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Simple one step synthesis of gemini cationic surfactant-based ionic liquids: Physicochemical, surface properties and biological activity

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ABSTRACT

In this work three gemini cationic surfactant-based ionic liquids were synthesized in one step. Alkylation of tridodecylamine was performed with 1,2-dibromoethane, 1,3-dibromopropane, and 1,6-dibromohexane in ethanol. Chemical structures of synthesized cationic surfactant-based ionic liquids were characterized using FTIR and ^{1}H NMR. The effect of spacer length of these types of ionic liquids on physicochemical properties such as melting point, density and viscosity has been investigated. The surface tension at different temperatures was measured and the surface parameters including: the critical micelle concentration (CMC), effectiveness (π_{cmc}), efficiency (Pc_{20}), maximum surface excess (Γ_{max}) and minimum surface area (A_{min}), were calculated. Adsorption and micellization thermodynamic parameters were calculated and shown that the two processes are spontaneous. It is clear that the synthesized surfactant ionic liquid showed their tendency towards adsorption at the interfaces and also micellization in the bulk of their solutions. The antimicrobial activity of the synthesized surfactant ionic liquids against gram-negative and gram-positive bacteria as well as fungi was evaluated. The efficiency of these compounds as antimicrobial agents was increased with the hydrophobicity and spacer length of the gemini ionic liquids.

1. Introduction

Ionic liquids (ILs) are organic salts with melting points below 100 °C and consider as a new type of non-molecular ionic solvent with ability for use in many applications as solvents, catalysts and electrolytes [1–4]. ILs are outstanding good solvents as they are non-volatile, non-flammable, have a high thermal stability and favorable solvation properties for a broad range of organic, inorganic and polymeric materials. Although earlier applications of ILs were mainly in chemical separations [5,6], organic chemistry [3,7] and electrochemistry [8], the scope of their application is now much broader and covers their use in biocatalysts [9], polymer science [10], sensors [11], solar cells [12], fuel cells [13] and biomass processing and as thermal fluids, ion gels and lubricants [14,15].

IL compounds are called 'green' usually because of their negligible vapor pressure. Low volatility, however, does not completely eliminate potential environmental hazards and can pose serious threats to aquatic and terrestrial ecosystems [16]. There are many other factors that determine whether ILs are or are not green. Today, it is very important that not only ILs themselves should be green (low toxicity or biodegradability), but also their synthesis [17]. In this respect, however, extensive studies on toxicity and biodegradability of ILs are necessary.

Ionic liquids with the chemical structure of gemini surfactants should have special properties and several applications in many areas, so synthesis of gemini ionic liquids and investigated their properties are interesting research. Furthermore, it is found that the length of the spacers and the number of carbon atoms in aliphatic chains can significantly affect the physicochemical properties of gemini surfactant ionic liquid. Although gemini ionic liquids with spacers of different lengths have been synthesized and their biological activity was investigated in previous studies [18–21].

Biological activity and toxicity of gemini ionic liquids are of great interest because of their increasing applications. Surfactants have a good antimicrobial activity against pathogenic bacteria and fungi as reported by several researchers [22–30]. These types of ionic liquids have significant toxic effects on pathogenic bacteria and fungi. The antimicrobial activity of 1-alkylquinolinium bromides was studied [31]. Pyridinium, imidazolium and quaternary ammonium salts were found to be toxic to pathogenic bacteria and fungi [32]. The toxicity of these compounds increases with increasing the length of the alkyl chain and spacer between two head groups [33,34].

In the present work three gemini cationic surfactants based on ionic liquids were synthesized and characterized. The effect of the alkyl chain, spacer attached to the head group and the nature of this cationic head group on the physicochemical, surface activities and antimicrobial activity was investigated. This study is intended to provide an improved

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understanding of the structural parameters affecting surface activity and biological activity of long-chain ionic liquids.

2. Materials and methods

2.1. Materials

Tridodecylamine (purity > 97%), 1,2-dibromoethane (purity > 98%), 1,3-dibromopropane (purity > 99%) and 1,6-dibromohexane (purity > 98%) were analytical grade chemicals which were obtained from Aldrich Chemical Company (Germany). All the solvent and reagents were used as received without further purification.

2.2. Synthesis

2.2.1. Synthesis of gemini cationic surfactant-based ionic liquids

The synthesized gemini ionic liquids were obtained by coupling reaction between 1,2-dibromoethane, 1,3-dibromopropane and 1,6-dibromohexane (0.1 mol) and tridodecylamine (0.2 mol) in 50 ml acetone. The reaction mixture was refluxed for 12 h and left for complete precipitation of the gemini compounds. Produced gemini surfactants ionic liquids were filtered off and recrystallized three times from acetone to produce the desired gemini cationic surfactants ionic liquids (G2IL, G3IL and G6IL), Scheme 1 [35].

2.3. Measurements

2.3.1. Density measurements

To measure the density, a standard 5 ml pycnometer was calibrated by using deionized water at 298 K (0.9970 g cm^{-3}) [36,37]. The pycnometer was filled with dried and degassed ionic liquid sample.

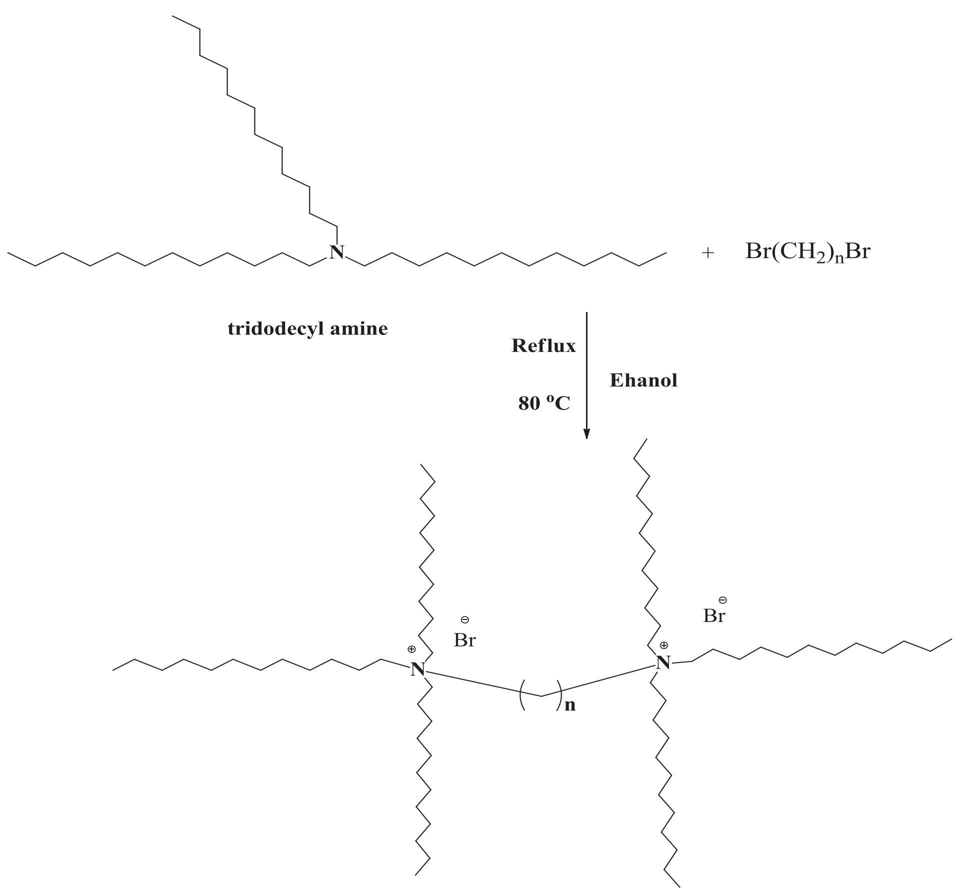
The working equation for calibration of pycnometer is

$$V = \left(m_{(w+e)} - m_e\right)_{/} p_{w=} m_{w/} p_w \quad (1)$$

where $m_w = 4{:}8381$ g is water mass filled in the pycnometer, the mass of empty pycnometer $m_e = 8.8033$ g. m_{w+e} is the mass of filled pycnometer, p_w is density of distilled water at 298 K (997.04593 ± 0.00081 $kg \cdot m^{-3}$). Masses were determined using Sartorius electronic analytical and precision balance (TE214S) with readability of 0.1 mg.

2.3.2. Viscometric measurements

The intrinsic viscosities (η) of the synthesized gemini ionic liquids was measured in distilled water at temperature range of (50–90 °C) using a capillary viscometer (Übbelhode suspended level type) under thermostated condition at surfactant concentrations 0.5 $g \cdot L^{-1}$ [38].



n= 2: N^1,N^1,N^1,N^2,N^2,N^2-hexadodecylethane-1,2-diaminium bromide

n= 3: N^1,N^1,N^1,N^3,N^3,N^3-hexadodecylpropane-1,3-diaminium bromide

n= 6: N^1,N^1,N^1,N^6,N^6,N^6-hexadodecylhexane-1,6-diaminium bromide

Scheme 1. The chemical structure of the synthesized gemini surfactant ionic liquids.