Choline Chloride Catalyzed Amidation of Fatty Acid Ester to Monoethanolamide: A Green Approach

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Abstract: Choline chloride catalyzed efficient method for amidation of fatty acid methyl ester to monoethanolamide respectively. This is a solvent free, ecofriendly, 100% chemo selective and economically viable path for alkanolamide synthesis. The Kinetics of amidation of methyl ester were studied and found to be first order with respect to the concentration of ethanolamine. The activation energy (Ea) for the amidation of lauric acid methyl ester catalyzed by choline chloride was found to be 50.20 KJ mol⁻¹. The 98% conversion of lauric acid monoethanolamide was obtained at 110°C in 1 h with 6% weight of catalyst and 1:1.5 molar ratio of methyl ester to ethanolamine under nitrogen atmosphere.

Key words: ionic liquid, monoethanolamide, amidation, choline chloride

1 INTRODUCTION

Fatty acid methyl esters are prepared by transesterification of renewable oil resources. It is non-toxic, ecofriendly so; we can convert it into value added chemicals by means of amidation of fatty acid methyl ester to monoethanolamide. The Surfactant derived from fatty materials is eco-friendly. The amide group in alkanolamide shows greater stability under alkaline condition, hence they are valid as stable emulsifier. The alkanolamide type of compound employed in pharmaceuticals products, cosmetic product and several speciality chemicals. They are used in the formulation of shampoos, bubble baths, synthetic toilet bars. The alkanolamide are compatible with other non-ionic and anionic surfactant. They are used in surfactant formulation in order to reduce zein no. of formulation. Some other applications are as a rust inhibitor in drilling oil and cutting oils.

There is more literature on synthesis of monoethanolamide from fatty acid and its methyl ester. The different catalytic system was used for synthesis of monoethanolamide like, Mg-Al layer double hydroxide solid base catalyst, micro spherical α-Zirconium phosphate enzyme synthesis of ethanol amide, direct aminolysis of triglyceride by heterogeneous catalyst. The enzymes and heterogeneous catalyst showed efficient activity but rate of reaction was slow, while in homogeneous catalysis showed the saponification of fatty materials during the reaction. Choline chloride based catalyst was employed for diverse chemical reaction likely; chemical transformation of bio based mass into valuable chemical compounds, synthesis of heterocyclic compound by condensation or cyclization reaction, synthesis of cyclic carbonate, chemo selective addition of organolithium and grignard reagents to ketone etc. which showed efficient catalytic activity.

The objective of this work is to study the amidation of methyl ester of fatty acid to respective monoethanolamide under solvent free system catalyzed by choline chloride (ionic liquid) as greener catalyst. We found that it showed greater catalytic property with 98% conversion and 100% selectivity at 110°C under solvent free condition. The kinetic study of reaction was studied by the changing concentration of the reactants and found to be a first order with respect to the concentration of ethanolamine.

2 EXPERIMENTAL

2.1 Materials and methods

Lauric acid, Myristic acid, Palmitic acid, Stearic acid, Methanol, ethanolamine, Choline chloride, p-Toluensulfonic acid etc. all chemicals are AR grade procured from M/s SD Fine chemicals Ltd. Mumbai. Fatty acid methyl esters were prepared in our laboratory using p-Toluensulfonic acid as a catalyst.
2.2 Preparation of fatty acids methyl esters

A 250 ml single neck round bottom flask containing fatty acids and methanol subjected to reflux temperature using 2% p-Toluenesulfonic acid catalyst for 6 hrs. The reaction mass was poured into separating funnel and washed with distilled water in order to remove the methanol. Then, reaction mass was solubilised into Hexane solvent and neutralised with 10% aqueous NaHCO₃ solution. Finally, the solvent was evaporated and product was used for further reaction.

2.3 Amidation reaction

Amidation reaction was carried out in 25 ml glass reactor. The fatty acid methyl ester and ethanolamine (1:1.5 molar ratios) with 6% choline chloride catalyst (weight of reaction mass) were added to the reactor under nitrogen atmosphere heated in an oil bath over the range of 90° to 110°C temperature for 1 hr. The general reaction has been shown in Scheme 1, where R is alkyl groups. The progress of amidation reaction was monitored by HPLC (Make: Agilent; Model 1200) with C-18 columns, using methanol and water as mobile phase in 9:1 ratio using a UV detector having wavelength 215 nm. The crude product was poured into hexane in order to extract methyl ester and ethanolamine from product; finally extracted with ethyl acetate solvent. Meanwhile, mass of the products was confirmed by LC-MS analysis.

Kinetic study of amidation of lauric acid methyl ester was determined by the initial rate of the reaction. The initial rate of reaction is the rate at which the reactants are first come together in reaction. Initial rate can be determined by plotting concentration of product against time of the reaction.

Lauric methyl ester + Ethanolamine →
Lauric ethanlamine + Methanol

The rate equation for the amidation of lauric methyl ester can be written as,

\[
\text{Initial rate} = \frac{d[\text{Lauric ethanlamine}]}{dt} = k[\text{Lauric methyl ester}][\text{Ethanlamine}] \tag{1}
\]

Where, k is rate constant of reaction.

The initial rate can be determined by plotting concentration of lauric ethanolamide against time of the reaction. The slope of plot will give the initial rate of reaction. We plot the graph of initial rate vs concentration of lauric methyl ester and ethanlamine using equation 1.

2.4 Characterisation of alkanolamide

The ethanlamine derivative of respective fatty acids were characterised by means of FT-IR, LC-MS and 1H-NMR analysis.

2.4.1 Lauric acid ethanlamine \((R = C_{12}H_{25})\)

FT-IR \(\nu = 3292\) (N-H), 2916 (O-H), 2848 (C-H), 1637 (C = O), 1558 (N-H bending), 1041 (C-N) cm⁻¹; MS (EI) \(m/z \) 244 \((M + H)^{+}, 80\% \) yield; \(^1\)H NMR (500 MHz, CD₃OD): \(\delta = 8.96\) (s, 1H, NH); 3.60 (t, 2H, CH₂, \(J = 6\) Hz), 3.33 (t, 2H, CH₂, \(J = 1.8\) Hz), 2.12 (t, 2H, CH₂, \(J = 7.2\) Hz), 1.62 (t, 2H, CH₂, \(J = 6.6\) Hz), 1.33 (m, 10H, CH₂ group), 0.92 (t, 3H, CH₃, \(J = 6.6\) Hz).

2.4.2 Myristic acid ethanlamine \((R = C_{13}H_{27})\)

FT-IR \(\nu = 3292\) (N-H), 2916 (O-H), 2848 (C-H), 1637 (C = O), 1556 (N-H bending), 1041 (C-N) cm⁻¹; MS (EI) \(m/z \) 272 \((M + H)^{+}, 65\% \) yield; \(^1\)H NMR (500 MHz, CD₃OD): \(\delta = 8.96\) (s, 1H, NH); 3.60 (t, 2H, CH₂, \(J = 6\) Hz), 3.33 (t, 2H, CH₂, \(J = 1.8\) Hz), 2.21 (t, 2H, CH₂, \(J = 7.8\) Hz), 1.62 (t, 2H, CH₂, \(J = 7.2\) Hz), 1.33 (m, 10H, CH₂ group), 0.92 (t, 3H, CH₃, \(J = 7.2\) Hz).

2.4.3 Palmitic acid ethanlamine \((R = C_{14}H_{29})\)

FT-IR \(\nu = 3294\) (N-H), 2916 (O-H), 2848 (C-H), 1637 (C = O), 1556 (N-H bending), 1039 (C-N) cm⁻¹; MS (EI) \(m/z \) 300 \((M + H)^{+}, 72\% \) yield; \(^1\)H NMR (500 MHz, CD₃OD): \(\delta = 8.96\) (s, 1H, NH), 3.60 (t, 2H, CH₂, \(J = 8\) Hz), 3.33 (t, 2H, CH₂, \(J = 1.8\) Hz), 2.21 (t, 2H, CH₂, \(J = 7.2\) Hz), 1.62 (t, 2H, CH₂, \(J = 6.6\) Hz), 1.33 (m, 10H, CH₂ group), 0.92 (t, 3H, CH₃, \(J = 7.2\) Hz).

2.4.4 Stearic acid ethanlamine \((R = C_{17}H₃₅)\)

FT-IR \(\nu = 3294\) (N-H), 2916 (O-H), 2848 (C-H), 1641 (C = O), 1584 (N-H bending), 1049 (C-N) cm⁻¹; MS (EI) \(m/z \) 328 \((M + H)^{+}, 88\% \) yield; \(^1\)H NMR (500 MHz, CD₃OD): \(\delta = 8.96\) (s, 1H, NH); 3.60 (t, 2H, CH₂, \(J = 6\) Hz), 3.33 (t, 2H, CH₂, \(J = 1.8\) Hz), 2.21 (t, 2H, CH₂, \(J = 7.2\) Hz), 1.62 (t, 2H, CH₂, \(J = 7.2\) Hz), 1.33 (m, 10H, CH₂ group), 0.92 (t, 3H, CH₃, \(J = 7.2\) Hz).

3 RESULTS AND DISCUSSION

Usually the reaction conversion relies on reaction temperature, time and the molar ratio of the initial reactant etc. we studied all those parameters which were influencing the amidation of fatty acid methyl ester by ethanlamine using choline chloride as greener catalyst.

3.1 Effect of temperature

Typically amidation of acid is an endothermic process requires energy to shift the equilibrium towards the forward direction. Likely, we studied the effects of temperature on amidation of fatty ester to respective ethanlamine...
were performed over the range of 90°C to 110°C. As evident from Fig. 1, ethanolamide conversion increased up to 98% with 100% selectivity at 110°C. So, we concluded that the variation in temperature enhances the rate of selective amidation reaction.

3.2 Effect of time
The effect of time on lauric acid ethanolamide conversion was studied with 1:1.5 molar ratio of lauric acid ester to ethanolamine along with 6% catalyst loading at 100°C (shown in Fig. 2). It showed that conversion increased with time i.e. 96% ethanolamide conversion after 80 min. Therefore, increase in time of reaction which imparts on enhancement in conversion for amidation reaction.

3.3 Mole ratio of ethanolamine
Selectivity being concern with a mole ratio of reactant during more than one reactive centre is present. It can be improved by increasing concentration of one of the reactant in excess amount in order to get 100% selective product. Similarly, we studied amidation to respective ethanolamide; the mole ratio of ethanolamine was varied from 1.2 to 1.5 we found that conversion of alkanolamide raised by 15% shown in Fig. 3. As the mole ratio of ethanolamine was increased, the rate of amidation of fatty acid methyl ester enhances consecutively.

3.4 Effect of catalyst loading
We studied the effect of catalyst loading on amidation reaction over the range of 4% to 8% with respective to reaction mass (Fig. 4). The conversion of the reaction enhanced from 58% to 88% with catalyst loading ranging...
from 4% to 6% at 105°C with 1:1.5 molar ratio of ester to ethanolamine. As the catalyst loading increased the rate of reaction enhanced by lowering activation energy of the reaction.

3.5 Kinetic study of selective Amidation

Rate of amidation of lauric acid methyl ester by ethanolamine with variable initial concentration of reactant was studied. The initial rate of amidation reaction with respect to methyl ester was constant i.e. the rate of the reaction was constant as the concentration of methyl ester was varied (shown in Fig. 5); while reaction rate increased with initial concentration of ethanolamine i.e. It exhibits first order reaction (From Fig. 5 and 6). So, we concluded that the rate of amidation of lauric methyl ester depends on concentration of ethanolamine.

The effect of temperature on rate constant (k) of reaction was determined by plotting Ink vs 1/T i.e. Arrhenius plot. Where, T is temperature. We plot the Ink vs 1/T for determining activation energy of amidation of lauric methyl ester by ethanolamine (Shown in Fig. 7). The activation energy was found be 50.20 kJmol⁻¹. It was observed to be kinetically controlled reaction as evident from the apparent activation energy.

4 CONCLUSIONS

Choline chloride catalyzed efficient, ecofriendly and solvent free system for amidation of fatty acid methyl ester with 98% conversion and 100% selectivity. The kinetics of amidation reaction was studied and found to be first order with respective to concentration of ethanolamine. While the apparent activation energy of the reaction was found to be 50.20 kJmol⁻¹ i.e. observed to be kinetically controlled reaction.

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