

Synthesis of Long Chain Wax Ester, using the Bronsted Acidic Ionic Liquid N-Methyl-2-Pyrrolidonium Methyl Sulphate ([NMP][CH₃SO₃])

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Abstract: The catalytic activity of Bronsted acidic ionic liquid N-methyl-2-pyrrolidonium methyl sulphate ([NMP][CH₃SO₃]) was studied in the esterification of oleic acid with oleyl alcohol under mild conditions and without any additional organic solvent. The effect of various reaction parameters were optimised to obtain a high percentage yield (%) of oleyl oleate. The optimal conditions for the ester synthesis were a reaction time of 8 h, temperature at 90°C, amount of catalyst 9.9% as a percentage of the weight of the oleic acid and a molar ratio of substrate of 1 which resulted in a maximum percentage yield of 86%. Analysis of the product of the reaction using FTIR, ¹H and ¹³C NMR showed the presence of oleyl oleate.

Key words: Wax ester, ionic liquid, esterification, oleic acid, oleyl alcohol, Malaysia

INTRODUCTION

Wax esters, consisting of long-chain fatty acids esterified to long-chain fatty alcohol have potential application as lubricants, plasticisers and cosmetics (Chen and Wang, 1997). These kinds of esters have excellent wetting properties at the interfaces. Two good examples of naturally occurring wax esters are jojoba oil and sperm whale oil. However, the supply of jojoba oil was inconsistent and sperm whale oil is depleting, so a substitute for this wax ester is desirable (Hadzir *et al.*, 2001).

Esterification of carboxylic acids with alcohols using homogeneous and heterogeneous catalysts is well known in the literature (Arfela *et al.*, 1999; Hino and Arata, 1985; Rama *et al.*, 2004). However, several limitations such as an excess of the catalysts or amounts of reactants to achieve efficient conversion, removal of water during the reaction, long reaction times and large amounts of effluent generation during work-up are associated with these processes (Sunitha *et al.*, 2007).

The catalysts used in traditional esterification are mainly sulphuric acid, p-toluene sulphonic acid and solid acid. Sulphuric acid cannot be reused and it has other disadvantages such as equipment corrosion, more byproducts, tedious workup procedure and environmental problem. P-toluene sulfonic acid also has some disadvantages such as higher cost, difficult separation from the products and more consumption of energy. Solid acid catalysts have attracted considerable attention in

recent years because of their significant advantages in eliminating corrosion and environmental and toxicity problems (Alpana and Uma, 2003).

Apart from recyclability and reusability, the disadvantages of solid acid catalysts are low activity, easy deactivation and difficult separation from the product (Zhang *et al.*, 2009). The room temperature Ionic Liquid (IL), a kind of environmentally friendly solvent and catalyst has gained wide attention from scholars from various fields such as synthesis, catalysis, separation and electrochemistry due to its adjustable physical and chemical properties (Swindall, 2004). Ionic liquid is non-flammable, thermally stable, exhibits negligible vapour pressure and offers the potential for recyclability. For these reasons, the replacement of the current esterification protocols with a more environmentally benign process involving the use of ionic liquids appears to be an area worthy of investigation. Deng *et al.* (2001) reported the esterification of carboxylic acids with alcohols in acidic chloroaluminate ionic liquid (Deng *et al.*, 2001). Since, then some Bronsted acidic ionic liquids including SO₃H-functionalised ionic liquid (Cole *et al.*, 2002).

Although, extensive research has been done in this area, some drawbacks in the above-mentioned catalytic systems still exist. Therefore, one of the driving forces for this research is the possibility of elucidating the merits of Bronsted acidic ILs for esterification and preparing synthetic wax esters which resemble naturally occurring waxes of commercial interest. The esterification reaction that was studied can be summarised as follows:

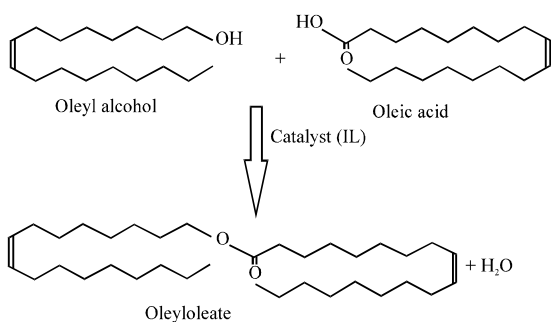


Fig. 1: Synthesis of oleyl oleate

In this study, the catalytic ability of N-methyl-2-pyrrolidonium methyl sulphate ([NMP][CH₃SO₃]) for synthesis of oleyl oleate was tested (Fig. 1). The effects of various parameters on the esterification reaction were investigated.

MATERIALS AND METHODS

Oleic acid (90%), oley alcohol (85%), N-methyl-2-pyrrolidone and methane sulphonic acid were purchased from Aldrich Chemical company (Germany). Ethyl acetate, benzene and sodium sulphate anhydrous were purchased from Systerm Chemical company (Malaysia).

Preparation of ionic liquid ([NMP][CH₃SO₃]) (Zhang *et al.*, 2009): Under vigorous stirring benzene (30 mL) was mixed with N-methyl-2-pyrrolidone (0.1 mol/9.9 g) in a 50 ML flask. Then, methane sulphonic acid (0.1 mol/9.6 g) was dropped slowly into the flask within 30 min in an ice bath. The reaction lasted for another 4 h at room temperature. Benzene was removed under reduced pressure and was further dried at 90°C under 1-5 mm Hg for 1 h giving ([NMP][CH₃SO₃]) as a light yellow viscous liquid with high percentage yield (94.0%).

Synthesis of oleyl oleate: A weighted amount of oleic acid (0.0125 mol/3.53 g), oleyl alcohol (0.0125 mol/3.35 g) and N-methyl-2-pyrrolidonium methyl sulphate ([NMP][CH₃SO₃]) (0.002 mol/0.35 g) were added to a flask having a reflux condenser, thermometer and a magnetic stirring apparatus. The esterification reaction was typically carried out for 8 h at a temperature of 90°C with vigorous stirring. After the completion of the reaction, the reaction mixture was transferred into a separatory funnel and then 5 mL of methanol was added into the funnel. Extraction (3X) was carried out. The aqueous layer was decanted and the product was dissolved with 20 mL of ethyl acetate followed by 10 mL of water to remove the remaining methanol. After the water layer was removed, the product

was dried in a conical flask with a sufficient amount of anhydrous Na₂SO₄. The hydrated Na₂SO₄ was filtered off. The dried product was rotary-evaporated to remove the solvent. The final ester product was analysed using FT-IR, ¹H and ¹³C NMR.

RESULTS AND DISCUSSION

Effect of molar ratio of substrates: The reaction mixture were reacted with different molar ratio of substrates, mol oleic acid/mol oleic acid (1:1, 1:2 and 1:3), respectively. While fixing the other condition. The effect of the molar ratio of the substrates on the esterification reaction is shown in Fig. 2.

Effect of reaction time: The effect of time in the wax ester synthesis was investigated by varying reaction period (2, 4, 6, 8, 10, 12 h) while fixing the other condition. The profile of wax esters produced at various time intervals is shown in Fig. 3.

Effect of reaction temperature: The reaction mixture were incubated at various reaction temperture (30, 50, 70, 90, 100 and 110) while fixing the other conditions. Figure 4 shows the influence of temperature on the esterification reaction within temperature range of 10-110°C.

Effect of amount of catalyst: The reactions were studied using various amount of ionic liquid catalyst (4.2, 5.7, 8.5, 9.9, 11.3 and 15.6%) as a percentage of the weight of oleic acid the influence of varying amounts of catalyst on the esterification reaction of oleyl alcohol and oleic acid is shown in Fig. 5.

Identification of functional groups of oleyl oleate wax ester using FTIR, ¹H and ¹³C NMR

Effect of molar ratio of substrates: The optimal molar ratio of oleic acid to oleyl alcohol was 1:1 at 86% of oleyl oleate. The results showed that increasing the molar ratio of oleyl alcohol to oleic acid beyond this molar ratio 1:1 would decrease the esterification activity. This observation may reflect that the excess of oleyl alcohol will hinder the interaction frequency between the substrate and catalyst (Kanasawud *et al.*, 1992; Claon and Akoh, 1994).

This is similar to the study which was reported by Chen *et al.* (1995) in which the optimal molar ratio to produce oleyl oleate was 1:1. The percentage yield of wax ester at a higher molar ratio was relatively lower which was due to the presence of a high amount of oleyl alcohol instead of the solvent. Oleyl alcohol has a higher

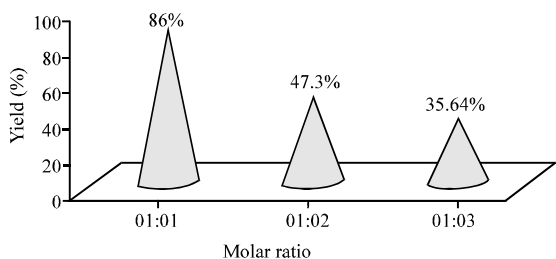


Fig. 2: The effect of the molar ratio of the substrates on esterification reaction

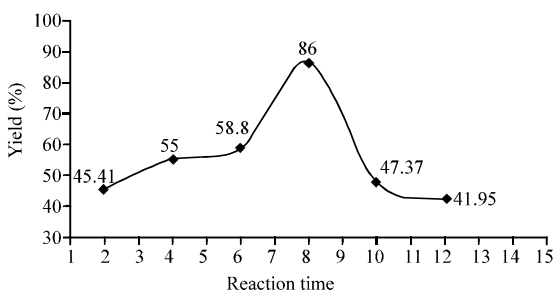


Fig. 3: The profile of wax esters produced at various time interval

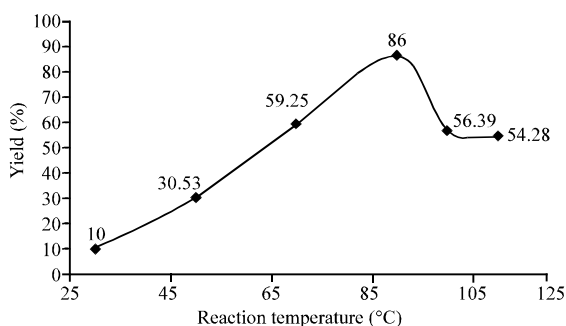


Fig. 4: The influence of temperature on the esterification reaction

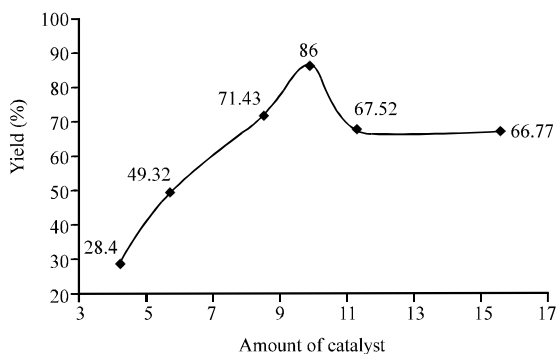


Fig. 5: Varying amounts of catalyst on the esterification reaction of oleyl alcohol and oleic acid

density than hexane thus, the interaction of the substrates and the catalyst may be inhibited. This result is identical with the result obtained because the solvent was not used in the reaction.

Effect of reaction time: The percentage yield of liquid wax ester increased with an increasing reaction time. The result suggested that the reaction took place over 8 h (86%). Thereafter, the percentage yield of oleyl oleate decreased at 10 h (47.37%) and remained constant up to 10 h (41.95%). According to Trubiano *et al.* (2007), the presence of water only has an unfavourable effect on the equilibrium conversion. Since, water is one of the products in the esterification reaction, it can promote the reverse hydrolysis reaction in the process. It is important to remove water during the course of the reaction to achieve a high product yield.

Effect of reaction temperature: Changes in the reaction temperature can affect the activity and stability of the catalyst and thus, the rate of reaction. Initially, the percentage yield of oleyl oleate increased with increasing temperature reaching a maximum at 90°C (86%). This is because the energy received from the heat from the higher temperature was used to increase the frequency of collision between the catalyst and substrate molecules resulting in accelerated rates of reaction (Syamsul *et al.*, 2010).

The percentage of yield started to decline to 56.39% at 100°C which as reported by Fannin *et al.* (1984) and Liao and Hussey (1996) is because at low temperature, the viscosity of ionic liquid is higher and it inhibits heat and mass transfer of the reaction system. (Fannin *et al.*, 1984; Liao and Hussey, 1996). When reaction temperature was increased, rate of esterification reaction increased and water simultaneously formed and dissolved in ionic liquid which diluted ionic liquid and greatly decreased its viscosity and acidity.

Effect of reaction amount of catalyst: The percentage yield increased from 4.2 (28.4%) to 9.9 (86%) and decreased when the amount of catalyst increased to 11.3 (67.52%). The amount of catalyst at 9.9% g was sufficient to catalyse this esterification reaction. This result shows that an excess of catalyst amount did not contribute to the increase in the percentage yield and sometimes, it would decrease the yield of the product. This is because at saturation point, all substrates are bonded to the catalyst and the added catalyst molecule could not find any substrate to serve as a reactant (Syamsul *et al.*, 2010). Based on the above experiments, optimum conditions were obtained as follows: Reaction temperature, 90°C; oleic acid to oleyl alcohol mole ratio, 1:1; amount of ([NMP][CH₃SO₃]), 0.35 g and reaction time

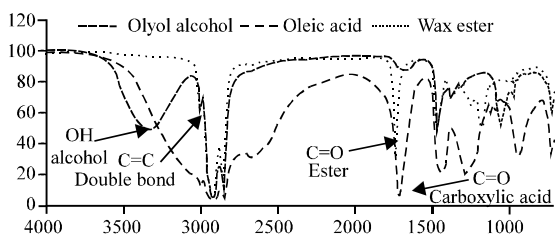


Fig. 6: FTIR spectra of the comparison between oleyl alcohol, oleic acid and oleyl oleate

8 h. Under these conditions, the percentage yield of oleyl oleate was 86%. The IL ([NMP][CH₃SO₃]) showed good catalytic performance in this case. The esterification was carried out at mild temperatures and the ester produced was isolated in high yield. It was reported that the bronsted IL [Hmim][BF₄] showed a satisfactory conversion (80-90%) for esterification (Zhu *et al.* 2003) but it needed a higher temperature 110°C. [C₃SO₃Hnhp][HSO₄] also had a good catalytic activity for esterification and the yield of n-butyl ester was >99% at optimised temperature 120°C (Huang *et al.*, 2007).

However, when the esterification was carried out at 96°C the yield of ester was <70% using [C₃SO₃Hnhp][HSO₄] as a catalyst. It was obvious that ([NMP][CH₃SO₃]) could benefit the esterification reaction of long chain fatty acids and long chain fatty alcohols in view of the low energy and easy operation. To prove the presence of C = O of wax ester (Oleyl oleate), the final product was tested by FTIR, ¹³C and ¹H. The comparison between oleyl alcohol, oleic acid and oleyl oleate FTIR spectra is shown in Fig. 6. The date of ¹³C-NMR and ¹H-NMR spectra is shown in Table 1 and 2. C = O group of wax esters can be detected at wavenumber 1735-1750 cm⁻¹ while the stretching vibration peak of =CH at 3000-3050 cm⁻¹, stretching vibration peak of free OH for alcohol can be detected at wavenumber 3300-3400 cm⁻¹ (Silverstein and Webster, 1998).

Based on Fig. 6, the FTIR spectrum of wax ester shows that stretching vibration peak at wavenumber 1739 cm⁻¹ is attributed to the carbonyl stretching frequency of ester moiety. This band combined with two C-O stretching bands, one stronger and broader than the other which occurred in the range 1172 and 1353 cm⁻¹, respectively. Whereas, the absorption due to OH of the hydroxyl group 3338 cm⁻¹ and carbonyl group of carboxylic acid at 1709 cm⁻¹ were not observed which confirms that the esterification reaction had taken place. Based on Table 1 and 2, the presence of C = O wax ester can be confirmed by comparison with the previous study by Awang *et al.* (2007).

The ¹³C chemical shift ranges for unsaturated bond was 100-150 ppm while for C-O it was 40-80 ppm and the

¹³C chemical shift value for C = O ester was 155-185 ppm. The ¹H chemical shift ranges for aliphatic protons, normally at about 1.25-2.53 ppm would also be shifted down field (Sharam *et al.*, 2006). However, the methine proton signal was shifted up field at about 4.60-5.30 ppm which indicates the presence of this type of proton (Hwang and Erhan, 2006). Furthermore, the most important feature for the success of esterification reaction is the presence of the COOCH₂ signal at about 4.02 ppm.

The spectral (¹H and ¹³C NMR and IR) data of the product matches with those reported in the literature (Awang *et al.*, 2007; Sunitha *et al.*, 2007).

CONCLUSION

The IL ([NMP][CH₃SO₃]) catalyst was active on the esterification of oleic acid with oleyl alcohol. The reaction yield was about 86% under optimal reaction conditions which were determined to be as follows: Duration, 8 h; temperature, 90°C; acid/alcohol molar ratio, 1:1; amount of catalyst, 4.1% of the weight of acid.

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