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NOTE

An Efficient Synthesis of Long-Chain Alkyl Sulphonated Acrylamides

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Long-chain alkyl sulphonated acrylamides can be synthesized *via* the Ritter reaction using acrylamide and acetic acid as promoters. This protocol has the advantages of easier work-up, higher yields and lower costs.

Key Words: Ritter reaction, Synthesis, Sulphonated acrylamide.

Long-chain alkyl sulphonated acrylamides exhibit surface-activities and polymerizable properties. They are an important class of compounds that can be applied as monomers for polymeric surfactants and polyampholytes[1-4]. Many methods were developed for the synthesis of sulphonated acrylamides. Among them, the multi-component one-pot synthesis *via* the Ritter reaction has received considerable importance[5-8]. But some of the reported methods suffer from drawbacks such as competing side reactions, poor yields and high costs[9].

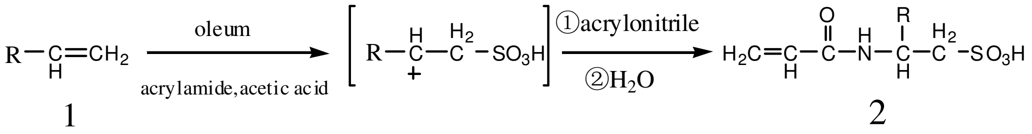
The amidation of olefins with nitriles in the presence of concentrated sulfuric acid is known as the Ritter reaction[10,11]. This method works well only in the case of branched olefins under strongly acidic conditions, thus limiting the scope of its use. Some alternative methodologies available are the use of oleum, reaction in nitrile solvents, reaction of olefins with nitriles in the presence of acid or anhydride and the use of promoters[12-17]. Reagents being used as sulfur trioxide stabilizers have been received increasing attention as a means to increase yields of the Ritter reaction[18]. These reagents contribute to the formation of SO_3H^+ and have many advantages such as easy workup procedures, higher yields and lower costs.

To our best of knowledge there is no method reported in the literature for the synthesis of long-chain alkyl sulphonated acrylamides from nitriles using acrylamide or weak acid as sulfur trioxide stabilizer. Although there are few reports about using them to improve the synthesis process of 2-acrylamido-2-methyl propane sulfonic acid (AMPS)[19]. We herein described an efficient synthesis of these compounds in nitrile solvents (**Scheme-I**). Acetic acid behaved as weak acid in the reaction.

Long-chain alkyl sulphonated acrylamides be synthesized *via* the Ritter reaction using acetic acid and acrylamide as promoters (**Scheme-I**).

General procedure: A dry 250 mL three-neck flask was charged with linear olefin **1** (0.2 mol), acrylonitrile (2 mol), acetic acid (0-2 g) and acrylamide (0-1.5 g). 10 % oleum (15 mL) was then added slowly to the solution with stirring at 0-5 ºC. The mixture was stirred at room temperature for 12-18 h and filtered. The crude product was washed by cold acetonitrile and dried to give long chain alkyl sulfonated arylamides (**2**).

Detection method: Primary purpose of this article is to describe a new synthetic PROCESS of long-chain alkyl sulphonated acrylamides. Identifications of the products are not the main part since they are known compounds reported in Ref.[9]. We also provide a rough characterization of one product (dodecyl sulphonated acrylamide) to prove this improved mehod has no negative effect. Melting point uncorrected. IR



yields increased from 20% to 37%

Scheme-I: Synthetic route for the long chain alkyl sulfonated acrylamides **2**

spectra were recorded on a Paragon-1000 spectrometer in KBr with absorptions in cm^{-1}. ^{1}H NMR was measured on a Avance-500 MHz spectrometer in D_2O with TMS as internal standard. High resolution mass spectra were obtained using a time-of-flight mass spectrometry (TOF-MS) instrument.

m.p. 129-131 ºC. ^{1}H NMR (500 MHz, D_2O) δ 0.8 (s, 3H), 1.2 (s, 18H), 6 (d, 1H); IR (KBr, ν_{max}, cm^{-1}): 3443, 2957, 2925, 2856, 1641, 1460, 1375, 1224, 1100, 1023, 625. HR MS. For $C_{15}H_{28}NO_4S$: 318.1748.

The results of the synthesis of long chain alkyl(dodecyl) sulphonated acrylamide promoted by acrylamide and acetic acid are summarized in Table-1. The rate of conversion of the olefin to the amide is dependent on the amount of acrylamide and the amount of acetic acid. After screening various reaction conditions to increase the rate of reaction, it was found that addition of acrylamide was very efficient for this transformation.

TABLE-1
EFFECTS OF THE AMOUNT OF ACRYLAMIDE AND ACETIC ACID ON THE SYNTHESIS OF DODECYL SULPHONATED ACRYLAMIDE

Entry	Acrylamide (g)	Acetic acid (g)	Isolated yield (%)
1	–	–	20
2	0.5	–	23
3	0.5	1	24
4	1.0	–	28
5	1.0	1	29
6	1.5	1	36
7	1.5	2	37

The optimum reaction conditions are as follows: tetradecene-1 (**1b**; 0.2 mol), was treated with 1.5 g of acrylamide, 2 g of acetic acid and 15 mL of oleum in 2 mol acrylonitrile for 12 h to obtain the corresponding amide in 37 % yield (Table-1, entry 7). To verify the effect of acrylamide, we have performed the synthesis of dodecyl sulphonated acrylamide without sulfur trioxide stabilizers; the yield of **1b** was 20 % (Table-1, entry 1). It was clear that acrylamide and acetic acid improved the reaction result. Under this condition, the acrylamide and acetic acid were used in the synthesis of long chain alkyl sulphonated acrylamides. The results are shown in Table-2.

As can be seen in Table-2, this protocol could be applied to long chain α-alkenes. Acrylamide and acetic acid can promote linear-alkenes to corresponding amides in better yields. It took 12-18 h to complete the transformation.

TABLE-2
SYNTHESIS OF LONG CHAIN ALKYL SULPHONATED ACRYLAMIDES PROMOTED BY ACRYLAMIDE AND ACETIC ACID

Compound	R	Time (h)	Isolated yield (%)
1a	$C_{10}H_{21}$	18	32
1b	$C_{12}H_{25}$	12	37
1c	$C_{14}H_{29}$	12	37
1d	$C_{16}H_{33}$	12	36

Conclusion

A simple, efficient and practical method for the conversion of long-chain linear-alkenes to the corresponding sulphonated acrylamides has been developed. This protocol has the advantages of easier work-up, higher yields and lower costs.

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