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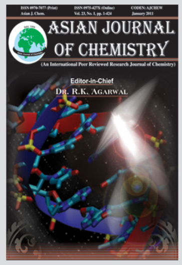

Development of Foam Indicator Based on Cationic Surfactant Quaternized Fatty Acid Triethanolamine Ester

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Quaternized fatty acid triethanolamine esters have been found to be used predominantly for commercial applications in recent years for preparing foam indicators. They possess low toxicity, high biodegradability, excellent hydrolytic stability, antistatic, softening, corrosion inhibition properties and excellent dispersing properties. Quaternized fatty acid triethanolamine ester is produced *via* a two-stage process in which triethanolamine is first esterified with a fatty acid followed by quaternization with alkylating agent. Foam indicator has been formulated based on this and evaluated its leak rate up to 10^{-4} mbar/s.

Key Words: Quaternized fatty acid triethanolamine ester, Foam indicator, Triethanolamine, Oleic acid.

INTRODUCTION

Quaternized fatty acid triethanolamine esters[1] (QFATE) belong to important class of cationic surfactants which have been found to be used predominantly for commercial applications in recent years for preparing the foam indicators. They are stable unlike foam indicators based on sodium salt of fatty acids which will forms heterogenous gels even at low concentrations of up to 5 % by weight[2]. Their uniqueness is due to the presence of at least one ester group between the long hydrocarbon chain and triethanolamine hydroxyl group. This ester link provides for easy hydrolysis to fatty acids and short chain quats[3]. Quaternized fatty acid triethanolamine esters possess low toxicity and high biodegradability and also has excellent dispersing properties in water due to its superior solubility in water[4-6]. Unlike other cationic surfactants they are good foaming agents and can be mixed in formulations which contain anionic surfactants. They have excellent hydrolytic stability, antistatic, softening and corrosion inhibition properties. The foam indicators obtained from them are meeting test guide lines of the Organization for Economic Cooperation and Development (OECD) and promised to become outstanding among the organic base soaps, because of the peculiar properties of the ethanolamine fatty acid compound, as well as the striking and unusual character of these hydroxyalkylamines themselves[7]. In this study, an attempt has been made to synthesize quaternized fatty acid triethanolamine esters by esterification of fatty acids and triethanolamine followed by quaternization in low polar solvents to introduce the positive charge to the molecule. Formulation of the foam indicator has been arrived with the prepared quaternized fatty acid triethanolamine esters.

EXPERIMENTAL

Triethanolamine (density: 1.12 g/mL; assay: > 97 %) was procured from E-Merck (India); oleic acid (density: 0.981 g/mL; assay: 65-70 %) was procured from SD Fine Chemicals, Mumbai and used for the experiments directly without any further purification

Synthesis of fatty acid triethanolamine ester (FATE): Oleic acid (147 g, 0.348 mol) and triethanolamine (26 g, 0.174 mol) were taken in a 250 mL beaker and mixed thoroughly which results in white gelly mass. The reaction mixture is heated at a temperature of 80-90 °C for 1 h to obtain dark brownish liquid. Cooled at room temperature and water is removed through vacuum to obtain fatty acid triethanolamine ester (FATE) (46 g, 50 % yield).

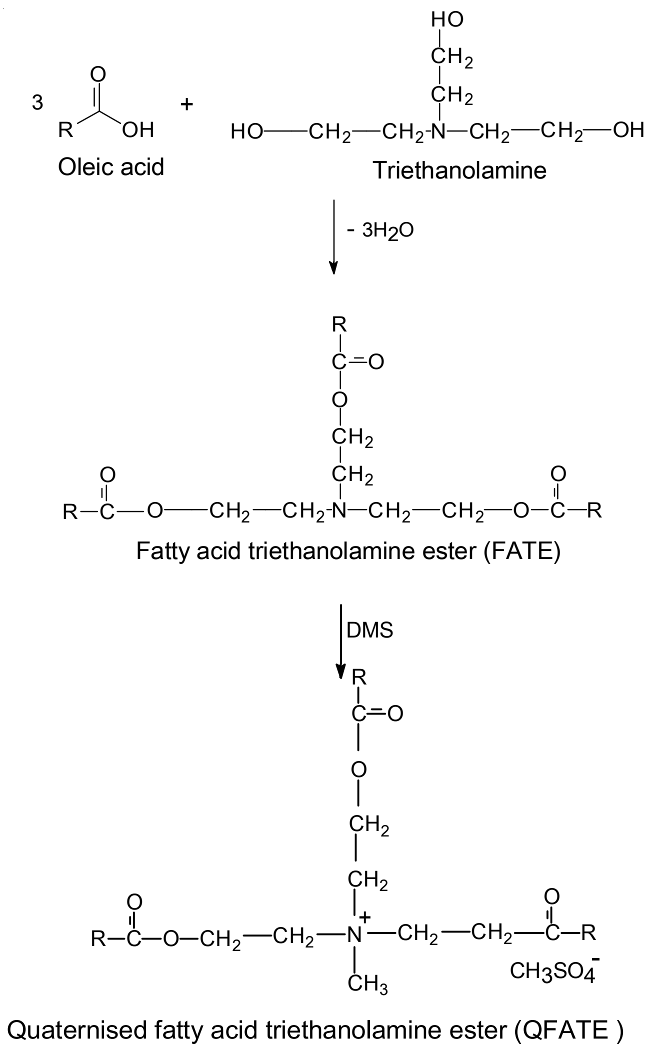
Synthesis of cationic surfactant, quaternized fatty acid triethanolamine esters: Fatty acid triethanolamine ester (192 g, 0.326 mol) taken in 500 mL beaker was dissolved in 200 mL of diethyl ether. Dimethyl sulphate (DMS) (61.71 g, 0.489 mol) was added drop by drop to it with constant stirring at room temperature. The reaction mixture was stirred for 3 h and allowed overnight to evaporate diethyl ether completely to obtain light brown coloured viscous liquid ester quaternized (191 g, 98.0 % yield).

Preparation of poly(vinyl alcohol)-glycerol (PVA-GLY) adduct: 1 g of poly(vinyl alcohol) (PVA) is powdered in piezal and mortar and kept in a 100 mL of beaker. 19 g of glycerol was added to the beaker and the reaction mixture was heated up to 170 ºC with constant stirring till complete dissolution to obtain PVA-GLY adduct.

Preparation of foam indicator: Quaternized fatty acid triethanolamine ester (10 g), PVA-GLY (20 g), ethylene glycol (65 g) and distilled water (5 g) were added in a 200 mL beaker and the reaction mixture was stirred for 1 h to obtain foam indicator which is ready to use in the leak testing. It is permissible to use more amount of distilled water to dilute the solution as per requirement.

RESULTS AND DISCUSSION

Synthesis of fatty acid triethanolamine ester: Esterification of triethanolamine with fatty acids results in corresponding ester derivatives[5,8,9]. Reaction between triethanolamine and fatty acid (oleic acid) results in the formation of fatty acid triethanolamine ester (Fig. 1). Here, hydroxy (-OH) moiety in triethanolamine reacts with carbonyl group of oleic acid (-COOH). Fatty acid triethanolamine ester synthesized using the above procedure was analyzed by using FT-IR and mass spectrometry. Mass spectrum shows molecular ion peak M^+: 414.3, corresponding to molecular weight of fatty acid triethanolamine ester. Fragmentation pattern at m/e:150 and m/e: 132 shows the presence of triethanolamine and fragmented oleic acid respectively. FT-IR shows the peak observed at 3324 cm^{-1} is due to free -OH group stretching vibration and O-H deformation was indicated by the peak at 1071 cm^{-1}. These two peaks were the confirmation of free OH groups of fatty acid triethanolamine ester. The peak obtained at 1714 cm^{-1} is due to the presence of -C=O group. The peaks appeared at 2923 and 1563 cm^{-1} confirmed the presence of tertiary nitrogen of triethanolamine present in the fatty acid triethanolamine ester.



where, R = CH_3—$(CH_2)_7$—C=C—$(CH_2)_7$—

Fig. 1. Synthesis of quaternized fatty acid triethanolamine ester (QFATE)

Synthesis of quaternary fatty acid triethanolamine esters (QFATE): Reaction of fatty acid triethanolamine ester with dimethyl sulphate undergoes quaternization which results in the formation of QFATE (Fig. 1). The two important parameters molar ratio of fatty acid triethanolamine ester:dimethyl sulphate and duration have been studied[8,10] during quaternization. Fatty acid triethanolamine ester was stirred for 2-4 h at room temperature with varying molar ratios of dimethyl sulphate *i.e.* 1.25; 1.50 and 1.75 to obtain QFATEs (QA_1-QA_9). Effect of duration of quaternization and molar ratios of dimethyl sulphate on cationic content and yield of QFATEs at 35 ºC is given in Table-1. Quaternization of FATE for 2 h using 1:1.50 molar ratio of ester: dimethyl sulphate results in quaternized ester having 35.4 % cationic content. When duration of quaternization increased to 3 h the cationic content further increased to 47 %. On increasing the duration of quaternization to 4 h by keeping constant the molar ratio of fatty acid triethanolamine ester: dimethyl sulphate, the cationic content was reduced to 28.4 %. Hence, increasing the duration of quaternization beyond 3 h could not increase the cationic matter. But increase in the molar ratio of dimethyl sulphate decreased the cationic content of QFATEs irrespective of duration of quaternization. The same trend was also observed with respect to yield percentage of QFATEs. The cationic content as well as yield percentage of QFATE, QA_5 was found maximum. Increase of cationic content of QFATE increases hydrolytic stability, antistatic and corrosion inhibition properties along with antimicrobial properties in the formulation of foam indicator.

TABLE-1
QUATERNIZATION OF FATTY ACID TRIETHANOLAMINE ESTER (FATE)

Molar ratio FATE:DMS	Duration (h)	QFATE	Cationic content (% wt.)	Yield (% wt.)
1:1.25		QA_1	27.6	91.1
1:1.50	2	QA_2	35.4	96.1
1:1.75		QA_3	30.1	92.3
1:1.25		QA_4	31.3	92.7
1:1.50	3	QA_5	47.0	98.0
1:1.75		QA_6	34.7	95.3
1:1.25		QA_7	18.4	90.1
1:1.50	4	QA_8	28.4	95.2
1:1.75		QA_9	22.7	92.0

TABLE-2
PERFORMANCE OF DIFFERENT FOAM INDICATORS AT DIFFERENT LEAK RATES

Foam indicator type	Leak rate of helium gas detected by helium gas detector (mbar/s)			
	10^{-3}	10^{-4}	10^{-5}	10^{-6}
Without PVA and water	Bubbles seen clearly	Very small bubbles difficult to be seen with naked eye	No bubbles	No bubbles
With PVA and water	Bubbles seen clearly	Bubbles seen clearly	No bubbles	No bubbles
With PVA and without water	Bubbles seen clearly	Very small bubbles difficult to be seen with naked eye	No bubbles	No bubbles

Formulation of foam indicator: Glycerol produces wetting effect to help dispersion of surface active agent and prevent it forming gel. Poly(vinyl alcohol) acts as a plasticizer and protects the bubbles from bursting by forming a poly(vinyl alcohol) film on the surface and increase its thickness and thus making the bubble touchable and unbreakable. The surfactant in the foam indicators acts to make the wall of water thin. So, a suitable mixture of glycerol and poly(vinyl alcohol) (PVA-GLY) has to be added to the mixture and it dissolves in water making the bubbles hard to pop. The glycols are completely miscible with water, acts as freezing point[11] and aid in the dissolution of various resins, gums and oils. They also add lubricity to the composition and permit solid particles to be easily wiped away before the surface dries[12]. Preferably about 10 to 65 parts of a glycol or mixtures of two or more are included in the composition of foam indicators. The laboratory prepared QFATE based foam indicator was tested as per MIL-PRF-25567E Standard and found to be meeting all the specifications.

Applications: The evaluation of leakage of foam indicator at different leak rates was done with helium leak detector with the closed container made with titanium alloy. Three different compositions of foam indicators prepared as per experimental procedure, was applied on the surface of the closed container which is already filled with *ca.* 80 % nitrogen gas and 20 % helium gas under pressure between 1.0 to 2.5 bars. Helium being lighter than nitrogen comes out first from the leaked areas which were detected by digital helium gas detector. The leak rate of helium gas shows the amount of leakage in the vessel. The test results shown in the Table-2 indicates that all the three type of foam indicators are able to detect leak rates at 10^{-3} mbar/sec but not at leak rates at 10^{-5} and 10^{-6} mbar/s. Foam indicator having both PVA and water in its formulation is capable to detect leak rate at moderate sensitivity 10^{-4} mbar/s. From this it was clearly evident that the formulated foam indicator is capable of checking leak detection even at moderate sensitivity. Bubbles detected during leak testing by the QFATE based foam indicator at the leak rate of 10^{-4} mbar/s of helium gas is shown as Fig. 2.

Fig. 2. Bubbles shown during leak testing of closed container made with titanium alloy

Conclusion

A synthetic protocol has been established for the preparation of cationic surfactant, quaternized fatty acid triethanolamine ester (QFATE). Formulation of foam indicator having high cationic content was successfully achieved and evaluation has been carried for its performance requirements on the basis of MIL-PRF-25567E in terms of both physical properties and chemical composition which was found satisfactory. The newly developed foam indicator has been able to detect the leak rate up to 10^{-4} mbar/s.

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REFERENCES

1. K. Holmberg, Novel Surfactants: Preparation, Application and Biodegradability, In Surfactant Science Series, CRC Press, Sweden, Vol. 14 (2007).
2. A.M.I. Beattie, US Patent 4430245 (1994).
3. R. Puchta, P. Krings and P. Sandkuhler, *Tenside Surfact. Deterg.*, **30**, 186 (1993).
4. B. Wahle, J.B. Llosas, R. Pi, A.S. Codina, E.B. Balague, Y. Reichert and P. Waltenberger, Process for the Production of Solid Esterquats, US Patent 5783534 (1998).
5. S. Mishra and V.K. Tyagi, *J. Oleo Sci.*, **56**, 269 (2007).
6. K. Holmberg, *Curr. Opin. Colloid Interface Sci.*, **1**, 572 (1996).
7. R.B. Trusler, *Ind. Eng. Chem.*, **21**, 685 (1929).
8. R. Tyagi, V.K. Tyagi and R.K. Khanna, *J. Oleo Sci.*, **55**, 337 (2006).
9. A.A. Haliza, P. Siwayanan and S. Ahmed, *J. Oil Palm Res.*, **18**, 305 (2006).
10. IS Standard 4955 (1978).
11. B. Berkeley, V. Stream, D. Schoenholz and N. Y. Bayswater, All-weather Surface Cleaner, US Patent 3057804 (1962).
12. C.J. Roscoe, Multi-Purpose Cleaning Concentrate, US Patent 3839234 (1974).