

Physicochemical studies of morpholinium based ionic liquid crystals and their interaction with cyclodextrins



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ARTICLE INFO

Article history:

Received 31 July 2013

Received in revised form 15 October 2013

Accepted 17 October 2013

Available online 29 October 2013

Keywords:

Inclusion complex
Aggregation number
Chemical shift
Packing parameter
Ionic liquids

ABSTRACT

The various physicochemical properties of morpholinium based ionic liquid crystals (ILC) (*N*-methyl-*N*-tetradecylmorpholinium bromide (M14) and *N*-methyl-*N*-hexadecylmorpholinium bromide (M16)) in the absence and presence of β -cyclodextrin (β -CD) and hydroxypropyl- β -cyclodextrins (HP β -CD) have been studied using conductance, surface tension, fluorescence and ^1H NMR measurements. The various micellar, interfacial and thermodynamic parameters such as critical micelle concentration (*cmc*), degree of counterion binding (*g*), association constants (*K*), surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}), aggregation number (N_{agg}), interaction parameter (β^m), standard Gibbs free energy of adsorption (ΔG_{ads}^0) and standard Gibbs free energy of micellization (ΔG_{m}^0) have been evaluated for mixtures of M14/M16+ β -CD/HP β -CD. Conductance study also shows that cyclodextrins (CDs) entraps in hydrophobic moieties of ILC to form inclusion complexes with stoichiometry of 1:1. The formation of inclusion complexes is confirmed by increase in *cmc* of synthesized ILC and changes in chemical shift of CDs and ILC protons in the presence of CDs. Forces responsible for the formation of inclusion complexes are van der Waals, hydrogen bonding, hydrophobic interactions, release of ring strain in cyclodextrin molecules and changes in solvent-surface tensions. The value of packing parameter ($p > 0.5$) for pure ILC which suggest a flexible bilayer arrangement for ILC.

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1. Introduction

Ionic liquid crystal (ILC) is an enthralling class of material that combines the properties of ionic liquids and liquid crystals [1]. Just as ionic liquids, the properties of ILCs can be tuned by an appropriate choice of anions and cations. These salts have been used as ordered solvents, templates for the synthesis of mesoporous and zeolitic materials, optoelectronics and dye-sensitized solar cells [2–7]. Among the known ILCs, imidazolium or pyridinium salts are the most studied compounds [8]. Only few thermotropic ILCs based on other cations have been reported [9]. Out of which morpholinium based ILCs received much attention because of their structural properties especially for the design of ILC and their mesomorphic behavior [10,11]. These are widely used for organic synthesis, heat stabilizers, and antioxidants for lubricating oils and for electrochemical purposes as corrosion inhibitors [12–14]. They have been considered in recent incoivity tests, among other commonly used ILs [15] and applied as gel polymer electrolytes [16]. Despite the argued advantage of having low vapor pressure, even the most hydrophobic ILs show some degree of solubility in water, allowing their dispersion into aquatic systems and raising

concerns on its pollutant potential [17]. So, the disadvantage is that once these ILC have been used it is essential to extract these compounds and for this purpose a material having extracting property is required. Hence, the present work was aimed to resolve this scientific challenge which would provide momentous information to the environmentalists.

CDs are well-known for including various guest molecules, and this unique ability makes them functional in cosmetics, pharmaceutical science, and several other fields [18,19]. CDs have homogeneous toroidal structures of different molecular sizes: most typical are cyclohexaamylose (α -CD), cycloheptaamylose (β -CD), and cyclooctaamylose (γ -CD). The primary hydroxyl groups are located at the wider rim and the secondary hydroxyl groups are found at the narrower rim [20,21]. The toroidal structure has a hydrophilic surface, making them water-soluble, whereas the cavity is composed of the glucoside oxygens and methylene hydrogens, giving it a hydrophobic character. As a consequence, the CDs are capable of forming inclusion complexes with compounds having a size compatible with dimensions of their cavity [22,23]. β -Cyclodextrin (β -CD) is of special consideration, since the size of its cavity is suitable for many donor molecules such as the surfactants' hydrophobic tail. Hydroxypropyl- β -cyclodextrins (HP β -CD) are nontoxic and biodegradable and, hence, widely usable without risk for the environment. They can be employed to remove non aqueous phase liquids from contaminated soils and

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groundwater as they enhance the water solubility of nonpolar organic compounds and their biodegradation and reduce their sorption onto the soil [24,25]. Thermodynamic properties are very sensitive to the hydrophobic, hydrophilic interactions and to a lesser extent, electrostatic interactions. Therefore these properties have been revealed as suitable to study the cyclodextrins in the presence of surfactants. The complex formation of CDs and surfactants has been examined by many techniques from physico-chemical point of view [26–28]. However there is no report in the literature comprises the interactions between the morpholinium ILC and CDs. As there are few reports on morpholinium salts with varying anionic species and alkyl chain length of cationic group [11,29,30].

Morpholinium ILC, *N*-methyl-*N*-tetradecylmorpholinium bromide (M14) and *N*-methyl-*N*-hexadecylmorpholinium bromide (M16) also show aggregation behavior as that of surfactants due to their amphiphilic properties. Hence, all the theories used to the study the behavior of surfactant+ CDs mixtures are applied on the ILC+ CDs systems. The objective of the present work is to study the encapsulation processes of cationic morpholinium ILC, *N*-methyl-*N*-tetradecylmorpholinium bromide (M14) and *N*-methyl-*N*-hexadecylmorpholinium bromide (M16) into the cavity of β -CD and HP β -CD and its effect on the micellization and interfacial properties of the surfactants. The various physicochemical techniques such as conductance, surface tension and fluorescence have been employed in order to predict different micellar, interfacial and thermodynamic parameters. However these techniques provide only indirect information on the molecular structure of the inclusion complexes. To understand the type of interactions and orientations of the molecules inside the cavity of CDs, ^1H NMR has been employed. The experimental results obtained through the present study might be practically useful because they will (1) assist researchers in determining whether their properties are practical for further applications, and (2) provide a useful background to investigate morpholinium ILCs with other species.

Table 1
Supplier and purity of chemicals used.

Chemicals	Supplier	Purity (%)
Pyrene	Sigma–Aldrich	≥ 99.0
1-Bromotetradecane	Sigma–Aldrich	≥ 99.0
1-Bromohexadecane	Sigma–Aldrich	≥ 99.0
4-Methylmorpholine	Sigma–Aldrich	≥ 99.0
β -CYCLODEXTRINS	Sigma–Aldrich	≥ 97.0
Hydroxypropyl- β -cyclodextrin	Sigma–Aldrich	≥ 98.0
Acetonitrile	Merck	≥ 99.9
Hexadecylpyridinium chloride	HIMEDIA	≥ 97.0

2. Experimental

2.1. Materials

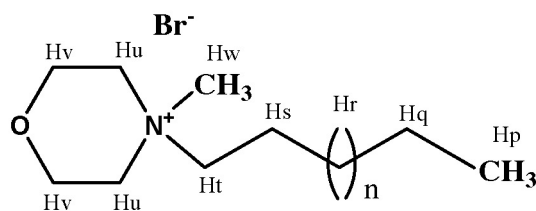
Morpholinium ILC, *N*-methyl-*N*-tetradecylmorpholinium bromide (M14) and *N*-methyl-*N*-hexadecylmorpholinium bromide (M16) (Fig. 1) were synthesized and purified as described in literature [11]. The purities of the chemicals used and their suppliers are given in Table 1. All the chemicals were of analytical grade and used without further purification. Purity of the products was assessed by ^1H NMR spectroscopy and surface tension. Double distilled water having specific conductivity of range $(1-2) \times 10^{-6} \text{ S cm}^{-1}$ was used for the solution preparations. The solutions were prepared by mass with an accuracy of $\pm 0.0001 \text{ g}$ using Sartorius analytical balance. All the measurements have been performed at $25.0 \pm 0.1^\circ \text{C}$ after giving overnight time for the stabilization.

2.2. Methods

2.2.1. Specific conductivity measurements

The specific conductivity (κ) measurements of morpholinium ILC (M14, M16) and their mixtures with β -cyclodextrin (β -CD) and hydroxypropyl- β -cyclodextrin (HP β -CD) were carried out at

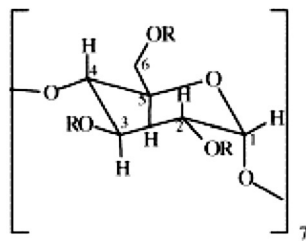
(a) *N*-methyl-*N*-alkylmorpholinium bromide



($n = 10$ for *N*-methyl-*N*-tetradecylmorpholinium bromide, M14)

($n = 12$ for *N*-methyl-*N*-hexadecylmorpholinium bromide, M16)

(b) Cyclodextrins



($\text{R} = \text{H}$ for β -cyclodextrin)

($\text{R} = \text{CH}_2\text{-CH}(\text{CH}_3)\text{-OH}$ for Hydroxypropyl- β -cyclodextrin)

Fig. 1. Molecular structures and their proton group assignments of morpholinium ILC and CDs.

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