



HAL
open science

Synthesis and characterization of analogues of glycine-betaine surface-active ionic liquids

Inês Cardoso, Emanuelle L.P. de Faria, Armando J.D. Silvestre, Mara Freire, Aminou Mohamadou

► **To cite this version:**

Inês Cardoso, Emanuelle L.P. de Faria, Armando J.D. Silvestre, Mara Freire, Aminou Mohamadou. Synthesis and characterization of analogues of glycine-betaine surface-active ionic liquids. *Journal of Molecular Liquids*, 2021, 342, pp.117440. 10.1016/j.molliq.2021.117440 . hal-03353168

HAL Id: hal-03353168

<https://hal.univ-reims.fr/hal-03353168v1>

Submitted on 16 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Synthesis and characterization of analogues of glycine-betaine surface-active ionic liquids

Inês S. Cardoso^{1#}, Emanuelle L. P. de Faria^{1#}, Armando J. D. Silvestre¹, Mara G. Freire¹,
Aminou Mohamadou^{2*}

¹CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro,
Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

²Institut de Chimie Moléculaire de Reims (ICMR), UMR CNRS 7312, Université de Reims
Champagne-Ardenne, Moulin de la Housse, BP 1039 – 51687 Reims cedex 2, France.

#equally contributing authors

* Corresponding author: Tel: +33 (0)32691 3334; Fax: +33 (0)32691 3243

E-Mail : aminou.mohamadou@univ-reims.fr

HIGHLIGHTS

- Synthesis and characterization of 8 ionic liquids with surfactant properties
- Thermal properties, micelle diameter and critical micellar concentration were determined
- Toxicity towards *Aliivibrio fischeri* was determined
- Most ionic liquids display more attractive properties than the conventional surfactant

Abstract

With the goal of finding sustainable solvents, novel ionic liquids (ILs) with low ecotoxicity features have been a target of research. Among these, ILs with surface-active characteristics play a significant role in the food, cosmetic, pharmaceutical, household cleaning and other detergent industries. Most surface-active ILs reported up to date are imidazolium-based, which may raise some environmental and health-related concerns. Aiming the development of ILs with surfactant properties and low ecotoxicity, in this work, novel surface-active analogues of glycine-betaine ILs (AGB-SAILS) combined with the dodecylbenzenesulfonate ([DBS]) anion have been synthesized and characterized. The synthesized AGB-SAILS were characterized chemically by elemental analysis and spectroscopic methods. Their thermal properties, critical micellar concentration, micelle diameter and ecotoxicity against *Aliivibrio fischeri* were determined, being these properties compared with the commercial surfactant sodium dodecylbenzenesulfonate (SDBS). It is shown that all investigated AGB-SAILS are liquid at room temperature and thermally stable. Furthermore, most of them display a lower critical micellar concentration and lower toxicity towards *Aliivibrio fischeri* than SDBS, thus being good alternatives to the commercial surfactant in a wide range of applications.

Keywords: surface-active ionic liquids, analogues of glycine-betaine, synthesis, thermal properties, toxicity, critical micellar concentration.

1. Introduction

Surfactants, which could be non-ionic, anionic, cationic and amphoteric compounds, constitute a class of chemical compounds with unique physical properties, including their ability to completely modify surface and interfacial properties and being capable to self-assemble into micelles [1]. These properties allow the application of surfactants to modify wetting and detergency features, in the displacement of liquid phases through porous media and to (de)stabilize dispersions [2]. Due to these properties, this group of chemicals is present in our everyday lives in endless ways, being applied in the textile, leather, food, cosmetic, pharmaceutical, household cleaning and other detergent industries [3]. However, many conventional surfactants used in those applications require a high concentration to form stable micelles in aqueous media, which may result in a high concentration of surfactants in both municipal and industrial effluents and in serious threats to the ecosystem and ultimately to human health [4]. To overcome environmental concerns [5], there is a growing interest to develop new surfactants with improved surface-active properties and lower environmental impact [6].

Amongst relatively recent surfactants, ionic liquids (ILs) have emerged as an alternative class. In short, these compounds are organic salts, composed of large organic cations and organic/inorganic anions, resulting in charge delocalization and low melting temperatures. It is also possible to adjust the solvent properties to a specific application by the proper design of the cation and/or anion chemical structure [7]. ILs containing long alkyl chain substituents (usually more than eight carbons) have been reported to be surface-active ionic liquids (SAILs), allowing the design of several families and types of surfactants, such as cationic, anionic, catanionic or gemini surfactants [7]. As the conventional surfactants, SAILs are able to self-aggregate or create micelles in aqueous and mixed solutions above the critical micelle concentration (CMC) [8], [9], and even in high salt concentration solutions [10], [11]. Therefore, they can be applied in a wide range of applications, such as cell disruption [7], proteins solubilization [12], biocatalysis [13] or extraction and purification processes [14], [15]. For instance, the high impact of SAILs was demonstrated by Vicente et al. [9], who investigated the effect of different SAILs as co-adjuvants upon the clouding behaviour of three nonionic commercial surfactants, proving that the nature of SAILs can significantly modify the micelles size and the temperature at which the mixture becomes turbid and phase-separate.

Despite the relevance of SAILs, the majority of the published research has focused on the study of the aggregation behaviour of cationic SAILs based on imidazolium cations, which may bring some environmental and health concerns [16]. Significant efforts have been carried out in the past years towards the design of environmentally safer SAILs, while exploring different

surfactant families, namely anionic surfactants. Several IL-based surfactants comprising a bio-based cation, such as those derived from cholinium, combined with counterions such as carboxylates and alkylsulfates, have gathered significant attention [17], [18]. Among these, Gehlot et al. [18] reported a cholinium-based surfactant synthesized from a commercial surfactant (sodium dodecylbenzenesulfonate - SDBS), demonstrating the surfactant low ecotoxicity towards freshwater microalgae of *Scenedesmus* genus. Biodegradable amino-acid-based SAILs showing better surfactant properties than conventional surfactants were reported by Trivedi et al. [19].

More recently, other ILs classes derived from several natural materials with improved biodegradability and low toxicity have been disclosed [17]–[25], e.g. analogues of glycine-betaine (AGB) ILs [20], [22], [26], [27]. Glycine-betaine is a relatively low-cost natural component, which can be obtained from sugar industry by-products, collected after the saccharose extraction step, accounting with 27 wt% of molasses of sugar beet [21], [23]. On the other hand, the use of glycine-betaine, as well as their derivatives, is currently acceptable in food supplements and health-care formulations [28]. The future application of these solvents requires adequate understanding of their physical properties and due to the “designer solvent” character of the ILs, there is a high number of unexplored cation/anion combinations able to boost the applicability of these solvents by covering a much wider polarity and affinity range. Given their high potential and lower toxicity [22], [26], [27], AGB-ILs with surface-active properties have been raising attention recently [29], [30]. Yet, to the best of our knowledge, these have not been investigated with the dodecylbenzenesulfonate anion ([DBS]⁻).

Due to the potential interest of analogues of glycine-betaine ILs with surfactant properties, herein we report the synthesis and characterization of 8 anionic AGB-SAILs comprising the [DBS]⁻. The novel AGB-SAILs were synthesised and characterized regarding their thermal properties (melting point, glass transition temperature and decomposition temperature), critical micellar concentration (CMC), size distribution by dynamic light scattering (DLS) and ecotoxicity against *A. fischeri*.

2. Experimental Section

2.1. Materials

Sodium dodecylbenzenesulfonate (SDBS) (purity > 99%), ethyl 2-bromoacetate (purity 98%), ethyl 4-bromobutyrate (purity 97%) were acquired from Sigma Aldrich, and triethylamine (purity 99%), tri(*n*-propyl)amine (purity 98%), tri(*n*-butyl)amine (purity 99%), and tri(*n*-butyl)phosphine (purity 95%) were acquired from Acros Organics.

Tri(*n*-alkyl)[2(or 4)-ethoxy-2-oxoethyl(or 4-oxobutyl)ammonium/phosphonium bromide ($[R_3NC_2]Br$ or $[R_3NC_4]Br$, and $[Bu_3PC_2]Br$ or $[Bu_3PC_4]Br$), were obtained by the methods earlier described [22], [26], [27]. These bromide salts were then applied to an anionic metathesis reaction protocol to prepare the dodecylbenzenesulfonate based ILs (AGB-SAILS).

Phosphate Buffer tablets (purity > 99%) was acquired from Sigma Aldrich.

2.2. Synthesis of AGB-SAILS

A hot aqueous solution of sodium dodecylbenzenesulfonate (17.42 g, 0.05 mol) in 150 mL of water was added to a solution of tri(*n*-alkyl)[2(or 4)-ethoxy-2-oxoethyl(or 4-oxobutyl)ammonium/phosphonium bromide (0.05 mol) in water (100 mL) and heated (70 °C) for 1 h whilst stirring. The mixture was then stirred at room temperature for 12h, and then allowed to settle into two phases. The bottom IL phase was extracted by ethyl acetate (3 × 50 mL) and the organic solvent was removed by under vacuum using a rotary evaporator. The resultant sample was dissolved in dichloromethane and washed with pure water several times, until no residual bromide was detected with the use of $AgNO_3$ test of the aqueous phase. Then, the organic phase was dried over anhydrous $MgSO_4$, filtered, and dichloromethane was evaporated under reduced pressure at 50 °C. The oily product obtained were re-dissolved in a minimum of dichloromethane (30 mL) and 3g of active charcoal was added and the mixture was stirred at room temperature. After 24 h, the mixture was filtrated, and the solvent was removed under reduced pressure. The obtained product was thereafter dried for 48 hours under vacuum to give the AGB-SAILS products. 1H spectra are given in Figs. S1 to S8 in the Supporting Information, showing the presence of both the organic cations and the corresponding organic anion. Their yields and synthesis characterization are given below. Fig. 1 comprises the acronym and chemical structure of these AGB-SAILS. The resonances assignment following the structures numbering. A commercially available surfactant (sodium dodecylbenzenesulfonate, SDBS) was used for comparison purposes.

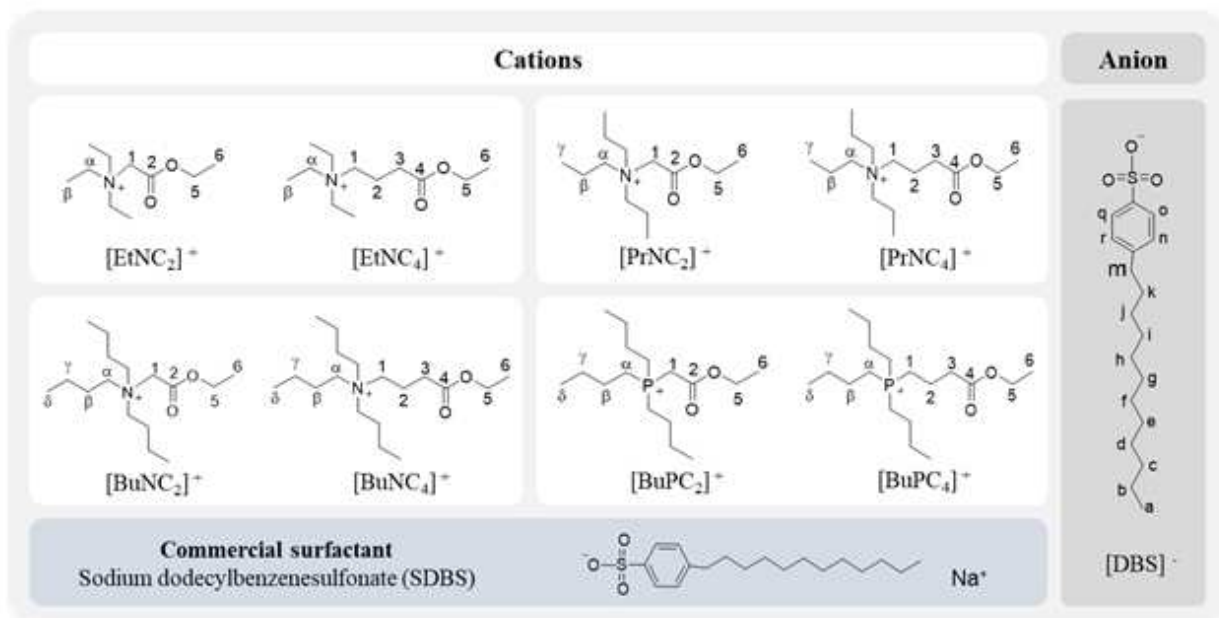


Fig. 1. Chemical structure of the synthesized AGB-SAILs and of the commercial surfactant SDBS.

2.2.1. *N,N,N*-tri(ethyl)(2-ethoxy-2-oxoethyl)-1-ammonium dodecylbenzenesulfonate ([EtNC₂][DBS]·0.5 H₂O)

Yield (20.28 g, 75%). Elemental analysis: Found: C, 63.98; H, 10.14; N, 2.59; S, 6.05%. Calculated for C₂₈H₅₂O_{5.5}NS (MW = 522.78 g·mol⁻¹): C, 64.33; H, 10.03; N, 2.68; S, 6.13%. ¹H NMR, δ/ppm (300 MHz, DMSO-*d*₆): 0.82 [3 H, t, CH₃(a)]; 1.45 [29 H, m, CH₂(β+b-k)]; 1.52 [2 H, m, CH₂(m)]; 3.50 [6H, m, CH₂(α)]; 4.25 [2 H, q, CH₂(5)]; 4.70 [2 H, s, CH₂(1)]; 7.11 [2 H, m, CH (n+r)]; 7.50 [2 H, dd, CH(q+o)].

2.2.2. *N,N,N*-tri(ethyl)(4-ethoxy-4-oxobutyl)-1-ammonium dodecylbenzenesulfonate ([EtNC₄][DBS]·0.5 H₂O)

Yield (23.04 g, 81%). Elemental analysis: Found: C, 65.54; H, 10.55; N, 2.72; S, 5.70%. Calculated for C₃₀H₅₆O_{5.5}NS (MW = 550.83 g·mol⁻¹): C, 65.42; H, 10.25; N, 2.54; S, 5.82%. ¹H NMR, δ/ppm (300 MHz, DMSO-*d*₆): 0.77-0.80 [15 H, m, CH₃(β+a+6)]; 1.21 [20 H, m, CH₂(b-k)] 1.65 [2 H, CH₂(l)]; 1.84 [2 H, m, CH₂(2)]; 2.45 [2 H, t, CH₂(3)]; 3.27 [8 H, m, CH₂(a+1)]; 4.11 [2 H, q, CH₂(5)]; 7.11 [2 H, m, CH(n+r)]; 7.50 [2 H, dd, CH(q+o)].

2.2.3. *N,N,N*-tri(*n*-propyl)(2-ethoxy-2-oxoethyl)-1-ammonium dodecylbenzenesulfonate ([PrNC₂][DBS]·0.4 H₂O)

Yield (25.20 g, 80%). Elemental analysis: Found: C, 66.10; H, 10.72; N, 2.52; S, 5.40%. Calculated for C₃₁H_{57.8}O_{5.4}NS (MW = 563.06 g·mol⁻¹): C, 66.13; H, 10.35; N, 2.49; S, 5.69%. ¹H

NMR, δ /ppm (300 MHz, DMSO- d_6): 0.81 [12 H, m, CH₃(γ +a)]; 1.20 [24 H, m, CH₃(6+b-k)]; 1.52 [8 H, m, CH₂(β)]; 2.45 [2H, m, CH₂(m)]; 3.16 [2 H, m, CH₂(α)]; 3.5 [2 H, s, CH₂(1)]; 4.27 [2 H, q, CH₂(5)]; 7.14 [2 H, m, CH(n+r)]; 7.60 [2 H, dd, CH(q+o)].

2.2.4. *N,N,N*-tri(*n*-propyl)(4-ethoxy-4-oxobutyl)-1-ammonium dodecylbenzenesulfonate ([PrNC₄][DBS]·0.3 H₂O)

Yield (25.20 g, 83%). Elemental analysis: Found: C, 67.02; H, 10.72; N, 2.45; S, 5.02%. Calculated for C₃₃H_{61,6}O_{5,3}NS (MW = 589.31 g·mol⁻¹): C, 67.26; H, 10.54; N, 2.38; S, 5.44%. ¹H NMR, δ /ppm (300 MHz, DMSO- d_6): 0.90 [12 H, m, CH₃(γ +a)]; 1.19 [21 H, m, CH₂(6+b-k)]; 1.65 [8 H, CH₂(β +2)]; 1,75 [2 H, m, CH₂(3)]; 2.40 [2 H, m, CH₂(m)]; 3.25 [8 H, m, CH₂(α)]; 4.11 [2 H, q, CH₂(5)]; 7.11 [2 H, m, CH(n+r)]; 7.50 [2 H, dd, CH(o+q)].

2.2.5. *N,N,N*-tri(*n*-butyl)(2-ethoxy-2-oxoethyl)-1-ammonium dodecylbenzenesulfonate ([BuNC₂][DBS]·0.3 H₂O)

Yield (24.81 g, 83%). Elemental analysis: Found: C, 67.50; H, 10.91; N, 2.12; S, 5.60%. Calculated for C₃₄H_{63,6}O_{5,3}NS (MW = 603.31 g·mol⁻¹): C, 67.69; H, 10.62; N,2.32; S, 5.31%. ¹H NMR, δ /ppm (300 MHz, DMSO- d_6): 0.80-0.82 [12 H, m, CH₃(δ +a)]; 1.25 [27 H, m, CH₂(6+ γ +b-k)]; 1.60 [8 H, m, CH₂(β +m)]; 3.45 [6 H, m, CH₂(α)]; 4.35 [2 H, q, CH₂(5)]; 4.50 [2 H, s, CH₂(1)]; 7.11 [2 H, d, CH(n+r)]; 7.50 [2 H, d, CH(o+q)].

2.2.6. *N,N,N*-tri(*n*-butyl)(4-ethoxy-4-oxobutyl)-1-ammonium dodecylbenzenesulfonate ([BuNC₄][DBS]·0.3 H₂O)

Yield (28.99 g, 90%). Elemental analysis: Found: C, 68.85; H, 10.92; N, 1.92; S, 5,45%. Calculated for C₃₆H_{67,6}O_{5,3}NS (MW = 631.39 g·mol⁻¹): C, 68.48; 10.79; N, 2.22; S, 5.08%. ¹H NMR, δ /ppm (300 MHz, DMSO- d_6): 0.97 [12 H, m, CH₃(d+a)]; 1.21 [21 H, m, CH₂(6+b-j)]; 1.33 [6 H, m, CH₂(g)]; 1.57 [10 H, m, CH₂(b+k+2)]; 1.84 [2 H, m, CH₂(3)]; 2.40 [2 H, t, CH₂(m)]; 3.20 [8 H, m, CH₂(a+1)]; 4.17 [2 H, q, CH₂(5)]; 7.11 [2 H, d, CH(n+r)]; 7.50 [2 H, d, CH(o+q)].

2.2.7. Tri(*n*-butyl)[2-ethoxy-2-oxoethyl]phosphonium dodecylbenzenesulfonate ([BuPC₂][DBS]·)

Yield (25.03 g, 80%). Elemental analysis: Found: C, 66,13; H, 10.52; S, 5.65%. Calculated for C₃₄H₆₃O₅PS (MW = 614.90 g·mol⁻¹): C, 66.41; H, 10.33; S, 5.91%. ¹H NMR, δ /ppm (300 MHz, DMSO- d_6): 0.80-0.92 [12 H, m, CH₃(δ +a)]; 1.16 [20 H, m, CH₂(6+b-j)]; 1.42

[14 H, m, CH₂(m+β+γ)]; 2.27 [6 H, m, CH₂(a)]; 3.80 [2 H, d, CH₂(1)]; 4.27 [2 H, q, CH₂(5)]; 7.12 [2 H, d, CH(n+r)]; 7.53 [2 H, dd, CH(o+q)].

2.2.8. Tri(*n*-butyl)[4-ethoxy-4-oxobutyl]phosphonium dodecylbenzenesulfonate ([BuPC₄][DBS])

Yield (27.93 g, 85%). Elemental analysis: Found: C, 67.52; H, 10.84; S, 4.98%. Calculated for C₃₆H₆₇O₅PS (MW = 642.95 g·mol⁻¹): C, 67.25; H, 10.50; S, 4.99%. ¹H NMR, δ/ppm (300 MHz, DMSO-*d*₆): 0.82-0.92 [12 H, m, CH₃(δ+a)]; 1.20 [24 H, m, CH₂(6+b-j)]; 1.37 [14 H, m, CH₂(β+γ+2)]; 1.75 [2 H, m, CH₂(k)]; 2.21 [8 H, m, CH₂(α+1)]; 2.45 [2 H, m, CH₂(3)]; 4.11 [2 H, q, CH₂(5)]; 7.11 [2 H, d, CH(n+r)]; 7.50 [2 H, dd, CH(o+q)].

2.3. Characterization of AGB-SAILS

All AGB-SAILS samples were dried under vacuum at room temperature for at least 48h before their characterization. The water content of the dried AGB-SAILS was determined by Karl Fischer coulometry using a Metrohm 787 KF Titrino coulometer, with Hydranal 34805 and Hydranal 37817 (from Fluka) as titrant. All samples have a water content lower than or equal to $3,5 \times 10^{-3}$ in mass fraction. The water content of each AGB-SAIL was considered in the preparation of the respective aqueous solutions.

The elemental analysis (C, H, N and S contents) of all synthesized AGB-SAILS was carried out on elementary CHNS thermo-electron FLASHEA 1112 series, whereas the ¹H Nuclear Magnetic Resonance (NMR) spectra were recorded at room temperature with a Bruker AC 30 spectrometer (250 MHz for ¹H) using DMSO as solvent.

The differential scanning calorimetry (DSC) assays were carried out using a TA Instruments Q100 (under controlled nitrogen atmosphere), at a cooling and heating rate of 10 °C·min⁻¹. The decomposition temperature of all AGB-SAILS was established by thermogravimetric analysis (TGA) using a Netzsch TG 209 F3 Tarsus thermogravimetric analyser (under controlled nitrogen atmosphere) with samples of 10 to 20 mg. The samples were heated from 30 to 600 °C, at a heating rate of 10 °C·min⁻¹.

The CMC of all SAILS was determined by electrical conductivity measurements. The electrical conductivity was determined using a SevenMulti™ conductimeter (Mettler Toledo Instruments) at 25°C, within an uncertainty of ± 0.01 mS·cm⁻¹. The CMC of each compound is given by the breaking point in the linear dependency of the specific conductivity as function of the IL concentration [31]. Since esters are normally stable in contact with water for long periods,

unless acidic or alkaline conditions conjugated with high temperature are used, it is expected that their application in neutral media at moderate temperatures does not raise stability problems, namely hydrolysis.

Dynamic light scattering (DLS) measurements, using a Malvern Zetasizer Nano-ZS from Malvern Instruments, were carried out to evaluate the micelle size of the novel AGB-SAILs. Aqueous solutions of AGB-SAILs were prepared above their CMC in Phosphate-Buffered Saline (PBS), at pH 7.2 and 25 °C. Samples were irradiated with red light (HeNe laser, wavelength of 665 nm) and the intensity fluctuations of the scattering light were detected at a backscattering angle of 173° to generate an autocorrelation function. For each sample at least 4 measurements were performed, and the average size and standard deviation determined.

The ecotoxicity of the novel synthesized AGB-SAILs was determined by the standard Microtox® liquid-phase assay [32]. In this technique it is assessed the inhibition of the luminescence of a specific bacteria (*Aliivibrio fischeri* - strain NRRL B-11177) [33]. These assays were carried out following the standard 81.9% test protocol [33], [34]. Firstly, the bacteria was exposed to a series of diluted aqueous solutions of each IL (from 0 to 81.9 wt%) [33], [34]. After 5, 15 and 30 min of exposure to each AGB-SAILs aqueous solutions, it was determined the light output of the microorganisms and compared with the light output obtained from the control. The EC₅₀ values, which represent a standard statistic parameter to evaluate dose-responsive relationships in which there is a 50% growth inhibition [35]. This acute test is assessed at 5, 15 and 30 min of exposure were determined through the available Microtox® Omni™ Software [33], [34].

3. Results and discussion

3.1. AGB-SAILs synthesis and characterization

The several AGB-SAILs listed in Fig. 1 were successfully synthesized by reaction between ethyl 2-bromoacetate and triethylamine, tri(*n*-propyl)amine, tri(*n*-butyl)amine, or tri(*n*-butyl)phosphine, followed by anion exchange (Fig. 2), obtaining yields ranging between 75% and 90% for [EtNC₂][DBS], [EtNC₄][DBS], [BuNC₂][DBS], [BuNC₄][DBS], [BuPC₂][DBS], [BuPC₄][DBS], [PrNC₂][DBS] and [PrNC₄][DBS]. Elemental analysis results and ¹H NMR spectra of all AGB-ILs, summarized above, reveal the ILs successful synthesis. ¹H NMR resonance assignments and reaction yields are given above, being the respective spectra provided in the Supporting Information.

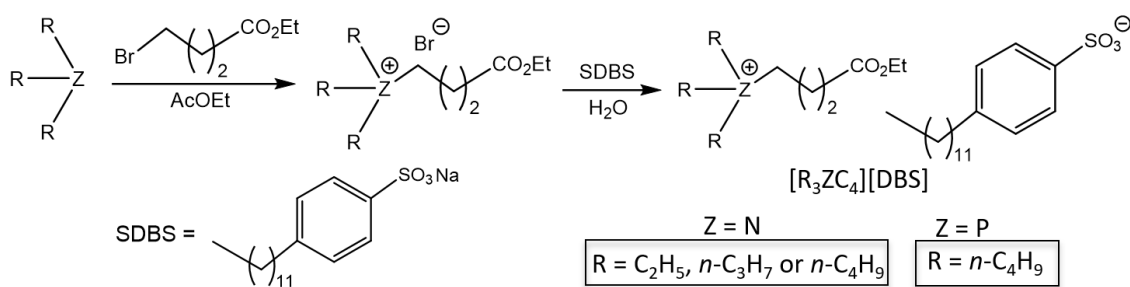


Fig. 2. Synthesis route for AGB-SAILs.

Remarkably, and contrarily to the commercial SDBS which shows a melting temperature of 300 °C [36], all the synthesized AGB-SAILs are liquid at room temperature, which is due to the bulky and asymmetric AGB cations with high charge dispersion, resulting in poor cation-anion interactions. This is a significant advantage comparing with the SDBS, allowing overcoming the energy associated to the melting enthalpy, thus improving the surfactant water solubility.

Table 1 summarizes the obtained AGB-SAILs glass transition (T_g) and thermal degradation or decomposition (T_{dec}) temperatures, the last one corresponding to a weight loss of 10%. The T_{dec} values of all prepared AGB-SAILs are within the range of 140 and 216 °C (TGA profiles given in Fig. S9 in the Supporting Information). This range is lower than the thermal stability of SDBS (380 °C) [37], being a consequence of the organic cation present. Although the T_{dec} values of the prepared AGB-SAILs (above 140 °C) are lower than of the SDBS, it is still high enough to enable their use in most applications requiring the use of bio-based surfactants. The most stable AGB-SAIL is [BuPC₄][DBS], whereas [PrNC₂][DBS] is the less thermally stable. Since all the AGB-SAILs share the same anion - [DBS]⁻ - the thermal degradation of the investigated AGB-SAILs follows the cation order: [PrNC₂]⁺ < [PrNC₄]⁺ < [EtNC₂]⁺ < [EtNC₄]⁺ << [BuNC₂]⁺ < [BuNC₄]⁺ < [BuPC₂]⁺ < [BuPC₄]⁺. In general, there is a slight increase in the thermal stability of all SAILs by increasing the length of the alkyl chain lengths of the cation. Regarding the SAILs containing ammonium and phosphonium cations with equivalent alkyl chains, namely [BuNC₂][DBS] and [BuNC₄][DBS] versus [BuPC₂][DBS] and [BuPC₄][DBS], the most stable SAIL is the one that holds shorter spacers. These results are in agreement with those from Gaetano et al. [32], who verified that the degradation temperature increases with the increasing number of carbon atoms in alkyl groups grafted on glycine-betaine ILs. A more significant increase in the thermal stability is observed for the phosphonium-based SAILs when compared with the ammonium-based analogues. These results are congruent with those of other phosphonium/ammonium-based ILs, where phosphonium-based ILs display higher T_{dec} values [26], [38], [39]. Tsunashima et al. [40] ascribed this trend to the existence of the empty *d*-orbitals on the phosphorus atom and Carvalho et al. [41] suggested that it is a result from weaker

interionic interactions due to the ionic volume increase, and that this substitution impacts bulk properties. The studied AGB-SAILs also allow to conclude that the longer the spacer, the more thermally stable is the respective AGB-SAIL. Parajó et al. [42] reported the T_{dec} values of the AGB-ILs comprising the $[\text{BuNC}_2]^+$, $[\text{BuNC}_4]^+$, $[\text{BuPC}_2]^+$ and $[\text{BuPC}_4]^+$ combined with the saccharinate anion. Comparing these AGB-ILs with the novel AGB-SAILs here reported, it is possible to verify that the combination of those cations with the $[\text{DBS}]^-$ anion leads to a decrease in the T_{dec} values.

Table 1. Glass transition (T_g) and decomposition (T_{dec}) temperatures of the synthesized AGB-SAILs and SDBS (for comparison).

AGB-SAILs	T_g (°C)	T_{dec} (°C)
$[\text{EtNC}_2][\text{DBS}]$	-53	149
$[\text{EtNC}_4][\text{DBS}]$	-51	153
$[\text{PrNC}_2][\text{DBS}]$	-52	140
$[\text{PrNC}_4][\text{DBS}]$	-53	143
$[\text{BuNC}_2][\text{DBS}]$	-53	187
$[\text{BuNC}_4][\text{DBS}]$	-53	193
$[\text{BuPC}_2][\text{DBS}]$	-51	209
$[\text{BuPC}_4][\text{DBS}]$	-53	216
SDBS	n.a.	380 [37]

n.a. - not available

The AGB-SAILs CMC data were further assessed since it is a key parameter for surfactants, being given in Table 2 (and Fig. S10 in Supporting Information). CMC values of AGB-SAILs range between 0.76 and 4.35 mM, with the highest CMC corresponding to $[\text{BuPC}_2][\text{DBS}]$ and the lowest associated to $[\text{EtNC}_2][\text{DBS}]$. The results further show that the CMC increases in the following cation order: $[\text{EtNC}_2]^+ < [\text{EtNC}_4]^+ < [\text{PrNC}_2]^+ < [\text{PrNC}_4]^+ < [\text{BuNC}_2]^+ < [\text{BuNC}_4]^+ < [\text{BuPC}_4]^+ < [\text{BuPC}_2]^+$. In general, an increase in both the aliphatic alkyl side and alkyl chains of the AGB-SAIL in the ammonium cation leads to an increase in the CMC, whereas the opposite is observed with the phosphonium-based SAILs. With the exception of $[\text{BuPC}_2][\text{DBS}]$, which presents a higher CMC (4.35 mM), the CMC values of the remaining AGB-SAILs in aqueous solutions are lower than SDBS (2.9 mM [31]), meaning that SAILs are in general highly effective surfactants. This observation is in agreement with the literature [9], [10], [18], [31], [43]. The decrease in the CMC with SAILs is mostly due to the large size cations, and the replacement of a more hydrated ion (Na^+) with a less hydrated and hydrophobic large organic cation, thus reducing electrostatic repulsion between the charged head groups in the surface layer, further decreasing the free energy required in the micellization phenomena. As expected, the weaker hydration of the bulky counterions allows the reduction of the electrostatic

repulsion of the electrostatic repulsion between headgroups more effective, promoting micelle formation [44].

With the exception of [BuPC₂][DBS], all the novel AGB-SAILs present higher micellar stability in aqueous solution comparing to the commercial surfactant. Given that most of the novel SAILs present a lower CMC than the commercial surfactant (SDBS) it can be emphasized the higher stability of the SAILs' micelles, since the lower the CMC of a given surfactant the more stable the resulting micelles [45]. This is particularly important from an industrial point of view.

Table 2. CMC values for the synthesized AGB-SAILs at 25 °C (in distilled water) compared to SDBS.

AGB-SAILs	CMC (mM)
[EtNC ₂][DBS]	0.76
[EtNC ₄][DBS]	0.84
[PrNC ₂][DBS]	0.91
[PrNC ₄][DBS]	0.90
[BuPC ₂][DBS]	4.35
[BuPC ₄][DBS]	2.78
[BuNC ₂][DBS]	2.44
[BuNC ₄][DBS]	2.66
SDBS	2.90 [31]

We also studied the micelle sizes of the AGB-SAILs investigated in this work, assuming the formation of spherical micelles, whose diameters, in nm, are presented in Fig. 3. When all the AGB-SAILs are compared, it can be observed that [EtNC₄][DBS] forms the smallest micelles, being also the only IL that presents smaller micelles comparing to the commercial surfactant (SDBS). By opposition, the [BuNC₂][DBS] forms the micelles with the largest diameter. This trend is mainly due to the head group electrostatic repulsions brought by the ionic nature of the AGB-SAIL and the higher steric effects arising from the larger bulk organic counterions [44]. For the aqueous solutions of AGB-SAILs, two distinct behaviours were observed: a slight decrease in micelle size induced by the larger spacers in the cations or micellar growth promoted by the increase in the alkyl chain length.

It is also possible to verify that phosphonium-based AGB-SAILs promotes the formation of smaller micelles than ammonium-based counterparts. This phenomena related to the effect of

the AGB-SAIL cation central atom (N vs. P) results from the charge distribution at the AGB-SAIL central heteroatom, which commands the SAIL water affinity and hydration spheres. As such, a greater charge delocalization closer to the central atom of the cation generates a stronger cation/anion interaction for the ammonium-based SAILs [41].

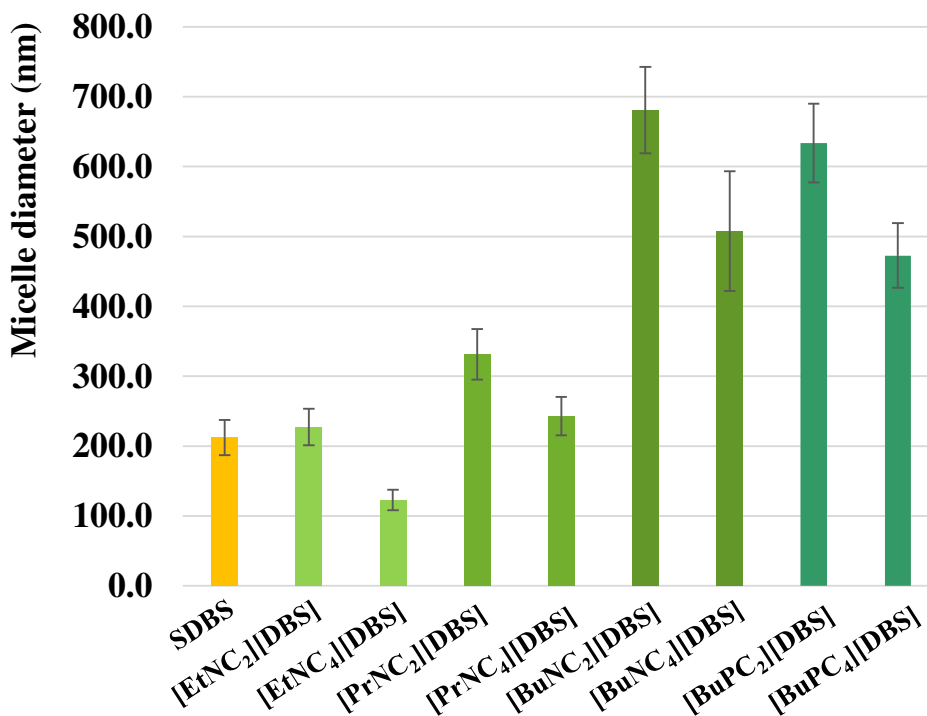


Fig. 3. Micelle size of AGB-SAILs in PBS (pH 7.2) at 25 °C compared to SDBS.

Taking into account the need of developing greener surfactants, it is mandatory to address their toxicity to foresee their potential use in the textile, leather, food, cosmetic, pharmaceutical and several detergent-related applications [4], [46]. In this sense, the impact of all AGB-SAILs against the marine luminescent bacteria *A. fischeri* for 30 min of exposure time was evaluated, being the correspondent EC₅₀ values with the respective 95% confidence limits summarized and compared with SDBS in Fig. 4. The EC₅₀ values at 30 min of exposure were specifically analysed to ensure enough exposition of the bacteria and assess the full impact in the luminescence inhibition [33], [34].

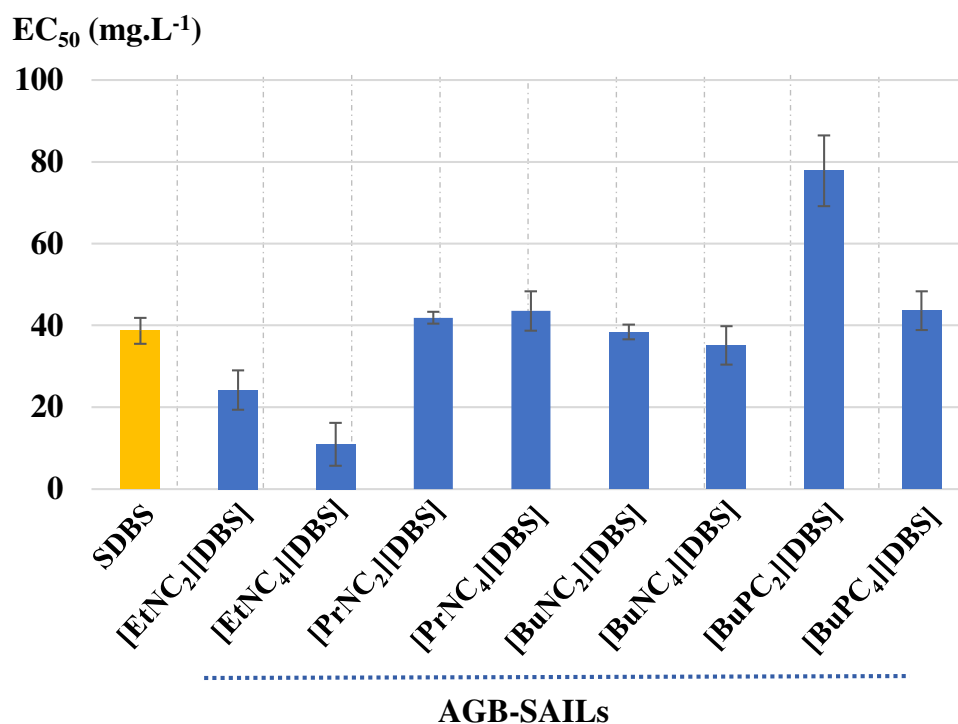


Fig. 4. Microtox[®] EC₅₀ values (mg.L⁻¹) for *A. fischeri* after 30 min of exposure time to aqueous solutions of AGB-SAILS and to a commercial surfactant (SDBS).

In general, the higher the EC₅₀ values, the lower the ecotoxicity of the target compound. Since the investigated SAILS share the same anion, the obtained results reveal that the toxicity of AGB-SAILS towards *A. fischeri* increases according to the following cation order: [BuPC₂]⁺ << [BuPC₄]⁺ ≈ [PrNC₄]⁺ ≈ [PrNC₂]⁺ ≈ [BuNC₂]⁺ < [BuNC₄]⁺ << [EtNC₂]⁺ << [EtNC₄]⁺. In this sense, the [BuPC₂][DBS] is the less toxic AGB-SAIL, whereas the [EtNC₄][DBS] is the most toxic SAIL investigated. Overall, phosphonium-based AGB-SAILS are less ecotoxic to the bacteria *A. fischeri* than the ammonium-based counterparts. Furthermore, an increase in the alkyl chain length leads to an increase of the IL ecotoxicity towards the same bacteria. Finally, no major ecotoxicity changes exist between the ILs with the propyl and butyl aliphatic groups, but an increase in the SAILS ecotoxicity is verified with the ones comprising the ethyl aliphatic groups.

According to previous studies [42], [48], it would be expected to have an increased ecotoxicity with increasing cation alkyl chain lengths, since it increases the IL hydrophobicity leading to a higher capacity to interact with phospholipid bilayers of cell membranes. This phenomenon is reported as ‘‘side-chain effect’’[47]. In addition, Parajó et al. [42] verified that the spacer in the cation of the AGB-SAIL plays a significant role in the toxicity of the SAIL, i.e. comparing the cations [Bu₃PC₂]⁺ and [Bu₃PC₄]⁺ (both sharing the saccharinate anion), with the latter one being less toxic. Parajó et al. [42] and Pereira et al. [22] also showed that the ammonium-based AGB-SAILS present a lower toxicity comparing to their phosphonium-based

counterparts. However, in the present work, opposite trends have been observed, demonstrating that the SAIL anion is playing the major role in defining these trends. In fact, in this work and contrarily to the previously cited works, we are dealing with an anionic surfactant where the toxicity is mainly defined by the long alkyl side chain at the anion. Therefore, the opposite trends observed in what concerns the IL cation is a consequence of the cation-anion interactions and synergistic effects.

It is known that the toxicity is related with the CMC; in general, the lower the CMC, which reflects a higher surface activity, the higher the toxicity of the respective compound [49]. However, in this work it is not possible to verify any correlation between the AGB-SAILS ecotoxicity and the CMC, as shown in Figure S11 in the Supporting Information, further reinforcing the role of the IL anion on determining the IL ecotoxicity towards *Aliivibrio fischeri* and the secondary effects manifested by the IL cation.

Overall, according to the Passino and Smith classification [50], all the AGB-SAILS investigated in this work are classified as slightly toxic (at 30 min of exposure: $10 \text{ mg.L}^{-1} \leq \text{EC}_{50} \leq 100 \text{ mg.L}^{-1}$). Despite the fact that [BuNC₄][DBS], [EtNC₂][DBS] and [EtNC₄][DBS] display a higher toxicity to *A. fischeri* than the commercially available surfactant (SDBS, $\text{EC}_{50} = 38.72 \text{ mg.L}^{-1}$), it should be remarked that the majority of the novel AGB-SAILS are good alternatives to the commercial SDBS surfactant in terms of toxicity and environmental risk. This fact coupled to the lower CMC values obtained with AGB-SAILS open the door to their use in a more eco-friendly and effective approach in a wide diversity of industries, such as food, cosmetic, pharmaceutical, household cleaning and other detergent industries.

4. Conclusions

This work reports the synthesis and characterization of eight new surface active analogues of glycine-betaine-based ionic liquids (AGB-SAILS) obtained by combination of analogues of glycine-betaine cations and the dodecylbenzenesulfonate anion. The respective thermal properties, namely glass transition and decomposition temperatures, were determined and discussed according to the IL chemical structure. All synthesized AGB-SAILS are liquid at room temperature, present degradation temperatures ranging between 140 °C and 216 °C, and glass transition temperatures ranging between -53 °C and -51 °C. The investigated AGB-SAILS have CMC values ranging between 0.76 and 4.35 mM, where the majority of these present lower CMC values than the respective commercial analogue (SDBS), and thus comparable or with higher micellar stability. Their toxicity against the marine luminescent bacteria *A. fischeri* showed that the studied AGB-SAILS are considered slightly toxic, but display a comparable or lower toxicity than the commercial surfactant. In this work, it is reported a singular synergistic

effect between the IL cations and the [DBS]⁻ anion since most hydrophobic AGB-SAILS are the less toxic.

Although surfactants derived from natural sources are a hot topic of research, their CMC is usually lower than that displayed by conventional surfactants, a trend that is not verified in the current work. Additionally, the low CMC values of AGB-SAILS, combined with their high thermal stability and low toxicity, allows to foreseen the future research of AGB-SAILS on the development of sustainable processes.

This work opens the door to the future introduction of AGB-SAILS in industrial processes, by enlarging the available data concerning novel and more benign SAILS, reinforcing the idea that the interfacial region can then be fine-tuned according to a specific application through the combination of the cation, including the nature of the substituents introduced and other structural modifications, and the counter-ion. Another advantage is that AGB-SAILS the favourable properties of most aprotic ILs, such as high polarity, high thermal and chemical stability, low melting point and negligible vapour pressure.

Author Contributors

I.S. Cardoso: Data curation, Investigation, Methodology, Writing - Original draft; **E.L.P. de Faria:** Data curation, Investigation, Methodology; **A.J.D. Silvestre:** Supervision, Methodology, Writing - Reviewing and Editing; **M.G. Freire:** Conceptualization, Methodology, Supervision, Writing - Reviewing and Editing, Funding acquisition; **A. Mohamadou:** Conceptualization, Methodology, Supervision, Writing - Reviewing and Editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. Inês S. Cardoso acknowledges the PhD grant SFRH/BD/139801/2018.

Appendix A. Supplementary data

Supplementary data to this article can be found online at

References

- [1] N. Dave, T. Joshi, A Concise Review on Surfactants and Its Significance, *Int. J. Appl. Chem.* 13 (2017) 663–672.
- [2] S. Kumar, A. Bhattarai, S. Chatterjee, Applications of Surfactants in modern Science and Technology, in: *Mod. Trends Sci. Technol.* 2013 pp. 147–158.
- [3] L. L. Schramm, E. N. Stasiuk, D. G. Marangoni, Surfactants and their applications, *Annu. Reports Prog. Chem. - Sect. C, Phys. Chem.* 99 (2003) 3–48.
<https://doi.org/10.1039/B208499F>
- [4] M. J. Scott, M. N. Jones, The biodegradation of surfactants in the environment,” *Biochim. Biophys. Acta - Biomembr.* 1508 (2000) 235–251.
[https://doi.org/10.1016/S0304-4157\(00\)00013-7](https://doi.org/10.1016/S0304-4157(00)00013-7)
- [5] A. Bhadani, A. Kafle, T. Ogura, M. Akamatsu, K. Sakai, H. Sakai, M. Abe, Current perspective of sustainable surfactants based on renewable building blocks, *Curr. Opin. Colloid Interface Sci.* 45 (2000) 124–135. <https://doi.org/10.1016/j.cocis.2020.01.002>
- [6] D. G. Hayes, G. A. Smith, Biobased Surfactants: Overview and Industrial State of the Art, in: *Biobased Surfactants (2nd Ed), Synthesis, Properties, and Applications*, 2019, pp 3–38.
<https://doi.org/10.1016/B978-0-12-812705-6.00001-0>
- [7] T. E. Sintra, M. Vilas, M. Martins, S. P. M. Ventura, Synthesis and Characterization of Surface-Active Ionic Liquids Used in the Disruption of Escherichia Coli Cells, *ChemPhysChem* 20 (2019) 727–735. <https://doi.org/10.1002/cphc.201801127>
- [8] N. A. Smirnova and E. A. Safonova, Ionic liquids as surfactants, *Russ. J. Phys. Chem. A* 84 (2010) 1695–1704. <https://doi.org/10.1134/S0036024410100067>
- [9] F. A. Vicente, I. S. Cardoso, T. E. Sintra, J. Lemus, E. F. Marques, S. P. M. Ventura, J. A. P. Coutinho, Impact of Surface Active Ionic Liquids on the Cloud Points of Nonionic Surfactants and the Formation of Aqueous Micellar Two-Phase Systems, *J. Phys. Chem. B* 121 (2017) 8742–8755. <https://doi.org/10.1021/acs.jpcc.7b02972>
- [10] M. U. H. Shah, M. Sivapragasam, M. Moniruzzaman, M. M. R. Talukder, S. B. Yusup, M. Goto, Aggregation behavior and antimicrobial activity of a micellar system of binary ionic liquids, *J. Mol. Liq.* 266 (2018) 568–576. <https://doi.org/10.1016/j.molliq.2018.06.101>
- [11] A. Z. Hezave, S. Dorostkar, S. Ayatollahi, M. Nabipour, B. Hemmateenejad, Dynamic interfacial tension behavior between heavy crude oil and ionic liquid solution (1-dodecyl-3-methylimidazolium chloride ([C12mim][Cl] + distilled or saline water/heavy crude oil)) as a new surfactant, *J. Mol. Liq.* 187 (2013) 83–89.
<https://doi.org/10.1016/j.molliq.2013.05.007>
- [12] P. Mester, M. Wagner, P. Rossmannith, Ionic liquids designed as chaotrope and surfactant for use in protein chemistry, *Sep. Purif. Technol.* 97 (2012) 211–215.
<https://doi.org/10.1016/j.seppur.2011.12.034>
- [13] S. P. M. Ventura, L. D. F. Santos, J. A. Saraiva, J. A. P. Coutinho, Ionic liquids microemulsions : the key to *Candida antarctica* lipase B superactivity, *Green Chem.*, 14 (2012) 1620–1625. <https://doi.org/10.1039/C2GC35197H>
- [14] V. Fernández-stefanuto, R. Corchero, I. Rodríguez-Escontrela, A. Soto, E. Tojo, Ionic Liquids derived from proline: application as surfactants, *ChemPhysChem*, 19 (2018) 2885–2893. <https://doi.org/10.1002/cphc.201800735>
- [15] F. A. Vicente, I. S. Cardoso, M. Martins, C.V.M. Gonçalves, A. C. R. V. Dias, P.

- Domingues, J. A. P. Coutinho, S. P. M. Ventura, R-phycoerythrin extraction and purification from fresh *Gracilaria* sp. using thermo-responsive systems, *Green Chem.* 21 (2019) 3816–3826. <https://doi.org/10.1039/C9GC00104B>
- [16] T. Ivanković, J. Hrenović, Surfactants in the environment, *Arch. Ind. Hyg. Toxicol.* 61 (2010) 95–110.
- [17] D. Rengstl, B. Kraus, M. Van Vorst, G. D. Elliott, W. Kunz, Effect of choline carboxylate ionic liquids on biological membranes, *Colloids Surfaces B: Biointerfaces* 123 (2014) 575–581. <https://doi.org/10.1016/j.colsurfb.2014.09.057>
- [18] P. S. Gehlot, A. Kulshrestha, P. Bharmoria, K. Damarla, K. Chokshi, A. Kumar, Surface-active ionic liquid cholinium dodecylbenzenesulfonate: Self-assembling behavior and interaction with cellulase, *ACS Omega*, 2 (2017) 7451–7460. <https://doi.org/10.1021/acsomega.7b01291>
- [19] T. J. Trivedi, K. S. Rao, T. Singh, S. K. Mandal, N. Sutradhar, A. B. Panda, A. Kumar., Task-specific, biodegradable amino acid ionic liquid surfactants, *ChemSusChem* 4 (2011) 604–608. <https://doi.org/10.1002/cssc.201100065>
- [20] , E. V. Capela, A. E. Santiago, A. F. C. S. Rufino, A. P. M. Tavares, M. M. Pereira, A. Mohamadou, M. R. Aires-Barros, J. A. P. Coutinho, A. M. Azevedo, M. G. Freire, Sustainable strategies based on glycine-betaine analogues ionic liquids for the recovery of monoclonal antibodies from cell culture supernatants, *Green Chem.* 21 (2019) 5671–5682. <https://doi.org/10.1039/C9GC02733E>
- [21] F. Goursaud, M. Berchel, N. Legros, Glycine betaine as a renewable raw material to ‘greener’ new cationic surfactants, *Green Chem.* 3 (2008) 310–320. <https://doi.org/10.1039/B713429K>
- [22] M.M. Pereira, M. R. Almeida, J. Gomes, A. F. C. S. Rufino, M. E. Rosa, J. A. P. Coutinho, A. Mohamadou, M. G. Freire, Glycine-betaine ionic liquid analogues as novel phase-forming components of aqueous biphasic systems, *Biotechnol. Prog.* 34 (2018) 1205–1212. <https://doi.org/10.1002/btpr.2685>
- [23] M. N. Belgacem, A. Gandini, Surfactants from Renewable Sources: Synthesis and Applications, in: *Monomers, Polymers and Composites from Renewable Resources*, Elsevier Science, 2008, pp. 153–178. <https://doi.org/10.1016/B978-0-08-045316-3.00007-7>
- [24] G. Singh, R. Kamboj, V. Singh, M. V. Chauhan, T. Kaur, G. Kaur, S. Singh, T. S. Kang, Nicotine-based surface active ionic liquids: Synthesis, self-assembly and cytotoxicity studies, *J. Colloid Interface Sci.* 496 (2017) 278–289. <https://doi.org/10.1016/j.jcis.2017.02.021>
- [25] G. Singh, M. Kaur, H. Kaur, T. S. Kang, Synthesis and complexation of a new caffeine-based surface active ionic liquid with lysozyme in aqueous medium: Physicochemical, computational and antimicrobial studies, *J. Mol. Liq.* 324 (2021) 115156–115166. <https://doi.org/10.1016/j.molliq.2020.115156>
- [26] M. M. Pereira, S. Pedro, J. Gomes, T. Sintra, S. P. M. Ventura, J. A. P. Coutinho, M. G. Freire, A. Mohamadou, Synthesis and characterization of analogues of glycine-betaine ionic liquids and their use in the formation of aqueous biphasic systems, *Fluid Phase Equilib.* 494 (2019) 239– <https://doi.org/10.1016/j.fluid.2019.05245>
- [27] Y. De Gaetano, A. Mohamadou, S. Boudesocque, J. Hubert, R. Plantier-royon, and L. Dupont, Ionic liquids derived from esters of Glycine Betaine : Synthesis and characterization, *J. Mol. Liq.* 207 (2015) 60–66. .

<https://doi.org/10.1016/j.molliq.2015.03.016>

- [28] A. M. Ferreira, E. S. Morais, A. C. Leite, A. Mohamadou, B. Holmbom, T. Holmbom, B. M. Neves, J. A. P. Coutinho, M. G. Freire, A. J. D. Silvestre, Enhanced Extraction and Biological Activity of 7-hydroxymatairesinol obtained from Norway Spruce knots using Aqueous Solutions of Ionic Liquids, *Green Chem.* 19 (2017) 2626–2635. <https://doi.org/10.1039/C7GC01091E>
- [29] D. K. Kaczmarek, D. Gwiazdowska, K. Juś, T. Klejdysz, M. Wojcieszak, K. Materna, J. Pernak, Glycine betaine-based ionic liquids and their influence on bacteria, fungi, insects and plants, *New J. Chem.* 45 (2021) 6344–6355. <https://doi.org/10.1039/D1NJ00498K>
- [30] T. Janek, K. Sałek, J. Burger, Ż. Czyżnikowska, S. R. Euston, Investigating the biomolecular interactions between model proteins and glycine betaine surfactant with reference to the stabilization of emulsions and antimicrobial properties, *Colloids Surfaces B: Biointerfaces*, 194 (2020) 111226. <https://doi.org/10.1016/j.colsurfb.2020.111226>
- [31] K. Ali, R. Moshikur, R. Wakabayashi, Y. Tahara, Synthesis and characterization of choline – fatty-acid-based ionic liquids : A new biocompatible surfactant, *J. Colloid Interface Sci.* 551 (2019) 72–80. <https://doi.org/10.1016/j.jcis.2019.04.095>
- [32] S. M. Steinberg, E. J. Poziomek, W. H. Engejmann, K. R. Rogers, A review of environmental applications of bioluminescence measurements, *Chemosphere*, 30 (1995) 2155–2197. [https://doi.org/10.1016/0045-6535\(95\)00087-O](https://doi.org/10.1016/0045-6535(95)00087-O)
- [33] F. A. e Silva, F. Siopa, B. F. H. T. Figueiredo, A. M. M. Gonçalves, J. L. Pereira, F. Gonçalves, J. A. P. Coutinho, C. A. M. Afonso, S. P. M. Ventura, Ecotoxicology and Environmental Safety Sustainable design for environment-friendly mono and dicationic cholinium-based ionic liquids, *Ecotoxicol. Environ. Saf.*, 108 (2014) 302–310. <https://doi.org/10.1016/j.ecoenv.2014.07.003>
- [34] A. G. Volpi, M. Girardini, D. Marchetto, C. Pantani, “Microtox s solid phase test : Effect of diluent used in toxicity test, *Ecotoxicol. Environ. Saf.*, 72 (2009) 851–861. <https://doi.org/10.1016/j.ecoenv.2008.01.011>
- [35] Z. A. Noel, J. Wang, M. I. Chilvers, Significant influence of EC50 estimation by model choice and EC50 type, *Plant Dis.* 102 (2018) 708–714. <https://doi.org/10.1094/PDIS-06-17-0873-SR>
- [36] A. T. Tyowua, S. G. Yiase, R. A. Wuanna, Manipulation of Concentration- Conductivity Data of Sodium Dodecyl Sulphate and Sodium Dodecylbenzene Sulphonate in KCl Solution in Relation to Micellisation Parameters Dodecyl Sulphate and Sodium Dodecylbenzene Sulphonate in KCl Solution in Relation to M, *Chem. Sci. J.* 79 (2012) 1–9.
- [37] L. T. Mukwada, M. J. Mochane, T. E. Motaung, S. V. Motloun, L. F. Koao, Effect of sodium dodecylbenzene sulphonate modifier and PP-g-MA on the morphology and thermal conductivity of PP/EG composites, *Plast. Rubber Compos.* 46 (2017) 469–475. <https://doi.org/10.1080/14658011.2017.1392713>
- [38] C. Maton, N. De Vos, C. V Stevens, Ionic liquid thermal stabilities: decomposition mechanisms and analysis tools, *Chem. Soc. Rev.* 42 (2013) 5963–5977. <https://doi.org/10.1039/c3cs60071h>
- [39] J. Kagimoto, K. Fukumoto, H. Ohno, Effect of tetrabutylphosphonium cation on the physico-chemical properties of amino-acid ionic liquids, *Chem. Commun.* 21 (2006) 2254–2256. <https://doi.org/10.1039/B600771F>

- [40] K. Tsunashima, S. Kodama, M. Sugiya, Y. Kunugi, Physical and electrochemical properties of room-temperature dicyanamide ionic liquids based on quaternary phosphonium cations, *Electrochim. Acta*, 56 (2010) 762–766. <https://doi.org/10.1016/j.electacta.2010.08.106>
- [41] P. J. Carvalho, S. P. M. Ventura, M. L. S. Batista, B. Schröder, F. Gonçalves, J. Esperança, F. Mutelet, J. A. P. Coutinho, Understanding the impact of the central atom on the ionic liquid behavior: Phosphonium vs ammonium cations, *J. Chem. Phys.* 140 (2014) 505–518. <https://doi.org/10.1063/1.4864182>
- [42] J. J. Parajóia, I. P.E. Macário, Y. De Gaetano, L. Dupont, J. Salgado, J. L. Pereira, F. J.M. Gonçalves, A. Mohamadou, S. P.M. Ventura, Glycine-betaine-derived ionic liquids: Synthesis, characterization and ecotoxicological evaluation, *Ecotoxicol. Environ. Saf.* 184 (2019) 109580. <https://doi.org/10.1016/j.ecoenv.2019.109580>
- [43] K. S. Rao, P. S. Gehlot, H. Gupta, M. Drechsler, A. Kumar, Sodium bromide induced micelle to vesicle transitions of newly synthesized anionic surface active ionic liquids based on dodecylbenzenesulfonate, *J. Phys. Chem. B* 119 (2015) 4263–4274. <https://doi.org/10.1021/jp512805e>
- [44] J. Jiao, B. Dong, H. Zhang, Y. Zhao, X. Wang, R. Wang, Li Yu, Aggregation behaviors of dodecyl sulfate-based anionic surface active ionic liquids in water, *J. Phys. Chem. B* 116 (2012) 958–965. <https://doi.org/10.1021/jp209276c>
- [45] A. Kapse, N. Anup, V. Patel, G. K. Saraogi, D. K. Mishra, R. K. Tekade, Polymeric micelles: A ray of hope among new drug delivery systems, in: *Drug delivery systems*, 2019, pp. 235-289. <https://doi.org/10.1016/B978-0-12-814487-9.00006-5>
- [46] S. Rebello, A. K. Asok, S. Mundayoor, and M. S. Jisha, Surfactants: Toxicity, remediation and green surfactants, *Environ. Chem. Lett.* 12 (2014) 275–287. <https://doi.org/10.1007/s10311-014-0466-2>
- [47] S. Stolte, M. Matzke, J. Arning, A. Bösch, W.-R. Pitner, U. Welz-Biermann, B. Jastorff J. Ranke, Effects of different head groups and functionalised side chains on the aquatic toxicity of ionic liquids, *Green Chem.*, 9 (2007) 1170–1179. <https://doi.org/10.1039/B711119C>
- [48] D. J. Couling, R. J. Bernot, K. M. Docherty, K. Dixon, E. J. Maginn, Assessing the factors responsible for ionic liquid toxicity to aquatic organisms via quantitative structure – property relationship modeling, *Green Chem.* 8 (2006) 82–90. <https://doi.org/10.1039/B511333D>
- [49] F. Ríos, A. Fernandez-Arteaga, M. Lechuga, and M. Fernandez-Serrano, Ecotoxicological characterization of surfactants and mixtures of them, in: *Toxicity and Biodegradation Testing, Methods in Pharmacology and Toxicology*, 2018, pp. 311–329. https://doi.org/10.1007/978.1.4939.7425.2_16
- [50] R. M. A. Y. Passino and B. Smith, “Acute bioassays and hazard evaluation of representative contaminants detected in great lakes fish,” *Environ. Toxicol. Chem.* 6 (1987) 901–907. <https://doi.org/10.1002/etc.5620061111>

Table 1. Glass transition (T_g) and decomposition (T_{dec}) temperatures of the synthesized AGB-SAILs and SDBS (for comparison).

Table 2. CMC values for the synthesized AGB-SAILs at 25 °C (in distilled water).

Figure captions

Fig. 2. Chemical structure of the synthesized AGB-SAILs and the commercial surfactant SDBS.

Fig. 2. Synthesis route for AGB-SAILs.

Fig. 3. Micelle size of AGB-SAILs in PBS (pH 7.2) at 25 °C compared to SDBS.

Fig. 4. Microtox® EC50 values ($\text{mg}\cdot\text{L}^{-1}$) for *A. fischeri* after 30 min of exposure time to aqueous solutions of AGB-SAILs and to a commercial surfactant (SDBS).