to a 2-D hexagonal lattice of pores. These aggregates are regularly stacked to from a 3D lattice in the intermediate phase (Fig. 3). The diameter of the rod-like segments was estimated from the data and is found to be consistent with the length of the surfactant molecule ($\sim$ 20 Å). Also the swelling behaviour of the random mesh phase is consistent with mesh-like aggregates with a micellar morphology in between a cylinder and a bilayer. The average mesh size is found to increase with ϕ_s in the random mesh phase and the transition to the intermediate mesh phase occurs when it is of the order of 1.4 times the lamellar periodicity. In the DTAB-SHN system, on the other hand, the average mesh size decreases with ϕ_s; which might me a reason for the absence of the intermediate phase in this system. The modulated part of the interaction potential between the planar surfaces (arising due to the structural inhomogeneity in the plane) decays exponentially with a decay length of the order of the in-plane periodicity. Only when the separation between the layers of random meshes is low compared to the pore separation, the interaction potential is strong enough to lock the meshes to give rise to a 3-D ordered phase. Most of the samples in the intermediate phase also give rather broad x-ray diffraction peaks in the small angle region, corresponding to average periodicities of around 25 nm. These peaks seem to be arising from some nodule-like structures seen in freeze-fracture electron micrographs of some samples in the intermediate phase.

In **chapter 4**, we describe the influence of the hydrophilic head group of the surfactant and the nature of the counetrions in determining the structure of mesh phases. The surfactant used is cetylpyridinium bromide (CPB). It has the same chain length as that of CTAB but with a pyridinium

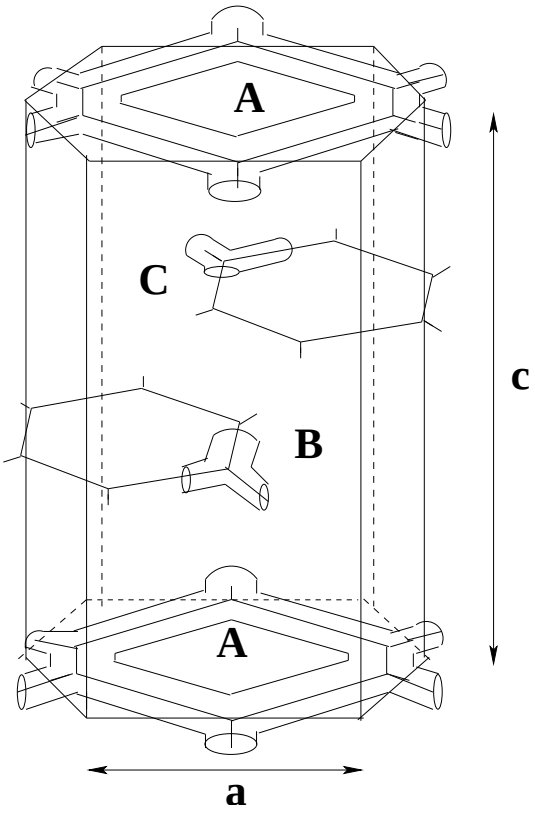

Figure 3: Model for the intermediate phase showing the unit cell of the hexagonal mesh structure.

instead of ammonium moiety in its head group. For low amounts of added SHN, the phase diagram is very similar to that of the CPB-water binary system. Higher amount of salt induces a lamellar phase with curvature defects. Interestingly, the mesh-like aggregates forming this phase have a four-fold symmetry axis normal to the plane, instead of the hexagonal symmetry seen in the mesh phases of the CTAB-SHN system. At still higher surfactant concentrations, an ordered mesh phase is formed, where the square mesh-like aggregates order in three dimensions in a body centred tetragonal lattice (Fig. 4). The radius of the cylinders is calculated from the surfactant volume fraction and is found to be comparable to the molecular length ($\sim$ 19 Å). The parameter γ which is the ratio of the mesh size to the lamellar periodicity increases with surfactant concentration in the random mesh phase and the transition to the ordered mesh phase occurs at around $\gamma \sim 1.3$. This observation is consistent with the similar trend found in the CTAB-SHN system indicating it to be a crucial feature necessary to induce the ordered mesh phase. The three component phase diagram is found to be symmetric about the equimolar CPB-SHN composition.

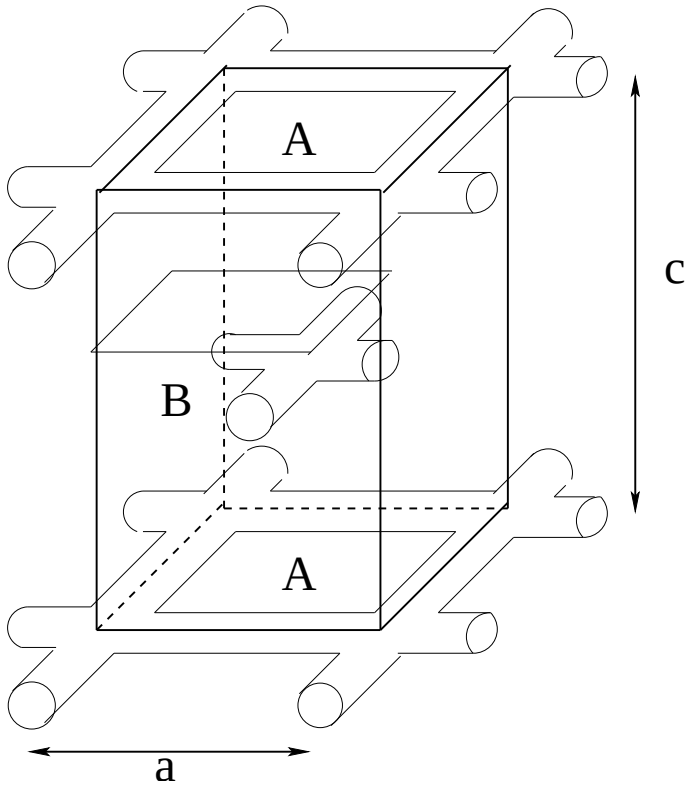

Figure 4: Model for the ordered mesh phase indicating the tetragonal unit cell.

To check the effect of the surfactant counterion, the phase diagram of the cetylpyridinium chloride (CPC)-SHN-water system has been determined. At equimolar composition this system forms a regular lamellar phase. Further the effects of the strongly bound counterion was probed by adding sodium salicylate (SS) and sodium *p*-toluene sulfonate (ST) to CPB. Both these salts give a very different phase diagram from that of SHN. These two salts do not alter the cylindrical morphology of the surfactant aggregates. At equimolar mixtures, only the hexagonal phase is observed as in the CPB-water binary system.

Chapter 5 deals with the influence of the organic salt *p*-toluidine hydrochloride (PTHC) on the phase behaviour of concentrated aqueous solutions of the anionic surfactant sodium dodecylsulfate (SDS). Very few systematic studies have been reported on the effects of organic salts on anionic surfactants in dilute aqueous solutions and there are no reports in the concentrated regime.

At low amount of added salt the diffraction patterns show three peaks with the corresponding spacings in the ratio $1{:}\frac{1}{\sqrt{3}}{:}\frac{1}{2}$ confirming the 2-D hexagonal structure, as in the system without salt. On increasing the concentration of the salt the hexagonal phase of SDS is found to show the fol-

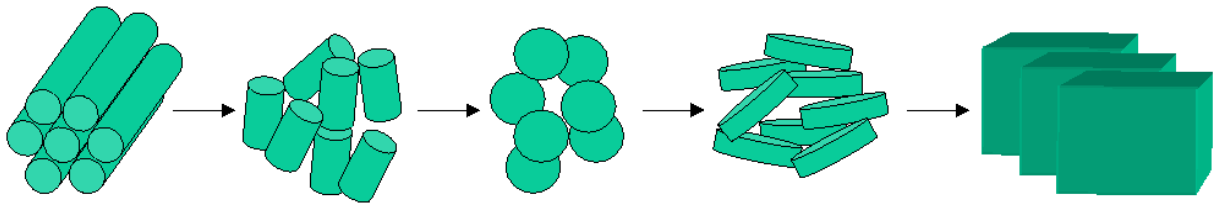

Figure 5: Schematic drawing of the sequence of aggregate morphologies seen in the SDS-PTHC-water system with increasing salt concentration.

lowing sequence of transformations: hexagonal → nematic → isotropic → nematic → lamellar (Fig. 5). The nematic near the hexagonal phase is most probably made up of rod-like aggregates, whereas the one near the lamellar phase is likely to consist of disc-like micelles. This has been proved by the presence of homeotropically aligned region under the crossed polarizers in the samples of the latter nematic phase. This sequence of phases suggests a gradual prolate to oblate change in the aggregate morphology with increasing counterion concentration. Such a morphological change seems to prevent the formation of other intermediate phases usually seen between the hexagonal and lamellar phases. Usually the addition of organic salts to a dispersion of rod-like aggregates is found to increase the length of the rods significantly, resulting in long worm-like micelles. But in the present system it seems that the addition of salt decreases the length of the rod like aggregate which is manifested by the monotonic decrease of the apparent viscosity within the hexagonal phase with increasing PTHC concentration. It is presently not clear if this behaviour is specific to PTHC or if it is more general. Further experiments are needed to clarify the situation. At much higher amount of PTHC, an isotropic-isotropic coexistence is observed. One of these is tentatively identified as a sponge phase, which seems to be different from the classical sponge phase of surfactants in some respects. Generally the classical sponge phase appears from a lamellar phase on dilution through a two-phase region which is not the case in the present system. Normally the x-ray diffraction pattern of the sponge phase shows a broad peak at around $q_o/3$, where q_o is the position of the sharp peak from the neighbouring L_α phase. However, in the present system the positions of the two peaks are almost identical. Further experiments are necessary to figure out the microstructure of this phase.

The ternary phase diagram is found to be asymmetric about the equimolar compositions of

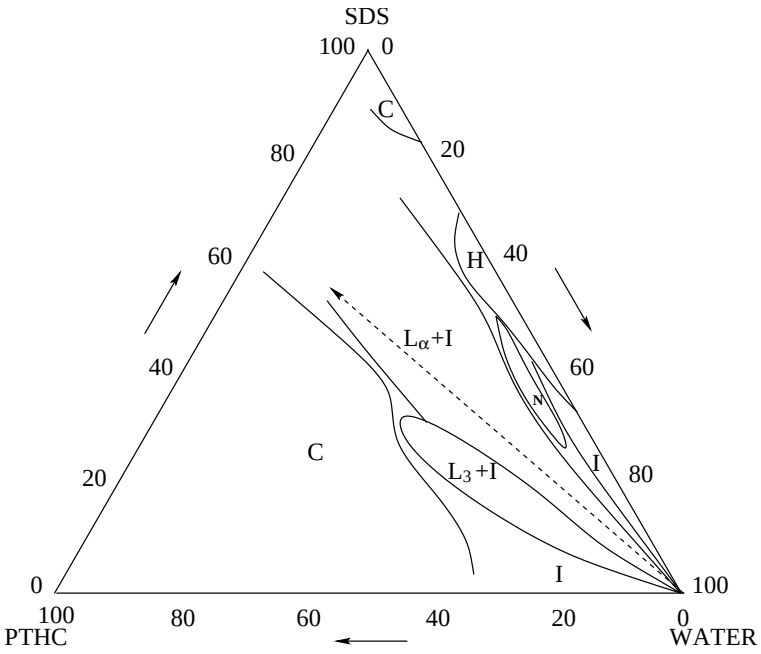

Figure 6: Partial ternary phase diagram of SDS-PTHC-water system at 30 °C. The concentrations are in wt %. I, N, L_α, H, L_3 and C denote the isotropic, nematic, lamellar, hexagonal, sponge and crystalline phases respectively. The dashed arrow indicates the equimolar compositions of SDS and PTHC.

the two species, unlike the systems described before. On each side of the equimolar line, the aggregates are either charged positively or negatively. The morphology of the aggregates usually depends only on the charge density but not on the type of the charge; with bilayers preferred close to the equimolar composition and cylindrical micelles away from it. Hence, the phase behaviour is usually symmetric about the equimolar axis. Strongly bound counterions, which are very weakly soluble in water, seem to behave similar to ionic surfactants. However, this is not the case in the present system. A possible reason might be that PTHC is reasonably soluble in water, unlike the other strongly bound counterions which were added to the cationic systems. This can destroy the symmetry of the aggregate charge density about the equimolar composition, thus giving rise to an asymmetric ternary phase diagram. Further experiments are needed to confirm this conjecture.

In **chapter 6**, we study the effect of different monovalent counterions on the lamellar-lamellar coexistence seen in the ionic surfactant, didodecyldimethylammonium bromide (DDAB). Inorganic salts, sodium bromide (NaBr) and sodium chloride (NaCl) and organic salts, 3-sodium-2-hydroxy naphthoate (SHN) and sodium salicylate (SS) were used to introduce the different counte-

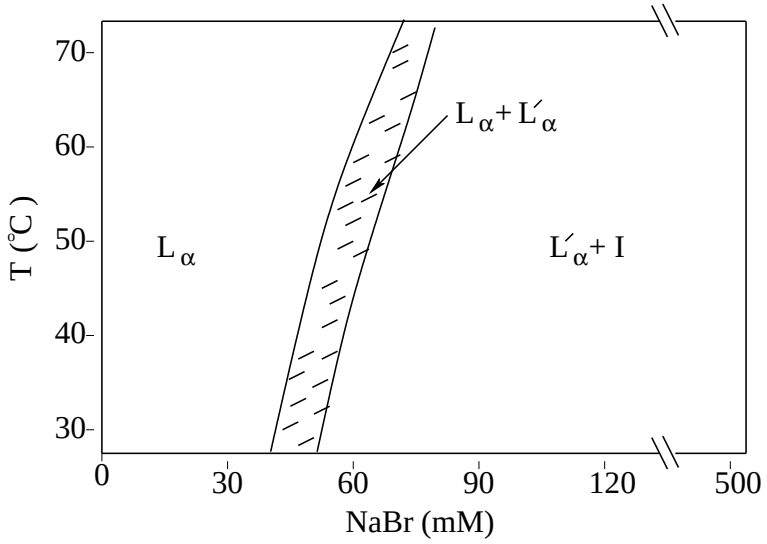

Figure 7: Phase diagram of DDAB-NaBr system at ϕ_s = 20. L_α and L´$_\alpha$ denote the swollen and collapsed lamellar phases respectively. I is the isotropic phase. The shaded region in the phase diagram denotes the coexistence of two phases.

rions. This double tailed surfactant has been known to exhibit a lamellar-lamellar coexistence over a range of concentration. Interestingly, the analogous surfactant with Cl^- counterion instead of Br^- does not show such a two phase region. Out results show that all the salts shift the coexistence region to much lower concentrations of the surfactant. Figure 7 shows the collapsed lamellar phase at 20 wt% of DDAB with NaBr whereas it shows a swollen lamellar phase without any added salt at the same concentration. Interestingly all the salts are found to be equally efficient in inducing the coexistence, in contrast to some recent theoretical predictions. The theory suggest that Br^- would be more efficient in inducing the coexistence than Cl^-. In the case of the organic salts, there is a striking different effect on the phase behaviour of DDAB compared to inorganic salts. At higher salt concentration, the collapsed lamellar phase is transformed into a viscous isotropic phase. Samples at these compositions show the coexistence of two isotropic phases (Fig. 8). X-ray studies show a number of sharp reflections from the viscous isotropic phase, indicating a high degree of positional ordering. These peaks are in the ratio $\sqrt{2}:\sqrt{3}:\sqrt{4}:\sqrt{6}:\sqrt{8}:\sqrt{9}:\sqrt{10}:\sqrt{12}$. The absence of the $\sqrt{7}$ reflection indicates the lattice to be a primitive cubic lattice corresponding to the space group $Pn3m$.

Present study suggests an alternative mechanism for the formation of the collapsed phase,

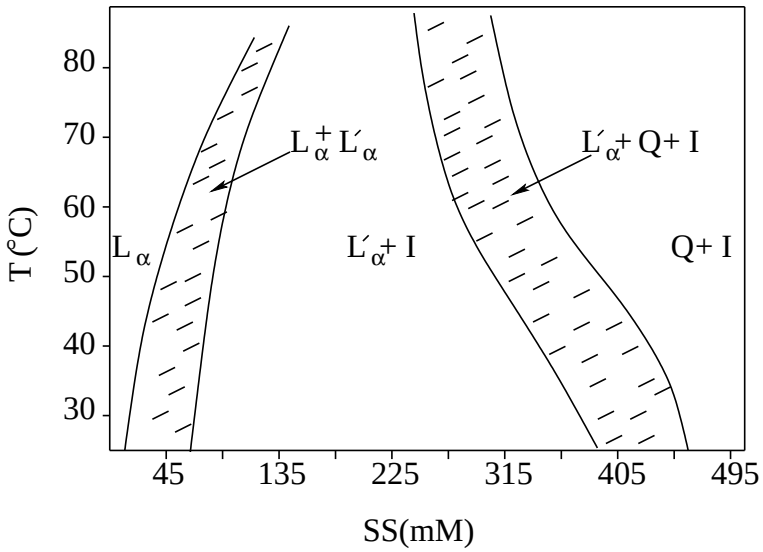

Figure 8: Phase diagrams of DDAB-SS system for $\phi_s = 30$. *Q* is the cubic phase corresponding to space group *Pn*3*m*.

which cannot be understood on the basis of present theories of these systems. As it is evident from previous chapters, some salts can bridge the cylindrical micelles to form a 2D network and give rise to mesh phases in systems which form rod-like micelles. One might expect a similar behaviour in a bilayer forming system. In that case it would form connections across bilayers and form a network. There are reports in the literature of 'stalk' formation in lipid bilayers, which are such interconnections. A gradual increase in the number of such interconnections might ultimately results in the lamellar to cubic transition.

In **chapter 7**, we address the role of a strongly bound counterion on the formation of cationic surfactant-DNA complexes and their structures. The cationic surfactant used is cetyltrimethylammonium tosylate (CTAT). The counterion in this case is the tosylate ion, which is relatively strongly bound to the surfactant micelles due to its aromatic nature, compared to the much more common Cl^- and Br^- counterions.

A partial phase diagram of the various structures formed by the complexes as a function of CTAT and DNA concentrations has been determined from x-ray diffraction data (Fig. 9). Four different structures have been observed, of which only the intercalated hexagonal has been seen earlier (Fig. 10A). At low DNA content we find a structure characterized by a two-dimensional square lattice over the whole range of CTAT concentration investigated. The lattice parameter of this

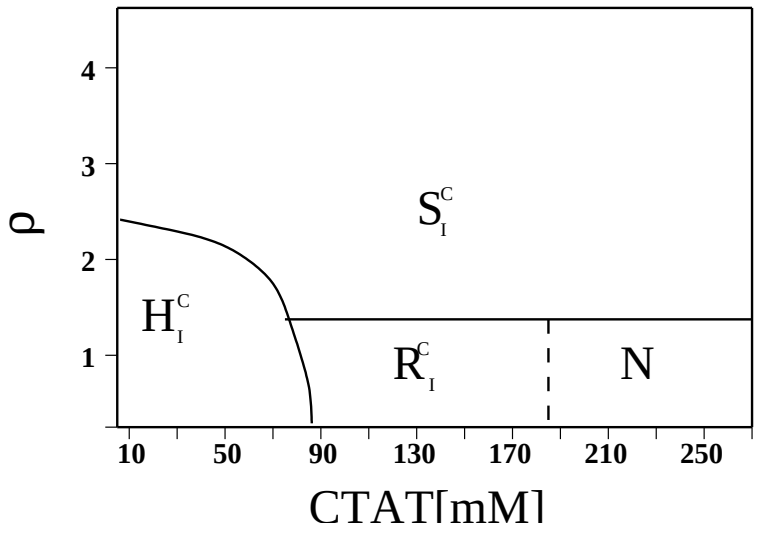

Figure 9: Partial phase diagram of DNA-CTAT complexes showing hexagonal (H_I^c), square (S_I^c) and rectangular (R_I^c) phases. N indicates the nematic phase which appears at very high surfactant concentrations in the presence of high amount of DNA.

square phase (S_I^c) is consistent with a closed-packed structure, where each micelle is surrounded by four DNA strands (Fig. 10B). We have carried out detailed analysis of the x-ray diffraction data to check the proposed structure. We model the two dimensional electron density of the square structure and compare the calculated relative intensities with those observed. The values of model parameters obtained from the best fit are found to be comparable to those reported in the literature and thus the intercalated structure of the square phase is consistent with the diffraction data. At high DNA content we find the intercalated hexagonal structure at low CTAT concentrations and a nematic phase with no long-range positional correlations but only long range orientational ordering at high CTAT content. Another structure is seen in between these two structures which shows a simple rectangular lattice. The packing of DNA strands and CTAT micelles in this lattice is yet to be determined.

The influence of the salts, NaCl and sodium tosylate (ST), on the structure of these complexes was also studied. The lattice parameter of the hexagonal phase is found to increase with increasing NaCl concentration. However, the addition of NaCl is not able to change the structure of the complex. At very high salt concentration, the complex melts into an isotropic dispersion. The behaviour is completely different when the organic salt is added to the complex. The hexagonal phase in this case is found to initially swell and then transform to the rectangular and then to the

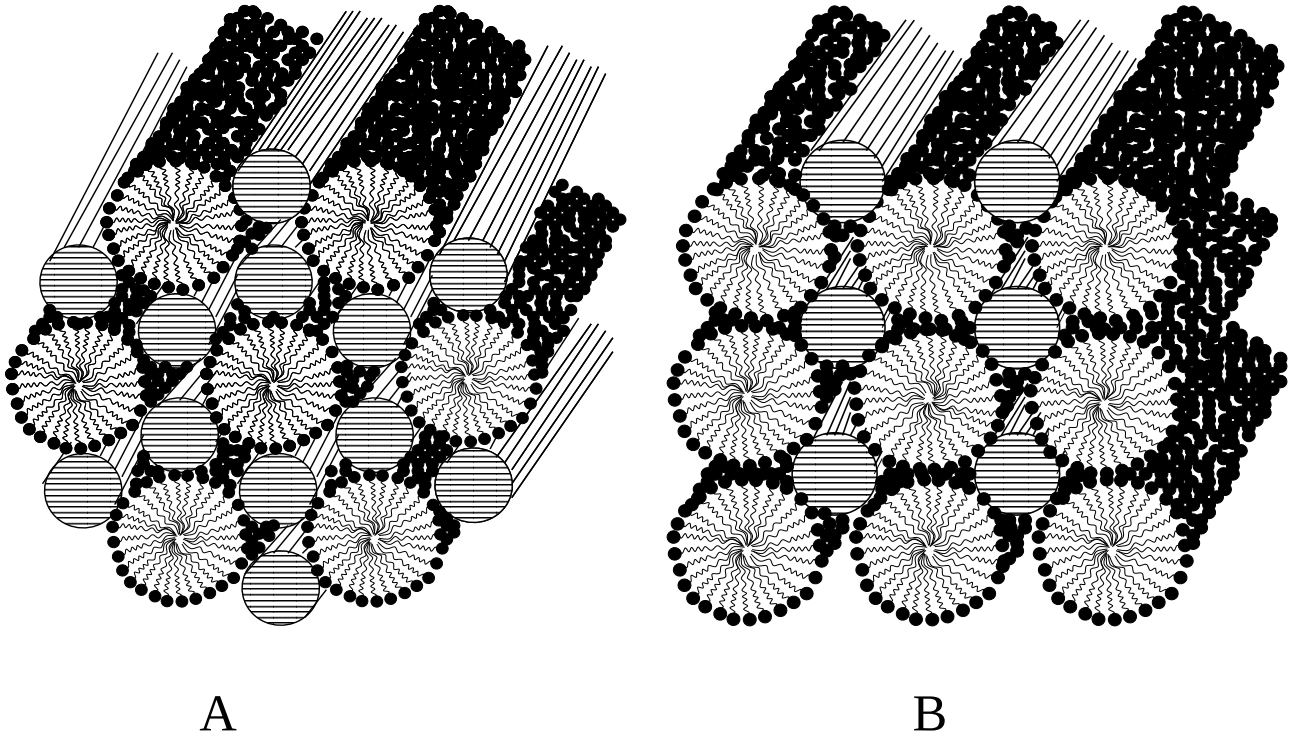

Figure 10: The schematic diagrams of (A) hexagonal and (B) square phases of CTAT-DNA complexes.

square phases with progressive addition of ST. At high salt concentration an isotropic dispersion is again formed.

In the present system there is a competition between the tosylate counterions and the phosphate ions on the DNA to bind to the micelle. At low DNA concentration, all the DNA molecules bind to the micelles with a minimal release of tosylate counterion to give rise the square phase. At higher DNA concentration, more DNA bind to the micelles at the expense of tosylate to give rise the hexagonal phase. From square to hexagonal phase, the number of DNA molecules to each micelle in the unit cell increases from one to two. This explanation is consistent with the observation on adding ST to the hexagonal phase. The rectangular phase found in between the hexagonal and square should have an intermediate structure. The appearance of nematic phase is the consequence of melting of ordered structure due to the dissociated salt. Similar melting of ordered structures on lowering the water content has been seen in other charged polyelectrolyte systems, again due to the released counterions.

The following papers contain the work described in this thesis

1. Structure of mesh phases in a cationic surfactant system with strongly bound counterions.
S. K. Ghosh, R. Ganapathy, R. Krishnaswamy, J. Bellare, V. A. Raghunathan and A. K. Sood.
Langmuir 2007, 23, 3606-3614.

2. Structure of an intermediate mesh phase of a mixed surfactant system.
S. K. Ghosh, R. Krishnaswamy, V. A. Raghunathan and A. K. Sood.
Proceedings of the DAE-Solid State Physics Symposium, India, Vol 51, 209, 2006.

3. Phase behavior of concentrated aqueous solutions of cetyltrimethylammonium bromide (CTAB) and sodium hydroxy naphthoate (SHN).
R. Krishnaswamy, S. K. Ghosh, S. Laksmanan, V. A. Raghunathan and A. K. Sood.
Langmuir 2005, 21, 10439-10443.

4. Novel structures of DNA-surfactant complexes.
S. K. Ghosh , A. V. Radhakrishnan, G. Pabst, V. A. Raghunathan and A. K. Sood.
To be submitted.