Synthesis and determination of Surface tension of 1-butyl-3-methylimidazolium lauroyl sarcosinate IL and Tween 80

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Abstract. Ionic liquids (ILs) have unique physicochemical properties. ILs with long carbon chains are called surface-active ILs, and they have surfactant properties. In this study, we synthesize (1-butyl-3-methylimidazolium lauroyl sarcosinate) [BMIM] [Lausar] IL that have surfactant properties. Nuclear magnetic resonance spectroscopy (NMR) was used to confirm the chemical structure of the synthesized IL. The surface tension of [BMIM] [Lausar] was determined that it was almost 37.1mN/m. Tween 80 is the most famous commercial surfactant, and we also determine the surface tension of Tween 80. Afterword, we make the binary mixture of Tween 80 and IL-based surfactants. Based on our results, we can conclude that Tween 80 and [BMIM] [Lausar] both reduced surface tension and have excellent surface properties when combining and can be used as surfactants in many sectors.

Keywords: Surfactants; Ionic liquid-based surfactants; Nuclear magnetic resonance; Surface tension.

1. Introduction

Ionic liquids (ILs) are an area of great interest for the scientific community, especially green chemistry [1]. ILs are called as green solvents because they have a green reaction without any by-product and have much application in the colloid and surface chemistry [2]. Ionic liquids are defined as salts that are liquid at room temperature with a melting point of less than 100 °C consisting of organic cations and inorganic or organic anions [3]. ILs, have unique physicochemical characteristics like low vapor pressure, non-
flammable, high solubility, toiler made properties, and excellent thermal stability [4]. These extraordinary characteristics led to the application of ILs in various industries, such as chemical, biotechnology, and membrane technology, etc. [5]. ILs that have a long hydrophobic tail and the hydrophilic head is called as ionic liquid-based surfactants, having amphiphilic properties [6]. SAILs are the best alternate of old surfactants in many processes like solubilization, protein folding because they are environmentally friendly and amphiphilic nature [7]. Different cationic head groups such as morpholinium, cholinium, imidazolium, and amino acid with a light alkyl chain many SAILs had been synthesized. Cationic head and alkyl chain played a vital part in the agglomeration nature and interfacial properties of ionic liquid-based surfactants solutions [8]. In current years, the synthesis of imidazolium-based SAIL had become much famous because of batter aggregation properties of imidazolium based ILs compared to others [9].

To increase the utilization and design understanding regarding the physical and chemical characteristic of SAILs is required. Notably, knowledge regarding interfacial and surface tension is more matter of concern [10]. Surface tension (γ) of ILs is a very significant physical characteristic; to determine interaction or synergism among ions, surface tension is an essential parameter. The surface tension of ILs showed cohesive forces among molecules of liquid that are present at the surface. Unfortunately, the information regarding the surface tension of ILs is still inadequate, erratic, and contradictory [11]. The surface tension of ILs could be determined by experimental methods and projected by models. Though, data regarding experimental surface tension of pure IL is very less [12]. Amino acid and fatty acid-based IL have been arisen as a new class of natural surfactants that are greener, halogen free with low toxicity and excellent biodegradability [13, 14]. Lauroyl sarcosinate ILs is almost new with limited available literature, therefore it has vast opportunities for future studies and research [15]. New biocompatible surface active lauroyl sarcosinate IL, (SALsILs) using cationic head group such as imidazolium is synthesized (Fig.1 b).

Tween 80 is a single-tailed nonionic surfactant that is mostly used as emulsifier and dispersant (Fig.1 a). Tween 80 has low viscosity and have low critical micelle concentration in comparison to another Tween family [16]. Tween 80 is a hydrophilic surfactant with hydrocarbon components such as Span 20 and formed densely packed interface, which in result significantly reduced IFT values compared to those values obtained from single surfactants [17].

Therefore, in our present study, we synthesize SAIL IL 1- butyl-3-methylimidazolium lauroyl sarcosinate [BMIM] [Lausar]. NMR confirms the chemical structure of synthesized SAIL. We also determine the surface tension of Tween 80 and IL 1- butyl-3-methylimidazolium lauroyl sarcosinate [BMIM] [Lausar].
2. Methodology

2.1. Materials

The chemicals utilized were; IL1-butyl-3-methylimidazolium chloride (from Merk Germany), N-lauroyl sarcosine sodium salt, ethanol, acetone, and Tween 80 were also obtained from Sigma-Aldrich (Malaysia).

2.2. Synthesis of IL 1-butyl-3-methylimidazolium lauroyl sarcosinate

[BMIM] [Lausar] was synthesized according to a well-known method [18]. The metathesis process prepared [BMIM] [Lausar]. In detail, the cationic chloride component and N-acyl amino sodium salt as an anion component with a 1:1 M ratio were mixed. Then ethanol was put in this mixture with (1:2; w/v) in the absence of nitrogen. This mixture was stirred for 46 h at 25 °C. Then the mixture was evaporated at a rotary evaporator at 85 °C under 650 bar pressure until the mixture became viscous and all ethanol evaporates. After evaporation, adds acetone and stirrer mixture for 20 minutes at 340 rpm then settled down for ten minutes. Remove the upper transparent layer and filter it. The resulted IL was collected from sodium chloride by the filtration method. The ethanol from the synthesized IL was evaporated using a rotary evaporator at 80 °C for 5h under 250 bar pressure.

![Synthesis process of [BMIM] [Lausar]](image)

2.3. Nuclear magnetic resonance (NMR) spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy, H NMR of [BMIM] [Lausar] was done using 500 MHz Bruker Avance III NMR spectrometer at 25 °C that is equipped with a superconducting magnet. For NMR analysis, almost 30 mg of [BMIM] [Lausar] was added into a 5mm NMR tube. The operational frequency of the instrument was 500.13 MHz for 1H NMR. The sample was dissolved in deuterated methanol (CH3OD) solution to get H NMR spectra. The signals at the 3.35, 4.25 ppm were used as an internal reference for 1H. The result of the analysis is given as follows:

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\begin{align*}
\delta & = 0.65 – 0.808 (3H, CH_3), 0.89 – 0.989 (3H, CH_3), 0.99 – 1.43 (18H, CH_2), 1.97 – 1.5 (2H, CH_2), 1.678 – 1.782 (2H, CH_2), 2 – 2.493 (2H, CH_2), 2.732 – 2.989 (3H, CH_2), 3.77 – 3.897 (5H, CH_3), 4 – 4.1 (2H, CH_2), 7.4-7.5 (2H, CH_3), 8.789-9.0012 (1H, CH_2).
\end{align*}
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2.4. Measurement of surface tension

The stock solution of Tween 80 and [BMIM] [Lausar] were prepared by adding ten times higher concentration than cmc of the pure component in double-distilled water. Tensiometer (Dataphysics DCAT 15 Germany) was used to measure the surface tension of Tween 80 as well as [BMIM] [Lausar]. The tensiometer was controlled by SCAT software, and measurement were performed using Wilhelmy platinum plate, with a thickness of 0.22 mm and area 3.99 mm$^2$ with accuracy ±1.4% at 25 °C ± 0.2 K. Before the start of experiment plate was washed by distilled water and dry at blue Bunsen flame before every measurement. Each experiment was performed in triplicate at the same circumstances, along with the ambiguity of 0.02 mNm$^{-1}$. At the start of the experiment, the accuracy of the instrument was confirmed by determining the surface tension of distilled water, which was found 71.99 mN/m, which is like previous studies.

3. Results and discussion

3.1. Nuclear magnetic resonance spectroscopy (NMR) of [BMIM] [Lausar]

The synthesis of IL was confirmed by $^1$H NMR spectroscopy to check the chemical structure. The $^1$H NMR spectra are shown in Fig.3. The three major peaks in this spectrum showed the presence of lauroyl sarcosinate anion with hydrogen bonding. The peak that is obtained among 2.3, as well as 2.45 ppm, is due to the reduction of a nuclear charge of fatty acid. Raley et al. also observed that fatty acid showed a peak at a range of 2.33 ppm, which is almost similar to our results [19]. The peak obtained at 0.82 ppm indicated the presence of CH$_3$; this is also confirmed by Abdullah et al. [20]. The other spike is obtained at 2.962 ppm that is due to the presence of electronegative nitrogen. Finally, the third peak is obtained in the range of between 3.88 and 3.95 ppm, which is more downfield due to the electronegativity of nitrogen and carbonyl group.

![Fig.3 $^1$H NMR of [BMIM] [Lausar]](image-url)
3.2. Determination of surface tension of Pure components

The variation in surface tension versus log C of Tween 80 and [BMIM] [Lausar] was determined at 25 °C and presented in fig. 4 (a, b), respectively. It is clear from Fig.4 that surface tension of [BMIM] [Lausar] and Tween 80 decrease with an increase in the concentration of surfactant in water. This showed that adsorption of surfactants at the air/solution interface and then surface tension concentration curve break at a specific point, and that point is called as critical micelle concentration. The surface tension of surfactants decreases rapidly with increase in the concentration of the surfactants and a point came where it became constant is called as critical micelle concentration. The critical micelle concentration of Tween 80 is similar to previous literature [21]. The decrease in surface tension is due to electrostatic repulsion between the hydrophobic chain and polar medium, which leads to the shifting of surfactant molecules toward the air/water interface.

![Fig.4](image)

Fig.4 Surface tension vs log concentration of (a) Tween 80 (b) [BMIM] [Lausar] at 25 °C.

The increase in chain length decreases the cmc value because the micelle formed more easily with the increase in the hydrophobic nature of surfactants [22].

3.3 Binary mixture of Tween 80 and [BMIM] [Lausar]

The cmc value of binary mixture of Tween 80 and [BMIM] [Lausar] at 70: 30 mol ratio is shown. It is clear from the fig that mixture of surfactants has low cmc value as compared to individual. Tween 80 lower the cmc value of [BMIM] [Lausar] molecules and start to form micelle at lower concentration. In individual and mixed surfactant system with the increase concentration of surfactants reduced the cmc value due to two factors first effect of solvency and second factor is electrostatic effect [23].
Conclusion

In the present study, we synthesize IL-based surfactants such as [BMIM] [Lausar] and determine its surface tension and critical micelle concentration. The chemical structure of synthesized SAIL was confirmed by NMR spectroscopy. We also assess surface tension and critical micelle concentration value of a famous chemical surfactant such as Tween 80. From results, it is cleared that [BMIM] [Lausar] and Tween 80 decrease their surface tension with increasing concentration of surfactant. The surface tension of [BMIM] [Lausar] and Tween 80 is 37.1 and 46 mN/m, respectively. The binary mixture of Tween 80 and [BMIM] [Lausar] have low cmc as compared to individual components. From these results, we can conclude that these two chemicals have surfactant properties and can be utilized in many sectors.

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