

# **Structure of Surfactant-Polyelectrolyte Complexes**

by  
*K. Rema*

**A Thesis submitted to the  
Jawaharlal Nehru University  
for the Degree of  
Doctor of Philosophy**

2003

*Raman Research Institute  
Bangalore 560 080  
India*

# *Certificate:*

---

This is to certify that the thesis entitled **Structure of Surfactant-Polyelectrolyte Complexes** submitted by K. Rema for the award of the degree of Doctor of Philosophy of Jawaharlal Nehru University is her original work. This has not been published or submitted to any other University for any other Degree or Diploma.

Prof. N. Kumar

Director

Raman Research Institute

Bangalore 560 080 INDIA

Dr. V. A. Raghunathan

(Thesis Supervisor)

## ***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.

(Dr. V. A. Raghunathan)

(K. Rema)

Liquid Crystal Laboratory  
Raman Research Institute  
Bangalore 560 080 - INDIA

# Acknowledgement:

The work in this thesis has been done under the supervision of Dr. V. A. Raghunathan. I thank him for everything I have learnt from him. Without his patience, support and encouragement, this thesis would not have been possible. I consider myself fortunate to have worked with him.

I thank Dr. Yashodhan Hatwalne and Dr. Madan Rao for their constant interest in this work. I thank Dr. G. V. Shivshankar for several discussions and for all the help received from his group. I thank Dr. J. Samuel and Dr. Bala Iyer for their concern and their encouragement. I thank Dr. Abhishek Dhar, it was a pleasure to discuss my work with him. I also thank Dr. R. Pratibha for all the help received.

I thank Mr. Dhason, Mr. Ram, Mr. Subramaniam, Ms. Vasudha, Mr. Ishaq and especially Mr. Mani, for their help in carrying out the experiments. I also thank the Chemistry lab for the help received at various stages of this work. I thank Mr. Raju for his help in developing photographs.

I thank all the library staff for their help, especially Patil, Ratnakar, Girija, Manjunath, Nagaraj, Geetha, Vrinda, Hanumanthappa and Chowdappa.

I thank Mr. Radhakrishna, Ms. Radha, Mr. Manjunath, Ms. Marissa and Ms. Lakshmi for their help in paper work. I also thank the computer department for all the help received.

I thank Sanat for all the discussions and help that I have received from him, he has been an ideal labmate and friend to me. I also thank him for patiently reading through my thesis. I thank Kheya for all the discussions that I have had with her and for her friendship. I thank

Rajkumar for all the help he has given me. I thank Lakshmanan for collaboration. I thank members of the LC group especially Manjula, Surajit, Viswa and Bala. I thank Sajal, Roopa and Dipanjan for discussions.

I thank all the staff and students at RRI, I will always cherish the wonderful atmosphere here.

I thank Mr. Ganguly for giving me the confidence to do research. I thank Sreedhar for the encouragement he gave me just before I joined RRI. I thank Naveen for all the physics that I learnt from him and for all the help he gave me. I thank Madhuri and Abhijit for the good times I had with them. I thank Usha for her help and advice when I needed it the most. I thank Gail and Pati for their wonderful company and help. I thank Niruj and Mamata for their friendship during my years at RRI. I thank Jishnu for constantly pushing me to finish my thesis and for keeping me in good humour. I thank my parents and my sisters, Shobha and Hema, for their support through all these years.

# Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Surfactants . . . . .	1
1.1.1	The Hydrophobic effect . . . . .	2
1.1.2	Self assembly of amphiphiles . . . . .	3
1.1.3	Phase behaviour of surfactant solutions . . . . .	6
1.2	Polymers . . . . .	10
1.2.1	Polyelectrolytes . . . . .	11
1.2.2	Counter ion condensation . . . . .	13
1.3	Formation of surfactant-polyelectrolyte complexes . . . . .	14
1.4	Theory of x-ray diffraction . . . . .	15
1.4.1	Polarization and geometric corrections . . . . .	17
1.4.2	Characterisation of liquid crystalline phases . . . . .	18
1.5	Experimental Procedure . . . . .	21
1.5.1	Experimental set up . . . . .	21
1.5.2	Sample preparation . . . . .	21
<b>2</b>	<b>Phase behaviour of the CTAB–SHN–water system</b>	<b>26</b>
2.1	Introduction . . . . .	26
2.2	Earlier studies . . . . .	27
2.3	Liquid crystalline phases of CTAB-SHN-water system . . . . .	28
2.4	Curvature defects in lamellar phases . . . . .	40
2.5	Discussion . . . . .	41

2.6	Conclusions . . . . .	46
<b>3</b>	<b>Structures of cationic surfactant-DNA complexes</b>	<b>49</b>
3.1	Introduction . . . . .	49
3.2	Earlier studies on surfactant-DNA complexes . . . . .	50
3.3	Structure of CTAB-DNA complex . . . . .	60
3.4	Modelling the structure of CTAB-DNA complex . . . . .	61
3.5	Tuning the structure of CTAB-DNA complex with SHN . . . . .	65
3.6	Discussion . . . . .	69
3.7	Conclusions . . . . .	71
<b>4</b>	<b>Influence of hexanol on the structure of CTAB-DNA and CTAB-SHN-DNA complexes</b>	<b>74</b>
4.1	Introduction . . . . .	74
4.2	Influence of a cosurfactant on the phase behaviour of surfactant-water systems	75
4.3	Theoretical studies on the phase behaviour of cationic lipid-DNA complexes	79
4.4	CTAB-DNA-hexanol Complexes . . . . .	84
4.5	CTAB-SHN-hexanol-DNA Complexes . . . . .	88
4.6	Discussion . . . . .	91
4.7	Conclusion . . . . .	97
<b>5</b>	<b>Structure of cationic-surfactant – polyelectrolyte complexes</b>	<b>101</b>
5.1	Introduction . . . . .	101
5.2	Earlier studies . . . . .	102
5.3	CTAB-polyelectrolyte complexes . . . . .	107
5.4	CTAB-SHN-polyelectrolyte complexes . . . . .	110
5.5	DDAB-polyelectrolyte complexes . . . . .	117
5.5.1	Phase diagram of DDAB-water . . . . .	117
5.5.2	Earlier studies on DDAB-polyelectrolyte complexes . . . . .	118

5.5.3	Structure of DDAB-polyelectrolyte complexes . . . . .	121
5.6	Discussion . . . . .	125
5.6.1	CTAB-SHN-polyelectrolyte complexes . . . . .	125
5.6.2	Structures in DDAB-polyelectrolyte complexes . . . . .	130
5.6.3	Surfactant content of the various polyelectrolyte complexes . . . . .	132
5.7	Conclusions . . . . .	134



## Synopsis

This thesis deals with the structure of complexes formed by deoxyribonucleic acid (DNA) and some other anionic polyelectrolytes with cationic surfactants in dilute aqueous solutions. X-ray diffraction studies on complexes of DNA with cationic double-tailed lipids have established some of the structures exhibited by these systems. The structures of complexes of some synthetic polyelectrolytes with many single-chained cationic surfactants have also been reported. Our objective was to study the structural modifications induced by sodium-3-hydroxy-2-naphthoate (SHN) and hexanol, on complexes of cetyltrimethylammonium bromide (CTAB) with various anionic polyelectrolytes. We also probed the influence of the chemical nature of the polyion on the structure of these complexes. In order to correlate the structure of the complexes, with the phase behaviour of the surfactant system, we have constructed a partial phase diagram of the CTAB-SHN-water system.

The CTAB-SHN-water system is found to exhibit a novel phase behaviour. It shows a lamellar phase with curvature defects at low surfactant concentrations. At high temperatures the defects disappear gradually on decreasing the water content and a lamellar phase without such defects is found at high surfactant concentrations; a similar behaviour has been observed earlier in some surfactant systems. Surprisingly, at lower temperatures, an intermediate ribbon phase appears between the two lamellar phases. Further theoretical work is required to understand this complex phase behaviour.

Cationic lipid-DNA complexes are known to form lamellar and inverted hexagonal structures. We have established a new structure, consisting of DNA strands intercalated into a direct hexagonal phase, in CTAB-DNA complexes.

Structural transitions of these complexes to lamellar and inverted hexagonal phases were observed with the addition of the cosurfactant hexanol. The transition from the lamellar to inverted hexagonal phase in the presence of hexanol has been observed earlier in lipid-DNA

systems. However, a transition from an inverted hexagonal to a lamellar structure driven by DNA concentration was observed for the first time; we propose that this transition is driven by the larger intake of DNA into the lamellar, as compared to the inverted hexagonal structure. We have constructed a partial phase diagram of the system which shows the different structures seen as a function of hexanol and DNA concentrations.

A variety of structures was observed in the complexes of various anionic polyelectrolytes with CTAB-SHN. Some of them have not been reported earlier in polyelectrolyte-surfactant systems. We could also correlate the structures observed in these complexes with those present in the surfactant system at similar surfactant content. Such a correlation has not been suggested in any of the earlier studies. The use of the surfactant system CTAB-SHN which has a rich phase behaviour made this possible in the present case.

In chapter-I, we discuss the phase behaviour of surfactant systems as well as the physical characteristics of polyelectrolytes that are relevant to our study. We also describe here briefly, the theory of x-ray diffraction. Further, we have outlined the experimental techniques employed to study the complexes.

Surfactants are amphiphilic molecules made up of one or more hydrophobic chains attached to a head group which is hydrophilic. In aqueous solutions, they form aggregates above a critical concentration known as the critical micellar concentration. These aggregates known as micelles, may be spherical, rod-like or disk-like in dilute solutions. At high surfactant concentrations, they form liquid crystalline phases with long range orientational order. Polyelectrolytes are polymers which acquire a charge in aqueous solutions by releasing their counter ions. The persistence length of a polymer is a measure of its flexibility, and it is the length below which the polymer chain behaves like a stiff rod. The number of charged groups on the polymer determines its bare charge density. In dilute solutions, the effective charge density of a polyelectrolyte can be much lower than the bare charge density since

some of the counter ions condense back on to the chain. This phenomenon known as the Oosawa-Manning condensation is essentially due to the competition between electrostatics and entropy. Electrostatics requires that the oppositely charged counter ions remain near the polyelectrolyte, whereas the entropy would prefer them to remain dispersed in the solution. Similar behaviour can also occur in the case of aggregates of ionic surfactants. When polyelectrolytes are added to a solution of oppositely charged surfactant, the polyion and the surfactant ion associate to form complexes releasing their respective counter ions into the solution. The resulting increase in the entropy of the counter ions is the main driving mechanism for the complex formation. These complexes form various liquid crystalline phases which may be characterized using x-ray diffraction.

In chapter-II, we describe the characterization of the liquid crystalline phases of CTAB-SHN-water system using polarizing microscopy and x-ray diffraction.

A partial phase diagram of CTAB-SHN-water system at 30 °C constructed from these studies is shown in fig 1. At low SHN concentrations, a direct hexagonal phase ( $H_I$ ) is observed which consists of long cylindrical micelles arranged on a 2D hexagonal lattice. On increasing the SHN concentration a phase consisting of ribbon-like aggregates arranged on a 2D oblique (O) lattice is obtained. These ribbon phases appear in general in surfactant systems, in between the hexagonal and lamellar phases. At high SHN concentrations, a lamellar phase ( $L_\alpha^D$ ) is observed over a wide range of surfactant concentration. It contains a large number of pores or slits in the plane of the bilayer. Such lamellar phases with curvature defects have been seen in a few surfactant systems. These defects are found to disappear gradually on increasing the surfactant content. A similar behaviour is observed in the present system at high temperatures (fig. 2). At low temperatures an intermediate centred rectangular phase made of ribbon-like aggregates (fig 3) appears between the two lamellar phases. More theoretical work is required to explain this novel phase behaviour.

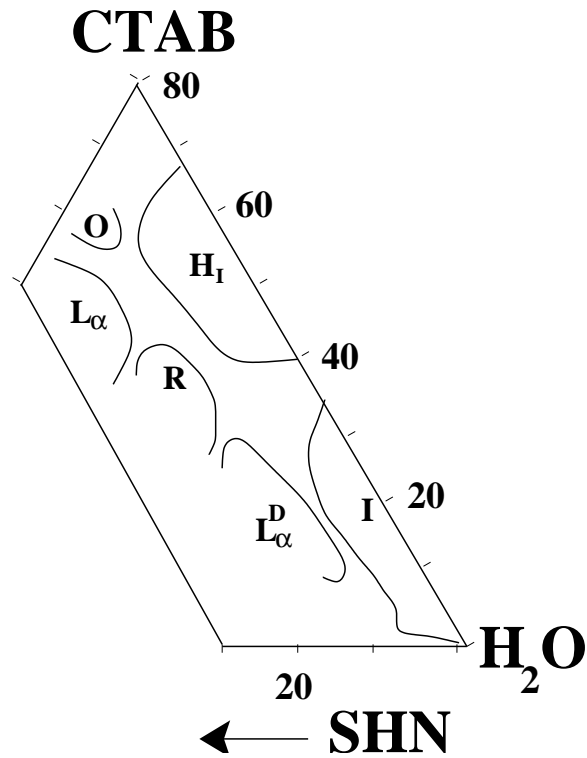


Figure 1: A partial phase diagram indicating the various liquid crystalline phases of CTAB-SHN-water system at 30 °C.  $L_{\alpha}^D$  denotes the lamellar phase with defects, O a phase with an oblique lattice, R a ribbon phase with a rectangular lattice, I the isotropic phase,  $L_{\alpha}$  the lamellar phase without defects and H the direct hexagonal phase.

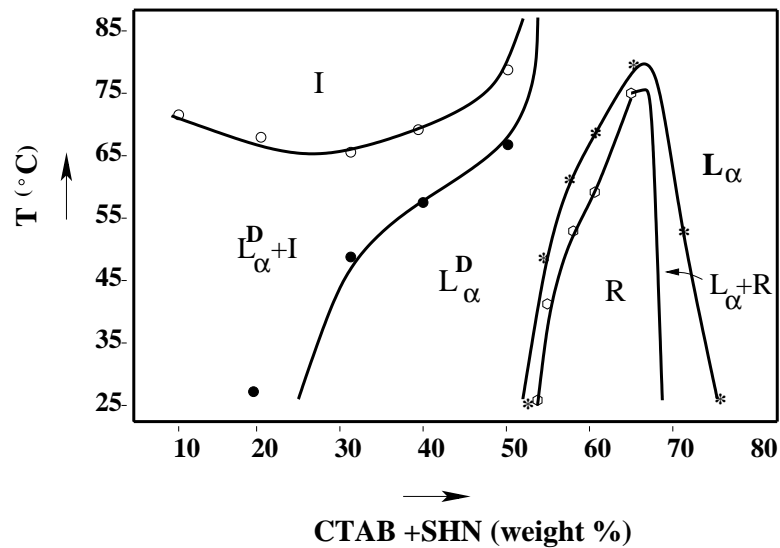


Figure 2: Temperature-composition phase diagram of CTAB-SHN-Water system at equimolar ratios of CTAB and SHN.

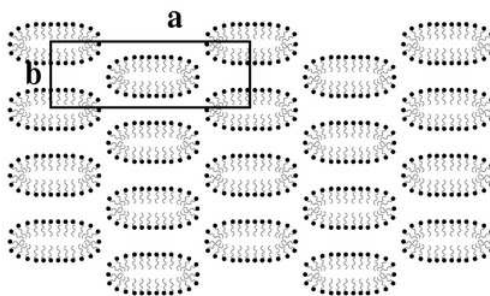


Figure 3: Schematic of the structure of the centred rectangular phase of CTAB-SHN-water system consisting of ribbon-like aggregates arranged on a 2D rectangular lattice. The long axes of the ribbons is normal to the plane shown.

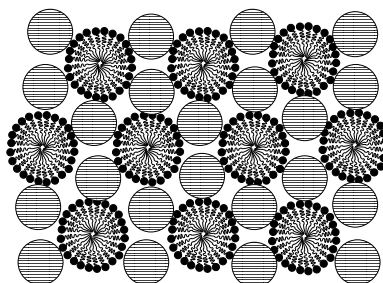


Figure 4: The intercalated hexagonal phase ( $H_1^C$ ), where each DNA strand (denoted by shaded circles) is surrounded by three cylindrical micelles.

In chapter-III, we discuss our x-ray diffraction studies on complexes of double stranded (ds) and single stranded (ss) DNA with CTAB. Since the addition of SHN decreases the spontaneous curvature of CTAB micelles, we have probed the structural modifications induced by SHN on CTAB-DNA complexes.

The diffraction pattern of CTAB-DNA complexes indicate a 2D hexagonal lattice. However the complex can in principle form either an intercalated hexagonal phase or an inverted hexagonal phase. The intercalated hexagonal phase consists of DNA strands intercalated into the direct hexagonal phase of CTAB (fig 4) where each DNA strand is in contact with three micellar cylinders. Though such a structure was proposed earlier for these complexes, it was not well established. An inverted hexagonal phase consisting of DNA strands covered by a surfactant monolayer and arranged on a 2D hexagonal lattice (fig 5), cannot be ruled

out. Such structures have been seen in cationic lipid-DNA complexes. To establish the structure of these complexes, we have modelled the 2D electron density in the plane normal to the axis of the DNA strands for both the structures. The relative intensities calculated from the models were compared with the experimentally observed values. Only the intercalated structure is consistent with the observed intensities. We conclude from here that CTAB-DNA complexes form an intercalated hexagonal phase.

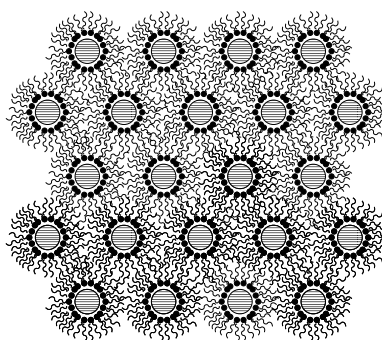


Figure 5: Schematic diagram of the inverted hexagonal phase ( $H_{II}^C$ ) where the DNA strands are confined to the aqueous cores of the micelles.

CTAB-SHN-DNA complexes also form an intercalated hexagonal phase at low SHN concentrations. At a higher SHN concentration, a lamellar phase is observed in the complex. An intercalated lamellar structure is proposed, consisting of DNA strands sandwiched between the bilayers (fig. 6). Similar structures have been observed in cationic lipid-DNA complexes. The hexagonal to lamellar transition of the CTAB-SHN-DNA complex and the cylinder to bilayer transformation of the aggregates in dilute aqueous solutions of CTAB-SHN, occur at

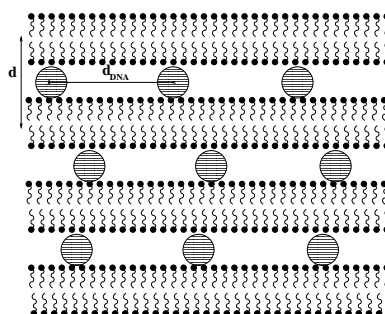


Figure 6: Schematic diagram of lamellar phase ( $L_a^C$ ) of DNA-surfactant complexes, where the DNA strands are sandwiched between surfactant bilayers.

similar SHN concentrations. We conclude from this that the structure of these complexes is determined by the morphology of the aggregates in the surfactant solution. The complexes of ss DNA with CTAB form a hexagonal phase at low SHN concentrations. Since ss DNA strands are highly flexible, the structure consists of cylindrical micelles bridged by the polymer chains. At high SHN concentrations the complex forms a lamellar phase which consists of bilayers bridged by the polymer chains. Thus complexes of ss and ds DNA with CTAB-SHN exhibit similar sequence of phase transitions, though their persistence lengths differ by almost two orders of magnitude.

In chapter-IV, we present our studies on the structural modifications induced by hexanol on CTAB-DNA complexes.

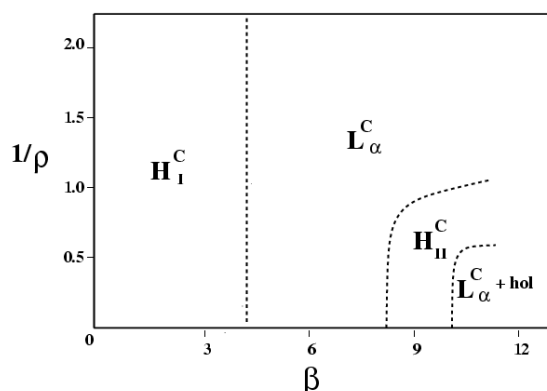


Figure 7: The phase diagram showing the different complexes obtained as a function of hexanol and DNA concentrations.  $\beta = [\text{hexanol}]/[\text{CTAB}]$ ,  $\rho = (\text{wt. of CTAB})/(\text{wt. of DNA})$ . hol denotes the hexanol rich phase coexisting with the complex. The locations of the different phase boundaries have not been precisely determined.

Three different structures and novel re-entrant phase transitions are found in CTAB-hexanol-DNA complexes as shown in fig 7. At low hexanol concentrations, the complex forms an intercalated hexagonal phase ( $H_I^C$ ) which transforms to a lamellar phase ( $L_\alpha^C$ ) on

increasing the hexanol concentration. These transitions are consistent with the cylinder to bilayer transformation of CTAB micelles in the presence of hexanol in aqueous solutions. Hexanol is also known to reduce the bending rigidity of bilayers. This leads to the formation of an inverted hexagonal phase ( $H_{II}^C$ ), at higher hexanol concentrations. The charges on the DNA are more effectively neutralized due to their greater proximity to the surfactant ions in this structure, as compared to  $L_{\alpha}^C$ . Hence the gain in the electrostatic contribution to the free energy is higher in the inverted phase. Further, the energy cost for bending the surfactant monolayer around the DNA is reduced due to their lower bending rigidity in the presence of hexanol thus accounting for the observed behaviour. Further addition of hexanol leads to a phase separation in the surfactant solution to a hexanol rich and surfactant rich phases. The inverted phase reverts back to a lamellar phase possibly due to the decrease in the hexanol content in the surfactant bilayers. At high hexanol content, increasing DNA concentration, leads to a transition from an inverted hexagonal to a lamellar phase. The transition is driven by the lower free energy of the DNA in the complex as compared with that of the uncomplexed DNA in solution. It has been estimated from the geometry of both the structures that nearly twice the amount of DNA can be incorporated into the lamellar phase as compared to the inverted phase at the same surfactant composition. The critical concentration at which the transition occurs can also be estimated. These estimates agree well with the experimentally observed values. Such phase transitions have been predicted earlier, but have not been observed prior to our studies.

In chapter-V, we describe studies on complexes of anionic polyelectrolytes like poly (glutamic acid) (PGA), poly (aspartic acid) (PAA) and poly (vinyl sulfonate) (PVS) with the CTAB-SHN surfactant system.

All complexes form a hexagonal phase at low SHN concentration. Two dimensional rectangular phases consisting of ribbon-like aggregates (fig 8) are formed at high SHN concentrations. The lattice parameters for PGA and PAA complexes are similar, whereas they



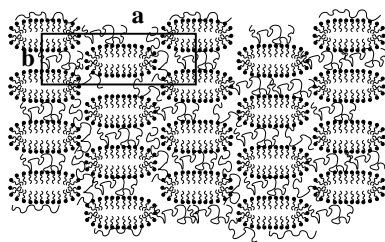


Figure 8: Schematic of the structure of the centred rectangular phase of CTAB-SHN-PAA/PGA/PVS complexes where the ribbon-like surfactant aggregates are bridged by the polyelectrolyte

differ for PVS which has a different charge moiety. The hexagonal phase of the complexes obtained at low SHN concentrations, is consistent with the fact that the surfactant solution consists of cylindrical micelles. The appearance of a rectangular phase in PAA/PGA/PVS complexes and a lamellar phase in DNA complexes, at similar SHN concentrations, is rather surprising. However on estimating the surfactant content in these complexes, we find that the structures seen in these complexes can be correlated with the structures seen in the surfactant system at similar surfactant content.

The dependence of the surfactant content of the complex on the polyelectrolyte used is rather intriguing. The flexibility of the polyelectrolyte cannot be a factor since single as well as double stranded DNA show similar structures at similar SHN concentrations. Since the polyelectrolytes used have comparable bare charge densities, this may also be ruled out as a possible cause. This indicates that the specific interactions between the polyion and the surfactant ion is the most likely cause of the observed behaviour. This conclusion is supported by the results of our studies on the complexes of these polyelectrolytes with the surfactant didodecyldimethylammonium bromide (DDAB).

**The following papers contain the work described in this thesis**

1. Tuning the structure of surfactant complexes with DNA and other polyelectrolytes,  
R. Krishnaswamy, P. Mitra, V. A. Raghunathan, and A. K. Sood,  
Europhys. Lett. **62**, 357 (2003).
2. Structures of some surfactant-polyelectrolyte complexes,  
R. Krishnaswamy, V. A. Raghunathan, and A. K. Sood,  
(to appear in Pramana-J. Phys).
3. Re-entrant phase transitions in DNA-surfactant complexes,  
R. Krishnaswamy, V. A. Raghunathan, and A. K. Sood,  
(submitted for publication).