Research Article

Effects of CuCl_2 on the Lyotropic Liquid Crystalline Behavior in Nonaqueous and Aqueous Medium

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Effects of varying doping concentrations (x) of CuCl_2 on the aggregation behaviour of cationic surfactant in nonaqueous and aqueous medium have been investigated. Mixed and pure lyotropic liquid crystalline LLC phases appeared in nonaqueous and aqueous ternary mixtures due to the fast quenching process and then characterized through polarizing optical microscopy and X-ray diffraction technique. The material parameters corresponding to these ternary nonaqueous and aqueous mixtures were evaluated to understand the mechanisms of deriving forces responsible for the modification of mesophases in the presence of metal salt.

1. Introduction

Lyotropic liquid crystals (LLCs) are the subset of the organic soft materials, self-assembled by the aggregation of amphiphilic molecules in the aqueous and nonaqueous domains. Their synthesis depends upon the micellization, reaction medium, thermodynamic equilibria, counter ion effect, optimal surface area of head group, and alkyl chain length [1]. These physicochemical conditions can be tuned to engineer new self-assembled structures, which exhibit unusual physical properties to enable them as prominent materials for variety of applications. The aggregation behaviour of micelles in aqueous medium is well documented in the literature and exploited in the key area of biology, cosmetics, and pharmaceuticals and as soft template to engineer functional nanomaterials [2–4]. New kinds of ternary systems like water, salt, and surfactant (WSS) have been synthesized and characterized to facilitate the development of modified mesostructured, mesoporous materials via self-assembly of ionic and nonionic amphiphilic molecules [3–9]. They could offer confinement of the metal ions in definite ordered geometry even at lower concentration, better control on shape, and size with higher yield [10–13]. However, due to the lack of stability at higher metal density and evaporation of water content from the media, these

systems could not be exploited for the industrial applications [14].

Nonaqueous solvents were found to overcome such problem, as they do possess cohesive energy, dielectric constant and hydrogen bonding ability to initialize the micellization, and thus produce water-free or water-poor stable mesophases (soft templates). Ray [15] first studied the micellar aggregation of dodecyl pyridinium bromide (C_{12}PBr) and tetradecyl trimethyl ammonium bromide (C_{14}TAB) in ethylene glycol. Later, Evans and coworkers reported the lamellar liquid crystals phase formation by lipids in ethylammonium nitrate (EAN) [16, 17]. With the consistent developments of this field, the cubic phase in N-alkylpyridinium surfactants in nonaqueous medium of EAN was reported by Bleasdale et al. [18]. Self-assembly of nonionic polyoxyethylene alkyl ether surfactants into lyotropic liquid crystals in EAN and other systems was reported [19–22]. Recently, we reported the aggregation behaviour of the cetyl pyridinium chloride in the nonaqueous solvent (ethylene glycol) producing mixed (hexagonal + lamellar) and pure lamellar LLC mesophases at lower and higher concentrations, respectively [23].

In this communication, we report on the effects of transition metal salt CuCl_2 on the mesogenic lamellar phase of binary [CpCl -EG (40:60 wt%)] system in nonaqueous and aqueous medium. We characterized them to understand

the packing behaviour of the micelles and the driving forces responsible for the self-assembly of surfactant molecules. In addition, the conductivity of nonaqueous ternary mixtures containing metal salt content $x = 0, 2$, and 4 wt% has been investigated.

2. Experimental

Cetyl pyridinium chloride [$(C_{21}H_{38}NCl)$ Merck, 99% purity], protic solvent ethylene glycol (EG) (SD Fine chemicals, 99% purity) and transition metal salt cupric chloride ($CuCl_2$) (Loba Chemie 99% purity) were used as received. The binary mixture (CpCl:EG) was prepared by dissolving appropriate amount of CpCl in the ethylene glycol (40:60 wt%) through several heating and cooling cycles between melting and room temperature followed by the sonication (37 KHz) for 1 hour near melting point of the surfactant material to ensure the homogeneity.

Nonaqueous ternary mixtures of CpCl: $CuCl_2$: EG were prepared by dissolving the appropriate amount of CpCl in ethylene glycol along with the varying concentration of TMS ($x = 1, 2, 4, 5, 6$, and 10 wt%). The resulting mixtures were homogenized by heating the sample to its melting point in a sealed glass vial followed by the sonication for 1 hour at elevated temperature. Similar procedure was employed to prepare CpCl: $CuCl_2$: H_2O systems. Nonaqueous ternary mixtures of 2 and 4 wt% concentrations (in which cubic rods) were washed with distilled water and ethanol to separate out the cubic rods from the mesogenic template.

The prepared samples were filled between cleaned glass slides and then placed in a temperature controlled hot stage (Linkam TP 94 and THMS 600) with in $\pm 0.1^\circ C$ temperature precision fitted on the polarizing microscope (Olympus BX-51P) stage. X-ray diffraction (XRD) patterns of the soft matter samples were scanned by diffractogram (Philips XPERT-PRO MPD) using $Cu\ \alpha$ radiation source and patterns were recorded at $2\theta = 1-10^\circ$ range. Scanning electron microscopic (SEM) textures were recorded through SEM Quanta, 200 (FEG and FEI Netherlands). Thermodynamical behaviour was investigated using differential scanning calorimeter (DSC model LINSEIS L-63) with heating @ 5 degree/minute for each case. The conductivity of these systems has been evaluated by RCL meter (Fluke model PM 6306).

3. Results and Discussion

3.1. Morphological and Structural Analysis

3.1.1. Nonaqueous Medium. Optical textures of the as prepared, quenched, and aged, metal salt-doped nonaqueous ternary mixtures ($x = 1, 2, 4, 5, 6$, and 10 wt%) recorded at room temperature are shown in Figure 1(a). We noticed the absence of ordering in the as prepared mixtures. It reflects the lack of liquid crystallinity in them at different concentrations as evident from Figure 1(a) (col. 1). However, ternary mixtures spontaneously attained some degree of ordering upon quenching from isotropic to room temperature. We noticed that systems with $x = 1, 2, 4$, and 5 wt% doping concentrations displayed fanlike textures though disrupted

focal cones and dendritic geometry did appear at $x = 6$ and 10 wt%. To further explore the structural information of these systems, XRD measurements were carried out. The diffractogram of these ternary nonaqueous mixtures are presented in Figure 2(a), whereas their consequent d spacing and (hkl) reflection are listed in Table 1. Four diffraction lines were noticed at $x = 2$ wt%, last three lines can be indexed as (001), (002), and (003) reflection of lamellar mesophases although first peak was matched with hexagonal phase. Peaks observed at $x = 4$ wt% is in $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$ ratio, characterized as reflection of hexagonal mesophase. At $x = 1$ and 5 wt%, diffraction peaks were found absent reflecting the lack of liquid crystallinity at these concentration. Diffraction peak observed at $x = 6$ indexed as reflection of lamellar mesophase. However, at $x = 10$ wt% system, diffract well-defined highly intense peaks indexed as (001), (002), and (003) planes of the layered lamellar phase Figure 2(a). Interestingly, some cubic rods, harvested at the nodal point of fan-like texture, were also found at 2 and 4 wt% concentrations. We presume that the growth of such well-ordered cubic rods at $x = 2$ and 4 wt% in the liquid crystalline moiety attributed to the confinement of released metal ions in the mesophase. In the pyridinium salts the following equilibrium exists

In the presence of $CuCl_2$ salt a solid complex separates

The resulting system is a complex mixture of liquid lyotropic and a solid system. The same should be observed for higher concentration of $CuCl_2$, but probably solid is separated in very small aggregates not confine into bigger crystals.

Origin of mesophase in nonaqueous mixtures attributed to the self-organization of amphiphilic and counter ions in the vicinity of solvophobic interactions and electrostatic forces. Structural studies infer that at low metal salt concentrations, disordering in the system owe to the strong attractive electrostatic interactions between Cl^- ion and the positively charged head group. Growth of ordered mesophases at $x = 4$ wt% could corresponds to the increase in the aggregation of number of salt ions near the positively charged hydrophilic crown head group, which certainly enhance the repulsive force between hydrophobic chains (because of the increase in the curvature of hydrophilic crown), thus resulting into hexagonal phase than that of layered lamellar mesophase. Aging effects studied for these ternary systems depicts hexagonal to lamellar transition up to 4 wt% concentrations; however, lamellar phase remains conserved at higher concentrations Figure 1(a) [Col. 3]. The cubic rods thus harvested at nodal point of the focal conic become eventually free from liquid crystalline moieties with the passage of time as system undergoes phase transition. The scanning electron micrograph of obtained rods is presented in the Figure 1(1.1).

A proposed model of the lamellar-hexagonal-lamellar transition observed from the textural and structural studies is illustrated in Figure 3. It is worth emphasizing to say that

FIGURE 1: The optical texture of fresh (Col. 1), quenched (Col. 2), and aged (Col. 3) nonaqueous ternary mixtures having metal salt ratio 1, 2, 4, 5, 6, and 10 wt%, respectively. The optical texture of fresh (Col. 1), quenched (Col. 2), and aged (Col. 3) aqueous ternary mixtures having metal salt ratio 1, 2, 4, 5, 6, and 10 wt%, respectively.

FIGURE 2: The XRD profiles of quenched ternary mixtures having metal salt ratio 1, 2, 4, 5, 6, and 10 wt% (a) nonaqueous (b) aqueous medium, respectively.

TABLE 1: d spacing value and (hkl) planes obtained from XRD patterns of (a) non-aqueous ternary mixtures (b) aqueous ternary mixtures.

(a)							
2 wt%		4 wt%		6 wt%		10 wt%	
d -spacing [Å]	[hkl]	d -spacing [Å]	[hkl]	d -spacing [Å]	[hkl]	d -spacing [Å]	[hkl]
30.65952	*	26.92937	10	10.42664	003	30.56	001
27.05235	001	15.51670	11	—	—	15.5491	002
13.85762	002	13.81812	20	—	—	10.41412	003
9.32170	003	10.41088	21	—	—	—	—
—	—	9.28521	30	—	—	—	—

(b)					
1 wt%		2 wt%		4 wt%	
d -spacing [Å]	[hkl]	d -spacing [Å]	[hkl]	d -spacing [Å]	[hkl]
26.98537	110	38.87693	10	15.71157	10
19.53447	210	27.29848	11	13.77588	11
13.81599	20	13.75712	20	10.35145	20
10.44494	21	11.32786	21	9.62659	21
9.30052	30	10.37896	30	—	—

FIGURE 3: Illustration of lamellar-hexagonal-lamellar transition in nonaqueous ternary mixtures.

such transition in these systems owes to the undulation at the interface.

3.1.2. Aqueous Medium. Micrographs of the freshly prepared, quenched, and aged aqueous ternary mixtures are presented in Figure 1(b). We noticed that the as-prepared systems did not show any ordered texture inferring the lack of liquid crystallinity in them Figure 1(b) (Col. 1). While, quenching (isotropic to room temperature) facilitates the development of well ordered fan like textures at $x = 1, 4$ wt% though no ordered texture has been seen at 2, 5, 6, and 10 wt% as shown in (Col. 2) Figure 1(b). In order to ascertain the validity of our morphological observations, XRD measurements were performed. The observed XRD profiles of aqueous ternary mixtures are shown in the Figure 2(b) and their corresponding d values are tabulated

in Table 1. Five diffraction peaks noticed at $x = 1$ wt%, indexed as reflection of cubic phase $\{(110) \text{ and } (210)\}$ and hexagonal LLC phase. Diffraction peaks at $x = 2$ and 4 wt% correspond to the 10, 11, 20, 21, and 30 plane of 2D hexagonal LLC phase. Liquid crystal order was found missing at $x = 5, 6$, and 10 wt%, as no diffraction was observed. The lack of liquid crystallinity at higher x may owe to the poor solubility of the metal salt. Mesophases observed in aqueous media were stable as a function of time, and no significant changes have been noticed in the optical texture at any concentration as evident from Figure 1(b) [Col. 3].

3.2. Thermodynamic Considerations. Thermodynamic response of both non-aqueous and aqueous ternary mixtures were investigated over wide temperature range 30°C – 120°C to ascertain their thermal parameters and stability.

TABLE 2: Thermodynamic parameters calculated on the base of DSC profiles (a) non-aqueous ternary mixtures (b) aqueous ternary mixtures.

(a)							
Concentration x (wt%)	Phase	Disordering temperatures ($^{\circ}\text{C}$)	Enthalpy (ΔH)	Entropy (ΔS)	Melting temperature ($^{\circ}\text{C}$)	Enthalpy (ΔH)	Entropy (ΔS)
Pure	L	—	—	—	104	-37.5	0.3
1%	No phase	42.6	5.05	-0.118	77	-173.9	2.26
2%	H + L	42.8	8.8	-0.2	73	-44.02	0.6
4%	H	45.4	14.2	-0.3	74	-38.49	0.5
5%	Disrupt	47.2	-32.43	0.6	79	-30.42	0.3
6%	One L peak	48.4	-123.19	2.5	76	-100.9	1.3
10%	L	46.7	-33.35	0.7	78	-45.39	0.5

(b)							
Concentration x (wt%)	Phase	Disordering temperatures ($^{\circ}\text{C}$)	Enthalpy (ΔH)	Entropy (ΔS)	Melting temperature ($^{\circ}\text{C}$)	Enthalpy (ΔH)	Entropy (ΔS)
Pure	No phase	42.1	-74	1.75	65	30.04	0.4
1%	Cubic + H	33.6	-22.2	0.6	76	-777.5	10
2%	2D H	35.1	-82.17	2.3	76	-527.80	6.9
4%	2D H	34.4	-63.03	1.8	74	-600.46	8.1
5%	No	35.6	-117.08	3.2	74	-533.81	7.5
6%	No	—	—	—	75	-454.7	6.0
10%	No	37.5	-97.59	2.6	70	-384.4	5.4

The observed exo and endothermic peaks for nonaqueous and aqueous ternary mixtures are presented in Figures 4(a) and 4(b) respectively. Exotherms observed at lower x (1, 2, and 4 wt%) indicates the nucleation of the ordered structures as shown in Figure 4(a) in the temperature range of 35°C – 50°C . The transition temperature of these mixture increased gradually up to $x = 6$ wt% which decreased at higher x values. The deviation in the transition temperature with the increment in the metal salt content in these systems may depend upon the ordering of the LLC phase (the fact that highly ordered geometries required higher thermal energy than that of less ordered during transitions). Endotherm noticed in high temperature range 65°C – 80°C corresponds to the melting of the parent amphiphilic molecules. We observed around 27°C ($\pm 3^{\circ}\text{C}$) decrease in the transition with respect to pure system.

Figure 4(b) shows the DSC spectra profiles of the aqueous ternary mixtures. We noticed that the transition temperature of dispersed matrix shifted to the lower value (ranging between 33°C – 37°C) than that of pure LC matrix (42°C) in the lower temperature region. Similarly, endothermic peaks were observed for these ternary mixtures in the high temperature region (65°C – 80°C) representing the melting of surfactant molecules. A small shift ($\approx 5^{\circ}\text{C}$) to the higher side in the anisotropic to isotropic transition has been noticed for the dispersed samples.

Entropy (ΔS) calculated for these disordered and melting transitions of nonaqueous and aqueous ternary mixtures are listed in Table 2. The variation of entropy for nonaqueous and aqueous medium corresponding to disorder transitions (in lower temperature region) is illustrated in Figure 5(a).

The entropy for the nonaqueous mixture in this temperature region was found less at lower x , which increased gradually with the variation in x and attained maxima at $x = 6$ wt%, whereas the system at $x = 10$ wt% shows decrease in the magnitude of ΔS . Such behaviour of the entropy corresponds to the order-disorder-order transition in these systems on the basis of structural considerations. The entropy of aqueous ternary mixture was found higher than that of nonaqueous mixture and did not display any regular trend as shown in Figure 5(a). We noticed that the entropy was low at lower x .

Figure 5(b) shows the variation of ΔS as function of metal salt concentration for aqueous and nonaqueous medium in higher temperature range (65°C – 80°C). We observed that the degree of ordering is a function of metal salt content and the temperature as the magnitude of the ΔS shifts to higher value. For nonaqueous ternary mixture the magnitude of the entropy at $x = 1$ wt% was maximum, inferring that addition of the small amount of CuCl_2 disturbed the system vigorously. Further increase in x , decreases the entropy of the system which remains almost constant up to 5 wt%. Similarly, the entropy of the aqueous ternary medium was found minimum for undoped matrix, while dispersion of the metal salt gives rise to ΔS . No specific pattern of the ΔS has been observed for these systems (entropy display minimum magnitude at higher x). It is quite reasonable to say on the basis of ΔS analysis that the nonaqueous ternary mixtures were more ordered than that of aqueous medium at lower and higher x . Our thermodynamical measurements suggest that the formation of LLC phases in these media depends on the quenching, physicochemical interaction and metal salt concentration.

(a)

(b)

FIGURE 4: DSC profiles of ternary mixtures having metal salt ratio 1, 2, 4, 5, 6, and 10 wt% (a) Nonaqueous (b) aqueous medium, respectively.

4. Conductivity Measurement

Figure 6 illustrates the variation of conductivity as a function of temperature for the nonaqueous ternary mixtures $x = 0, 2, 4$ wt%. Undoped liquid crystalline matrix was found metallic in nature though systems with $x = 2$ wt% exhibit semiconducting nature as evident from the Figure 6. It seems quite reasonable to say that such transitions attributed to the percolated defects in the LLC matrix, which consequently decreased the mean-free path of the conduction electrons and likely metal to semiconductor transition takes place. Note that the different subphases being observed in this semiconducting matrix are due to the changes in the morphological structures with the increase in the temperature as displayed in the Figure 6. At $x = 4$ wt%, system shows metallic nature, which may be due to increase in the metal salt density. It seems that the released metal ions in the LLC

(a)

(b)

FIGURE 5: Variation of entropy versus metal salt concentrations ($x = 1, 2, 4, 5, 6$, and 10 wt%) (a) lower temperature region (35°C–50°C) (b) higher temperature region (65°C–80°C), respectively.

matrix are not percolated in the matrix but forming the cluster, which enhances such conduction in the system.

5. Conclusions

In summary, we have investigated the effects of transition metal salt on the aggregation of cationic surfactant in nonaqueous and aqueous medium.

- (1) Highly ordered mixed (lamellar + hexagonal), 2D hexagonal and lamellar layered mesophases were

FIGURE 6: Variation of conductivity as a function of temperature for pure, 2 and 4 wt% metal salt concentrations in nonaqueous medium.

observed in the ternary nonaqueous medium at lower and higher value of x ; however, the liquid crystalline order was found restricted to the lower value of metal salt content in the aqueous media.

- (2) Nonaqueous ternary mixtures with 2 and 4 wt% metal salt content was found stable template as it facilitates the in situ growth of cubic rods ($4\text{--}5\text{ }\mu$ diameter) in the mesophase. These phases can be exploited as soft templates for the fabrication of various metallic and semiconducting materials ranging from micro to nanometer length scale.
- (3) Calorimetric measurements indicate the formation of stable mesophase in nonaqueous and aqueous medium due to fast quenching process.
- (4) The conductivity measurement hints at the use of such soft conducting matrix in many technological applications.

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