

**STRUCTURAL MODIFICATION IN REVERSE  
MICELLES AND GROWTH OF ANISOTROPIC  
NANOSTRUCTURES**

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**DEPARTMENT OF CHEMISTRY  
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**STRUCTURAL MODIFICATION IN REVERSE  
MICELLES AND GROWTH OF ANISOTROPIC  
NANOSTRUCTURES**

by

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*in fulfilment of the requirements of the degree of Doctor of Philosophy*

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## CERTIFICATE

This is to certify that the thesis entitled, “**STRUCTURAL MODIFICATION IN REVERSE MICELLES AND GROWTH OF ANISOTROPIC NANOSTRUCTURES**” being submitted by **Ms. Vaishali Sethi** to the Indian Institute of Technology, Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. **Ms. Vaishali Sethi** has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this dissertation have not been submitted in part or full, to any other university or institute for award of any degree or diploma.

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## ABSTRACT

One of the crucial factors in implementation of nanomaterials for fabrication of devices with desired function is precise control of their dimensions. Novel applications of these materials are attainable due to extraordinary chemical and physical properties governed by their shape and size. Designing nanostructures of desired morphology require development of new synthetic protocols to stimulate structural alterations in templates, modulating the architecture of nanometric structures. Systematic efforts have been made to design variable templates for fabrication of fascinating nanostructures. Self-assembly of amphiphilic molecule results in nanostructures of diverse size and shape which can be used for tailored synthesis of nanomaterials. This thesis is an endeavour to develop structural modifications in a tunable soft template, reverse micelles and to evaluate the growth of nanostructures within these nanotemplates. Small-angle X-ray scattering (SAXS) studies were performed to elucidate the morphology and dimensions of these nanotemplates.

Chapter 1 provides details regarding various shape and size dependent properties of nanomaterials, variable templates used for the synthesis of nanomaterials, reverse micelles, literature review and scope of the problem addressed in this thesis. In Chapter 2 synthetic methodology for preparation of hydrotrope-based reverse micellar systems studied in this thesis have been described.

In chapter 3 various aspects of structural transitions in the reverse micellar solution of a cationic surfactant, cetyltrimethylammonium bromide (CTAB) with aliphatic headgroup have been investigated. SAXS studies were designed to understand the effect of hydrotrope (sodium salicylate) concentration and water-to-surfactant molar ratio ( $W_x$ ) on the shape, size, intermicellar interaction and other structural parameters in CTAB /butanol/water/isooctane reverse micellar system. Hydrotrope location inside the micellar assembly is probed with the

help of  $^1\text{H}$ NMR studies on the basis of the changes in the environment polarity of the protons upon its interaction with different components of reverse micellar system.

Chapter 4 demonstrates the morphology of reverse micellar system of a cationic, quaternary pyridinium surfactant was tuned by varying the hydrotrope concentration. SAXS studies were performed on cetylpyridinium bromide/butanol/water/isooctane reverse micellar system to understand the effect of salicylate ion concentration on the dimensions of these systems. Formation of reverse-worm like micelles was evident in these systems. Also interaction between aromatic surfactant headgroup and salicylate ion was investigated with the help of proton NMR studies.

Chapter 5 presents the effect of nature of co-surfactant and organic solvent on the structural aspects of CTAB/hexanol/water/heptane reverse micellar system. SAXS studies have been carried on these reverse micellar assemblies by varying concentration of sodium salicylate and  $W_x$ . Herein, the bridging interactions between hydrotrope-based CTAB/heptane reverse micellar droplets came into picture and is described in terms of stickiness parameter calculated with the help of Baxter sticky hard-sphere model.

Chapter 6 deals with understanding the growth mechanism of formation of anisotropic  $\text{YF}_3$  nanobundles in CTAB/pentanol/aqueous/cyclohexane reverse micellar system.  $\text{YF}_3$  is an important host lattice material for visible and infra-red emission lanthanide-doped upconversion nanoparticles (UCNPs) due to their low phonon energy and thus preventing quenching of excited states of the rare earth ion. Thus, elucidating the fundamental mechanism behind formation of bundle-like morphology of  $\text{YF}_3$  is helpful in developing synthetic strategies for other morphologies and hence helpful in modulating the optical properties of the UCNPs.  $\text{YF}_3$  bundles were obtained by mixing reverse micelles loaded with  $\text{YCl}_3$  and NaF as aqueous phase. Series of time-dependent SAXS measurements were performed to understand morphological evolution of  $\text{YF}_3$  nanobundles within CTAB/cyclohexane reverse micellar pool.

## सार

वांछित कार्य के साथ उपकरणों के निर्माण के लिए नैनोमटेरियल्स के कार्यान्वयन में महत्वपूर्ण कारकों में से एक उनके आयामों का सटीक नियंत्रण है। इन सामग्रियों के उपन्यास अनुप्रयोग उनके आकार और आकार द्वारा शासित असाधारण रासायनिक और भौतिक गुणों के कारण प्राप्य हैं। वांछित रूपरेखा के डिजाइन नैनोस्ट्रक्चर को नैनो-मीट्रिक संरचनाओं के आर्किटेक्चर को संशोधित करने, टेम्पलेट्स में संरचनात्मक परिवर्तन को प्रोत्साहित करने के लिए नए सिंथेटिक प्रोटोकॉल के विकास की आवश्यकता होती है। आकर्षक नैनोस्ट्रक्चर के निर्माण के लिए परिवर्तनीय टेम्पलेट्स को डिजाइन करने के लिए व्यवस्थित प्रयास किए गए हैं। एम्फिलिक अणु के स्व-असेंबली के परिणामस्वरूप विभिन्न आकार और आकार के नैनोस्ट्रक्चर होते हैं जिनका उपयोग नैनोमटेरियल्स के अनुरूप संश्लेषण के लिए किया जा सकता है। यह थीसिस एक ट्यूनेबल मुलायम टेम्पलेट, रिवर्स माइसल्स में संरचनात्मक संशोधनों को विकसित करने और इन नैनोटेम्पलेट्स के भीतर नैनोस्ट्रक्चर के विकास का मूल्यांकन करने का एक प्रयास है। छोटे-कोण एक्स-रे स्कैटरिंग (एसएएक्सएस) अध्ययन इन नैनोटेम्पलेट्स के रूपरेखा और आयामों को स्पष्ट करने के लिए किए गए थे।

अध्याय 1 नैनोमटेरियल्स के विभिन्न आकार और आकार निर्भर गुणों, नैनोमटेरियल्स के संश्लेषण के लिए उपयोग किए जाने वाले परिवर्तनीय टेम्पलेट्स, रिवर्स माइसल्स, साहित्य समीक्षा और इस थीसिस में संबोधित समस्या का दायरा के बारे में विवरण प्रदान करता है। इस थीसिस में अध्ययन किए गए हाइड्रोड्रॉप-आधारित रिवर्स माइसल्स सिस्टम की तैयारी के लिए अध्याय 2 सिंथेटिक पद्धति में वर्णित किया गया है।

अध्याय 3 में एक cationic surfactant के रिवर्स माइसेलर समाधान में संरचनात्मक संक्रमण के विभिन्न पहलुओं, एलीफटिक हेडग्रुप के साथ cetyltrimethylammonium ब्रोमाइड (सीटीएबी) की जांच की गई है। SAXS (एसएएक्सएस) अध्ययनों को हाइड्रोड्रॉप (सोडियम सैलिसिलेट) एकाग्रता और पानी से सर्फैक्टेंट दाढ़ी अनुपात (डब्ल्यू<sub>एक्स</sub>) के आकार, आकार, इंटरमीसेलर इंटरैक्शन और CTAB / Butanol/ water / isoocatne रिवर्स माइसेलर सिस्टम में अन्य संरचनात्मक मानकों के प्रभाव को समझने के लिए डिज़ाइन किया गया था। माइसेलर असेंबली के अंदर हाइड्रोड्रॉप स्थान को रिवर्स माइसेलर सिस्टम के विभिन्न घटकों के साथ बातचीत पर प्रोटॉन की पर्यावरण ध्रुवीयता में परिवर्तन के आधार पर <sup>1</sup>H NMR अध्ययनों की सहायता से जांच की जाती है।

अध्याय 4 एक cationic quaternary pyridinium surfactant की रिवर्स माइसेलर प्रणाली की रूपरेखा का प्रदर्शन करता है, हाइड्रोड्रॉप एकाग्रता बदलकर ट्यून किया गया था। SAXS अध्ययन इन प्रणालियों के आयामों पर salicylate आयन एकाग्रता के प्रभाव को समझने के लिए cetylpyridiniumbromide / butanol / water / isooctane रिवर्स माइसेलर प्रणाली पर किया गया था। इन प्रणालियों में माइसेलर जैसे रिवर्स-वर्म का गठन स्पष्ट था। प्रोटोन एनएमआर अध्ययनों की मदद से सुगंधित सर्फैक्टेंट हेडग्रुप और सैलिसिलेट आयन के बीच भी बातचीत की जांच की गई।

अध्याय 5 सीटीएबी / हेक्सनॉल / पानी / हेप्टेन रिवर्स माइसेलर प्रणाली के संरचनात्मक पहलुओं पर सह-सर्फैक्टेंट और कार्बनिक विलायक की प्रकृति का प्रभाव प्रस्तुत करता है। एसएक्सएस अध्ययन सोडियम सैलिसिलेट और डब्ल्यूएक्स की विभिन्न एकाग्रता से इन रिवर्स माइसेलर असेंबली पर किए गए हैं। यहां, हाइड्रोड्रॉप-आधारित सीटीएबी / हेप्टेन रिवर्स माइसेलर बूंदों के बीच ब्रिजिंग इंटरैक्शन चित्र में आया और बैक्सटर चिपचिपा हार्ड-स्फेयर मॉडल की मदद से गणना की गई चिपचिपा पैरामीटर के मामले में वर्णित है।

अध्याय 6 सीटीएबी / पेंटनॉल / जलीय / साइक्लोहेक्सन रिवर्स माइसेलर सिस्टम में एनीसोट्रॉपिक  $YF_3$  नैनोबंडल्स के गठन की वृद्धि तंत्र को समझने के साथ संबंधित है।  $YF_3$  उनके कम फोनन ऊर्जा के कारण दृश्यमान और इन्फ्रालाल उत्सर्जन लान्टेनहाइड-डोपड अपकवर्जन नैनोकणों (यूसीएनपी) के लिए एक महत्वपूर्ण मेजबान जाली सामग्री है। इस प्रकार,  $YF_3$  की बंडल जैसी मॉर्फोलॉजी के निर्माण के पीछे मौलिक तंत्र को स्पष्ट करना अन्य रूपों के लिए सिंथेटिक रणनीतियों को विकसित करने में सहायक है और इसलिए यूसीएनपी के ऑप्टिकल गुणों को संशोधित करने में सहायक है।  $YF_3$  बंडल को  $YCl_3$  और NaF के साथ जलीय चरण के रूप में लोड रिवर्स माइसेलस मिलाकर प्राप्त किया गया था। सीटीएबी / साइक्लोहेक्सेन रिवर्स माइसेलर पूल के भीतर  $YF_3$  नैनोबंडल्स के आकार के विकास को समझने के लिए समय-निर्भर SAXS (एसएक्सएस) माप की श्रृंखला का प्रदर्शन किया गया था।

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## LIST OF ABBREVIATIONS

Aerosol OT	AOT
Atomic force microscope	AFM
Cetyltrimethylammonium bromide	CTAB
Critical micellar concentration	CMC
Cetylpyridinium bromide hydrate	CPB
Charge coupled device	CCD
Chemical vapor deposition	CVD
Cornell High Energy Synchrotron Source	CHESS
Deuterium oxide	D <sub>2</sub> O
Deoxyribonucleic acid	DNA
Diamond light source	DLS
Ditetradecyltrimethylammonium chloride	DTDAC
European synchrotron radiation facility	ESRF
High – performance liquid chromatography	HPLC
Hydrogen bonds	HBs
Imaging-plate	IP

Indirect Fourier transformation	IFT
Institute of solid state Physics	ISSP
Linear accelerator	LINAC
Localized surface plasmon resonance	LSPR
Micellar droplets	MDs
Minimum hydrotrope concentration	MHC
Multi-wire proportional counter	MWPC
Near-infra red	NIR
Non-linear optical	NLO
One-dimensional	1D
Pair distance distribution function	PDDF
Percus–Yevick approximation	PY
Polymer reference interaction site model	PRISM
poly (p-phenyleneethylene)	PPE
Proton nuclear magnetic resonance	$^1\text{H}$ NMR
Quasi-Light Scattering	QLS
Radius of hard sphere	RHS

Rescaled mean spherical approximation	RMSA
Ribonucleic acid	RNA
Scanning tunneling microscope	SEM
Scattering length density	SLD
Small angle X-Ray scattering	SAXS
Small angle neutron scattering	SANS
Stanford synchrotron research laboratory	SSRL
Surface-enhanced Raman spectroscopy	SERS
Transmission electron microscopy	TEM
Two-dimensional	2D
Three-dimensional	3D
Upconversion nanoparticles	UCNPs
Vacuum ultra violet	VUV
Water-in-oil	W/O
Wormlike micelles	WLMs
YF <sub>3</sub> nanoparticles	YNP
Zero-dimensional	0D