



# Effect of hygroscopicity of the metal salt on the formation and air stability of lyotropic liquid crystalline mesophases in hydrated salt–surfactant systems



Cemal Albayrak, Gözde Barım, Ömer Dag\*

Bilkent University, Department of Chemistry, 06800 Ankara, Turkey

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## ABSTRACT

It is known that alkali, transition metal and lanthanide salts can form lyotropic liquid crystalline (LLC) mesophases with non-ionic surfactants (such as  $C_iH_{2i+1}(OCH_2CH_2)_jOH$ , denoted as  $C_iE_j$ ). Here we combine several salt systems and show that the percent deliquescence relative humidity (%DRH) value of a salt is the determining parameter in the formation and stability of the mesophases and that the other parameters are secondary and less significant. Accordingly, salts can be divided into 3 categories: Type I salts (such as LiCl, LiBr, LiI,  $LiNO_3$ ,  $LiClO_4$ ,  $CaCl_2$ ,  $Ca(NO_3)_2$ ,  $MgCl_2$ , and some transition metal nitrates) have low %DRH and form stable salt–surfactant LLC mesophases in the presence of a small amount of water, type II salts (such as some sodium and potassium salts) that are moderately hygroscopic form disordered stable mesophases, and type III salts that have high %DRH values, do not form stable LLC mesophases and leach out salt crystals. To illustrate this effect, a large group of salts from alkali and alkaline earth metals were investigated using XRD, POM, FTIR, and Raman techniques. Among the different salts investigated in this study, the  $LiX$  (where  $X$  is  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ , and  $ClO_4^-$ ) and  $CaX_2$  ( $X$  is  $Cl^-$ , and  $NO_3^-$ ) salts were more prone to establish LLC mesophases because of their lower %DRH values. The phase behavior with respect to concentration, stability, and thermal behavior of Li(I) systems were investigated further. It is seen that the phase transitions among different anions in the Li(I) systems follow the Hofmeister series.

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## 1. Introduction

Oligo(ethylene oxide) type surfactant molecules ( $C_nH_{2n+1}(OCH_2CH_2)_mOH$  denoted as  $C_iE_j$ ) form lyotropic liquid crystalline (LLC) mesophases with water [1], ionic liquids [2], supercritical carbon dioxide [3,4], organic solvents [5–7], and molten hydrated salts [8–11]. The molten hydrated salts are usually divalent transition metal or lanthanide aqua complexes that have melting points close to room temperature (RT). The hydrogen bonding interactions between the coordinated water molecules and ethylene oxide units of the surfactant play an important role in the self-assembly process. In addition to molten hydrated transition metal and lanthanide salt [12], the hydrated lithium salts ( $LiX \cdot nH_2O - C_{12}E_{10}$  systems) also exhibit LLC mesophases at very high salt and very low water concentrations [10], where the salt–water couple collaboratively acts as the solvent component in the system. In these highly concentrated systems water molecules are responsible for the hydration of the ions in the LLC mesophase and the water/salt mole

ratio can be as low as 2 [10]. We refer to such mesophases as salt–surfactant systems in order to distinguish them from the systems at low salt concentrations, where the solvent is merely water rather than the salt–water couple. To the best of our knowledge, the effect of electrolytes on the  $H_2O - C_iE_j$  mesophases has been investigated only at low salt concentrations and the salt species were considered as an additive in the mesophase [13–22].

The behavior of the mesophases at high salt concentrations is significantly different and complex as compared to binary  $H_2O - C_iE_j$  systems [10–11,23]. In the salt–surfactant systems the interactions between the solvent (salt + water) and the surfactant are stronger because of the higher acidity of the coordinated water in the medium. The strong interactions lead to higher stability at both high and low temperatures [11] and may also lead to the emergence of more complex mesocrystalline phases [23]. Moreover, the LC phases of salt–surfactant systems are stable under open atmospheric conditions, while in the  $H_2O - C_iE_j$  systems the water molecules loosely hydrate the surfactant head groups and are prone to water evaporation. Understandably, the phase behavior of the salt–surfactant system significantly depends on the salt species and each salt–surfactant system may exhibit its unique

\* Corresponding author.

E-mail address: dag@fen.bilkent.edu.tr (Ö. Dag).

phase behavior. For instance, the meso-crystalline phases are observed only in LiI, and some Ca(II) and Mg(II) salts [23].

We believe that in such a complex and unexplored area it is important to present a general behavioral study of different salt-surfactant systems (under open atmospheric conditions), that is their LLC mesophase formation tendencies. This kind of a study can also be very helpful for those who would like to use the salt-surfactant LLC systems as medium for material synthesis. In our experiments with many different salts, we observed that some salts are more prone to form LLC phases while others quickly leach out salt crystals or stay as disordered mesophases. Usually, the coordinated/hydration waters are non-volatile at very low relative humidity (RH) levels (10% RH) and they are stable for short time-scales even under a few mbar vacuum conditions. However, the strength of the hydration (or the hydration energy) is not the only determining parameter. For example the LiF·nH<sub>2</sub>O–C<sub>i</sub>E<sub>j</sub> systems are unable to form LLC mesophases because of the very low solubility of the LiF in water. Other parameters are also important such as the strength of the cation···H<sub>2</sub>O···C<sub>i</sub>E<sub>j</sub> and the cation···C<sub>i</sub>E<sub>j</sub> interactions (valence of the cation), and the position of the anion in the Hofmeister series [24]. Nevertheless, we have found out that most of these effects can be summarized by the percent deliquescence relative humidity (%DRH) value of the salt. The %DRH is defined as the percent relative humidity of the surrounding atmosphere at which the material begins to absorb moisture. Therefore, low %DRH means the salts dissolve by absorbing water from the surrounding at lower humidity. Another words, the deliquescence occurs at a critical relative humidity, where a salt spontaneously dissolves by absorbing the ambient water from the air. If the equilibrium vapor pressure of water in a saturated solution is lower than the vapor pressure of water in the air, the salt spontaneously absorbs water from the air until a thermodynamic equilibrium is established. The saturated solutions of such salts are expected to be stable above their %DRH value, see Table 1. To summarize, the tendency of the salt to retain the water is reflected on its %DRH value. We observed that this is also true when the salt species is in the LC mesophase.

In this investigation, we demonstrate that the salts with low %DRH values are more prone to form LLC mesophases in the salt-nH<sub>2</sub>O-surfactant systems. Note also that without water, the salt–C<sub>i</sub>E<sub>j</sub> systems do not form an LLC mesophase unless the melting point of the salt is around RT, and without salts the C<sub>12</sub>E<sub>10</sub>–H<sub>2</sub>O system is unstable under our experimental conditions, because the water evaporates and leaves the system. A large group of salts has been studied over a broad range of salt concentrations, their general tendencies are outlined and their compatibility with the salts %DRH value is presented. The salt-surfactant mesophases need to be further investigated to enable the synthesis of new porous materials [30,31] and as ion membranes [10]. This investigation has been carried out using thin films of the spin coated solutions (salt–C<sub>i</sub>E<sub>j</sub> in excess water) or gels (hydrated salt–C<sub>12</sub>E<sub>10</sub>), and characterizations were done using x-ray diffraction (XRD), polarized optical microscopy (POM), Fourier Transform-Infrared (FT-IR) and Raman spectroscopy techniques.

## 2. Materials and methods

### 2.1. Materials

Tap water was distilled and deionised using a Millipore Synergy 185 water purifier and used without further treatment. Other chemicals were obtained from the following companies and used without further treatment: Sigma Aldrich: LiBr, LiCl, LiNO<sub>3</sub>, LiClO<sub>4</sub>, KSCN, KCl, KClO<sub>4</sub>, KNO<sub>3</sub>, NaI, NaCl, NaNO<sub>3</sub>, NaSCN, NaClO<sub>4</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, C<sub>12</sub>E<sub>18</sub>, C<sub>12</sub>E<sub>10</sub>, and CH<sub>3</sub>COONa. Merck: NaBr, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, KI, and CaCl<sub>2</sub>·6H<sub>2</sub>O. Riedel-de Haen: MgCl<sub>2</sub>·6H<sub>2</sub>O.

### 2.2. Preparation of the LLC gel samples

The LLC gel samples were directly prepared by mixing the required weight of the ingredients without further treatment. This procedure allows definite control and knowledge of the amount of the ingredients. Some samples of LiCl·nH<sub>2</sub>O–C<sub>12</sub>E<sub>10</sub>, LiClO<sub>4</sub>·nH<sub>2</sub>O–C<sub>12</sub>E<sub>10</sub> and H<sub>2</sub>O–C<sub>12</sub>E<sub>10</sub> were also prepared in this way. The

**Table 1**

Percent deliquescent relative humidity of salts [25–29] at 25 °C – except otherwise noted. Color codes are used to categorized salts: Type I salts with blue, Type II salts with green and Type III salts with red color. Other salts were not investigated except NaOH which is air reactive.

Salt	%DRH [25]	Salt	%DRH [25]
<b>H<sub>2</sub>O</b>	100	<b>NaBr</b>	57.0
K <sub>2</sub> SO <sub>4</sub>	100	NaBr-KBr mixture	56.0
KClO <sub>3</sub>	98.0	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> ·1/2H <sub>2</sub> O	55.0 (27°C)
CaHPO <sub>4</sub> ·2H <sub>2</sub> O	97.0	NH <sub>4</sub> Cl-NaBr mixture	54.0
KH <sub>2</sub> PO <sub>4</sub>	96.6	NaNO <sub>3</sub> -KBr mixture	54.0
<b>KNO<sub>3</sub></b>	95.0-91.0	<b>Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O</b>	52.0(24.5°C)
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	93.0	<b>Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O</b>	51.0
Na <sub>2</sub> C <sub>2</sub> H <sub>4</sub> O <sub>6</sub> ·2H <sub>2</sub> O	92.0	<b>NaClO<sub>4</sub></b>	43-46 [27,28]
ZnSO <sub>4</sub> ·7H <sub>2</sub> O	88.5	K <sub>2</sub> CO <sub>3</sub> ·2H <sub>2</sub> O	43.0
BaCl <sub>2</sub> ·2H <sub>2</sub> O	88.0 (24.5°C)	<b>NaI</b>	38.17 [26]
Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O	87.0	<b>MgCl<sub>2</sub>·6H<sub>2</sub>O</b>	33.0
<b>KCl</b>	89.0-84.5	<b>CaCl<sub>2</sub>·6H<sub>2</sub>O</b>	31.0
C <sub>12</sub> H <sub>22</sub> O <sub>17</sub>	85.0	CH <sub>3</sub> COOK	19.0
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	83.0-81.1	<b>LiI</b>	17.56 [26]
<b>KBr</b>	79.0	(CH <sub>3</sub> COO) <sub>2</sub> Ca·H <sub>2</sub> O	17.0
NH <sub>4</sub> Cl	79.3-77.0	<b>LiCl·H<sub>2</sub>O</b>	13.0
CH <sub>3</sub> COONa	77.0	<b>LiNO<sub>3</sub></b>	12.86 [29]
CO(NH <sub>2</sub> ) <sub>2</sub>	76.7-76.0	<b>H<sub>3</sub>PO<sub>4</sub>·1/2H<sub>2</sub>O</b>	9.0
<b>NaCl</b>	76.5-75.0	NaOH	6.5
<b>NaNO<sub>3</sub></b>	76.0-74.0	<b>LiBr</b>	6.37 [28]
K <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·1/2H <sub>2</sub> O	75.0	P <sub>2</sub> O <sub>5</sub>	0.0
<b>LiClO<sub>4</sub></b>	~70 [28]		
<b>KI</b>	68.86 [26]		
NH <sub>4</sub> NO <sub>3</sub>	63.5		

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