Engineering Chemistry
ISSN: 2813-6535, Vol. 9, pp 53-60
doi:10.4028/p-MxwzR2

Submitted: 2024-11-14
Revised: 2025-01-26
Accepted: 2025-01-27
Online: 2025-03-10

Synthesis and Investigation of Surface Tension Properties of Fatty Pyrimidinium betaines

Malki Fatiha[1,a*], Missoum Amina[1,b] and Hamza Kahina[1,c]
[1]Laboratoire de recherche sur les produits bioactifs et valorisation de la biomasse, Ecole Normale Supérieure, BP 92, Kouba, Algiers, Algeria
[a]*malki_fatiha76@yahoo.fr, [b]missoumamina09@gmail.com, [c]kahina_hamza@yahoo.fr

Keywords: amphoteric surfactant, pyrimidinium betaine, synthesis, surface activity, critical micelle concentration (CMC).

Abstract. A novel series of fatty betaines containing a pyrimidine ring with different alky chain lengths were synthesized by condensation of fatty N,N'-diphenylalkylamidines with a specific highly reactive malonic ester derivative under mild conditions. The chemical structures of products were characterized by common spectroscopic analyses (FTIR, mass spectra, ^{1}H NMR, and ^{13}C NMR spectrometry). Equilibrium surface tension and conductivity as a function of concentration of dodecyl pyrimidinum betaine (betaine with a 12 -carbon alkyl chain) in ethanolic solutions were measured and the critical micelle concentration (CMC) was determined at 30 °C. The results showed that the critical micelle concentration (CMC) of dodecyl pyrimidinum betaine is 0.925 mmol/L and the corresponding surface tension (γ_{CMC}) is 25.38 mN/m respectively. These results revealed that the synthesized fatty pyrimidinium betaines are efficient amphoteric surfactants making them promising candidates for applications in a very large number of areas.

Introduction

Amphoteric surfactants possess long hydrophobic chain with positively and negatively charged hydrophilic head groups [1]. Due to the various properties demonstrated in the amphoteric surfactants (remarkable interfacial activity, lower CMC, solubility, less harm to the skin, less toxic and more biodegradable-depending on the polar headgroups), they have a lot of different uses in cosmetics, enhanced oil recovery, electrochemistry, nanoscience, polymer chemistry, etc …[2-3].
In recent decades, amphoteric surfactants have attracted considerable interest in academic and industrial research, due to their unique properties such as: solubility, micellization and surface tension [4].

Betaine amphoteric surfactants contain both a positively charged group and a negatively charged group within the same molecule . Betaine- type amphoteric surfactants have been shown to exhibit antimicrobial activity against various microorganisms [5]. They have a variety of applications in biological research, medicine, pharmacy and other scientific fields [6-8]. Betaine derivatives are widely used in personal care products, detergents, as antistatic agents and are applied in enhanced oil recovery [9]. An important factor determining the properties of betaine surfactants is their chemical structure. The zwitterionic form of betaine exhibits a much lower CMC and a much higher surface activity [10], favoring the formation of micelles and a greater surfactant activity at the air-water interface [11].

Betaines containing a pyrimidine ring are a special class of mesoionic compounds [12]. Mesoionic pyrimidinium betaines have been of a great interest for their particular structure [13] and their chemical stability [14]. They also possess various bioactivities [15, 16] which have raised much interest as biologically active compounds [17].

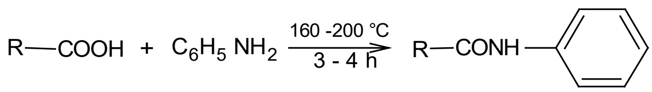
In recent years, many studies have been conducted on the effect of modifying hydrophobic groups, hydrocarbon chain length and types of hydrophilic head group [18]. Several works have focused on the synthesis of imidazolinium-based fatty surfactants and have studied their surface activity [19, 20, 21]. No studies on the surface tension of alkyl pyrimidinium betaines were reported.

In the present work, a series of novel betaines containing a pyrimidine ring with different alkyl chain lengths were synthesized, and characterized by FTIR, ^{1}H NMR, ^{13}C NMR and mass spectrometry. In addition, the surface tension of the prepared compounds was investigated using both tensiometric and conductometric techniques [22]. The critical micelle concentration (CMC) and the corresponding surface tension (γ_{CMC}) were measured at 30° C.

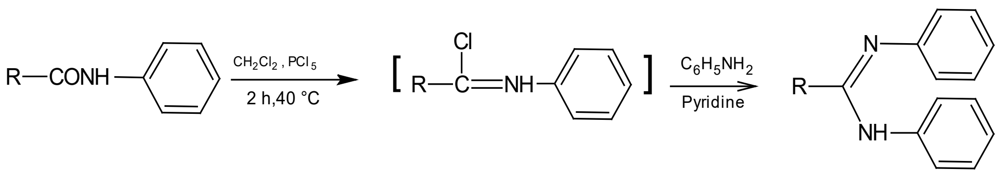
Materials and Methods

Materials. All of the chemicals and reagents used were of analytical grade and used directly without purification. Chemicals were purchased from Sigma-Aldrich, Merck, Fluka and Prolabo and were of analytical grade purity. Triethylamine was purified by distillation and the solvents were dried using conventional techniques. Thin layer chromatographic analysis, using Aluminum plates precoated with silica gel was used to monitor the reaction's progress and the chromatograms were visualized using UV at 254. Melting points were measured in a capillary tube, using a Büchi 540 type digital apparatus. UV-Visible absorption spectra were carried out using a Shimadzu 160 double-beam spectrophotometer. FTIR spectra were recorded as KBr pellets on a Jasco system 4100. ^{1}H NMR and ^{13}C NMR spectra were acquired on a Bruker AC 200 instrument at 300 and 75MHz respectively. Electron impact mass spectra (EIMS) were performed on a Nermag R10-10 type apparatus**.**

Synthesis. The synthesis of pyrimidinium betaine surfactants involves three steps.The first step consists of the synthesis of fatty N,N'-diphenyalkylamidines **3a-e**, from the corresponding alkylanilides **2a-e**, themselves prepared from the homologous carboxylic acids **1a-e** [23] (Scheme 1). The second step includes the synthesis of bispentachlorophenyl ester of phenyl malonic acid **5** by the action of pentachlorophenol on phenyl malonic acid **4** [24] (Scheme 2). The third step involves the synthesis of fatty pyrimidinium betaines **6a-e** from the condensation of fatty amidine derivatives **3a-e** with malonic ester derivative **5**, according to a previously reported procedure [23, 25, 26] (Scheme 3). The synthesis pathways of the reagents **3a-e** and **5** are as follows :



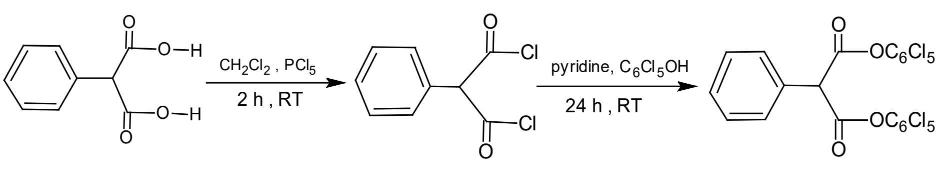
1a-e **2a-e**



2a-e **3a-e**

6a. R=C_9H_{19}, **6b.** R=$C_{11}H_{23}$, **6c.** R=$C_{13}H_{27}$, **6d.** R=$C_{15}H_{31}$, **6e.** R=$C_{17}H_{35}$

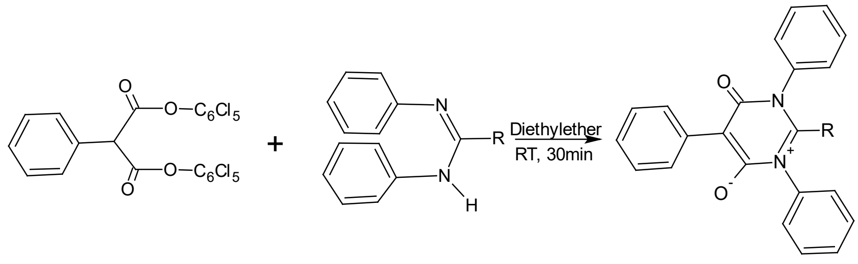
Scheme 1. Synthesis route of fatty N, N'- diphenylalkylamidines **3a-e**



4 **5**

Scheme 2. Preparation of bispentachlorophenyl ester of phenyl malonic acid **5**

General procedure for the synthesis of fatty chain pyrimidinium betaines 6a-e. Fatty chain pyrimidinium betaines **6a-e** were synthesized according to the Dvortsak procedure [25] by reacting 1 mmol of fatty N,N'-alkylamidines **3a-e** with 1 mmol of the bis pentachlorophenyl ester of phenyl malonic acid **5** in diethyl ether [26] under stirring at room temperature (Scheme 3), To the milky suspension obtained, 2 mmol of triethylamine was added. Less than a minute after this last addition a white solid precipitated. The entire system was then stirred for 30 min. The products were isolated by filtration. Their purification after several successive extractions afforded powdery white solids [26]. The purity of the synthesized fatty betaines was confirmed by TLC technique.



5 **3a-e** **6a-e**

6a. R=C_9H_{19}, **6b.** R=$C_{11}H_{23}$, **6c.** R=$C_{13}H_{27}$, **6d.** R=$C_{15}H_{31}$, **6e.** R=$C_{17}H_{35}$

Scheme 3. Synthetic pathway of fatty pyrimidinium betaines **6a-e**

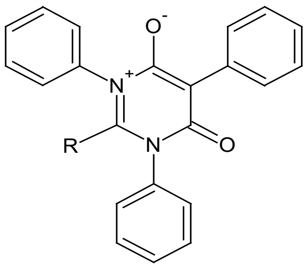
Measurements. In this work our study focused on a pyrimidinium betaine with a 12 -carbon alkyl chain **6b** (dodecyl pyrimidinium betaine BT12) as an example.

Surface tension measurements. A series of ethanolic solutions of dodecyl pyrimidinium betaine surfactant BT12 were prepared at different concentrations from 0.1 mmol/L to 10 mmol/L. The surface tension was measured at 30 ºC using a Krüss GmbH, K6 tensiometer by the ring tear-off method. All measurements were repeated three times and the average value was taken [9, 27, 28].

Conductivity measurements. The conductivity of ethanolic solutions of dodecyl pyrimidinium betaine surfactant BT12 was measured by a HI 8633 conductivity meter. The conductivity measurements were carried out at different concentrations at 30° C [22, 29].

Results and Discussion

Characterization of synthesized compounds. Betaines with fatty alkyl chain **6a-e** containing a pyrimidine moiety were realized according to a previously reported procedure [23, 26]. As presented in Table 1, the different alkyl betaines were isolated in low to moderate yields, 30-45 % .



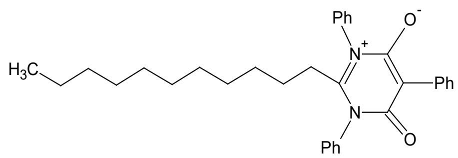
R = C_nH_{2n+1} ; $9 \leq n \leq 17$

Table 1. Yields of synthesized fatty alkyl pyrimidinium betaines **6a-e**

Betaine	R	Aspect	Yield (%)
6a	C_9H_{19}	white solid	39
6b	$C_{11}H_{23}$	white solid	45
6c	$C_{13}H_{27}$	white solid	31
6d	$C_{15}H_{31}$	white solid	30
6e	$C_{17}H_{35}$	white solid	35

The fatty pyrimidinium betaines **6a-e** were also characterized by the spectral analyses and their different spectra were found to be identical. As an example, UV-Visible, FTIR, MS, ^{1}H NMR and ^{13}C NMR spectral results of dodecyl pyrimidinium betaine **6b** are compiled in Table 2.

Table 2. UV-Visible, IR, and NMR spectral results of dodecyl pyrimidinium betaine **6b**



6b

Dodecyl pyrimidinium Betaine **6b** (BT12).	Chemical formula	Mol. Mass. (g/mol)	m.p. (°C)	UV-Visible (dioxane) λ_{max} (nm)	IR (KBr) $\bar{\upsilon}$ (cm^{-1})	^{1}H NMR ($CDCl_3$) δ (ppm)	^{13}H NMR ($CDCl_3$) δ (ppm)	EI Mass
(6-oxo-2-dodecyl,1,3,5-tripheny-1,6-dihydropyrimidin-3-ium-4-olate)	$C_{33}H_{38}N_2O_2$	494	124–128	352	3055 (C-H, Ar.), 1647 (C=O), 1597 (C=C, Ar.)	7.91–7.14 (15H, Ar.), 2.41–0.78 (23H, aliph.)	161.42 (C-14,16), 159.00 (C-12) , 136.27-125,76 (C, Ar.), 32.77–14.11 (C, aliph.)	495[M+1]$^{+}$

Surface Activity

Surface tension measurements. Measuring surface tension allows us to know the surface free energy per unit area at the air-liquid interface. This data is necssary to establish the CMC and study the micellization and adsorption properties [22]. The surface tension of dodecyl pyrimidinium betaine surfactant BT12 as a function of concentration at 30 ºC was determined and plotted in Figure 1.

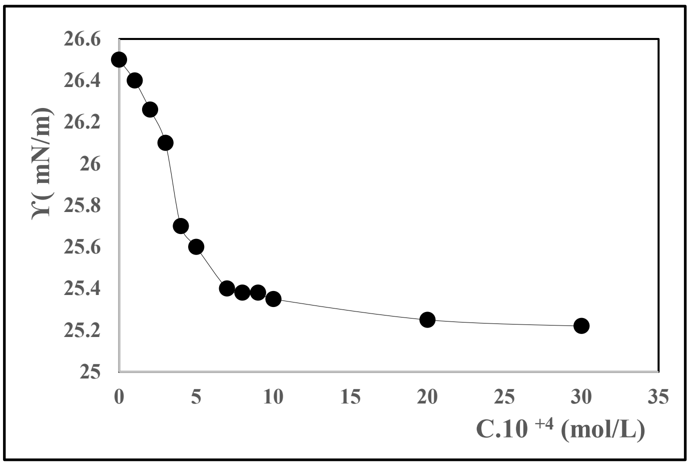


Fig. 1. Variation of surface tension as a function of the concentration of the pyrimidinium betaine surfactant BT12 in ethanolic solution at 30 °C

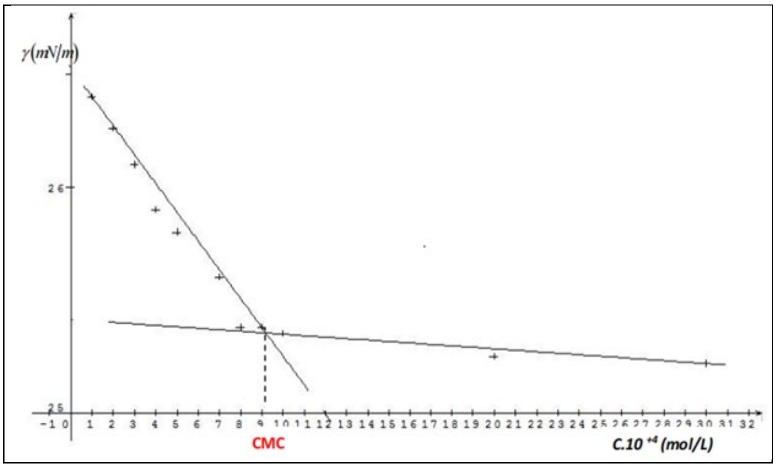


Fig. 2. Determination of CMC value by tensiometric technique

As illustrated in the figures above, the surface tension values decrease rapidly with increasing surfactant concentration due to the adsorption of molecules at the air–liquid interface. Then a distinct break point appears, known as critical micelle concentration (CMC) [29]. At the CMC values the surfactant begins to form micelles to decrease the electrostatic energies of the system [20]. The CMC and surface tension at CMC (γ_{CMC}) values were estimated from the breakpoints of these plots. After the breaking point, the surface tension remains almost constant with increasing BT12 concentrations [18]. This is due to the saturation of the air–liquid interface with BT12 molecules [28] **.** Figure 1 and 2 show that γ_{CMC} and CMC values of BT12 are 25.38 mN/m and 0.915 mmol/L respectively. The results obtained reveal that the synthesized pyrimidinium betaine surfactant has a great ability to reduce the surface tension of the system [28]. It appears that the length of the alkyl chain of the fatty pyrimidinium betaine studied has a significant effect on the reduction of surface tension [19, 29].

In general, the CMC value of surfactants is a sign of surface properties. The corresponding surface tension γ_{CMC} value indicates the ability of surfactants to reduce surface tensions and, therefore, the CMC indicates the effectiveness [9]. This means that BT12 with a long alkyl chain has excellent micellization capacity at low concentrations.

Conductivity measurements. The variations of conductivity against concentration of BT12 at 30° C are shown in Figure 3.

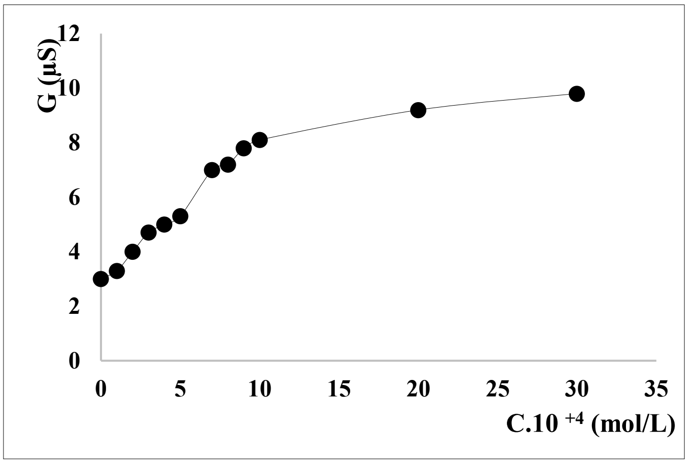


Fig. 3. Dependence of conductivity on the concentration of the pyrimidinium betaine surfactant BT12 in ethanolic solution at 30 °C.

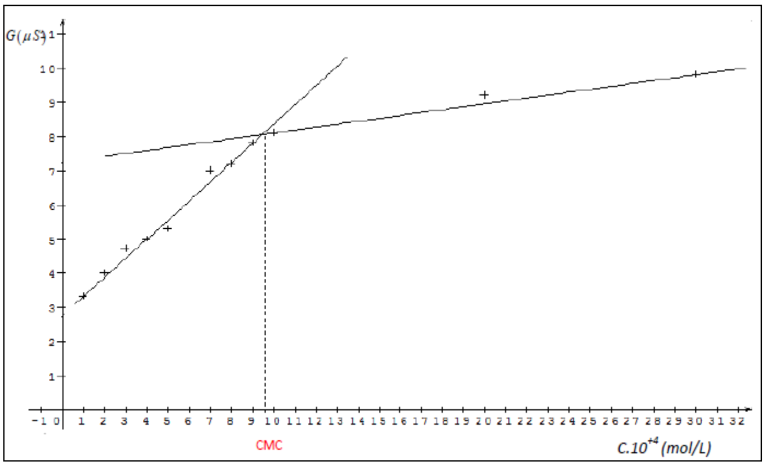


Fig. 4. Determination of CMC value by conductometric technique

As showed in Figures 3 and 4, the experimental results correspond in two straight lines with a significant change in direction at the breakpoint [22, 30]. The conductivity of the solution increases rapidly in the pre-micellar region. This is due to the increase in the concentration of current carriers which increases with increasing surfactant concentration. Regarding the conductivity measurements, CMC value was obtained at the point of intersection of the linear parts of the conductivity versus concentration plots [28]. As depicted in Figure 4 the value of CMC obtained is 0.935 mmol/L.

By comparing the results obtained using both tensiometric and conductometric techniques we concluded that the CMC values are very close.

Summary

In the present work, a series of new fatty betaines containing a pyrimidine ring were prepared and their chemical structures were characterized using FTIR, ^{1}H NMR , ^{13}C NMR and mass spectra.
The surface activity of dodecyl pyrimidinium betaine surfactant in ethanolique solutions at 30 °C was investigated by surface tension and conductivity measurements. The synthesized surfactant has proved satisfactory surface properties.This work has demonstrated that it is possible to obtain amphoteric surfactant with appropriate surface properties based on fatty acids, available and inexpensive products. The synthesized compounds could therefore have wide potential applications. They can be used in several industrial application such as laundry detergent, corrosion/rust inhibitor and lubricating emulsion.

Acknowledgements

Authors are grateful for the financial support from the Algerian Ministry of Higher Education and Scientific Research (Projet de Recherche Formation-Universitaire. PRFU n° B00L01EN160220180003). Authors deeply thank the researchers of Laboratory of organic synthesis, university of science and technology, Houari-Boumédiène (USTHB) , Algiers, Algeria, for kindly providing a tensiometer. We are also grateful to Doctor Michel Baltas for the NMR and mass spectra performed in the Laboratory of Synthesis and Physiochemistry of Molecules of Biological Interest, UMR 5068, University Paul Sabatier Toulouse, France.

References

[1] Sarkar, A. Pal, A. Rakshit, B. Saha, Properties and applications of amphoteric surfactant: A concise review, J. Surfact. Deterg. (2021) 1–22.

[2] G. Savary, M. Grisel, C. Picard, Cosmetics and personal care products, In: O. Olatunji (Ed.), Natural polymers: industry techniques and applications, Springer International Publishing, Basilea (2016) pp. 219–261.

[3] V. Seredyuk, E. Alami, M. Nydén, K. Holmberg, Micellization and adsorption properties of novel zwitterionic surfactants, Langmuir, 17 (2001) 5160–5165.

[4] L. M. Jansen et al., Synthesis and performance of bio-based amphoteric surfactants, chemistry - A European Journal , 30(38) (2024)1-6.

[5] M. Lindstedt, S. Allenmark, A.R. Thompson, L. Edebo, Antimicrobial activity of betaine esters, quaternary ammonium amphiphiles which spontaneously hydrolyze into nontoxic components, Antimicrob. Agents Chemother. 34 (1990) 1949–1954.

[6] C.R. Birnie, D. Malamud, R.L. Schnaare, Antimicrobial evaluation of N-alkyl betaines and N-alkyl-N,N-dimethylamine oxides with variations in chain length, Antimicrob. Agents Chemother. 44 (2000) 2514–2517.

[7] M.A. Gonzalez, J.C. Royero, A. Mesa, L.B. Galvis, Synthesis and biological evaluation of pyridine betaine A and B, Natl. Prod. Res. 23 (2009) 1485–1491.

[8] A. Cosquer, Antibacterial activity of glycine betaine analogues: involvement of osmoportes, Bioorg. Med. Chem. Lett. 14 (2004) 2061–2065.

[9] J. Zhao, C. Dai, Q. Ding, M. Du, H. Feng, Z. Wei, A. Chen, M. Zhao, The structure effect on the surfacial and interfacial properties of zwitterionic sulfobetaine surfactants for enhanced oil recovery, RSC Adv. 18 (2015) 13993-14001.

[10] X. Wang, J. Liu, L. Yu, J. Jiao, R. Wang, L. Sun, Surface adsorption and micelle formation of imidazolium-based zwitterionic surface active ionic liquids in aqueous solution, J. Colloid Interface Sci. 391 (2013) 103–110.

[11] X. Liu, L. Dong, Y. Fang, A novel zwitterionic imidazolium-based ionic liquid surfactant: 1-carboxymethyl-3-dodecylimidazolium inner salt, J. Surfact. Deterg. 14 (2011) 497–504.

[12] A. Koch, U. Jonas, H. Ritter, H.W. Spiess, Extended mesoionic systems: synthesis and characterization of monocyclic, polycyclic and macrocyclic pyrimidinium-olate derivatives and their photochemical behavior, Tetrahedron 60 (2004) 10011–10018.

[13] C. Kratky and T. Kappe, “Mesoionic six-membered heterocycles. XIV.Crystal structure of a pyrimidine betaine”, J. Heterocycl. Chem., 18, 05(1981) 881-883.

[14] G. Wenska, M. Insińska, and B. Skalski, Synthesis and solvatochromism of 2-(N-pyridinio)-pyrimidin-4-olate and related betaines derived from uracils, Polish J. Chem., 74 (2000) 659-672.

[15] J. Pan, L.Yu, D. Liu, and D. Hu, Synthesis and Insecticidal Activity of Mesoionic Pyrido[1,2-α]pyrimidinone Derivatives Containing a Neonicotinoid Moiety, Molecules, 23 (5) (2018) 1217-1228.

[16] F. Malki, A. Alouache, S. Krimat, Effects of various parameters on the antioxidant activities of the synthesized heterocyclic pyrimidinium betaines, Indones. J. Chem. 23 (2023) 90-100.

[17] F. Malki, A. Alouache, A. Meklat, Synthesis of heterocyclic mesoionic betaines derivatives containing a pyrimidine ring for screening of their biological activities, Res. J. Chem. Environ. 28 (2024) 43-47.

[18] Q. Zuo, Z. Wang, P. Li, L. Yang, Z. Song, Studies on the synthesis and application properties of a betaine surfactant with a benzene ring structure, Appl. Sci. 13 (2023) 4378.

[19] A.L. Chong, M. Forsyth, D.R. MacFarlane, Novel imidazolinium ionic liquids and organic salts, Electrochim. Acta 159 (2015) 219–226.

[20] C.M. Phan, et al., Micelle and surface tension of double-chain cationic surfactants, ACS Omega 3 (2018) 10907–10911.

[21] A. Ghanem, R.D. Alharthy, S.M. Desouky, R.A. El-Nagar, Synthesis and characterization of imidazolium-based ionic liquids and evaluating their performance as asphaltene dispersants, Materials 15 (2022) 1600.

[22] A. Gharbi, L. Badache, L. Berriche, S. Habi Ben Hariz, Synthesis and characterization both micellization and thermodynamic parameter of cationic surfactant mixture derived from vegetable oil, J. Iran. Chem. Soc. (2020).

[23] F. Malki, A. Touati, S. Rahal, S. Moulay, Total synthesis of monocyclic pyrimidinium betaines with fatty alkyl chain, Asian J. Chem. 23 (2011) 961–967.

[24] M. Huhn, E. Somfai, G. Szabo, G. Resofszki, Ger. Offen. 26 27 709. (1976).

[25] P. Dvortsak, G. Resofszki, M. Huhn, L. Zalantai, A.I. Kiss, Reactions of pentachlorophenyl esters of malonic acid derivatives—II: preparation and investigation of pyrimidine betaines, Tetrahedron 32 (1976) 2117–2120.

[26] F. Malki, A. Touati, S. Moulay, Extraction and recrystallization of mesoionic pyrimidinium betaines, IJCEA 5 (2014) 151–154.

[27] K.D. Danov, S.D. Kralchevska, P.A. Kralchevsky, K.P. Ananthapadmanabhan, A. Lips, Mixed solutions of anionic and zwitterionic surfactant (betaine): surface tension isotherms, adsorption and relaxation kinetics, Langmuir 20 (2004) 5445–5453.

[28] D. Fu, X. Gao, B. Huang, J. Wang, H. Jiang, M. Zheng, P. Li B. Huang[1], K. Kan , X.n Zhang, Micellization and thermodynamics study of ester functionalized picoline-based ionic liquid surfactants in water, RSC Adv 23 (2022) 14477–14484.

[29] L. Shi, J. Ma, Y. Chen, Synthesis and surface properties of sodium sulfonate amphoteric surfactants having different hydrophobic carbon chain length, Research on Chemical Intermediates, (2022) 48:2509–2533.

[30] A. Bratovcic, S. Nazdrajic, A. Odobasic, I. Sestan, The Influence of Type of Surfactant on Physicochemical Properties of Liquid Soap,International Journal of Materials and Chemistry, 8(2) (2018) 31-37.