Asian Journal of Chemistry; Vol. 33, No. 2 (2021), 333-337

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.22999

Synthesis and Performance Evaluation of Green Anionic Polymeric Surfactant for Detergent Application

NEETA SINGH[1,*], P.K.S. YADAV[2] and S.K. GUPTA[1]

[1]Department of Chemical Engineering, Harcourt Butler Technical University, Kanpur-208002, India
[2]Department of Oil Technology, Harcourt Butler Technical University, Kanpur-208002, India

*Corresponding author: E-mail: neetasinghrana90@gmail.com

Received: 22 September 2020; *Accepted*: 9 November 2020; *Published online*: 15 January 2021; AJC-20217

The main role of this study is to prepare the green polymer based anionic surfactant as an alternative to non-biodegradable surfactant for detergent applications. The detergent properties *i.e.*, surface tension measurements, foaming property, emulsifying ability, dispersing property, FTIR analysis and wetting behaviour were studied using several rheological techniques. The critical micelle concentration (CMC) value was obtained at 6 mg/L of surfactant concentration showing no further remarkable changes in surface tension with increases in concentration. Low surface tension value was correlated with decrease in cohesive force exist between the molecules and allowed the surfactant easily adsorbed on the pore surface. The low surface tension value, reliable wetting characteristic, excellent emulsifying power, benchmark dispersing behaviour and suitable foaming property assuring the successful utilization of polymer based anionic surfactant for detergent applications.

Keywords: Polymeric surfactant, Odium methyl ester, Critical micelle concentration, Surface tension, Detergent.

INTRODUCTION

Non-biodegradable surfactants *i.e.*, petroleum-derived materials, have affected several environmental aspects and created environment imbalance conditions for surrounding human life [1,2]. Hence, this imbalance condition has triggered many researchers to prepare green anionic polymer surfactants for daily applications [3]. Moreover, green anionic surfactant is generally plant-based originated ecofriendly materials with desirable detergent properties *i.e.* low surface tension, remarkable foaming characteristics and appropriate critical micelle concentration with maintaining low cost [4-8]. Anionic polymers surfactants are generally classified as negatively charged water-soluble group. In addition, green anionic polymer surfactants have been frequently used in daily applications for their benchmark ability to enhance wetting characteristics of the materials with no environmental issue. Moreover, many anionic polymers *i.e.*, ammonium lauryl sulfate, sodium myreth sulfate, sodium lauryl sarcosinate, sodium pareth sulfate, sodium stearate, sodium lauryl sulfate, sodium laureth sulfate have been widely used for detergent applications [9-14]. So, the industrialist can be dealt with the complexity of global demand by providing a reliable product using anionic polymer surfactant material [15,16].

Extensive use of non-biodegradable petroleum surfactant products can potentially harm the plants and animal lifes. To overcome this issue, many researchers have focused on using the combination of polymer and green surfactants [17,18]. This environmentally friendly anionic polymer surfactant has hydrophilic and hydrophobic characteristics that lower the surface tension of liquid by increasing the distance between the molecules. Sodium methyl ester sulfonate is a green anionic polymer surfactant that is derived from rice bran oil with polymerizing by a free radical technique using acrylamide as a monomer [19].

Many researchers have applied the theory of ionic polymer based surfactant materials to attain the promising value of desirable characteristics *i.e.*, wetting behaviour, foaming properties, emulsifying ability and surface tension value for detergent applications. Fernandez *et al.* [15] prepared nonylphenol ethoxylates based green surfactants with high filler content for emulsion applications. Yu *et al.* [20] reviewed several types of surfactants like non-ionic, anionic and cationic for detergent applications. Chu and Feng [3] synthesized erucic acid derived from rapeseed oil based vegetable green surfactant for detergent applications. Raffa *et al.* [4] reviewed various types of surfactants like anionic, cationic for printing, detergent and coatings applications. Kumar *et al*. [1] investigated the physico-chemical properties of sodium methyl ester sulfonate based materials using potassium bisulfate as an indicator for enhanced oil recovery applications. Kumar *et al*. [19] prepared anionic polymeric surfactants based on sodium methyl ester sulfonate with potassium persulfate as an indicator of enhanced oil recovery applications. Lim *et al*. [21] examined the performance of alpha-sulfo fatty methyl ester sulfonate/linear alkyl sulfonate based surfactant for detergent applications. Kakizawa and Miyake [22] studied the combination of surfactant/polymer based material for body wash applications. Kumar *et al*. [19] studied only rheological properties of sodium methyl ester sulfonate based surfactant for enhanced oil recovery purposes. To our best of knowledge, no literature has been carried using sodium methyl ester sulfonate for detergent applications.

In this study, sodium methyl ester sulfonate/acrylamide monomer based surfactant material has been synthesized using the free radical technique. Further, the synthesized material was characterized using different analyses techniques like surface tension measurement, FTIR analysis, foaming properties, emulsifying ability and wetting behaviour to determine the suitability of this material for detergent applications.

EXPERIMENTAL

Rice bran oil was purchased from local industry, Kanpur, India. The saponification value is 194.68, iodine value is 101.25 and specific gravity is 0.9003 at 30 ºC of the purchased rice bran oil. Acrylamide (*m.w*. 71.08) and potassium metabisulphite were procured from Loba Chemie Pvt. Ltd, India. All other solvents like acetone, methanol, pyridine (99.5%), hydroquinone, sodium carbonate, ether (99.7), cholorosulfonic acid, were procured from Sigma-Aldrich, USA.

Synthesis of sodium methyl ester sulfonate: In first step, acid-catalyzed esterification reaction was carried out to reduce the acid value of rice bran oil (3.358 mg KOH/g). In this step, different methanol/oil molar ratios were poured in beaker at a temperature of 60 ºC for 2 h using 1% sulfuric acid as a catalyst. Further, the methanol-water was removed using separating funnel after 3 h. The resultant product has desirable acid value (< 1 mg KOH/g).

In second step, the transesterifiaction reaction was carried out at 105 ºC for 30 min using KOH as catalyst. After this, the solution was allowed to cool and settled down for 8 h. The extra top layer of H_2O-KOH-CH_3OH was removed using separating funnel. Resultant solution was washed and heated up to 105 ºC for 10 min.

Cholorosulfonic acid (2.63 g) and pyridine (15 mL) were added slowly in fatty acid methyl ester solution (2.60 g) and heated in the steam bath until the resultant solution became crystal clear. The solution was quenched using sodium bicarbonate (33 g/300 mL) with appropriate quantity of sodium bicarbonate and prepared sodium salts. Subsequently, this solution was washed three times with butanol and evaporated the solvent using evaporation unit.

Preparation of anionic surfactant: The selective quantity of acrylamide (10 g) and methyl ester sulphonate (5 g) were placed in a conical flask. Further, 250 mL of double distilled water was added in the solution and heated at 70 ºC in an inert atmosphere. In addition, potassium persulphate (0.5 wt. %) was added dropwise in that solution for 12 h. After that, the resultant concentrated solution was filtered out using an acetone solution. The resulting product was dried in an oven at 70 ºC.

FTIR analysis: In order to visualize the structural groups present in the surfactant, FTIR analysis was recorded using Thermo-Nicolet 5700, USA over the 4000-500 cm^{-1} wavelength range in a transmittance mode.

Surface tension measurement: The Du-Nouy tensiometer was used for the measurement of surface tension of the prepared surfactants. In this method, the platinum ring was carefully washed using acetone and red-hot heated in an ethyl alcohol flame for every concentration.

Foaming characteristics analysis: Foaming characteristics of the synthesized anionic polymer based surfactants were measured using the Ross mile method in accordance with ASTMD 1173. In this method, the stability of foam was demonstrated on the basis of height change measurement after 3 min [23].

Emulsifying ability measurement: The emulsifying ability of the synthesized polymer based surfactant was calculated using the emulsifying power analysis method proposed by Eissa *et al*. [23]. In this method, a similar amount of surfactant and oily materials have been taken mixed properly in a tube at 25 ºC and noted the separation time of two liquids that is the emulsifying ability of the synthesized surfactants.

Wetting characteristics: The wetting behaviour of the synthesized surfactants was analyzed using standard draves method in accordance with ASTM D2281. In this method, a weighted skein was used to demonstrate the wetting properties of the synthesized surfactants [24].

Dispersing characteristics: In this method, equal amount of commercial dye and surfactant were mixed in 100 mL distilled water at pH 5 and heated to 130 ºC for 1 h. Subsequently, the solution was cooled at 90 ºC and filtered using the filtration unit. The concentration of dye in the filtered solution was determined using Elico SL 210 UV VIS spectrophotometer. Dispersibility (D) was calculated using the following equation:

$$D\ (\%) = \frac{\text{Dye concentration in filterate}}{\text{Dye concentration in native solution}} \quad (1)$$

RESULTS AND DISCUSSION

FTIR analysis for anionic polymeric surfactants: In order to visualize the functional groups present in the sample, FTIR analysis for surfactant has been recorded over the wavelength range of 4000-500 cm^{-1} (Fig. 1). A peak at 1060-1020 cm^{-1} represents sulfonate group present in the surfactants, while the band at 3421-3410 cm^{-1} exhibits acrylamide exist in the sample. A characteristic peak at 1680-1670 cm^{-1} signifies the amide group. The collective information shows that the present sample is mixture of acrylic acid and methyl ester sulfonate.

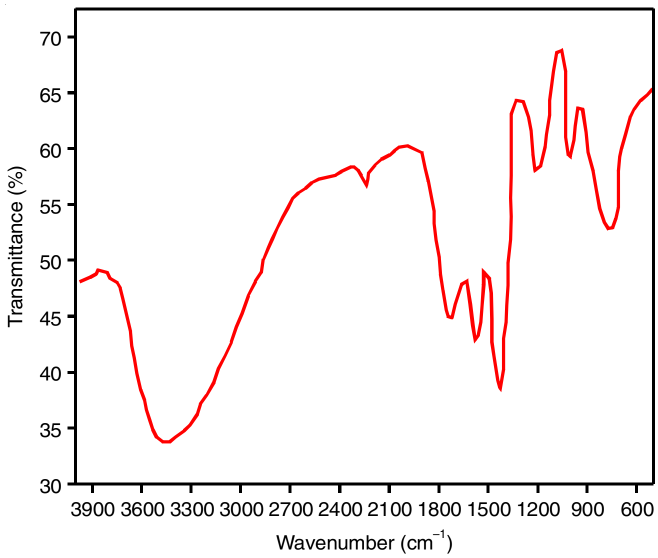

Fig. 1. FTIR analysis for anionic surfactant

Surface tension measurements and critical micelle concentration of anionic polymeric surfactants: The surface tension property of different concentrations of surfactants was investigated using Du-Nouy international tensiometer (platinum ring). This test reveals the shrinking availability of the surfactant molecules in the minimum surface area. Fig. 2 reveals the surface tension decreases with increasing the concentrations of surfactants. This happens due to the adsorption of materials on the air-liquid interface. Eissa *et al*. [25] prepared hydrophilic polymeric surfactants and observed the similar results. The authors also explained the decrement in the surface tension had been correlated with the addition of surfactants due to amphipathic structure of the material. Moreover, the optimized concentration of surfactants at which no further reduction in surface tension was also observed. The CMC value at 6 mg/L concentration of surfactant is 33.7 mN/m. At this CMC, the formation of micelle was occurred and no further significant change in surface tension as concentration surges. At CMC, surfactants separate the liquid molecules and allow the detergent to adsorb at the pore surface. This behaviour suggests the suitability of this material for detergent applications.

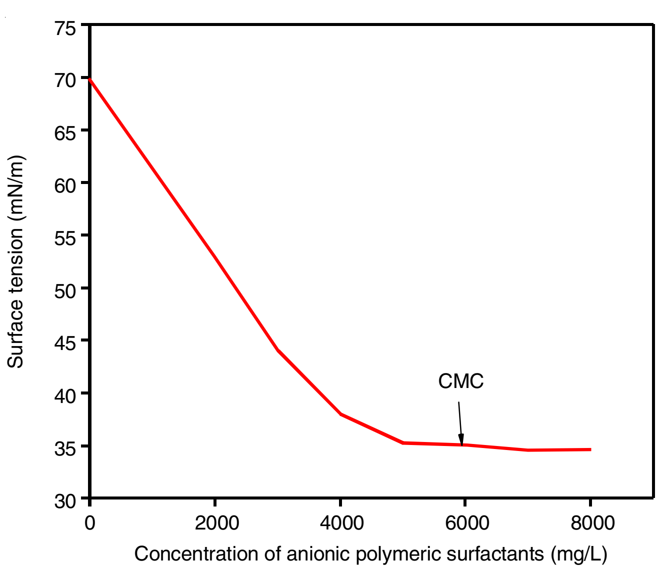

Fig. 2. Surface tension *versus* different concentrations of surfactant curve

Foaming characteristics of anionic polymeric surfactants: The desirable foaming characteristic of anionic surfactants is an important parameter for selecting assured detergent using Ross miles foam analyzer in accordance with ASTM D1173. This characteristic measurement process is generally unsteady state thermodynamic phenomena. The foam height was 86 mm for 2 mg/L, 91 mm for 4 mg/L, 95 mm for 6 mg/L and 99 mm for 8 mg/L of surfactants, respectively at 25 ºC. The foam height was 83 mm for 2 mg/L, 87 mm for 4 mg/L, 91 mm for 6 mg/L and 93 mm for 8 mg/L of surfactants, respectively at 85 ºC. The foam height increased as the concentration of surfactant surges (Fig. 3). The foam height is completely decayed at 3 min and generally depends on the multi hydrophilic group present in the material. These groups lower the cohesive force exists between the liquid molecules, additionally, it also surges the electrostatic repulsion in between the molecules. Chen *et al*. [24] synthesized the anionic surfactants and reported the similar results. The suitable foaming property of the synthesized materials shows the reliability for detergent applications.

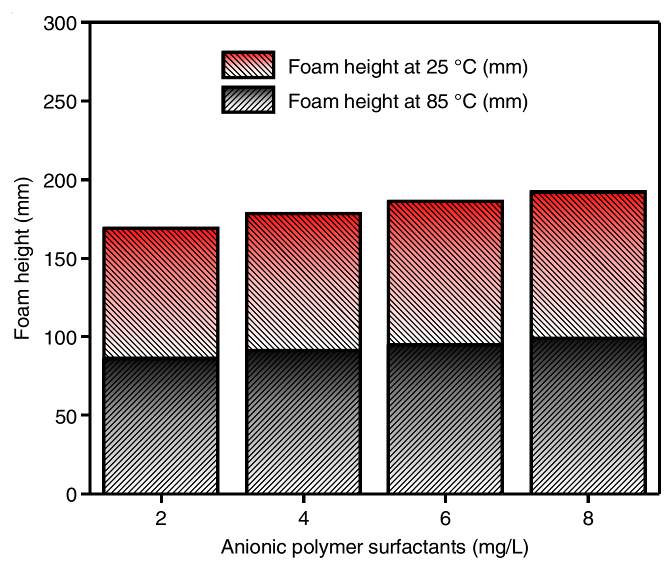

Fig. 3. Foaming characteristics of anionic surfactant at different temperatures

Emulsifying ability of anionic polymeric surfactants: In order to visualize the impact of increasing concentration of surfactants on emulsion stability, emulsifying ability of anionic polymeric surfactants were investigated. The separation time for kerosene is 171 s for 2 mg/L, 189 s for 4 mg/L, 251 s for 6 mg/L and 309 s for 8 mg/L of surfactants, respectively (Fig. 4). The separation time for liquid paraffin was 1161 s for 2 mg/L, 1780 s for 4 mg/L, 2027 s for 6 mg/L and 2057 s for 8 mg/L of surfactants, respectively. The separation time for *o*-dicholorobenzene is 1534 s for 2 mg/L, 1641 s for 4 mg/L, 1811 s for 6 mg/L and 2007 s for 8 mg/L of surfactants, respectively. From results, it reveals that the surfactants represent an excellent emulsifying ability towards various oils. Higher concentrations are responsible for longer separation time of various solutions. Therefore, higher concentrations of surfactants exhibit more

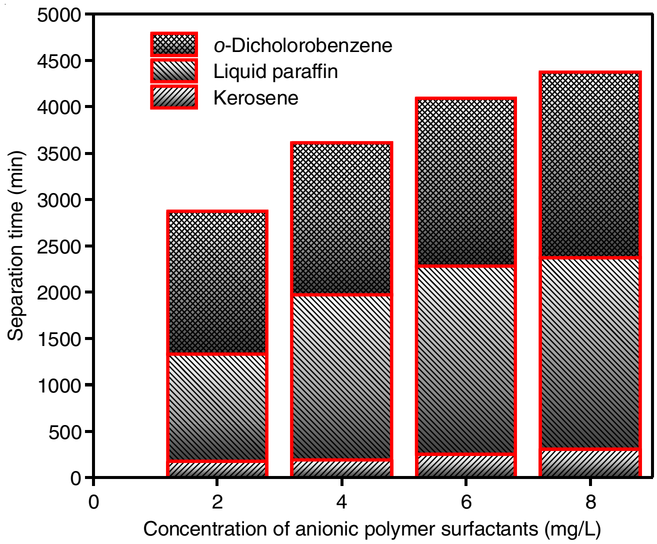

Fig. 4. Emulsifying abilities of different concentrations of polymeric surfactant

stable emulsifying solutions. Kamba *et al*. [26] also observed the similar results.

Wetting characteristics of anionic polymeric surfactants: This wetting behaviour of surfactants has attracted the commercial industries to use this surfactant for removing oil and dye by washing. In order to elucidate the penetrating properties of samples, the wetting characteristics of surfactants have been investigated using Drave's method. The wetting time was 25 min for 2 mg/L, 22 min for 4 mg/L, 18 min for 6 mg/L and 17 min for 8 mg/L of surfactants, respectively (Fig. 5). The wetting time for pure water was around 40 min. Higher concentrations of surfactants increase the capability to remove air from the interface.

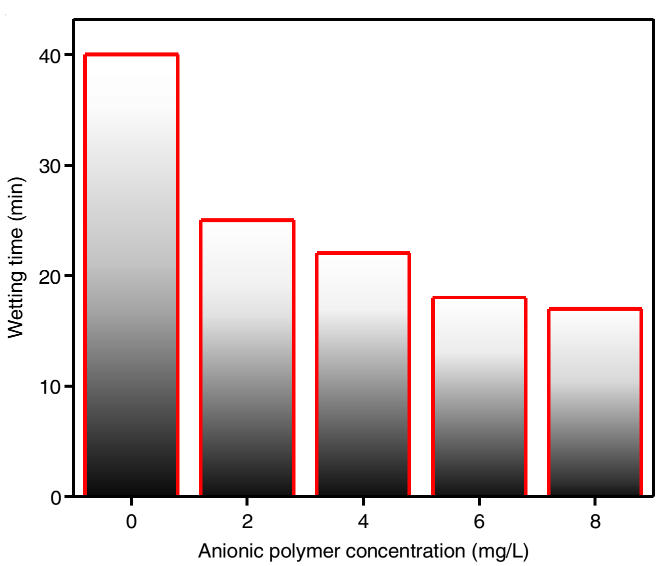

Fig. 5. Wetting characteristics of different concentrations of polymeric surfactant

Dispersing properties: The dispersing properties of the various concentrations of anionic polymeric surfactants have been studied. The dispersing behaviours of surfactants have been analyzed in yellow and blue dyes. The dispersibility in yellow dye is 47.29% for 2 mg/L, 50.54% for 4 mg/L, 55.47% for 6 mg/L and 56.11% for 8 mg/L, respectively (Fig. 6). The dispersibility in blue dye was 28.39% for 2 mg/L, 31.21% for 4 mg/L, 35.67 % for 6 mg/L and 36.15% for 8 mg/L, respectively. The dispersability increases with an increase in concentrations of surfactants due to a reduction in cohesive force between the liquid molecules.

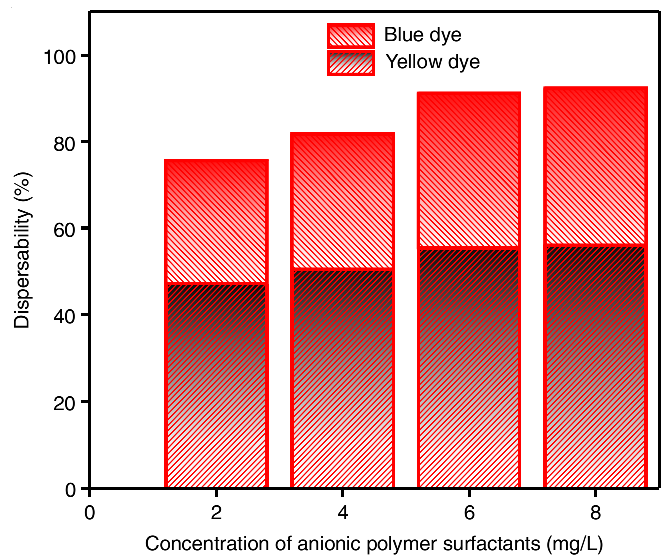

Fig. 6. Dispersing properties of different concentrations of polymeric surfactant

Conclusion

In this study, sodium methyl ester sulfonate/monomer acrylamide based anionic polymer based surfactant material had been prepared using a free radical technique for detergent applications. The cleaning performance of the synthesized surfactant was evaluated on the basis of various properties. The optimized surface tension value was 6 mg/L, while the CMC value at 6 mg/L concentration of surfactant was found to be 33.7 mN/m. At this CMC value, surfactant easily adsorbed at the pore surface and enhances the quality of surfactant for the detergent applications. The foaming height was increased with an increase in concentration due to a reduction in cohesive force between the molecules of the liquid. The longer separation time for oil removal was showing the noticeable emulsifying ability of the surfactant. Higher concentration of surfactant was responsible for reducing the wetting time of the resultant materials. So, it can be concluded that sodium methyl ester sulfonate/monomer acrylamide based anionic polymer based surfactant material is suitable for the detergent applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. S. Kumar, N. Saxena and A. Mandal, *J. Ind. Eng. Chem.*, **43**, 106 (2016); https://doi.org/10.1016/j.jiec.2016.07.055
2. D. Jenkins, W.J. Kaufman, P. McGauhey, A.J. Horne and J. Gasser, *Water Res.*, **7**, 265 (1973); https://doi.org/10.1016/0043-1354(73)90168-1

3. Z. Chu and Y. Feng, *ACS Sustain. Chem. Eng.*, **1**, 75 (2013); https://doi.org/10.1021/sc300037e
4. P. Raffa, D.A.Z. Wever, F. Picchioni and A.A. Broekhuis, *Chem. Rev.*, **115**, 8504 (2015); https://doi.org/10.1021/cr500129h
5. Z. Zhang, J. Li and J. Zhou, *Transp. Porous Media*, **86**, 199 (2011); https://doi.org/10.1007/s11242-010-9616-6
6. H.L. Chang, *J. Petrol. Technol.*, **30**, 1113 (1978); https://doi.org/10.2118/7043-PA
7. B. Sandiford, *J. Petrol. Technol.*, **16**, 917 (1964); https://doi.org/10.2118/844-PA
8. K.D. Danov, R.D. Stanimirova, P.A. Kralchevsky, E.S. Basheva, V.I. Ivanova and J.T. Petkov, *J. Colloid Interface Sci.*, **457**, 307 (2015); https://doi.org/10.1016/j.jcis.2015.07.020
9. G. Martins and M.F.R.G. Dias, ed.: M. Miteva, Hair Cosmeceuticals. In *Alopecia*, Elsevier, Chap. 27, pp 285-293 (2019).
10. A. de Lucas, L. Rodríguez, J. Lobato and P. Sánchez, *Chem. Eng. Sci.*, **57**, 479 (2002); https://doi.org/10.1016/S0009-2509(01)00372-4
11. B. Kapur, J. Solomon and B. Bluestein, *J. Am. Oil Chem. Soc.*, **55**, 549 (1978); https://doi.org/10.1007/BF02668068
12. Y. Lim, R.D. Stanimirova, H. Xu and J. Petkov, *Household and Personal Care Today*, **11**, 47 (2016).
13. W. El-Dougdoug and E. El-Mossalamy, *Appl. Surf. Sci.*, **253**, 2487 (2006); https://doi.org/10.1016/j.apsusc.2006.05.006
14. D. Hall and G. Tiddy, *Surfactant Science Series*, **11**, 60 (1981).
15. A.M. Fernandez, U. Held, A. Willing and W.H. Breuer, *Prog. Org. Coat.*, **53**, 246 (2005); https://doi.org/10.1016/j.porgcoat.2004.12.011
16. L. Cohen, A. Moreno and J. Berna, *J. Am. Oil Chem. Soc.*, **70**, 79 (1993); https://doi.org/10.1007/BF02545372
17. P.E. Throckmorton, R.R. Egan, D. Aelony, G.K. Mulberry and F.H. Otey, *J. Am. Oil Chem. Soc.*, **51**, 486 (1974); https://doi.org/10.1007/BF02635857
18. X. Li and W. Eli, *J. Mol. Catal. Chem.*, **279**, 159 (2008); https://doi.org/10.1016/j.molcata.2007.08.032
19. S. Kumar and A. Mandal, *Polymer*, **120**, 30 (2017); https://doi.org/10.1016/j.polymer.2017.05.051
20. Y. Yu, J. Zhao and A.E. Bayly, *Chin. J. Chem. Eng.*, **16**, 517 (2008); https://doi.org/10.1016/S1004-9541(08)60115-9
21. Y.S. Lim, N.B. Baharudin and Y.W. Ung, *J. Surfactants Deterg.*, **22**, 549 (2019); https://doi.org/10.1002/jsde.12230
22. Y. Kakizawa and M. Miyake, *J. Oleo Sci.*, **68**, 19081 (2019); https://doi.org/10.5650/jos.ess19081
23. A. Eissa, M. El-Hefnawy, S. Bader and M. Radwan, *J. Surfactants Deterg.*, **15**, 411 (2012); https://doi.org/10.1007/s11743-011-1324-x
24. Y.-F. Chen, C.-H. Yang, M.-S. Chang, Y.-P. Ciou and Y.-C. Huang, *Int. J. Mol. Sci.*, **11**, 4417 (2010); https://doi.org/10.3390/ijms11114417
25. A. El Menam Eissa, M. El Hefnawy, S. Bader, M. Radwan and M. Deef Allah, *J. Surfactants Deterg.*, **15**, 411 (2012); https://doi.org/10.1007/s11743-011-1324-x
26. E. Kamba, A. Itodo and E. Ogah, *Int. J. Mater. Chem.*, **3**, 69 (2013); https://doi.org/10.5923/j.ijmc.20130304.01