Selective esterification of triethylene glycol with methacrylic acid using methane sulphinic acid

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The esterification of triethylene glycol with methacrylic acid under identical conditions of catalyst concentration, for synthesis of triethylene glycol di-methacrylate using sulphuric acid and methane sulphinic acid as catalyst is discussed. The reaction by-products are lesser in case of methane sulphinic acid catalyst, in comparison to sulphuric acid catalyst. Therefore the yield of ester product, triethylene glycol di-methacrylate, achieved during the synthesis is higher with the use of methane sulphinic acid as a catalyst, than on use of sulphuric acid as catalyst. This concludes that methane sulphinic acid has better catalyst selectivity in comparison to sulphuric acid, for the synthesis of triethylene glycol di-methacrylate. Methane sulphinic acid when neutralized is easily biodegradable which is also desirable from environmental point of view.

The esters of triethylene glycol (TEG) and methacrylic acid (MA) are commercially very important. Methacrylate esters of TEG find applications in, the manufacture of plastic lenses, anaerobic adhesive having good bond strength, formulation of adhesives for Acrylonitrile Butadiene Styrene (ABS) plastics, manufacture of polymers with high refractive index and optical articles, orthopedic plastic brace, adhesives specially useful for bonding a ferrite core of induction coil, formulation of composition used for dental application, and propellants industry as moderator.

The literature available on the manufacture of methacrylate esters of TEG is very scanty. The catalyst used for industrial/commercial scale manufacture of esters are mainly mineral acids. The methacrylate ester of TEG is manufactured using sulphuric acid (SA) as catalyst. Detailed study was carried out to investigate the comparative performance of MSA and SA catalysts from selective catalysis point of view for development of ester product, Triethylene Glycol Di-Methacrylate (TEGDM). The potential of methane sulphinic acid (MSA) catalyst over SA catalyst for industrial/commercial scale production of high purity ester of glycol and MA is presented in this paper.

Experimental Procedure

Materials

Following chemicals were used during the investigation: Methacrylic acid, assay 99% (E-Merck, Germany); Methane sulphinic acid, assay 98% (SD Fine Chemicals, Mumbai); Sulphuric acid, assay 98%; Hydroquinone, assay 99%; Toluene, assay 99% (Qualigens Fine Chemicals, Mumbai) and Triethylene glycol, assay 97% (Fluka).

Experimental set-up

The reaction was carried out in a three-necked half litre round bottom flask at atmospheric pressure. A magnetic stirrer was placed inside for stirring the reaction mixture. The central neck was fitted with Dean and Stark apparatus. A condenser was placed over Dean and Stark apparatus. One neck was stoppered, and the other neck was used for inserting thermowell for temperature recording.

Method

TEG, MA and toluene were taken in the mole ratio of 1:2.2:11.3. The catalyst concentration employed was 9.86 meq per 100 g of the reaction mixture. Hydroquinone was employed as a polymerisation inhibitor. Temperature was maintained around 378-388 K. The water produced in the reaction was continuously removed azeotropically from the reaction system, till there was no further formation of water in the reaction system. The central neck was fitted with Dean and Stark apparatus. A condenser was placed over Dean and Stark apparatus. One neck was stoppered, and the other neck was used for inserting thermowell for temperature recording.
water layer and ester product in toluene medium separate easily into two layers and it makes separation very easy.

The washed ester product TEGDM in toluene medium is subjected to vacuum distillation to recover toluene.

Results and Discussion

The samples were subjected to Gas Chromatography Mass Spectrograph Test (GCMS). The results of the test revealed that the desired ester product TEGDM, obtained was 94.03% with the use of novel catalyst MSA, and 85.19% only with the use of conventional SA catalyst, under identical catalyst concentration. The comparative analysis of ester product TEGDM and by-product formation for the catalyst SA and MSA is shown in Table I.

Based on the yield of esters achieved, the performance of catalyst MSA was found to be superior to the conventional SA catalyst. Thus from catalyst selectivity point of view MSA is far more superior as compared to SA catalyst, because of reduced by-product formation and higher yield of TEGDM. The achievement of this investigation is that, the by-products with molecular weight (MW) 114 and 132 obtained during synthesis of TEGDM have been identified. The by-product with molecular weight of 132 is formed due to dehydration of one molecule of water from TEG and by-product with molecular weight of 114 is formed due to dehydration of two molecules of water from TEG. The product developed using novel catalyst MSA has low free acidity in comparison to conventional SA catalyst. This concludes that MSA has better catalyst selectivity in comparison to SA for synthesis of TEGDM. From environmental point of view also, when neutralized, MSA is considered as a better choice because it is readily biodegradable. Thus, MSA catalyst holds vast potential to replace mineral acid catalyst like SA for industrial and commercial production of high purity esters of glycols and MA.

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